THE TROPOSPHERIC AEROSOL- MEASUREMENTS AND MODELLING

CASE STUDIES IN TANZANIA AND SOUTHEAST ASIA AND DEVELOPMENT OF MODELS FOR SIZE RESOLVED AEROSOL SIMULATIONS ON THE REGIONAL SCALE

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ABSTRACT

The tropospheric aerosol is a complex constituent of the atmosphere that has impacts on health and the climate. This thesis presents five different studies from Tanzania, Southeast Asia and Europe dealing with urban measurements of particle mass and elemental composition, regional scale modelling of ozone and particle mass of inorganic aerosols and development of modules for sea salt emissions and size resolved aerosol particles with aerosol dynamical mechanisms implemented in a regional scale chemistry and transport model (CTM).

The first research task, which was measurements in Dar es Salaam, Tanzania, uses information on elemental composition and temporal behaviour to find sources of particulate mass with a simple statistical model. The second research task used available monitored species in Asia to set up and evaluate a regional chemical transport model developed and used for European conditions. This model was then compared to other models in the Asian region. The regional scale model was also set up for Europe to test new parameterisations of sea salt emissions and size distributed aerosols.

A conclusion drawn from measurements in Dar es Salaam is that there is an enhanced concentration of small particles of anthropogenic origin in the city.

In Southeast Asia, the evaluation of the CTM with respect to ozone was found to be difficult as a result of unrepresentative monitoring data. The study does indicate that the model performance is representative, but more comparisons should be made before concluding that the model is as valid as it is in Europe.

An ensemble of models set up for East and Southeast Asia was able to reproduce the temporal variation for monitored particulate nitrate and sulphate. For simulations of the annual mean of nitrate, most models underestimated the measured values. All models in the ensemble either underestimated or overestimated total ammonium at five different stations, indicating that the emission inventory used by all the models considered here might be the reason for the bias of models to measurements.

The new sea salt emission module overestimated the value of monitored sodium, but the correlation was good. Introducing aerosol dynamics in the model made the bias smaller, but also the correlation decreased.

An aerosol dynamics module was successfully implemented in a regional scale CTM and can produce size distributed number and mass of several species. The introduction of aerosol dynamics did not degrade the performance of the model with respect to total inorganic particle mass.

Keywords: Aerosol, PM, Source assignment, Chemical Transport Modelling, Model inter-comparison, Sea salt emissions and Aerosol dynamics.

PREFACE

This thesis consists of a summary of research reported in five appended publications:

I. *Concentrations and sources of trace elements in particulate air pollution, Dar es Salaam, Tanzania, studied by EDXRF,* **Bennet, C**. ,P. Jonsson, and E. Selin-Lindgren, 2005, X-Ray Spectrometry, v. 34, p. 1-6.

II. *A regional model for surface ozone in Southeast Asia,* **Bennet, C**. and M. Engardt, 2008, Tellus B, v. 60, p. 718-728.

III. *MICS-Asia II: Model intercomparison and evaluation of particulate sulphate, nitrate and ammonium,* Hayami, H., T. Sakurai, Z. Han, H. Ueda, G. R. Carmichael, D. Streets, T. Holloway, Z. Wang, N. Thongboonchoo, M. Engardt, **C. Bennet**, C. Fung, A. Chang, S. U. Park, M. Kajino, K. Sartelet, K. Matsuda and M. Amann, 2008, Atmospheric Environment, v. 42, p. 3510.

IV. *Sea salt generation, dispersion and removal on the regional scale,* Foltescu, V. L., S. C. Pryor and **C. Bennet**, 2005, Atmospheric Environment, v. 39, p. 2123.

V. *Optimizing aerosol dynamics parameterisations for regional scale chemical transport modelling,* **Bennet C**., Bergström R. and Kokkola H. Presented at ICCE 2009 Stockholm.

The publications are referred to by their roman numerals.
The introduction gives a broad background of the tropospheric aerosol, its health and climate implications and a short presentation of the research methods used in state of the art research in the area. Five research objectives are presented at the end of the introduction, and the remainder of the thesis is organised according to these. The chapter that treats methods presents, models, statistical and physical principles, and this is followed by selected results from the studies. The last chapter gives conclusions and a brief outlook on what can be done in the field in the future.

SCIENTIFIC PUBLICATIONS NOT INCLUDED IN THE THESIS

Suspended particulate matter and its relations to the urban climate in Dar es Salaam, Tanzania, Jonsson, P., **C. Bennet**, I. Eliasson and E. Selin Lindgren, 2004, Atmospheric Environment, v. 38, p. 4175.

MICS-Asia II: The model intercomparison study for Asia Phase II methodology and overview of findings, Carmichael, G. R., T. Sakurai, D. Streets, Y. Hozumi, H. Ueda, S. U. Park, C. Fung, Z. Han, M. Kajino, M. Engardt, **C. Bennet**, H. Hayami, K. Sartelet, T. Holloway, Z. Wang, A. Kannari, J. Fu, K. Matsuda, N. Thongboonchoo and M. Amann, 2008, Atmospheric Environment, v. 42, p. 3468.

MICS-Asia II: Model intercomparison and evaluation of ozone and relevant species, Han, Z., T. Sakurai, H. Ueda, G. R. Carmichael, D. Streets, H. Hayami, Z. Wang, T. Holloway, M. Engardt, Y. Hozumi, S. U. Park, M. Kajino, K. Sartelet, C. Fung, **C. Bennet**, N. Thongboonchoo, Y. Tang, A. Chang, K. Matsuda and M. Amann, 2008, Atmospheric Environment, v. 42, p. 3491.

MICS-Asia II: Impact of global emissions on regional air quality in Asia, Holloway, T., T. Sakurai, Z. Han, S. Ehlers, S. N. Spak, L. W. Horowitz, G. R. Carmichael, D. G. Streets, Y. Hozumi, H. Ueda, S. U. Park, C. Fung, M. Kajino, N. Thongboonchoo, M. Engardt, **C. Bennet**, H. Hayami, K. Sartelet, Z. Wang, K. Matsuda and M. Amann, 2008, Atmospheric Environment, v. 42, p. 3543.

MICS-Asia II: Model inter-comparison and evaluation of acid deposition Wang, Z., F. Xie, T. Sakurai, H. Ueda, Z. Han, G. R. Carmichael, D. Streets, M. Engardt, T. Holloway, H. Hayami, M. Kajino, N. Thongboonchoo, **C. Bennet**, S. U. Park, C. Fung, A. Chang, K. Sartelet and M. Amann, 2008, Atmospheric Environment, v. 42, p. 3528.

CONTENTS

1 INTRODUCTION

1.1 The nature of the tropospheric aerosol

The atmospheric aerosol is a versatile system that interplays with the biosphere, technosphere, weather and climate at the same time as physical interactions and heterogeneous and homogeneous chemical reactions take place within the aerosol itself. The atmospheric aerosol is a multi-phase system with solid or liquid particles suspended in the ambient gas, the air. There are several quantities that can represent a particular aerosol, such as the composition of the gas mixture, bulk concentration of particulate matter (PM), size distributions of the chemicals present, number of particles surface area and volume. These are mostly treated as statistical quantities while, in reality each particle in the aerosol has its individual properties, such as its form or chemical content. With these follow different physical, thermodynamic and chemical properties such as electric charge, optical scattering and absorption, hygroscopicity, chemical potential, melting and vaporisation points, and effect properties such as poisoning, acidifying and fertilizing abilities.

There are multiple ways of classifying the aerosol. Based on the size of the particles in the aerosol, there are e.g. ultrafine particles, with diameters less than 0.1 μm, particulate matter, PM2.5, with particle diameters less than 2.5 μm, and PM10, with diameters less than 10 μm. PM2.5 is also called the fine PM fraction while the range between PM10 and PM2.5 make up the coarse particle fraction. In some contexts the term totally suspended matter (TSP) is used.

Some aerosol particles are also hydrometeors. This is the case for liquid aerosol particles such as sea spray and fog and cloud drops smaller than 100 μm in diameter. When a particle in high ambient relative humidity reaches a certain size and hygroscopicity and starts to grow rapidly by condensation of water it, is called cloud condensation nuclei (CCN). The resulting, larger sized cloud or fog drop is not classified as an aerosol particle.

Particles emitted directly to the air are called primary particles; if formed from precursor gases in the atmosphere, they are called secondary particles. Based upon source, the particles (and thus aerosols) are either anthropogenic or natural.

The size distribution of an aerosol can be represented in different ways. The mass is important when addressing health guidelines, while the total surface is interesting when studying surface reactions. The number of particles is more important than mass in studies of the microphysics, cloud processes and climatic effects of the aerosol.

The number size distribution is often described by three or four lognormal modes. The nucleation mode [1], where the main source of particles is nucleation, consists of particles having diameters between 2 and 20 nm. The Aitken mode [1] has diameters from 20 to 200 nm, and the accumulation mode [1] ranges from 0.5 to 2 µm; here the mass is accumulated by the physical processes of condensation and coagulation. Finally, the coarse mode [1] is made up of particles over 2 µm, produced by mechanical processes. With this classification, the size distribution can be described by three parameters per mode: mean, standard deviation and number at mean. Figures 1 and 2 illustrate the volume, mass and number distribution of two hypothetical aerosols. The mean mode diameters of measurement data fitted to this kind of function often do not coincide with the size ranges used for classification [2].

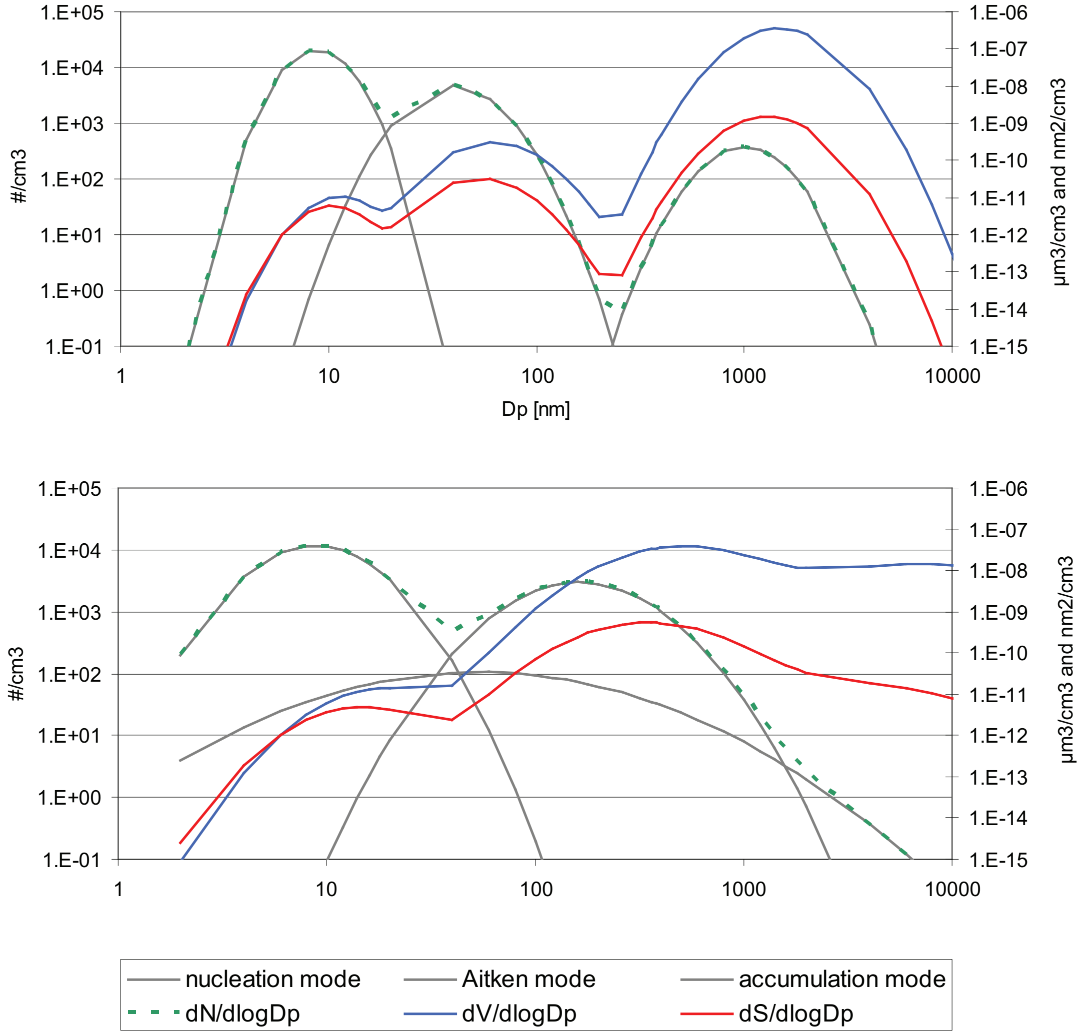

Figure 1. Idealised picture of the size distribution with three modes (upper). Size distribution with three lognormal modes of a rural aerosol according to [2] (lower).

1.2 Health effects

Particulate matter has documented health effects in the urban population in both developed and developing countries, summarised in an extensive review of epidemiological studies and clinical studies of the characterisation of inhaled particles, considerations of deposition and clearance in the respiratory tract and doses delivered to the upper and lower airways and the alveoli [3]. From this review the World Health Organisation, WHO, has recommended guidelines for concentrations of PM10 and PM2.5 that are 20 and 10 $\mu g/m^3$ respectively for annual mean, and 50 and 25 $\mu g/m^3$ for 24-hour mean [3]. The smaller the particles, the more easily they bypass the human body's respiratory defences. There are as yet no health guidelines for the number of ultrafine particles. Emerging research however supports relationships between these particles and use of medical resources [4] and coughing [5] among asthmatics, as well as cardiovascular mortality [6]. There are also measurement studies that indicate a poor correlation between the ultrafine number concentration and fine mass concentration [7, 8]. As the guideline for PM2.5 does not cover the number of ultrafine particles, even though they are part of that quantity it is interesting to further investigate ultrafine particles.

Some chemical species of the aerosol are considered to be hazardous to health. Among the organic species, several are known to be carcinogenic, for example the group of polycyclic aromatic hydrocarbons [9, 10], monitored for regulatory purposes. This is also the case for the trace elements and heavy metals arsenic, cadmium and nickel [9, 10]. Lead is also regulated as it causes a wide range of damages such as neuro developmental effects in children and hypertension in adults [11]. There is an ongoing discussion concerning how to regulate aerosols in order to achieve the best effect on human health. As an example, Graham et al. [12] suggest that it is more important to restrict certain emissions from transport rather than to monitor and regulate PM2.5 as though all PM therein were equally toxic.

1.3 Effects on climate

Aerosols have several and possibly large effects on climate. The IPCC reports a total net global negative radiative forcing that can be of the same magnitude as the warming from greenhouse gases [13]. The direct effect is the scattering and absorption of incoming light by the aerosol. The secondary effects, also called indirect effects, concern the aerosol's interactions with clouds. The direct effect on the radiative budget can be either positive or negative depending on the optical properties of the aerosol. Here it is important which species are included in the particles and how they are mixed [14]. The indirect effects are more complicated, and several mechanisms are proposed [15]. The first secondary effect, also called the Twomey effect or cloud albedo effect, is the effect of more particles being present, resulting in smaller cloud droplets that increase the cloud albedo by reflecting more solar radiation back to space. The second indirect effect, also called the cloud lifetime effect, concerns the fact that smaller cloud droplets decrease the precipitation efficiency and thereby prolong the cloud lifetime, the distribution of clouds and the hydrological cycle [16]. At the same time, latent heat from condensation and evaporation is affected, leading to changes in the atmospheric circulation within and outside the clouds. Both the first and second indirect effects result in a net cooling of the atmosphere. There is another effect when absorbing aerosols, which create heat in their surroundings, come into play. The heating of air in the atmospheric boundary layers influences the formation of cumulus clouds. The extra heat from absorbing aerosols makes the layer more stable, resulting in lower humidity and fewer clouds. This is the semi-direct effect, which can be dominant in highly polluted regions. It is important in climate modelling to have a correct representation of the processes that involve aerosol particles as well as a good microphysical cloud model. A recent suggestion regarding requirements for the description of an aerosol particle population is that the number of particles is of greater importance than their chemical composition [17].

1.4 Research approaches

To understand this multifaceted and important constituent of the atmosphere, several approaches are used in state of the art research and air quality monitoring. Measurements with *in situ* and remote sensing techniques, laboratory experiments, theoretical studies, computer modelling from box models to global three-dimensional models and emission inventories are all fundamental tools. This section is not an attempt to catalogue all methods but is a brief presentation of different approaches that are fundamental to the present knowledge of aerosols in the atmosphere.

Particles can be collected on different types of filters for analysis of mass and chemical components. Total suspended matter, PM10 and PM2.5 are usually collected as health guidelines (national and those issued by WHO) stipulate. As a consequence, this type of monitoring is common in Europe and other parts of the world both in urban and remote locations.

Most collectors separate particles of different sizes by using the inertia of particles in an airstream that makes them continue in a straight line and later impact on a surface when the flow of air bends. This process is called impaction and the collecting device an impactor. Another method for separating particles of different sizes is to force an airstream into a cyclonic movement where centrifugal, gravitational and inertial forces sort out particles of a calculated cut-off size. The studies described in Paper I involved a dichotomous virtual impactor as well as a sharp cyclone used to collect PM1, PM2.5 and PM10-PM2.5 (PMcoarse) on filters.

The semi-volatile fraction of the aerosol is difficult to measure correctly by capture on filters [18]. Such species exist in an equilibrium state between the gaseous, liquid and solid phases and can either evaporate from the filter or the gas in which they are present can condense on the filter sample. To solve this problem, filter packs with several filters having different properties are used in sequence after each other, or the total amount of species, both gaseous and solid, is measured .

The chemical composition of collected particles can be analysed in various ways. For example, detailed information on the chemical constituents of individual particles, as well as their size and structure, can be studied with electron microscopy (EM) (see Figure 3). These pictures reveal the different size, composition and form of four particles. In several analysis methods and models these particles are represented by a sphere, often of unit density, that is assumed to behave like the real particle in the instrument. The characteristic diameter of such a particle is called the aerodynamic diameter.

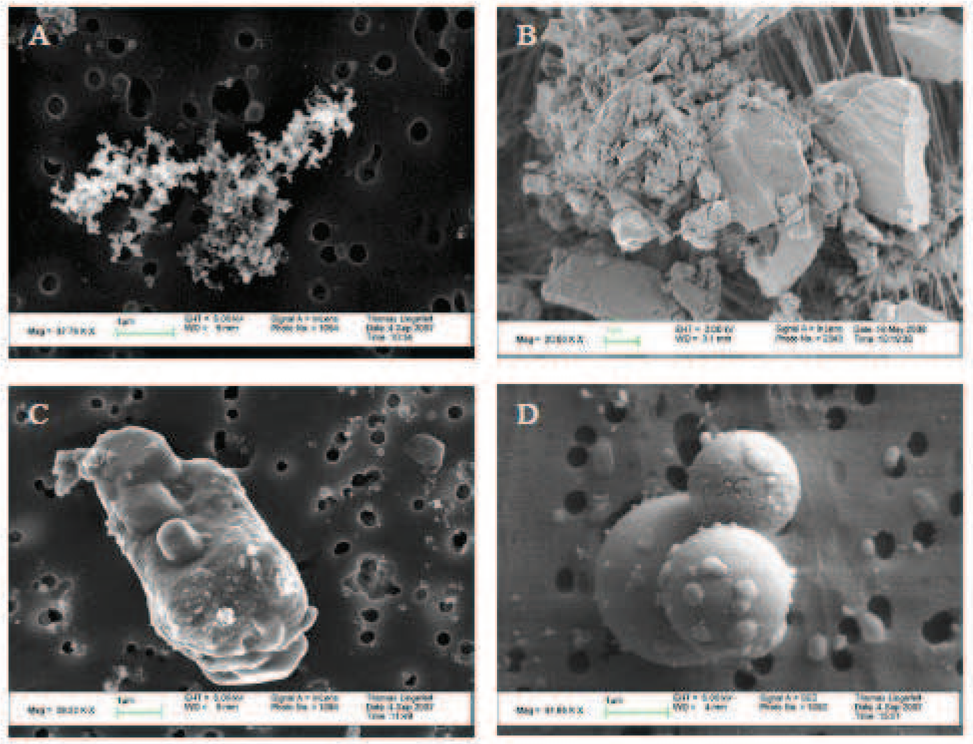

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Figure 3. Electron microscopy pictures of particles from Linköping, Sweden. A: Typical exhaust particle. B: Mineral content. C: NaCl with deposits on the surface. D: Flyashes.

An efficient way to analyse the elemental content of a sample is to use X-ray techniques, while ion chromatography is often used for measurements of ammonium, nitrate, chloride and sulphate ions. Soot can most easily be measured by light absorption measurements. However, when the objective is to distinguish between organic and elemental carbon, methods for analysis are more complicated and include destructive techniques involving incineration of the filter sample and analysis of the emanated gases.

Some instruments use optical methods to count particles instead of collecting them. The simplest method is the use of a small laser particle counter to detect particles in their ambient state. These instruments estimates the size of the particles by measuring the scattered light from individual particles. This type of instrument gives a rough but fast number of differently sized particles. When studying the dynamic processes of aerosols, e.g. nucleation, coagulation and condensation, the measurements require more sophisticated instruments. Either a D/SMPS system (Differential /Scanning Mobility Particle Sizer) or an APS (Aerodynamic Particle Sizer) can be used. The APS measures the individual particle's aerodynamic size by detecting the time of flight for a particle in a known airflow. The DMPS lets the particles pass through several steps. The ambient particles are first dried, then charged electrically and later passed through a DMA (Differential Mobility Analyser), where electrical mobility is used as a means for size separation. The last step is to count the size fractions of particles entering a CPC (Condensation Particle Counter), where the particles grow by condensation to 10-12 μm, which makes them easy to detect by laser scattering.

Ground based instruments and satellite based optical instruments measuring scattering, backscattering, attenuation and absorption of radiation from the atmosphere or parts of the atmosphere are often referred to as remote sensing. With ground based remote techniques it is possible to obtain vertical profiles of the aerosol backscattering coefficient, while satellite measurements give the most correct measures of the integrated atmospheric total column. A weakness of satellite based information is that it is difficult to distinguish between surface, cloud and aerosol properties, and the time resolution for measurements at one location is often rather poor as the satellite orbits the earth. New instruments and satellites make this area of aerosol research promising for answering questions about the aerosol's effect on clouds and climate [17, 19]. As it gives a spatially integrated measure, it can also be of value for evaluation purposes or data assimilation into larger scale atmospheric models.

Chemical and physical experiments in a controlled environment are used to investigate isolated processes and phenomena involving aerosols. The output of these is empirical mathematical descriptions called parameterisations that are valid under certain circumstances. Thermodynamic, physical and chemical theories on the behaviour of gaseous, solid and liquid compounds and their interactions are also analytical mathematical descriptions of isolated and linked phenomena. Assumptions and simplifications can sometimes give simpler mathematical descriptions of the aerosol systems. These can be used to understand measured data or can be used to make simulations in different computer models.

Computer models in one dimension simulating chemistry and aerosol dynamics over time are commonly called box models. They combine descriptions and facts originating from theoretical studies, laboratory studies and remote and *in situ* measurements. Box models are important tools for optimising simplified descriptions with accurate results to be implemented in three-dimensional models.

The most advanced circulation and dispersion models for the atmosphere or parts of the atmosphere are three dimensional. The spatial extension and resolution, together with available computational power, decide the detail in which processes can be described. Weather forecast models often do not include atmospheric chemistry processes or aerosol dynamics in detail, even though precipitation, clouds and radiative properties are influenced by aerosols. Models for simulations of climate, i.e. GCMs (General Circulation Models), frequently include simplified descriptions of chemistry and aerosol dynamics. Chemical transport models (CTMs) generally include the most detailed chemistry schemes, and advanced descriptions of the aerosol processes. They are developing with the growing amount of knowledge of aerosol processes. The three-dimensional aerosol models are thus summations of the collected knowledge in the aerosol field, and using them can teach us about the strengths and weaknesses of that knowledge and where effort is needed for a correct understanding of the atmosphere.

The mass of sulphate, nitrate and ammonia is relatively well modelled in CTM [20, 21] while the modelling of the number concentration is still a challenge. Modelling of primary natural particles, dust and sea salt is often carried out by empirically derived algorithms that take into consideration wind speed, salinity [22] and, in the more advanced models, the size distribution of sand in different arid regions [23].

Model studies can be used to investigate the response of different emission scenarios [24] and thus be an important tool for policymakers, for example in developing cost-effective air pollution control strategies.

Important inputs to all models are the emissions of primary particles and precursor gases. The atmospheric aerosol contains particles of both anthropogenic and natural sources. There are global to local databases where extensive information has been compiled to describe these emissions. Most often, the data are assembled for different source sectors, such as traffic, domestic burning and industry. Two different emission inventories are used in this thesis and are described in Chapter 2. Natural sources of primary particles are primarily sea salt emitted from the oceans, windblown dust and volcanic emissions. Primary particles of anthropogenic origin consist mainly of re-suspended dust from roads and farming, particles abraded from tyres and carbon from incomplete combustion. In terms of secondary particles, volatile organic compounds (VOC) from soil, wetlands and vegetation are important precursors, along with anthropogenic emissions of gaseous NH_3 from agriculture, SO_2, NO_X and VOCs from fossil fuel burning, biomass burning and the use of solvents.

1.5 Ozone

A secondary air pollutant that is certainly better understood than the particulate part of the aerosol is ozone. Ozone is produced in the atmosphere from NO, NO_2 and VOC or carbon monoxide (CO). Several reactions in its production scheme are photochemical, i.e. dependent on sunlight. Precursors of secondary organic aerosol (SOA), an important part of the aerosol that is still fairly uncovered in research [25], are dependent on the same type of photochemical reactions as is ozone. Biogenic VOCs have both an ozone forming potential and form semi-volatile products that condense onto particles or even contribute to the nucleation of new particles [26]. Precursors of ozone are also often emitted from the same sources as primary carbon particles. Ozone is well monitored and modelled [21, 27] in Europe and industrialised parts of the world as it has been recognized to have health implications and degrading effects on crops. This makes it a suitable species to use as an indicator of how well photochemical modelling set-ups perform.

1.6 Aerosol dynamics

The processes that control the size distribution of particle number, mass and chemical species are together termed aerosol dynamics. These involve transport in the atmosphere, dry and wet deposition, condensation of gases onto particles, nucleation of particles from gas mixtures and coagulation – particles colliding with and sticking to each other.

The atmospheric transportation of aerosols is determined by the motion of air at different temporal and spatial scales such as turbulence, wind, vertical uplifting and atmospheric waves. Dilution is important close to aerosol sources.

Aerosol particles are removed from the atmosphere by wet and dry deposition. In the case of coarse particles, dry deposition is most important owing to gravitational settling; for particles with diameters below 100 nm, dry deposition is most important because of Brownian diffusion. Wet deposition, deposition by precipitation or fog, is more efficient for particles between 0.1 and 1 μm.

Condensation takes place as the particle-gas system strives to achieve equilibrium between the gaseous and the particle phases. The gas phase concentration at equilibrium is called the equilibrium vapour pressure. For a curved surface – the surface of a particle – the equilibrium vapour pressure is always higher than for a flat surface of the same substance. This is called the Kelvin effect and means that condensation is more efficient for a larger particle than a smaller one. The equilibrium vapour pressure is also dependent on the substances involved.

Homogeneous nucleation is the case in which new particles are formed from gaseous precursors. The initial size of a stable particle is of the order of one nm in diameter. There are large uncertainties in measuring and modelling nucleation, and several pathways have been suggested: binary water-sulphuric acid nucleation, ternary water sulphuric-acid-ammonia ion induced nucleation and activated nucleation.

Coagulation is mainly controlled by the collision rate between particles, as low kinetic energy bounce off is unlikely and the probability of unity sticking can be assumed. Brownian motion is most efficient for all sizes, while gravitational settling and turbulent shear coagulation become significant when the particle diameter exceeds a few micrometers. Coagulation is important for depletion of the smallest particles, which effectively coagulate with coarser particles.

1.7 Objectives of the studies conducted in three different world regions

The overall aim of this thesis was to improve knowledge of the atmospheric aerosol. As there are differences in the knowledge base in different parts of the world, a variety of approaches have been taken in the research:

In Tanzania, Africa, few field measurement studies had been undertaken before. The consequence was that a modelling study would have suffered in the validation of its results. For this reason, a measurement campaign was the choice in this study of air pollution in Africa (Paper I). The study in Tanzania had the following objective:

Thesis objective 1: Assess the concentrations and chemical contents of PM2.5 and PM10 in a rural background and in the urban air of Dar es Salaam, Tanzania (Paper I).

Measurements are made of gaseous species at several stations for air quality and of particulate matter at a few stations in East and Southeast Asia. Regional scale CTMs with photochemistry and aerosol descriptions are not uncommon in this region. The approach chosen to study the Asian atmospheric composition was to model the chemistry with a CTM and compare the results with those of other models while also validating the CTM with available monitoring data.

Thesis objective 2: Investigate whether ozone can be modelled at the regional scale in Southeast Asia with a fair degree of accuracy. Identify the difficulties in applying a CTM developed for another climate zone (Paper II).

Thesis objective 3: Investigate how harmonious is the performance of various CTMs in East and Southeast Asia. Compare the performance of the models with respect to available monitoring data (Paper III).

Monitoring the atmospheric aerosol and gaseous air pollutants is widespread in Europe. Chemical transport modelling has also been applied on the regional scale and evaluated for several decades. Knowledge of the amount of particulate matter originating from some sources, such as sea spray, is not complete, however, although measurements are made routinely at certain locations. More recently, a growing number of measurement stations have focused on the number concentrations of fine and ultrafine particles. Box models of the aerosol dynamics have been developed and are steadily being improved and implemented in a three-dimensional regional scale CTM.

Thesis objective 4: Investigate the spatial distribution and concentration levels of aerosols from sea spray (Paper IV).

Thesis objective 5: Implement and optimise an aerosol dynamics routine coupled to the chemistry in a regional scale CTM (Paper V) in order to investigate the possibilities of mapping the spatial distribution of the size resolved aerosol.

2 METHODS

2.1 Measurements

2.1.1 Impactor and cyclone measurements

Paper I addresses particle measurements made with an impactor and cyclone for particle separation and sizing. The dichotomous impactor (Figure 4 a) uses the inability of particles of larger sizes to follow a turning airflow. In a sharp bend, the particle inertia can be described by a centrifugal force that makes the heavier particles follow a straighter path. The major flow through the instrument has a 90-degree turn, which separates most of the heavier particles that follow a straight minor flow. In the cyclone (Figure 4 b) the air is forced into a cyclonic trajectory, making the heavier particles impact on the walls while the smaller particles follow the air and can be collected on a filter.

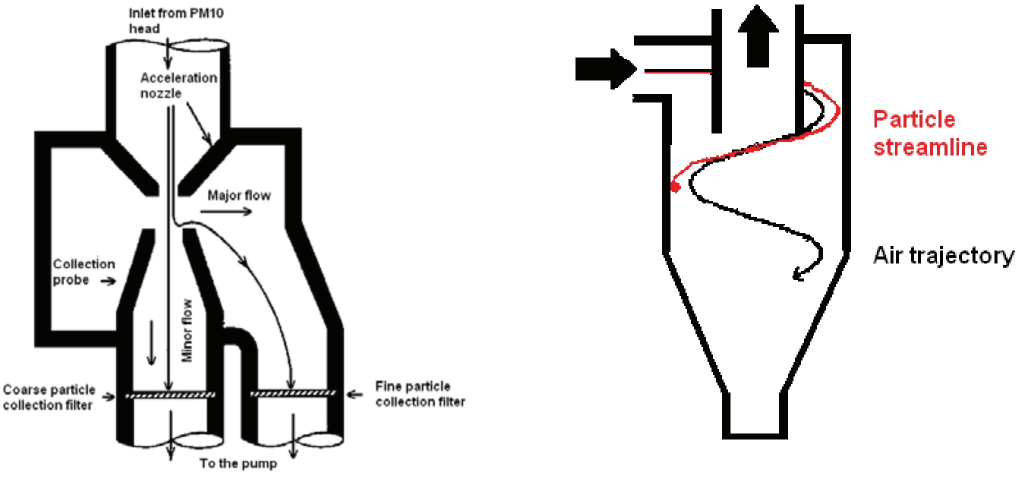


Figure 4. Schematic pictures of the dichotomous impactor (left) and the cyclone (right).

2.1.2 Analysis by EDXRF

Particles collected on filters were subsequently analysed with energy dispersive X-ray fluorescence spectrometry (EDXRF). This non-destructive analytical technique can detect multiple elements with weights between Beryllium (Be) and Uranium (U). The sample was irradiated with X-rays that excite the elements which then send fluorescent radiation characteristic for the elements. This radiation is translated to the masses of species via a spectrum analysing software. S, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr and Pb were found in the particulate sample (Paper I).

2.1.3 Multi-component Correlation Analysis

In an attempt to make a source assignment of particles present in an African city, the work reported in Paper I investigated the correlation of the collected and analysed elements. The statistical analysis technique used here was principal component analysis (PCA), which starts from a number of possibly correlated variables (original species concentrations time series in the dataset) and whose objective it is to propose new variables that are uncorrelated to each other. These new variables are called the principal components of the data. The first principal component accounts for most of the variability in the dataset. The assumption is that species originating from the same source are correlated to each other and thus end up in the same principal component. The principal components are assigned to sources with knowledge of the elemental signatures from emission sources .

2.2 Regional chemistry and transport model - MATCH

MATCH, the multiscale atmospheric transport and chemistry model, was used on the regional scale over East and Southeast Asia (Papers II-III) and Europe (Papers IV and V). The MATCH model is a three-dimensional Eulerian model developed at the Swedish Meteorological and Hydrological Institute [28]. It was used in Model Inter-Comparison Study (MICS) Asia, Phase I, to simulate sulphur transport and deposition [29] [30], for studies of ozone [27], and for modelling climate change influences on nitrogen transport [31] .

MATCH can be used with a number of different chemistry, deposition and transport schemes. The most advanced chemistry scheme is based on thermal and photochemical gas phase chemistry described by Simpson et al. [32]. It considers 70 species and includes 110 thermal, 28 photochemical, two aqueous phase, five aerosol reactions and four gas phase, aqueous phase and aerosol equilibrium. The formation of ammonium sulphate ($(NH_4)_2SO_4$) is modelled followed by the formation of ammonium nitrate (NH_4NO_3). If there are both H_2SO_4 and NH_3 (taken both from the gas NH_3 and the NH_3 part of NH_4NO_3), $(NH_4)_2SO_4$ is formed. If, after that reaction, there is still available NH3 and NO_3, those two species react in an equilibrium reaction between gas and particle phase to form NH_4NO_3. These heterogeneous reactions are partly replaced by dynamical condensation in Paper V described in Section 2.5.

The model includes the following organic compounds: methane, ethane, ethene, methanol, ethanol, formaldehyde, acetaldehyde, butanone, propene, n-butane, o-xylene, isoprene and their reaction products. They are chosen to represent different volatile organic molecules emitted to the atmosphere. They span the normal range of photochemical ozone creation potential (POCP) for most important organic pollutants [33].

Different meteorological input data can be employed in CTM modelling. In the Asian studies (Papers II-III), data from the European Centre for Medium-Range Weather Forecasts, ECMWF, were used with a horizontal resolution of 0.5º * 0.5º. These were updated every six hours and interpolated to one-hour resolution and showed very good agreement with radiosonde measurements over Japan [34]. The correlation coefficient was above 0.65 for wind direction and 0.8 for wind speed, while the relative humidity was more poorly reproduced, with a correlation coefficient of 0.4. The correlation of modelled to measured temperature was never below 0.98. For the development of the model, investigations (Papers IV-V) that were set up for Europe, a region with an availability of high quality monitoring of meteorological variables, data from the High Resolution Limited Area Model, HIRLAM [35], were used.

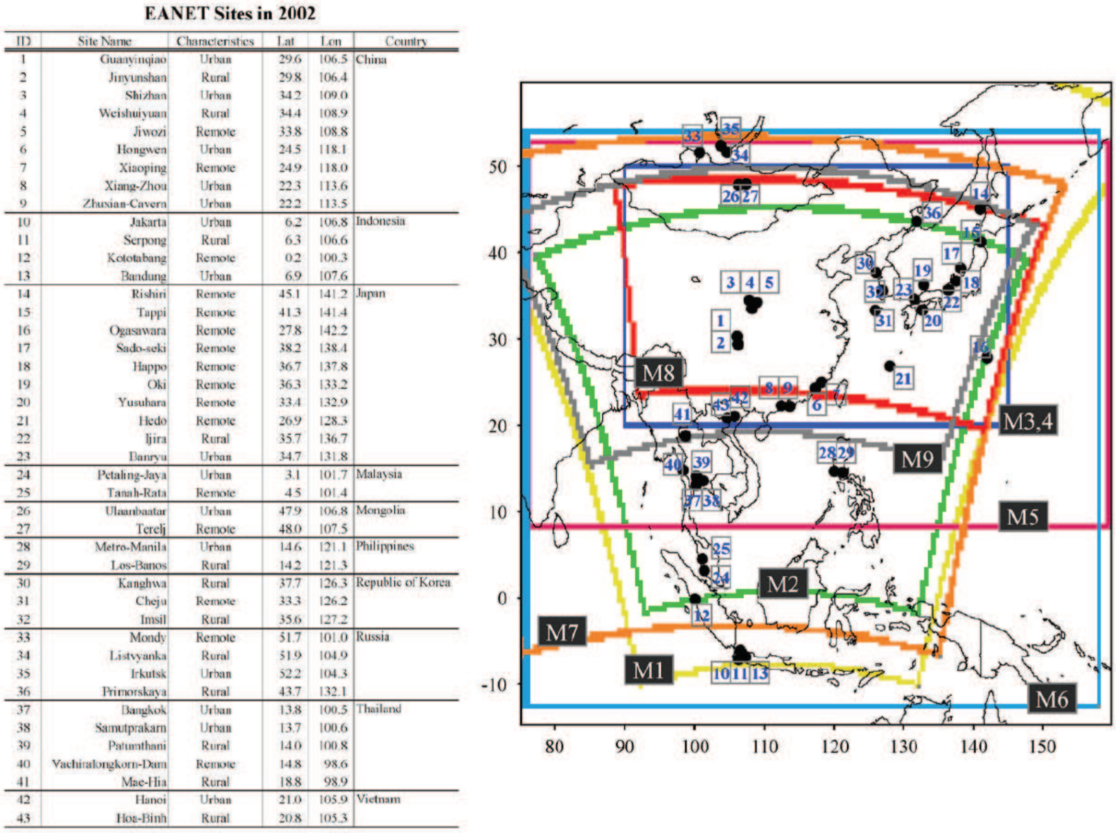
In both the European set-up (Papers IV-V) and the Asian set-up (Papers II-III), the horizontal resolution in the model was 0.4-0.5º * 0.4-0.5º, with 25 vertical layers reaching the top boundary at approximately 8 km.

Dry deposition velocities for the modelled chemical species were derived as a function of stability and were given a diurnal variation over land, as the activity of the biota increases the uptake and depletes the species from the atmosphere during the day.

2.3 Model Inter Comparison Study, MICS Asia

The Model Inter Comparison Study, MICS in Asia (Phases I and II), was set up to compare the performance of several high performing regional scale CTMs in Asia [29, 34, 36-38]. The MATCH model qualified for this study. Investigating differences between models provides an opportunity to estimate the uncertainty of assumptions made in the model and to better understand the controlling processes. In MICS-Asia Phase II, nine models (M1-M9) including MATCH were set up for the same geographical area, period of time, emissions and boundary conditions. Different meteorological inputs were used in the models, but these differences were taken into consideration when the resulting differences in performance were analysed. The species compared were ozone and its precursors and aerosol mass concentrations of nitrogen and sulphuric compounds. The simulations were carried out for 14 months in an attempt to see year-to-year differences for two months. All data were reported to the coordinators, and preliminary results were then presented and discussed at a workshop, and leading authors appointed to joint articles. The purpose of taking part in the MICS study was to investigate how well the MATCH model photochemistry descriptions would operate in another part of the world prior to implementing new aerosol descriptions.

The investigated area is depicted in Figure 4 together with a list of all measurement stations. The monitoring data from these stations are from the Acid Deposition Monitoring Network in East Asia, EANET [39]. The MATCH model is identified as number six (M6) and covers the entire region envisioned for the comparison.



EANET Sites in 2002

ID	Site Name	Characteristics	Lat	Lon	Country
1	Guanyinqiao	Urban	29.6	106.5	China
2	Jinyunshan	Rural	29.8	106.4	
3	Shizhan	Urban	34.2	109.0	
4	Weishuiyuan	Rural	34.4	108.9	
5	Jiwozi	Remote	33.8	108.8	
6	Hongwen	Urban	24.5	118.1	
7	Xiaoping	Remote	24.9	118.0	
8	Xiang-Zhou	Urban	22.3	113.6	
9	Zhuxian-Cavern	Urban	22.2	113.5	
10	Jakarta	Urban	6.2	106.8	Indonesia
11	Serpong	Rural	6.3	106.6	
12	Kototabang	Remote	0.2	100.3	
13	Bandung	Urban	6.9	107.6	
14	Rishiri	Remote	45.1	141.2	Japan
15	Tappi	Remote	41.3	141.4	
16	Ogasawara	Remote	27.8	142.2	
17	Sado-seki	Remote	38.2	138.4	
18	Happo	Remote	36.7	137.8	
19	Oki	Remote	36.3	133.2	
20	Yusuhara	Remote	33.4	132.9	
21	Hedo	Remote	26.9	128.3	
22	Ijira	Rural	35.7	136.7	
23	Banryu	Urban	34.7	131.8	
24	Petaling-Jaya	Urban	3.1	101.7	Malaysia
25	Tanah-Rata	Remote	4.5	101.4	
26	Ulaanbaatar	Urban	47.9	106.8	Mongolia
27	Terelj	Remote	48.0	107.5	
28	Metro-Manila	Urban	14.6	121.1	Philippines
29	Los-Banos	Rural	14.2	121.3	
30	Kanghwa	Rural	37.7	126.3	Republic of Korea
31	Cheju	Remote	33.3	126.2	
32	Imsil	Rural	35.6	127.2	
33	Mondy	Remote	51.7	101.0	Russia
34	Listvyanka	Rural	51.9	104.9	
35	Irkutsk	Urban	52.2	104.3	
36	Primorskaya	Rural	43.7	132.1	
37	Bangkok	Urban	13.8	100.5	Thailand
38	Samutprakarn	Urban	13.7	100.6	
39	Patumthani	Rural	14.0	100.8	
40	Vachiralongkorn-Dam	Remote	14.8	98.6	
41	Mae-Hia	Rural	18.8	98.9	
42	Hanoi	Urban	21.0	105.9	Vietnam
43	Hoa-Binh	Rural	20.8	105.3	

Figure 4. Locations for model evaluation and domains for models participating in the MICS-Asia study. M6 is the MATCH model. Adapted from [34].

The emissions were provided by the Center of Global and Regional Environmental Research, Iowa University, and were based on the TRACE-P emission inventory [40, 41]. The emissions refer to the following sectors: non domestic, domestic biofuels, domestic fossil fuels, biomass burning and large point sources, together with data from natural emissions of volcanoes. The TRACE-P inventory has been compared to a comprehensive national inventory of Japan and shown good results [42], although the authors warn about using the techniques they applied in their work for developing countries, where there are less detailed activity data and information on local emission factors. Isoprene emissions from the Global Emission Inventory Activity, GEIA database [43], were added for the MATCH model.

Most models used boundary data from the global CTM MOZART [44]. In the inter comparison study, the global model was also used to estimate the contribution of transport from North America and Europe to the ozone concentration in Asia [44]. The European contributions were 5-8% in spring and autumn, while the North American contribution peaked at 10% of the monthly mean O_3 during the winter months.

Measurement data on particulate sulphate, total nitrate (gaseous HNO_3 and particulate NO_3) and total ammonium (gaseous NH_3 and particulate ammonium) from 14 EANET stations were used to evaluate the performance of eight models for March, July and December 2001 and March 2002 (Paper III). Among the EANET stations, six are classified as rural stations, five as urban and only three as remote. This is optimal for a comparison of regional scale modelling results, as the results of this modelling represent mean values over extended areas of hundreds of kilometres for each grid point in the model.

2.4 Sea salt aerosol emission module

A sea salt aerosol emission module including two different parameterisations for different size ranges was developed and implemented in MATCH (Paper IV). Sea salt particles are generated by bubble bursting, which ejects jet and film drops to the atmosphere over the seas [45]. The bubbles are thereby formed within breaking waves but also to a minor degree by the splashing of precipitation on the sea surface [46]. The module was originally developed with the sea salt aerosol particles being represented by eight fixed size bins, where the four finer size bins were parameterised according to Mårtenson et al. [41] and the coarser bins were parameterised according to Monahan [45]. The module has more recently been updated to allow for an arbitrary number of size bins. New modelling results are presented in section 3.4.

The Mårtensson parameterisation is valid for dry diameters <2µm, and the following expression is used for the production flux, F ($m^{-2}s^{-1}$):

$$\frac{dF}{d\log D_p} = 3.84 * U_{10}^{3.41}(A_k T_w + B_k)$$

$$A_k = c_4 D_p^4 + c_3 D_p^3 + c_2 D_p^2 + c_1 D_p + c_0$$

$$B_k = d_4 D_p^4 + d_3 D_p^3 + d_2 D_p^2 + d_1 D_p + d_0$$

U_{10} is the wind speed at a height of 10 meters ($m\ s^{-1}$) and A describes the influence of the water temperature, T_w (K). A and B are functions of the dry particle diameter, D_p, and empirical coefficients c0-4 and d0-4 that are reported in [41] for three size ranges (k=1,2,3), respectively.

The sea salt generation function according to Monahan [45] is expressed as a function of the wet particle radius (r_w) at 80% relative humidity. It is valid for particles larger than r_w=0.8 µm or D_p=1-2 µm.

$$\frac{dF}{dr_w} = 1.373 U_{10}^{3.41} r_w^{-3}(1 + 0.057 r_w^{1.05}) * 10^{1.19e^{-B*B}}$$

The empirically derived B = (0.380-log(r_w)/0.650.

The model was compared to measurements of sodium at ten European stations in Norway, Denmark and the Netherlands.

2.5 Aerosol dynamics module - SALSA

The work presented in Paper V was preceded by several studies dealing with aerosol dynamics coupled to chemistry in chemical transport models[47-55]. An extensive search among these for readily available aerosol modules led to the choice of the SALSA aerosol module [54], originally developed at the Finnish Meteorological Institute. SALSA had been optimised to work fast enough to be implemented in large three-dimensional models such as GCM or CTM. In the SALSA implementation in MATCH, three dynamic particle features are processed: nucleation – how particles are formed from gases; condensation – how gas phase species are transferred to the solid phase on the surface of already existing particles; and coagulation – how particles collide with each other and coalesce to form larger particles. Other important mechanisms that influence the particle population are deposition and transport, which are treated outside SALSA in MATCH.

The aerosol distribution is represented by ten size bins, divided into three regimes representing particles with different characteristics. Regime 1, with three size bins logarithmically distributed between 3 and 50 nm, contains one internal mixture of organic carbon and sulphate. Regime 2, with four size bins between 50 and 0.7 μm, contains one population of sulphate, organic carbon and black carbon and another with sea salt, sulphate, organic carbon and black carbon. The third regime, with three size bins starting from 0.7 μm, contains three externally mixed classes: a. sea salt; b. primary organic carbon; and c. dust (Figure 6).

The number of particles within a size section is monodisperse, meaning that there is no distribution within the section, even though the distribution of size bins is logarithmic, motivated by the normally logarithmical behaviour in measurement data [56]. Size bins 1-7, regimes 1 and 2, are dealt with by the moving centre technique [57] while the larger sizes, regime 3, are fixed. The moving centre method implicates size bins with fixed upper and lower limits of the section, but the size can move within the bin. When the size reaches one of the boundaries, all mass is transferred to the next bin and a new characteristic size of the bins is achieved by averaging and conserving both the number and volume of the particles. While this may lead to empty size bins, this is smoothed out by the transport from adjacent cells in the three-dimensional model.

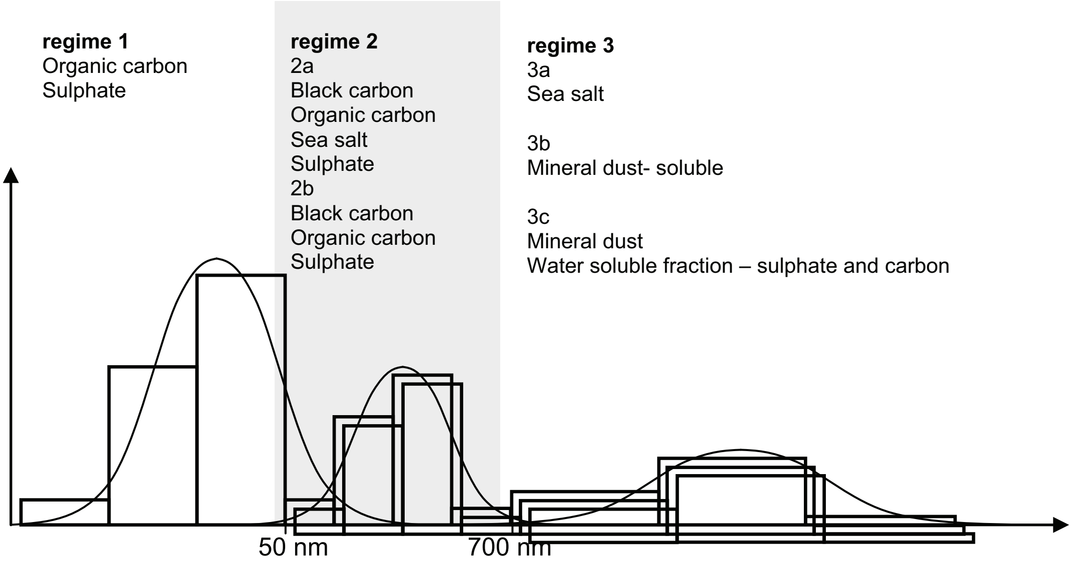


Figure 6. The distribution of size bins in the SALSA model.

New particles are formed by nucleating gases, and this adds particles to the particle population of the smallest size bin. The process is modelled together with condensation, as these two processes compete for the available gas: the question is whether it will nucleate to new particles or will condense on already existing particles. The nucleation parameterisation describes the nucleation of 3 nm particles, which is the lower limit of the model and not the sub micrometer particles that are created very first. The growth rate needed for this shift in size-space is reported in [58]. The real nucleation rate can be calculated in the default set-up by binary nucleation [59], ternary nucleation [60], kinetic nucleation [61] or activation type nucleation [26], but so far the MATCH model can only provide information for binary nucleation, H_2SO_4 and H_2O, and ternary nucleation, H_2SO_4, H_2O and NH_3.

The condensation of sulphuric acid to all sizes and regimes is determined by the collision rate between particles and gas molecules and consequently by the surface of the particle population, the temperature, i.e. the speed of the gas molecules and the diffusion coefficients of the particles (considered only for the smaller particles), and the gas. For a gas to condense, the partial vapour pressure of the gas in the atmosphere must exceed the saturation vapour pressure for the gas over the particle surface. The saturation vapour pressure is very small for sulphuric acid, and is approximated in the model to zero.

The mass transfer from gas to particle is calculated using the condensation equation for the gas concentration (C_i) or the particle concentration (c_i) of compound *i* summed over all bins [62]:

$$\frac{dC_i}{dt} = -\sum_{j=1}^{n} \beta_{i,j} C_i$$

where $\beta_{i,j}$ is the collision rate between particles in bin *j* and gas molecules.

$$\beta_{i,j} = \frac{2(d_i + d_j)(D_i + D_j)(Kn + 1)}{0.377Kn + 1 + \frac{4}{4\alpha}(Kn^2 + Kn)}$$

dependent on d_i and d_j, the diameters of the condensing molecule and the particle, as well as D_i and D_j, their respective diffusion coefficients. K_n, the Knudsen number, is a relation between the mean free path of the condensation process (λ) and the characteristic size of the particles involved.

$$Kn = \frac{2\lambda}{d_i + d_j}$$

The mean free path, λ, is dependent on the diffusion coefficients and the thermal speeds of the particle and the molecule (c_i and c_j).

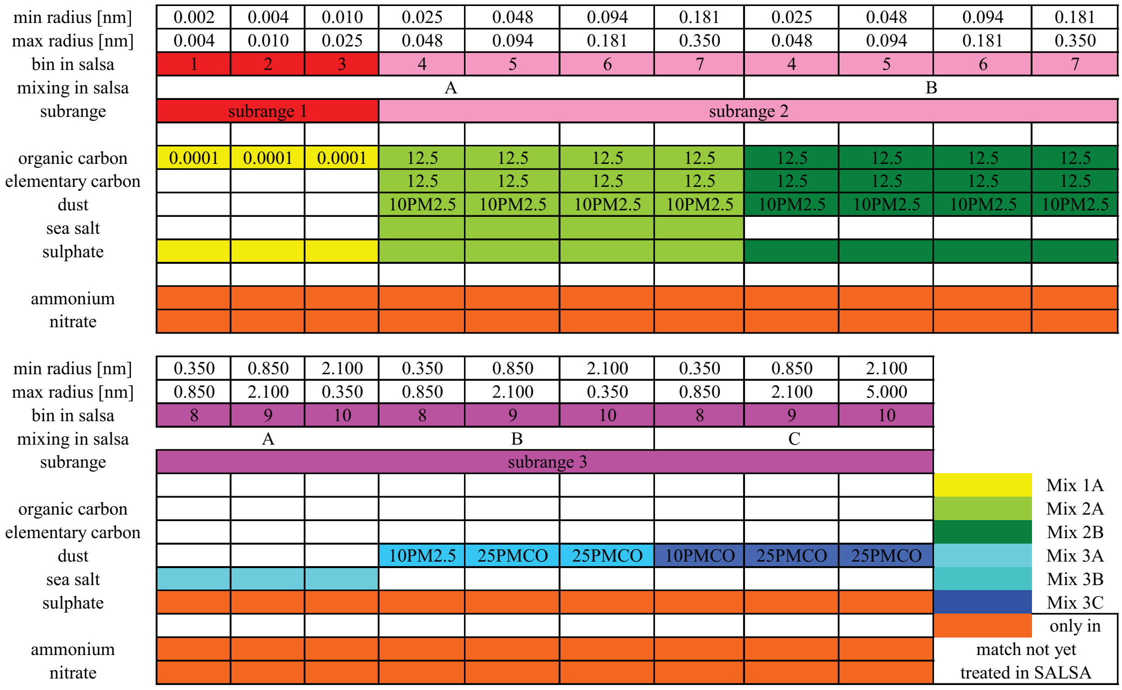
As modelling coagulation can be a computationally expensive process, the coagulation coefficients for each size bin pairs and pressure level are calculated once at the beginning of a simulation. The dry mean diameter for each size bin is used, and the coefficient is then scaled according to the actual wet diameter in each time step. What makes it costly is the number of different combinations between classes, which is why the coagulation in SALSA is not calculated for all collision pairs but only where they have a significant effect on the number or volume. The changes in particle number and volume are then calculated according to [57], a semi-implicit scheme that requires no iterations.

SALSA was originally optimised for use in a general circulation model, GCM, where one of the main purposes is to get a correct radiative budget on a longer time scale. It thus has some different requirements than a CTM, which is used for air quality and long range transport of air pollutants. Some changes were made to adjust it to MATCH. The mass and number of the larger sized particles were also saved; these are not of importance for climatic effects but for the total deposition of PM (Paper V).

In the MATCH-SALSA model, the reactions for ammonium sulphate and ammonium nitrate are replaced by the dynamic condensation in SALSA. After SALSA, the ammonium is distributed in the size bins where there is available sulphate, and the residual ammonium together with the HNO_3 are put in equilibrium with the ammonium nitrate, meaning that ammonium nitrate can either form (condense) or be consumed (evaporate). The ammonium nitrate is then apportioned to the size classes.

The emissions used in the first model set-up with SALSA were originally developed for the EURODELTA modelling inter-comparison exercise for regional scale CTMs in Europe [21]. They have also been used in several other studies [24, 28, 31]. The emissions are assembled for eight main sectors:

combustion in energy and transformation industries, non-industrial combustion plants, combustion in manufacturing industry, production processes, solvent and other product use, road transport, other mobile sources and machinery, and agriculture. The sectors all have different emission patterns with regard to their vertical profiles and temporal diurnal, weekly and seasonal distributions. The way in which total NMVOC is distributed among the species is also prescribed for each sector.



min radius [nm]	0.002	0.004	0.010	0.025	0.048	0.094	0.181	0.025	0.048	0.094	0.181
max radius [nm]	0.004	0.010	0.025	0.048	0.094	0.181	0.350	0.048	0.094	0.181	0.350
bin in salsa	1	2	3	4	5	6	7	4	5	6	7
mixing in salsa	A							B			
subrange	subrange 1			subrange 2							
organic carbon	0.0001	0.0001	0.0001	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
elementary carbon				12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
dust				10PM2.5	10PM2.5	10PM2.5	10PM2.5	10PM2.5	10PM2.5	10PM2.5	10PM2.5
sea salt				🟩	🟩	🟩	🟩				
sulphate	🟨	🟨	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
ammonium	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧
nitrate	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧

min radius [nm]	0.350	0.850	2.100	0.350	0.850	2.100	0.350	0.850	2.100
max radius [nm]	0.850	2.100	0.350	0.850	2.100	0.350	0.850	2.100	5.000
bin in salsa	8	9	10	8	9	10	8	9	10
mixing in salsa	A			B			C		
subrange	subrange 3								
organic carbon									
elementary carbon									
dust				10PM2.5	25PMCO	25PMCO	10PMCO	25PMCO	25PMCO
sea salt	🟦	🟦	🟦						
sulphate	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧
ammonium	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧
nitrate	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧

🟨	Mix 1A
🟩	Mix 2A
🟩	Mix 2B
🟦	Mix 3A
🟦	Mix 3B
🟦	Mix 3C
🟧	only in match not yet treated in SALSA

Table 1. Size distribution of emissions in chemically external mixes. xPM2.5 and xPMCO refer to x % of the total emissions of PM2.5 and coarse PM, respectively.

The aerosol species that have previously been modelled without aerosol dynamics by the MATCH model. These simulations will hereafter be called MATCH-Europe. Results from SALSA-MATCH and MATCH-Europe simulations (Paper V,[63]) are assessed at 13 European stations from the co-operative program for monitoring and evaluation of long-range transmissions of air pollutants in Europe (EMEP) [64]. (Section 3.2)

3 SELECTED RESULTS AND DISCUSSION

3.1 Impactor and cyclone measurements

The element concentrations of particles in urban and rural Dar es Salaam are presented in Table 5 together with data from Khartoum [65] and Gaborone [66]. The elements identified as originating from crustal material in Khartoum, Si, K, Ca, Mn, Fe, Ni, Cu, Rb and Sr, are all, except for Ca, of significantly higher amounts in Khartoum - where the source is Saharan dust - than elsewhere. The exception, Ca, is higher in Dar es Salaam. The source of Ca might be the cement industry at Waso hill, a few km north of Dar es Salaam, which quarries limestone from a coral limestone bed [67]. Cl of sea salt origin in a coastal city is expected to be present in higher amounts. This is indeed the case in Dar es Salaam as compared to Gaborone and Khartoum.

The source assignment by PCA gave two to three principal components for each dataset (rural fine particle fraction, urban fine fraction, rural coarse fraction, urban coarse fraction), presented in Table 2.

Particle samples				
Rural		Urban		
Fine particles	Coarse particles	Fine particles	Coarse particles	Identified Source
Cl, Se	Br, Cl	Cl, Se	Br, Cl, S	Sea spray
	Fe, K, Mn, Rb, Si, Ti		Fe, K, Mn, Rb, Ti	Soil
			Ca, Cu, Ni, Pb, Sr, Zn	City road dust
Br, K, BC, Rb		Br, K, BC, Rb		Biomass
Cu, Fe, Mn, Ti, Pb		Cu, Fe, Mn, Ti, Pb, Br Ni, Zn		Industrial and traffic

Table 2. Source assignment from principal component analysis for elements present in particle samples in Dar es Salaam.

Comparisons of concentrations of elements in PM1 to PM2.5 (Figure 7) show five elements, K, Zn, BC, Pb and Br, for which most of the mass appeared to reside in the PM1 fraction, and one element, Cl, for which there was no linear correlation between PM1 and PM2.5, the latter possibly indicating different sources of Cl in small and larger particles.

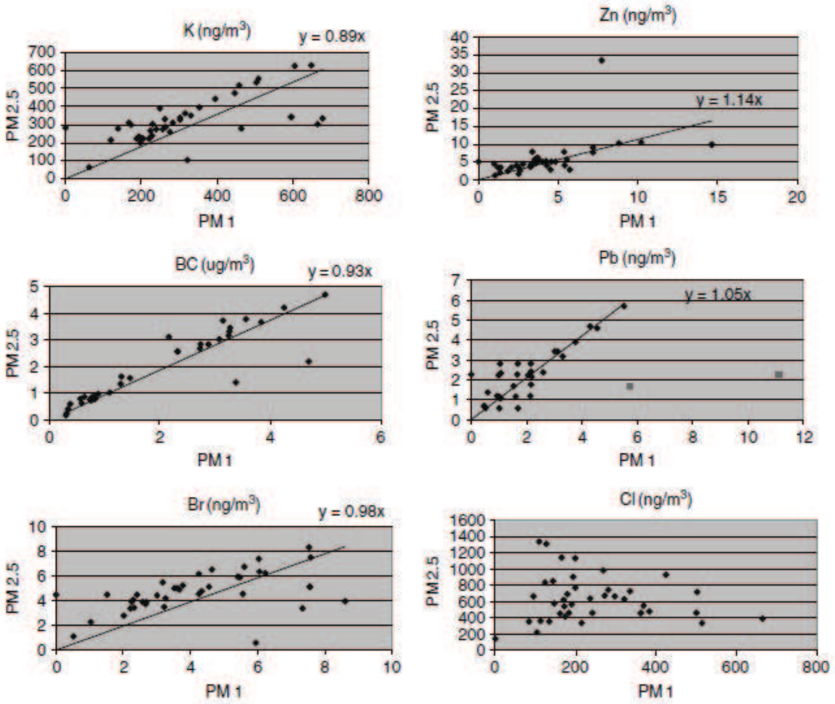


Figure 7. Adapted from Paper 1. Relation between the mass of PM 1 and PM 2.5 for six elements in urban Dar es Salaam. Note that two values were excluded for Pb in calculating the regression curve.

	Khartoum		Gaborone		Dar es Salaam	
	Coarse	Fine	Coarse	Fine	Coarse	Fine
Si	16500	6430	4443	ND	ND	ND
S	250	430	127	1161	680	1000
Cl	ND	ND	112	104	4500	1200
K	2750	510	593	645	420	350
Ca	4700	1460	763	162	4900	270
Ti	700	195	188	41	100	7.6
Mn	70	36	53	14	27	2.5
Fe	5650	1790	2365	604	610	44
Ni	7	3	ND	ND	1.2	1.6
Cu	8	3	10	7	3.6	6.4
Zn	25	19	21	28	40	91
Br	2.5	4	15	116	3.1	9.3
Rb	5	2	12	3	1.1	1
Sr	30	9	6	2	12	0.9
Pb	8	7	38	232	12	25
BC	300	3000	ND	1300	250	3600

Table 5. Mean values of element concentrations and BC (Black Carbon) in ng/m^3 within PM10 measured in Khartoum, April-May 2001 [65], Gaborone, July-August 1999 [66] and urban Dar es Salaam, October 2001 (Paper I). ND = Not detectable.

3.2 MATCH model performance in Asia as compared to Europe

3.2.1 Surface ozone

In Southeast Asia, 55 stations that measured ozone were compared to the output of the model (Paper II). Unfortunately, only 19 of them were categorised as remote. As ozone varies on a sub-grid scale near the emission sources, urban and rural stations can not represent the modelled concentrations for the 40*40 km^2 grid cell. Where the emission of NO is large, the reaction $NO+O_3\text{->}NO_2+O_2$ is enhanced and thus the ozone concentrations decrease. This may be the explanation for the model's overestimation of the ozone concentrations as compared to measurements. This is also confirmed by the underestimation of NO_x and VOC at some of these stations. The remotely located stations were better reproduced, but still with a mean bias of 7 ppbv, and for individual stations of -7 to 17. European MATCH results for 85 stations showed a bias of only -0.08 ppbv and a correlation of 0.71; however, for single stations, the bias ranged from -8 to +8 and the correlation from 0.45 to 0.86 [63]. Noteworthy is that the measured mean for all European stations was 32 ppbv while the mean of data from Asian stations was 16. Comparing the only 13 Asian stations where the ozone exceeded 20 ppbv to measurements, the relative bias falls to 4 ppbv, indicating that the model performs better for higher concentrations or that the lower measurements originate from less representative locations.

No correlation at remote stations in Southeast Asia could be made as the measurements were only monthly or annual averages. The best correlated non remote stations had correlations above 0.6, while this was around 0 for the most poorly correlated case; these data came from a station situated near the coast, which can explain the deviant model behaviour as the spatial integration in the model involves a part of sea with lower deposition and less diurnal variation, as opposed to vegetated land. There might also be local wind patterns, such as the land-sea breeze, that are not reproduced by the model but influence the actual ozone variation.

The isoprene emissions were varied in a sensitivity test to biogenic VOCs in Southeast Asia. The isoprene increased ozone where NO_X was high and decreased it where NO_X was low. The only available inventory in this study was from 1995 [43]. At present, it should be possible to obtain better emission estimates globally by using models that simulate the exchange of gases between the biosphere and the atmosphere (e.g. MEGAN) [68].
Both Paper III and [44] conclude that the upper boundary condition has an effect on the surface ozone concentration. For this reason, attributing correct boundary values might help in improving the model simulations for Asian conditions.

3.2.2 Concentrations of particulate nitrate, ammonium and sulphate

Nitrate

The Japanese station, Fukue Island, had daily measurements of nitrate and sulphate for one month. For nitrate, the correlations of diurnal means for the different models varied from 0.46 to 0.74 with a mean of 0.63. For MATCH in Europe, the corresponding results for nitrate at different stations ranged from 0.18 to 0.84, and the mean for 29 stations was 0.64. Including SALSA aerosol dynamics in MATCH, the correlations were 0.13 to 0.87 with a mean of 0.60. The results in Asia are thus well within the range of the modelling performance in simulating day-to-day variation at remote measurement sites in Europe. The biases of annual mean concentrations were not as good, however. More stations were available for the comparison of the annual mean concentration. The annual mean of nitrate is shown in Figure 8 for Asian sites and in Figure 9 for remote European sites. Nitrate is underestimated at most sites. The inclusion of the SALSA aerosol dynamics module however improves the bias in Europe. A comparison of the relative biases for individual stations and models shows that the European simulations reproduced the annual means with relative biases in the worst cases 82% vs 67% (MATCH-Europe vs MATCH-SALSA) and in the best -2% vs -1%. The mean bias was -27% (both MATCH-Europe and MATCH-SALSA). In Asia, models underestimate the measured concentrations with a negative relative bias up to 99% (worst case) and at best 40%. At one station, remote station nr 25 situated at an altitude of 1470 m, the models overestimate the measured concentrations. The reason for this could be the models' mean altitude for that specific grid box being lower than the actual altitude at the measurement site. This can lead to higher nitrate concentrations in the models' results. Finally, at the remote station at Fukue, four models overestimate the monthly mean while three models underestimate it. The consequence is that the model ensemble mean exhibits a relative bias of +30%.

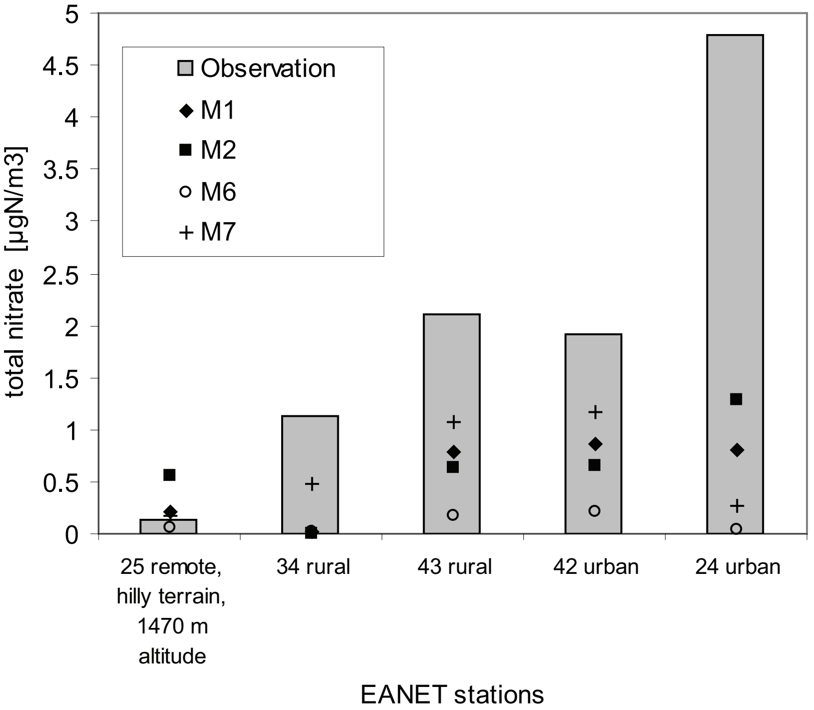


Figure 8. Annual mean concentrations of total nitrate measured at six stations in Asia and modelled with six models, including MATCH (M6). The annual means are calculated from four months of data representing three seasons.

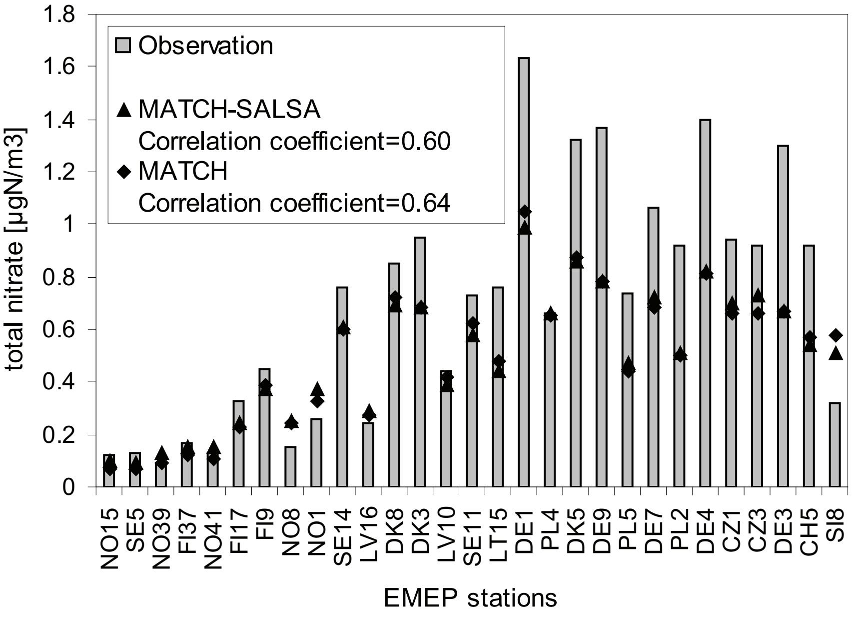


Figure 9. Annual mean concentrations of total nitrate measured at EMEP [51] stations in Europe and calculated with MATCH-Europe (original configuration) and MATCH-SALSA. The correlation coefficients presented in the frame are for diurnal means and are averaged for all stations.

Ammonium

For ammonium, there were no time series with diurnal measurements in the Asian study (Paper III). There were measurements in Europe with diurnal resolution at 28 remote stations. The correlations for MATCH-Europe and MATCH-SALSA (within brackets) to measurements range from 0.18 (0.09) to 0.84 (0.86) with a mean of 0.61 (0.56). Ammonium is also mostly underestimated, but the negative bias decreases with the new aerosol dynamics module SALSA (Figure 11). The relative bias for all stations was -34% (-13%). The five stations presented in Figure 10 show five very different behaviours. Station 25, the remote Malaysian site at high altitude, is overestimated by all models. In a comparison with Figure 8 it appears that the reasons for this can be the same as for nitrate. The measurements made at the Russian rural station 34 and the urban Malaysian site nr 24, in Petaling-Jaya, are underestimated by all models, but this is also the case for nitrate (Figure 8) and sulphate (Figure 12).

The concentrations at two Vietnamese stations 43 (rural) and 42 (urban) are both strongly overestimated. The models also overestimate sulphate (Figure 12) at the urban station, indicating that the ammonium sulphate in the models is high. At the rural station both the measured sulphate and nitrate are higher than the results given by the models, which indicates that the models overestimate ammonia emissions. The spread of the models' results is high for these stations, which could be caused by differences in emissions in the models. The height of the lowest layer and the vertical emission distribution are plausible reasons for the spread among the modelled results.

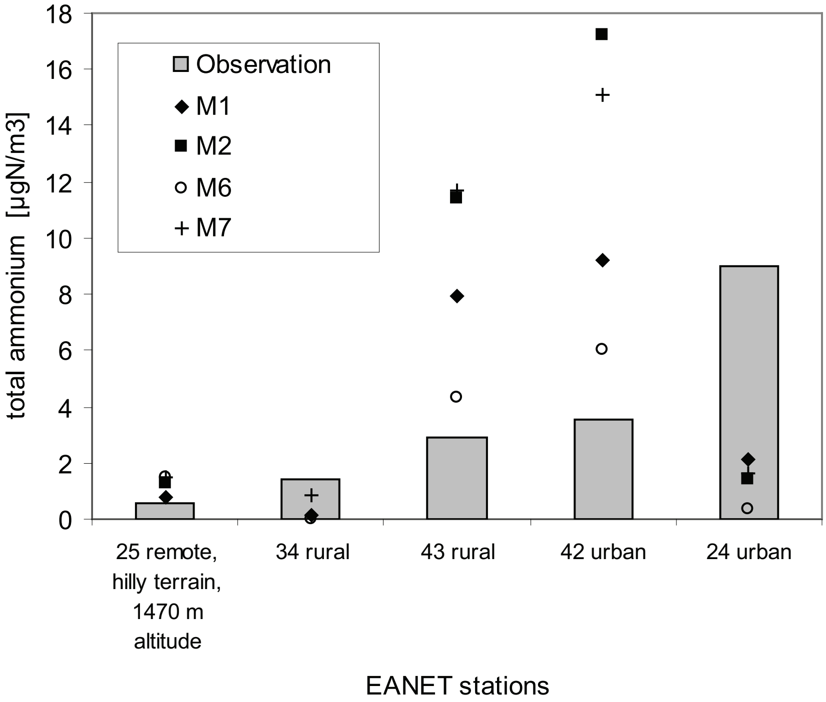


Figure 10. Annual mean concentrations of total ammonium measured at five stations in Asia and modelled with four models, including MATCH (M6). The annual means are calculated from four months of data representing three seasons.

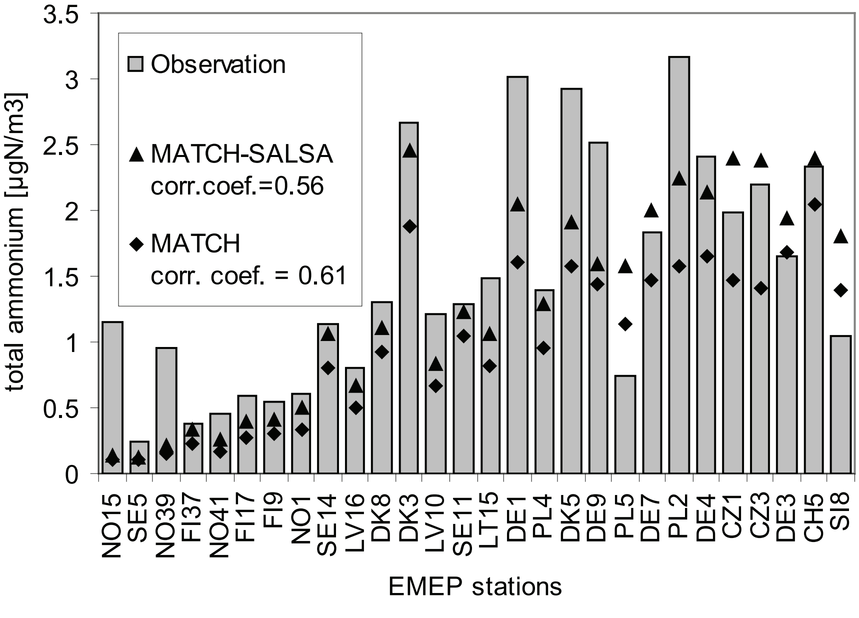


Figure 11. Annual mean concentrations of total ammonium measured at EMEP stations in Europe and calculated with MATCH-Europe and MATCH-SALSA (aerosol dynamics configuration). The correlation coefficients presented in the frame are for diurnal means and are averaged for all stations.

Sulphate

The correlation for modelled sulphate at Fukue Island varies between 0.11 and 0.83 among the eight models, with a mean correlation of 0.57, where the MATCH model displayed 0.83. The relative bias of the ensemble mean is -47% and is even higher for the MATCH model, namely -59%. The relative bias for 46 stations in Europe is -7% for MATCH-SALSA and -25% for MATCH-Europe (Figure 13). The better bias for all stations in MATCH-SALSA is an effect of overestimation at some stations and underestimation at others. When looking at the absolute bias, it is seen to be of the same magnitude for both the European simulations. The mean correlation coefficient for all European stations is 0.48 in MATCH-SALSA and 0.59 in MATCH-Europe. The correlations are as good for single stations in Europe as for Fukue Island in Asia.

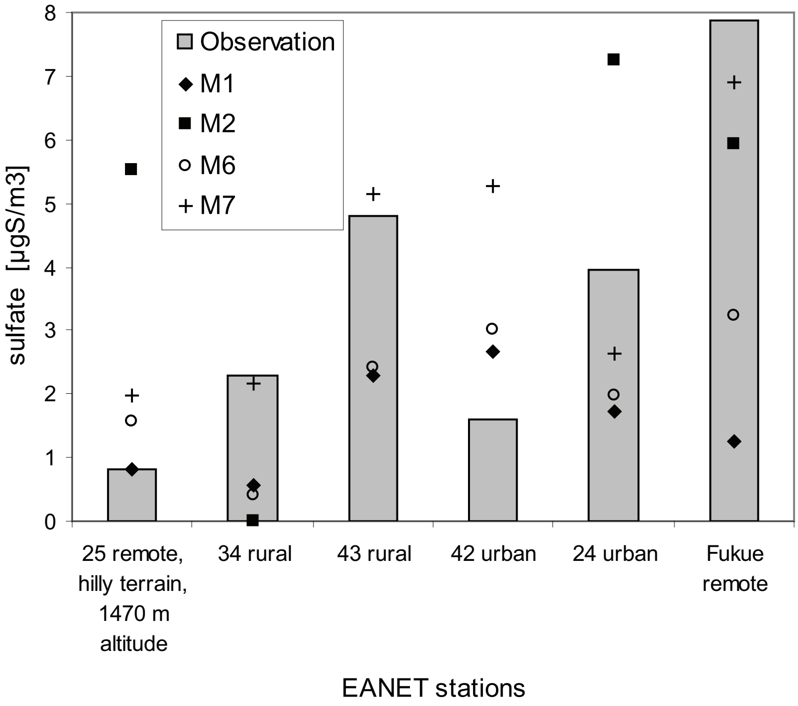


Figure 12. Annual mean of sulphate measured at six stations in Asia and modelled with four models, including MATCH (M6). The annual means are calculated from four months of data representing three seasons.

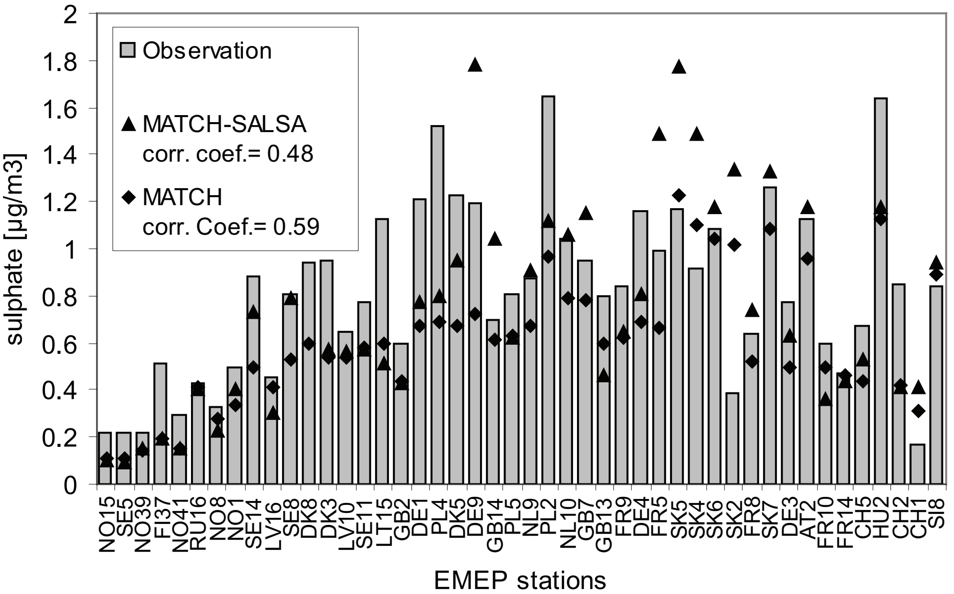


Figure 13. Annual mean concentrations of total sulphate measured at EMEP stations in Europe and calculated with MATCH-Europe (original configuration) and MATCH-SALSA (aerosol dynamics configuration). The correlation coefficients presented in the frame are for diurnal means and are averaged for all stations.

3.3 Model to model comparisons in Asia

Four models in the Asian study had size resolved aerosol dynamic mechanisms and another four models, one being MATCH, had bulk representation of the aerosol. Later work with implementation of the SALSA aerosol dynamics in MATCH allows for representation of the number of particles of different sizes and different chemical content. The results from MICS Asia indicate that the MATCH results for bulk properties and partitioning between gas and particle species in the original configuration were similar to results obtained with sophisticated aerosol dynamics schemes in other models. Model M1 had the most comprehensive size resolved particle representation, with 16 size bins and the SCAPE2 thermodynamic scheme [69], dynamic condensation, coagulation and sea salt emission (which MATCH did not include at that time), while MATCH (M6) had a simple bulk description with equilibrium for total NH_3 and NH_4NO_3. Figure 14 shows that the performance of M6 is very similar to that of M1 in terms of gas-to-particle partitioning of three main species. As highlighted earlier, the bias with respect to measurements increases when more detailed aerosol descriptions are introduced in MATCH.

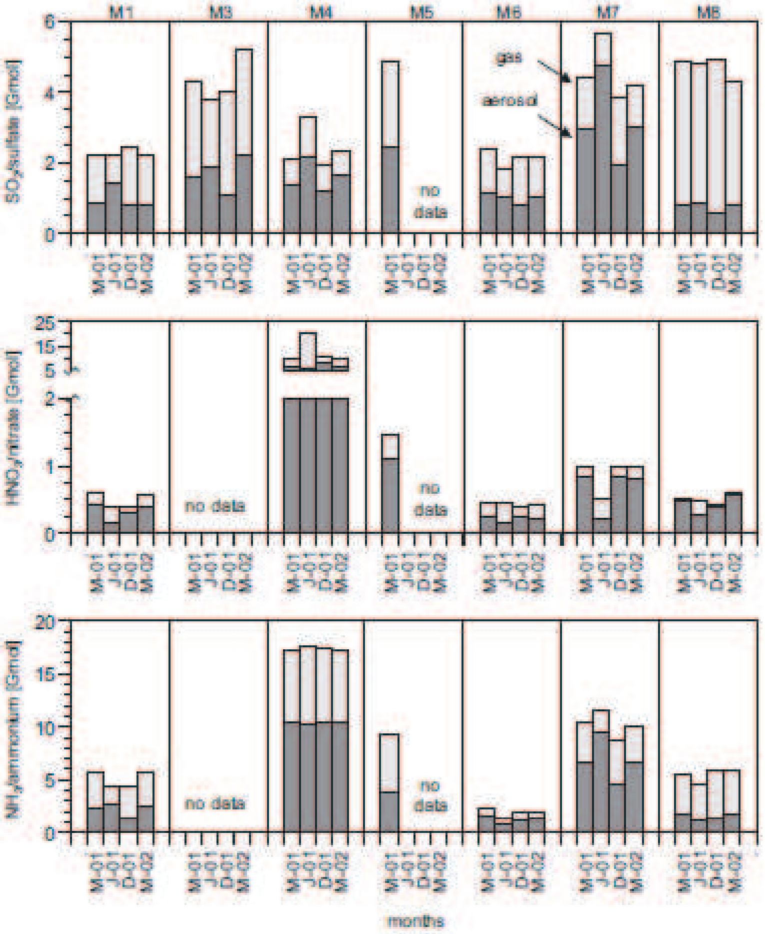


Figure 14. Adapted from Paper III. Model to model comparison of models M1 to M8 for the months of March, July and December 2001 and March 2002.

3.4 Particles from sea spray

The first evaluation of the sea salt emission formulation with Na concentrations from eight measurement stations showed high correlations with respect to modelled concentrations: minimum 0.4, average 0.6 and max 0.7. The relative bias ranged from 0.3 to 7.6, with a mean for all stations of 3.6. When the parameterisation was generalised to an arbitrary number of size bins, the mean relative bias decreased to 2.4 but the correlations also decreased to a minimum of 0.2, an average of 0.4 and a maximum of 0.5. The latter investigation was carried out for 364 daily values from the SALSA-MATCH simulation of 2003.

The species compositions of PM at the Hyytiälä and Birkenes field stations (both in Scandinavia) are somewhat different (Figure 15). Sea salt clearly dominates the mass at both stations, but the mass load for sea salt is 10.0 $\mu g/m^3$ for Birkenes (situated near the Norwegian coast) and only 1.6 for Hyytiälä (in inland Finland).

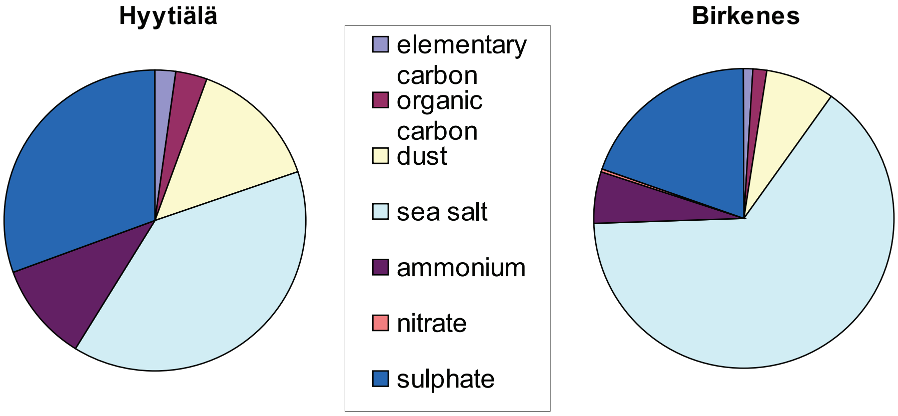


Figure 15. The modelled mass distribution in terms of species. The total particulate mass was 15.6 µg/m^3 at Birkenes and 4.0 µg/m^3 at Hyytiälä.

The simulation shows different dispersion patterns for sea salt particles of different sizes. The smallest particles of size class four (to the left in Figure 16) are rapidly transformed to larger particles and thus not transported far over land, while the larger particles (to the right in Figure 16) reach further from the coast. This result strictly shows the effect of transport, transformation and deposition, leaving out the effect of chemical reactions that emitted sea salt undergoes.

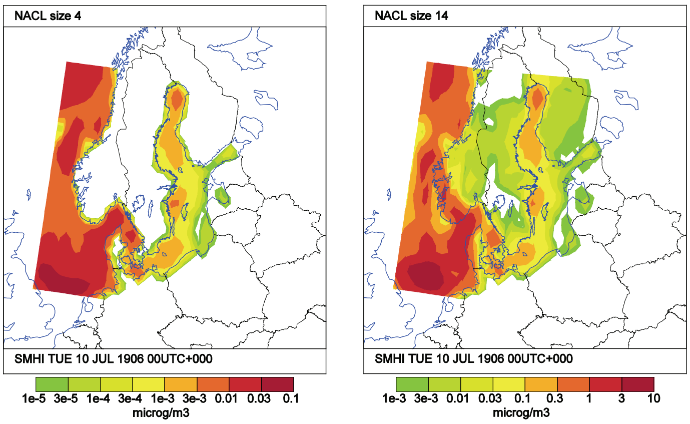


Figure 16. Modelled NaCl concentrations in Northern Europe illustrating different dispersion patterns for small particles (class 4, size bin 4), left, and larger particles (class 14, size bin 7), right.

3.5 Size distribution of particle mass and number at European stations

All evaluations of the SALSA-MATCH model presented in this section can be seen as a first comparison of model to measurement, which is a first step in finding out how to proceed with the development of the aerosol dynamics representation in the CTM.

The modelled species composition of the total particulate mass was compared with measurements from the Birkenes field station for July 2006 (Figure 17). The elemental carbon was well simulated, while the organic carbon is underestimated in the model - as expected, as there is no condensation of secondary organic aerosol in the model. Both ammonium and sulphate are slightly too high in the model, while nitrate is far too low. The dust in the model should resemble the measured potassium, magnesium and calcium, and the missing mass in measurements is the difference between the measured mass of PM10 and the total mass of measured chemical components.

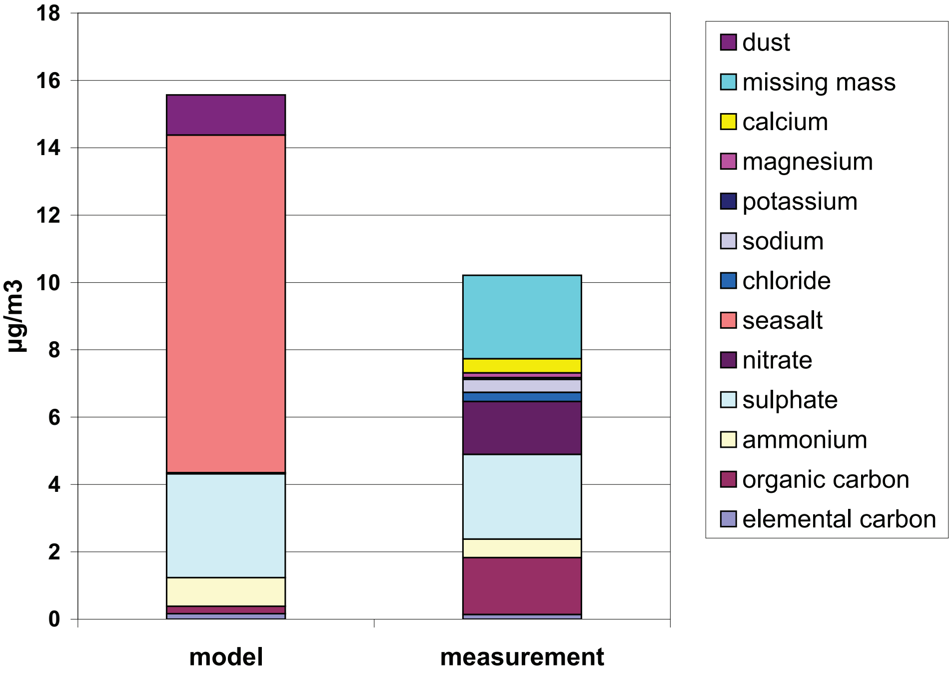


Figure 17. Modelled and measured elemental concentrations at Birkenes. Monthly mean for July 2006.

The size distributions of different elements at two stations in Scandinavia are presented in Figures 18 and 19. The size distribution of sea salt particles shown in these figures has a mass peak near 1 µm. Sulphate and ammonium follow each other, and no particulate nitrate is present at the Birkenes station location (Figure

17), which suggests an environment rich in sulphate, i.e. the available sulphate in the model is larger than the total ammonia and ammonium.

The organic and elemental carbon concentrations are similar to each other for size bins 3-6. For the smaller particles, classes 1-3, the source of particle matter is condensation and a small primary emission of organic carbon. These emissions have large uncertainties as the size distribution of emissions is not fully understood.

For one station, Birkenes, the number size distribution was compared to DMPS measurements (Figure 20). The very high number of particles in the smallest nucleation bin shows that the nucleation in the model is too prominent, or occurs too often. As nucleation takes place only when there is not enough surface for the gas to condense on, this might be solved by a higher attribution of emissions in the accumulation mode size bins. It is expected that new, size dependent emission factors for primary particles will soon be available through the emission initiative in the European integrated project on aerosol cloud climate air quality interactions, EUCAARI [70]. This will possibly improve the simulation of number size distributions.

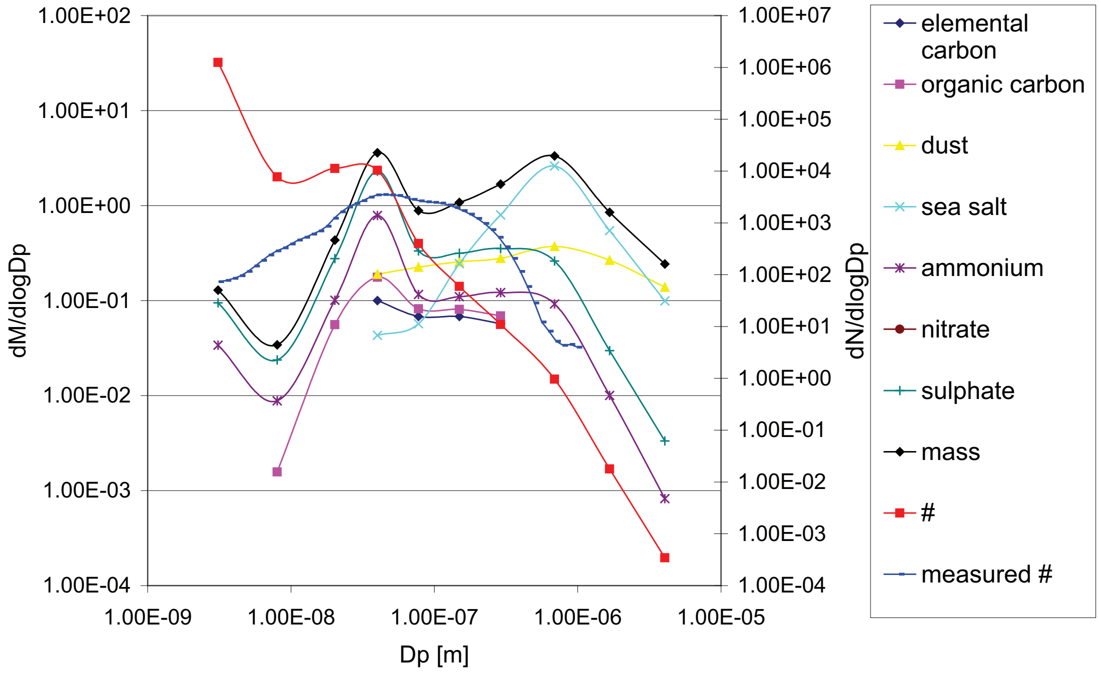


Figure 18. Size distributions of mass and number concentration in Hyytiälä, Finland.

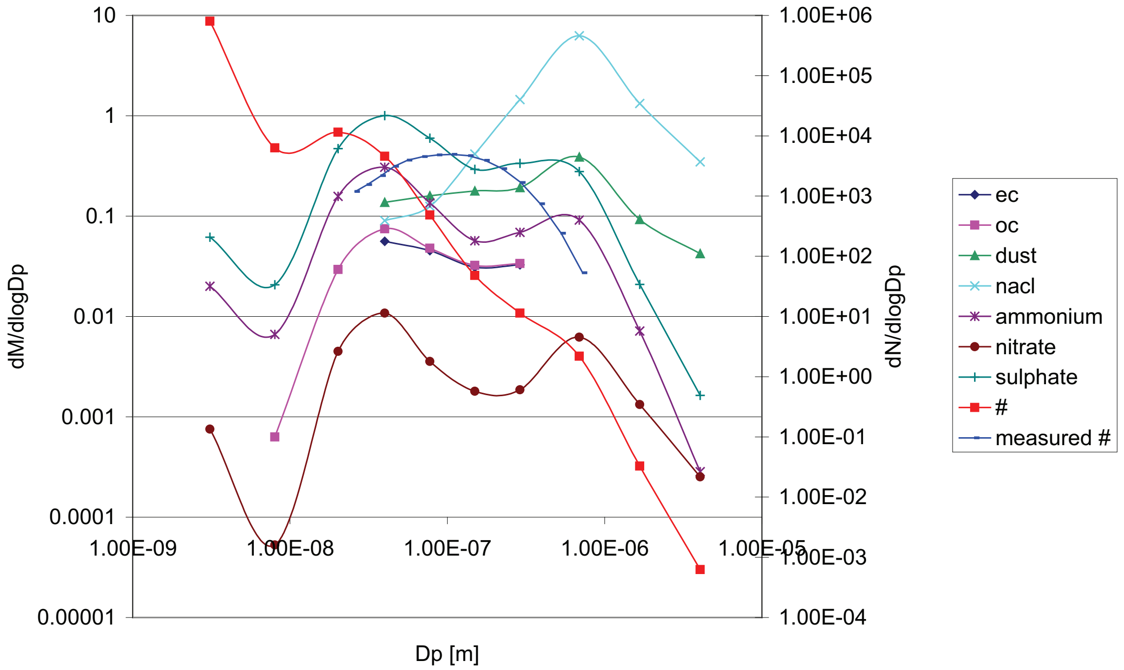


Figure 19. Size distributions of mass and number concentration in Birkenes, Norway.

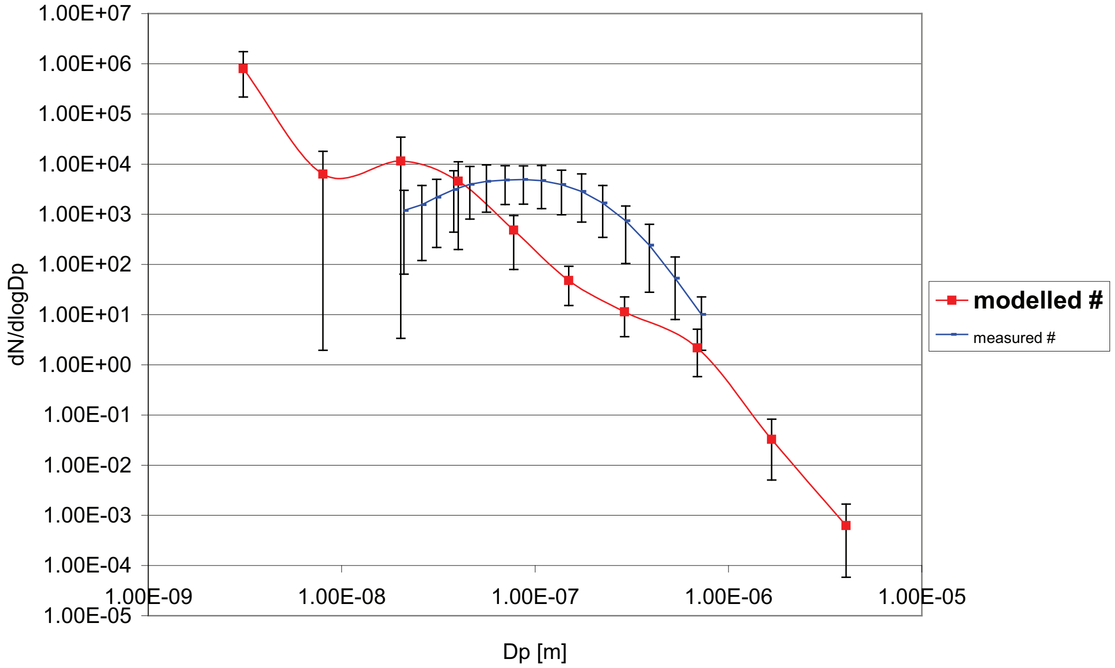


Figure 20. Average for July 2006 of counted ultrafine particles by DMPS at Birkenes, Norway, compared to the model output. The error bars indicate the 10 and 90 percentiles for hourly data during the month.

4 CONCLUSIONS AND OUTLOOK

4.1 Airborne particles in Dar es Salaam

This study suggested five major sources of particulate air pollution within and outside Dar es Salaam. These are sea spray, soil, city and road dust, biomass and industrial/traffic. The city itself contributes to the concentrations of elements in the particulate air pollution in Dar es Salaam. The comparison between PM1 measurements by cyclone and PM2.5 measurements by the conventional dichotomous impactor indicates that especially anthropogenic particles showed enhanced concentrations within the city which to a large extent originate from particles smaller than 1 μm. As they are in the smaller size fraction of PM2.5, this implies that the particles are more numerous than if they had been more evenly distributed in the size range. This is important, as there are indications that such fine particles are of greater harm to human health than larger particles. The result also encourages the use of the cyclone as a relative simple, low cost sampling technique that gives relevant information on the hazardous sub-micron particles in the environment.

Designing a measurement campaign stretching over different seasons is important as the levels of air pollution may differ over the year. Most concentrations of elements are higher in the dry month of October but the exceptions, Br, Pb (both elements being fingerprints of traffic) and BC (fingerprint of biomass burning), indicate that there is higher traffic and more domestic biomass burning during the cooler month of May.

A few studies have been carried out in Dar es Salaam after 2001. One of the studies [71] recommended air quality monitoring on a regular basis and the use of non leaded petrol to control the damages from air pollution in Dar es Salaam. The National Environmental Management Council of Tanzania ran the Air Quality Monitoring Capacity Building Project during the period 2005-2007 with the aim of collecting baseline data on PM10 and other air quality variables at five different locations in Dar es Salaam [72]. Paper I and [72] conclude that there is a need for much longer time series.

4.2 Ozone in South East Asia

The MICS Asia study on ozone [37] concluded that most of the participating models captured the key features in ozone distribution such as O_3 enhancement in the Western Pacific in March and in Northeast Asia in July, although the absolute model values differed from each other. This means that the models are approaching good results, but there is room for improvement. For Southeast Asia the MICS study concludes [37] that the models are more diverse here and their ability can not be clearly established because of lack of databases of observations. In paper III one model was compared to additional measurement data in

Southeast Asia and the conclusion was drawn that most of these data seem to be affected on a local scale, as they are often too low, compared to remote European stations. These weaknesses in the measurements make it difficult to say whether the absolute model output is strictly correct. For some Southeast Asian stations, the performance of the model was comparable to the European case, which indicates that the model is successful in Asia as well.

4.3 Model harmonization in Asia

Studying how several models perform with respect to each other is an important evaluation tool when other validation data are sparse. In MICS Asia this was done for photochemistry and bulk particulate species, as not all the models had detailed aerosol size distribution representations. With respect to the MATCH model, a conclusion was that the performance for total amount of nitrate, ammonium and sulphate was similar to other models with more highly developed aerosol dynamics schemes. For the ensemble of models, the conclusion is that there is a spreading in the output from the different models, and the ensemble mean at stations with annual measurements is most often not better than individual results. Most often all the models overestimate or underestimate the measurements. Concerning the correlation of models to measurements done at one station, Fukue Island, for nitrate and sulphate, the ensemble mean is good, around 0.6.

4.4 Improvements on the knowledge of sea spray aerosol

Sea salt is an important contributor to the levels of concentration of particles, especially near coasts and for the coarser fraction. They scatter solar radiation, participate in cloud processes and, with their seasonal variation as well as total loading, they may have an impact on both local and global climate [73].

Paper IV concludes that the correlation of modelled sea salt to measurements is good but that the model bias is high.

For the newest sea salt formulation (Paper V), the bias was better but the model still over predicts most measurements.

For the newest sea salt formulation (Paper V) only 2003 and July 2006 were simulated for the smaller geographical area shown in Figure 16. As more measurement data are available for later years in Europe, a future aim is to use those to improve the model formulation and also to investigate the sensitivity to emission formulations. In addition to NaCl originating from the ocean, DMS (Dimethyl Sulphide) could be interesting to model as a precursor to particulate sulphate as well as the organic part of sea spray that can be up to 90% of the emitted submicron mass in the summer period [74].

The aerosol dynamics of the equilibrium between the gas and particle phase of chlorine will also be an interesting topic for future studies.

4.5 Better understanding of the dispersion of aerosol particles of different sizes

A size distributed aerosol dynamics scheme was tested together with a well functioning regional CTM. The first results were compared to a few measurements with varying results. The conclusion of this study so far is that the SALAS module is fast enough to use in a regional CTM. The coupling between SALSA and the CTM MATCH works, and the system delivers reasonable particle concentrations with regard to the input of emissions to the model.

The total modelled annual nitrate, ammonium and particulate sulphate were compared to 29 representative European stations with and without SALSA. The results was that the correlation mean for all stations decreased a little when adding the aerosol dynamics, but the best correlation at a single station was even better and the worst was even lower. The mean bias did not change for nitrate but was lower with SALSA for ammonium and sulphate.

Tunved et al. [75] propose two important branches in the aging of the size distribution. The first is the same as the one modelled in SALSA-MATCH, consisting of growth by condensation and coagulation. The second is processing by non precipitating clouds. The latter is not yet included in the MATCH model system. For better modelling results employing aerosol dynamics calculations, it is crucial to use size dependant emissions as well as representative measurement stations [76] in model validation. It is problematic to measure a remote/background value that should represent a larger area while the biosphere emits organic condensing gases causing nucleation events at the site [26]. Other important improvements would be better condensation routines for both semi-volatile inorganic and organic species, with consideration taken to equilibrium of semi-volatile gases condensing to available particles, including mixed particles. When this is achieved it is possible that we will have a regional model that gives us consistent and useful information about species, size distributions and masses.

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Contribution to the papers

Paper I.
I conducted the field work together with Per Jonsson. The idea for the paper was Prof. Selin Lindgren's, who also assisted in the writing of the paper. All analyses and preparations of particle measurements were done by me with the assistance of the staff at the Environmental Physics group at the Physics Department of the University of Gothenburg.

Paper II.
The model was set up, the results analysed and the paper written by me with the supervision of Dr. Engardt at SMHI. Emissions were prepared by Professor Streets in the MICS Asia study.

Paper III
I produced and reported data from the MATCH model to the MICS Asia study. I prepared the presentation to and joined discussions at the MICS workshop 2005. The author of the paper was Dr. Hayami.

Paper IV
I carried out the programming of the Mårtensson parameterisation and worked with the evaluation with respect to measurements. Dr. Foltescu was the main author of the article.

Paper V
I carried out the implementation of SALSA in the MATCH model together with Robert Bergström. The evaluation with respect to size distributions and the writing was made by me.

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Paper 1