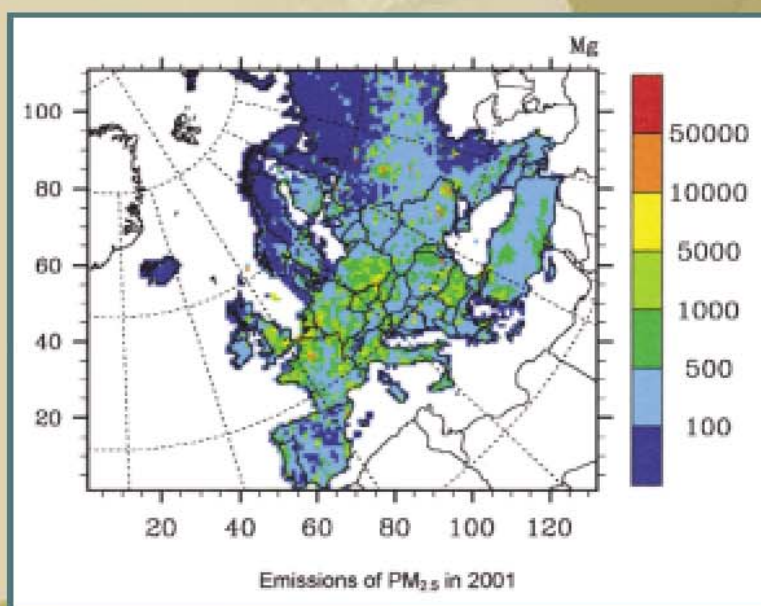


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Transboundary particulate matter in Europe

Status Report 4/2003



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**EMEP Co-operative Programme for Monitoring and Evaluation of the
Long-Range Transmission of Air Pollutants
in Europe**

**Transboundary particulate matter in Europe
Status report 4/2003**

**Joint
CCC & MSC-W & CIAM
Report 2003**



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Executive Summary

This status report on Particulate matter (PM) presents information compiled within EMEP and co-operating programmes on regional PM emissions and concentrations for years 2000 and 2001. The main purpose of this report is to provide a critical discussion of the information on aerosols currently available from EMEP's observational data, modelling results, and emission inventories, to point out strengths and shortcomings, and to make specific recommendations for future improvements. Special emphasis has been placed on interlinking the discussions on monitoring and modelling results, on investigating as to what extent currently available observations suffice for validating the EMEP model, and on identifying future tasks for improving both the emission compilation, the model development and the observational programme.

Fulfilling EMEP's objectives poses a significantly larger challenge for particulate matter than for many other single-component pollutants due to the highly complex and variable nature of particles in air. EMEP's monitoring network for PM mass concentrations is relatively young and still expanding. Clearly, monitoring of PM mass concentrations of fine and coarse mode particles still need to be extended significantly. Currently, only six countries have reported PM₁₀ and PM_{2.5} data to EMEP. By also considering data from AIRBASE this figure is increased to 25 countries.

There exists a partial overlap between EMEP and Airbase monitoring stations for PM₁₀, and it is important that both networks make use of relevant data and exchange information. However, measurements of policy-relevant quantities (PM₁₀, PM_{2.5}) under the EC-requirements for PM monitoring are not sufficient to meet EMEP's objectives. More detailed information on chemical and physical properties of aerosols is needed in order to understand and correctly predict long-range trans-boundary transport of aerosols, their deposition, and their effects on human health. EMEP therefore needs to pursue a dual strategy of extending its own aerosol monitoring programme of particulate matter and of obtaining supplemental information from external data providers. In particular, for obtaining information from advanced and resource-intensive measurement techniques it is essential to intensify cooperation with the research community.

Special attention has been given to the characterisation of the integrated mass of particles up to 2.5 µm (PM_{2.5}). This is because the recent WHO review recommended to use PM_{2.5} as the indicator for health effects induced by particulate pollution, such as increased risk of mortality in Europe (WHO, 2003). It should be noted that PM_{2.5} is most frequently used in health studies as an indicator for fine particles. PM_{2.5} has been selected as the indicator for fine particles to include all accumulation-mode particles during high relative humidity, while recognising that it also includes some coarse-mode particles between 1 and 2.5 µm.

In the future, when sufficient monitoring data is compiled, PM₁ is likely to be a better metric for health assessments, since in a typical aerosol size distribution the minimum between the fine and the coarse mode is found around 1 µm. PM₁ would also facilitate to separate long-range transported accumulation mode

particles with relatively large anthropogenic contributions from coarse particles with a large contribution of natural sea salt and/or mineral dust and with much higher deposition rates.

At present, however, PM_{2.5} is to be used for health assessment of particulate matter, and the capability of EMEP to provide reliable PM_{2.5} mass concentration data over Europe should be evaluated. Comparison of modelled results with few available observations has indicated reasonably high correlation coefficients (0.5-0.6) and a general underestimation of PM_{2.5} mass by 20-30%. The underestimation amounts to 30-50% for PM₁₀. To understand the reasons for this systematic underestimation of the modelled mass concentrations with respect to observations a study of the separate chemical aerosol components has been presented.

The comparison of chemical speciation of modelled and observed aerosol concludes that the model reproduces aerosol inorganic composition reasonably well, but problems still remain in reproducing the organic fraction and in attaining full mass closure. The main discrepancies are found to be related to carbonaceous and mineral dust constituents and the unaccounted part of the aerosol. The main reasons for these discrepancies are most likely due to:

- **measurement artefacts:** evaporation of volatile organic compounds and volatile NH₄NO₃, as well as water in aerosols
- **model limitations:** secondary organic aerosols and re-suspended and wind eroded mineral dust are not yet included in the model calculations, mostly due to a lack of reliable measurement information to parameterise these processes.
- **Emission assumptions** on the chemical composition of PM anthropogenic emissions in the model: appropriate information on the chemical speciation of PM emissions is crucial for adequate modelling of the aerosol chemical composition

Thus, the major error sources are volatile species, water, and, perhaps most importantly, an insufficient characterisation of “elemental” and organic carbon (EC/OC). This implies that priority should be given to the compilation of EC/OC measurements on a regular basis with a reasonably high spatial coverage.

Introduction and characterisation of organic aerosol in the Unified EMEP model should now receive first priority, in particular work addressed to distinguish between the biogenic and anthropogenic contribution to organic aerosol mass. More complete information on the EC/OC content of aerosols is required, both concerning primary emissions of the aerosol and air concentrations. Such information is a prerequisite for improving the parameterisation of EC/OC in the EMEP Unified model.

While requirements for PM emission reporting are concerned only with PM mass, information concerning the chemical speciation of primary PM emissions has been left to dedicated expert studies. In 2003, 24 Parties submitted data for primary PM mass emissions, the level in reported detail varies significantly. In

many cases, the largest disagreements between nationally reported data and model estimates from the RAINS model can be traced back to different estimates for a few sectors. Assuming the implementation of present emission control legislation, PM emissions are expected to further decline in the future, with larger reductions of the coarse fraction than of PM_{2.5}.

Preliminary estimates of black carbon emissions suggest a share of typically 10 percent in total PM_{2.5} emissions. In the EU-15, the majority of black carbon originates from the transport sector, while in Central and Eastern European countries domestic combustion of solid fuels makes the largest contribution. These types of studies are extremely useful to analyse the actual share of mineral components, black or elemental carbon and organic carbon in primary PM emissions, and further efforts in this respect are both welcomed and encouraged.

Finally, there is a general recommendation to include advanced techniques for measuring more detailed particle properties, such as particle number distributions and optical particle properties at a limited number of EMEP sites. Such data could also be obtained by intensifying EMEP's cooperation with the scientific community and will become essential for understanding cloud processes and analysis of synergies with climate effects.

1. Physical characterisation of particulate matter across Europe in 2000 and 2001

by Svetlana Tsyro, Michael Kahnert and Leonor Tarrasón

Information available to EMEP on the physical properties of the aerosol, mass and particle number distributions are presented in this chapter. The information compiled from most recent EMEP monitoring results, AIRBASE data, national networks and research campaigns is compared here with EMEP modelling results. No effort has been made to combine model and measurement data at this stage but rather to indicate short-comes and progress in the data compilation.

Special attention is given to compilation of PM_{2.5} data as it has been recommended as indicator for health effects by the latest WHO report (WHO, 2003). In addition, arguments are given on the need to compile particle number concentration data for future analysis of health impacts and analysis of synergies with climate.

1.1 Measured and modelled European PM₁₀ and PM_{2.5} mass concentrations

EMEP network

The geographical distribution of the annual averages of PM concentrations in Europe in year 2000 is shown in Figure 1.1. The upper panels show modelling results for PM₁₀ and PM_{2.5} from the EMEP aerosol research model for 2000, using emissions of gaseous precursors SO₂, NO_x, NH₃, NMVOC and primary PM_{2.5} and coarse PM reported to UNECE/EMEP (Vestreng, 2003). The middle panels show PM₁₀ and PM_{2.5} results measured at various EMEP stations. Only six sites measured PM_{2.5} in 2000, and only four of these had data coverage over 50% to provide temporally representative annual average values. The lower panel is showing total suspended particle (TSP) mass concentrations observed at EMEP sites.

The model consistently underestimates the measured PM₁₀. This is because not all aerosol components were included in the present calculations, i.e. Secondary Organic Aerosol (SOA), re-suspended and wind blown dust were not accounted for in the model. On the other hand, the model correctly predicts rather low PM₁₀ values in the Alpine region, which is in accordance with the measurements. In Central Europe (Central and Southern Germany, Switzerland, Austria), model calculated PM₁₀ are rather close to the measurements, although the modelled PM₁₀ gradients in those regions (it is very pronounced!) appear lower than the measured ones.

The geographical distribution of PM concentrations in Europe in year 2001 is shown in Figure 1.2. The most significant difference between 2000 and 2001 is that more observational data is available for 2001.

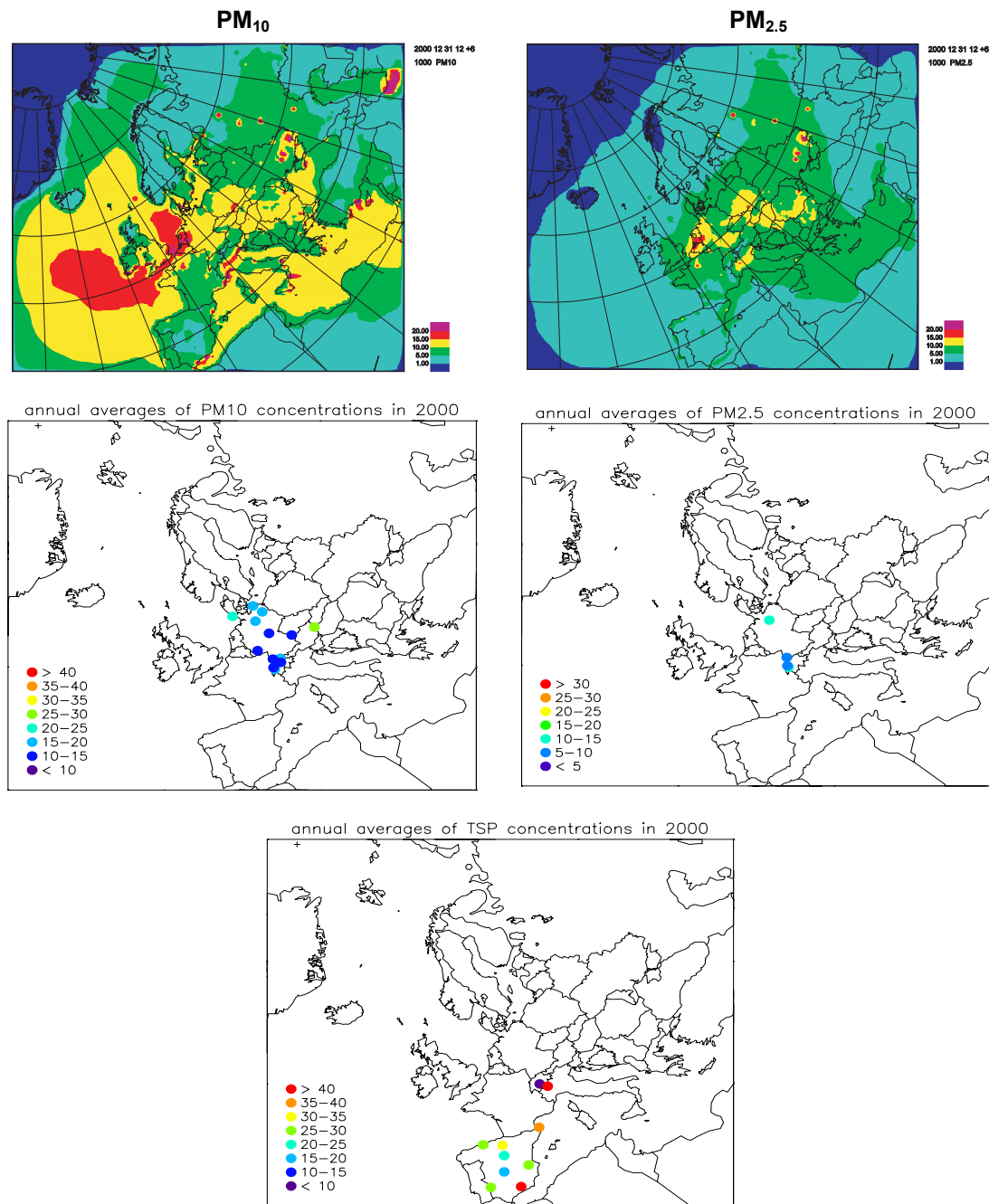


Figure 1.1: Annual averages of calculated and measured PM concentrations in 2000: PM₁₀ and PM_{2.5} calculated with the EMEP aerosol model - the upper two panels, PM₁₀ and PM_{2.5} measured at EMEP stations - the middle two panels, and TSP measured at EMEP stations – the lower panel (only stations with data coverage over 50% are shown).

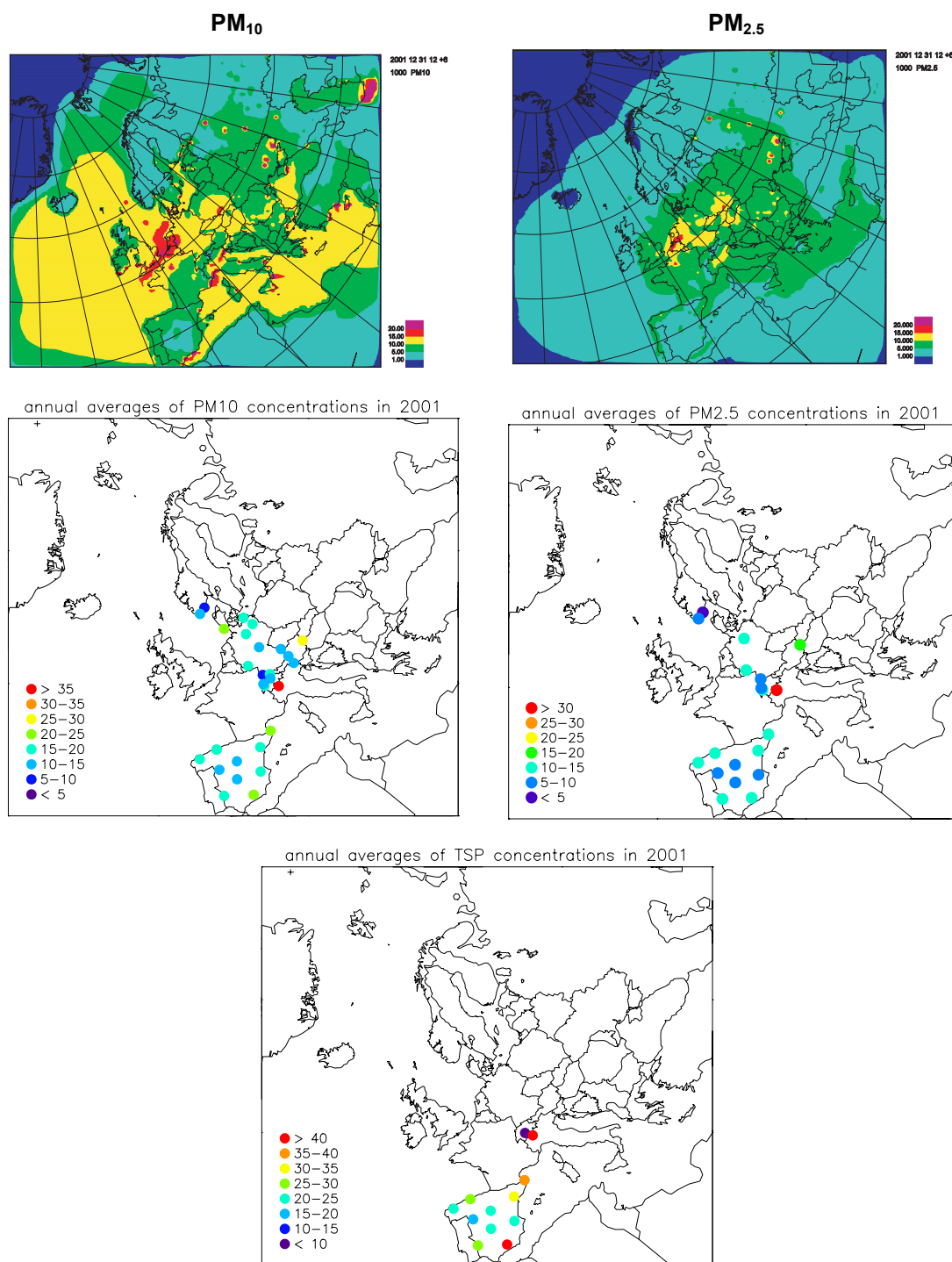


Figure 1.2: Annual averages of PM₁₀ and PM_{2.5} concentrations calculated with the EMEP aerosol model (upper panels) and observed at EMEP stations in 2001 (middle panels), as well as observed TSP mass concentrations observed in 2001.

Particularly notable are the Spanish observations, which show a relatively large difference between PM_{2.5} and PM₁₀ values, and again between PM₁₀ and TSP values. The significant amount of coarse mode particles observed in Spain indicates a high contribution from mineral dust aerosols. A good example of a

station strongly influenced by long-range transport of aerosols is Birkenes in Southern Norway. The annual average of PM₁₀ and PM_{2.5} concentration in 2001 is 6.06 µg/m³ and 4.04 µg/m³, respectively. The relatively high contribution of fine particles is mostly due to secondary inorganic and secondary organic aerosols. However, coarse mode particles (mostly due to sea salt) also play a role at Birkenes (see also Figure 2.17).

AIRBASE stations

Figure 1.3 and Figure 1.4 show bar graphs of the country- and annual averages of PM₁₀ concentrations. For comparison, we also show PM₁₀ concentrations from rural, urban, and street sites that were reported into the AIRBASE database maintained by the European Topic Centre on Air and Climate Change (ETC/ACC) under contract of the European Environmental Agency (EEA). Many of the AIRBASE data from rural sites are actually EMEP data that have been quality assured at and delivered by CCC to ETC/ACC. Note that differences across countries are of the same order of magnitude as differences between rural and kerbsite stations.

Figure 1.5 compares annual mean PM₁₀ concentrations in 2000 calculated with the EMEP aerosol model with data from the EMEP monitoring network and with rural measurements from AIRBASE. A fairly good agreement has been found between model calculated PM₁₀ and observations. The correlation coefficients between modelled and measured annual mean PM₁₀ are 0.68 for EMEP sites and 0.63 for AIRBASE rural sites, indicating that the model manages to predict the regional PM₁₀ gradients. Correlation coefficients vary for different countries from 0.51 at EMEP German sites to 0.81 at AIRBASE Dutch sites.

The aerosol research model underestimates the observed PM₁₀ concentrations by 31% at EMEP stations and by 44% at AIRBASE rural sites. Several factors can contribute to the discrepancy of model predictions and observations of PM₁₀.

- 1) The model does not account for Secondary Organic Aerosol (SOA), and re-suspended and wind eroded mineral dust (also biogenic aerosols can be important).
- 2) Anthropogenic emissions of primary PM are rather uncertain and difficult to verify, in particular concentrations of primary anthropogenic OC and anthropogenic dust. As we will see in the next chapter, the organic fraction can contribute substantially to the PM₁₀ mass, sometimes being the dominating aerosol component (even contributing more than sulphate).
- 3) There are several uncertainties in the measurements. Volatile species, such as water and volatile organic compounds in the condensed aerosol and in the gaseous phase are in thermodynamic equilibrium with each other at the time of sampling. Changes in the ambient conditions during transport and conditioning of the filter samples will shift this equilibrium and thus lead to the loss or addition of aerosol mass. Likewise the partitioning between gaseous and condensed chemical species, such as nitric acid and ammonia on the one hand and ammonium nitrate on the other hand, can change with shifting temperature, relative humidity, and pressure.

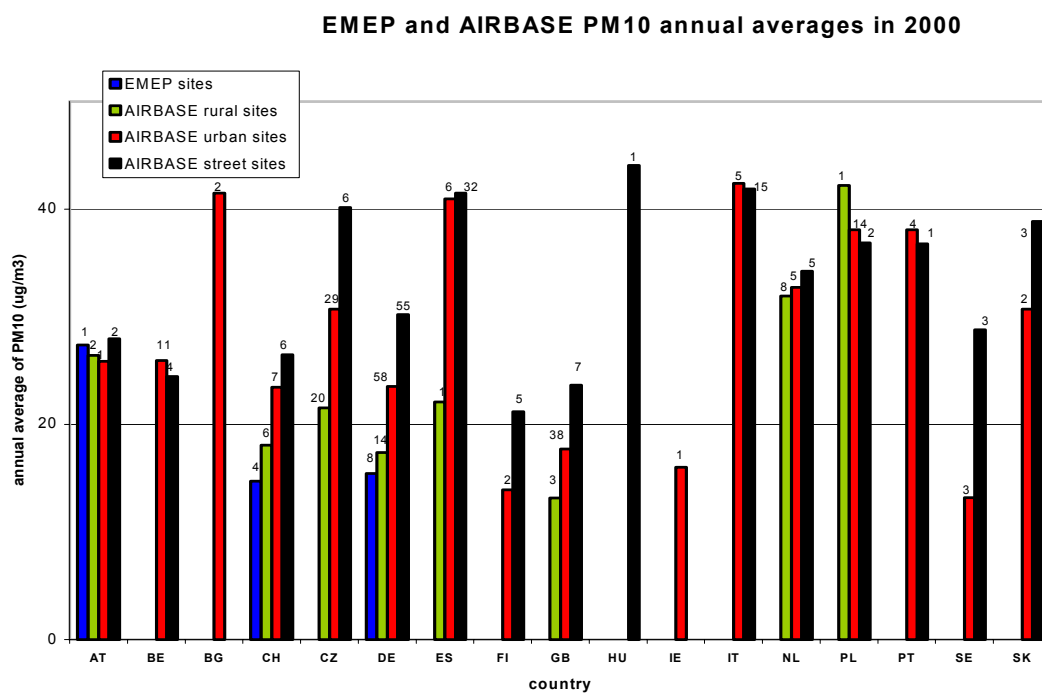


Figure 1.3: Annual country averages of PM₁₀ at EMEP stations and at rural, urban, and AIRBASE street sites in 2000. Numbers over each bar indicate the number of observation stations contributing to each country average.

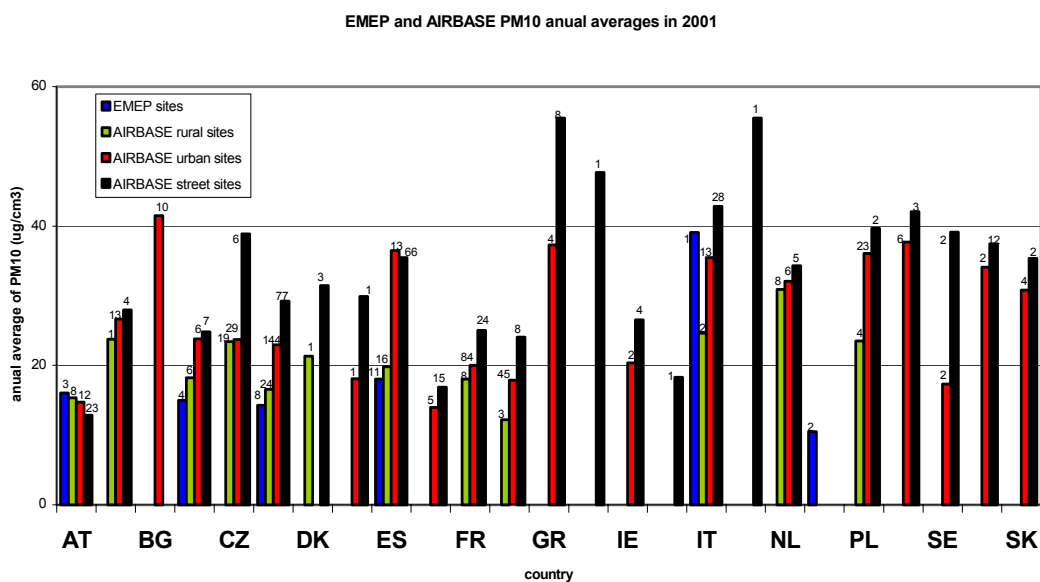


Figure 1.4: As Figure 1.3, but for 2001.

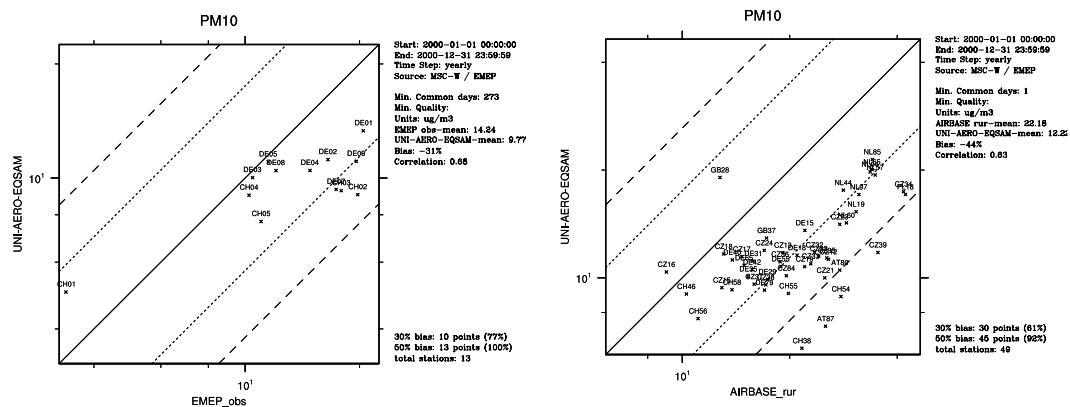


Figure 1.5: Scatter plots for PM_{10} : comparison between the EMEP aerosol model and EMEP observations (left panel), and between the EMEP aerosol model and AIRBASE rural data (right panel). Notice that here relative bias is calculated as $(Model-Obs)/Obs$.

1.2 Analysis of PM_{2.5} data: national Austrian network

WHO has recently completed a review on health aspects of air pollution by particulate matter (PM), ozone (O₃) and nitrogen dioxide (NO₂) (WHO, 2003). The review compiles strong evidence to conclude that fine particles (< 2.5 µm, PM_{2.5}) are more hazardous than larger ones (coarse particles) in terms of mortality and cardiovascular and respiratory endpoints in panel studies, and recommends to use fine particulate matter (PM_{2.5}), as the indicator for health effects induced by particulate pollution such as increased risk of mortality in Europe (WHO, 2003).

It should be noted however that PM_{2.5} is most frequently used in health studies as an indicator for fine particles. PM_{2.5} has been selected as the indicator for fine particles to include all accumulation-mode particles during high relative humidity, while recognizing that it also includes some coarse-mode particles between 1 and 2.5 µm. From a scientific standpoint PM₁ is likely to be a better metric, since in a typical aerosol size distribution the minimum between the fine and the coarse mode lies around 1 µm.

The recommendation of using PM_{2.5} as indicator for health effects demands reliable characterization of PM_{2.5} mass concentrations across Europe. Modelling and observed data are necessary for such characterization. However, rather little monitoring data is available for verification of PM_{2.5} concentrations. Here, we compare modelled PM₁₀ and PM_{2.5} with measurements at two Austrian and one Swedish site.

Modelled PM₁₀ and PM_{2.5} has been compared with the measurements from the Austrian AUPHEP research project of the Clean Air Commission of the Austrian Academy of Science together with a number of other Austrian institutions. The first site, AU01, is located in a residential area of Wien affected by traffic ("urban background"). The second site, AU02, is rural, with some influence of traffic (Streithofen). The measurement period was from 1.06.1999 to 31.05.2000. PM₁₀ and PM_{2.5} mass was continuously monitored with TEOM and measured with High-Volume Filter-Samplers. The TEOM method typically underestimates PM mass as compared to the gravimetric recommended methods due to heating of the sampled aerosols, which results in the loss of water and in losses of volatile NH₄NO₃ and organic matter in TEOM. This implies that we can expect lower PM₁₀ and PM_{2.5} concentrations from the measurements with TEOM methods as compared to gravimetric methods measurements.

Time series of daily averages of PM₁₀ and PM_{2.5} values calculated and determined with the gravimetric method are presented in Figure 1.6. For comparison, calculated PM₁₀ and PM_{2.5} are also plotted versus data from TEOM (see example for AU02 in 2000). Model calculated and measured PM₁₀ and PM_{2.5} show high daily correlation coefficients at the two different sites. The correlation coefficients vary from 0.57 to 0.68 for PM₁₀ and from 0.60 to 0.67 for PM_{2.5}.

In Figure 1.6, the mean PM_{2.5} and PM₁₀ concentration levels increase from the second half of 1999 to the first half of 2000. However, the model calculates a larger increase of mean PM concentrations than observed. The verification of model results showed that the model calculates noticeably lower average SO₄, NO₃ and NH₄ concentrations in 1999 than in 2000. Initial analyses have revealed

that the overestimation by the model of NO_3 and NH_4 concentrations in January-May 2000 is considerably greater than in June-December 1999. This is thought to be due to the effect of meteorological conditions in 1999 and 2000 on the gas/aerosol partitioning in the model, but needs more thorough examination. To verify the contribution of the other PM components was not feasible at the moment

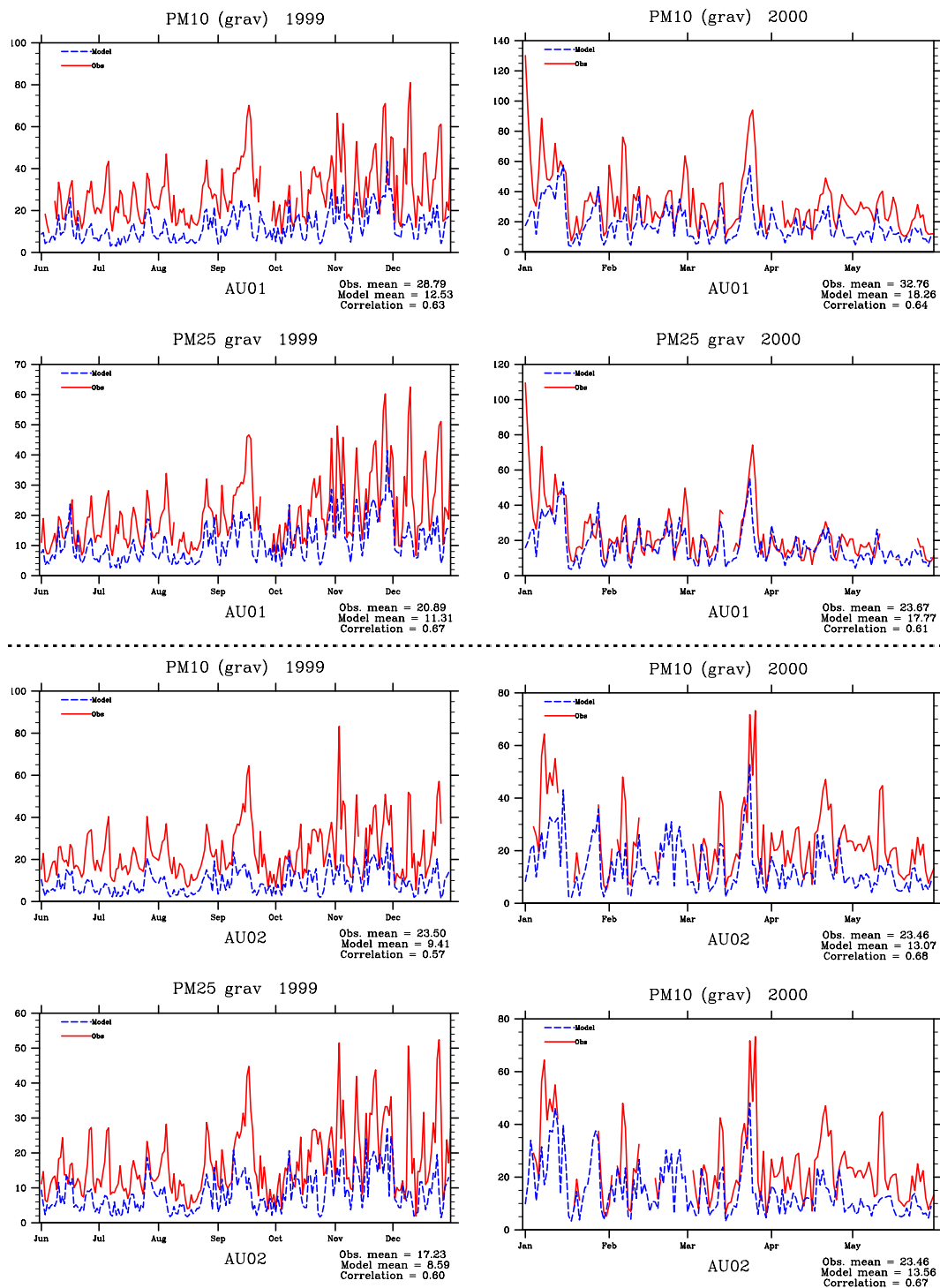


Figure 1.6: Time series of daily averages of PM_{10} and $\text{PM}_{2.5}$ concentrations calculated with the aerosol model (blue dashed curve) and measured (red solid curve) at Austrian sites (using the gravimetric method).

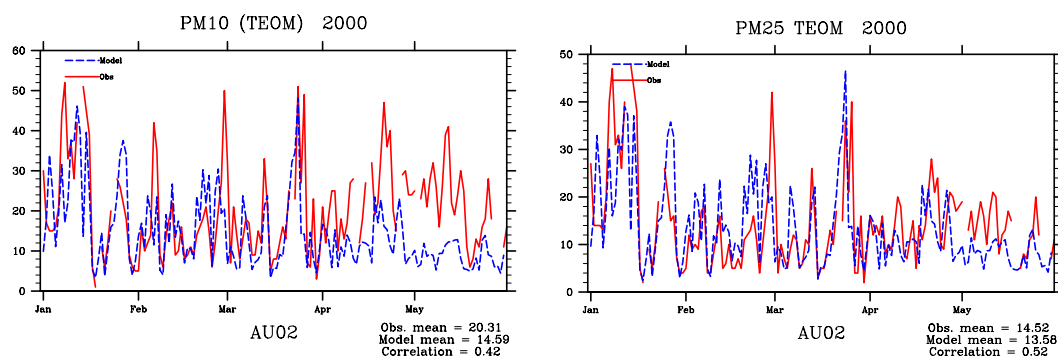


Figure 1.7: Time series of daily averages of PM_{10} and $PM_{2.5}$ concentrations calculated with the aerosol model (blue dashed curve) and measured (red solid curve) at AU02 in 2000 with TEOM.

Figure 1.6 and Figure 1.7 reveal that the model's underestimation of PM_{10} is larger than the overestimation of $PM_{2.5}$. This indicates that the model underestimation is more significant for coarse particle mass. This result was expected as re-suspended and wind blown dust, which can be important contributors to the coarse fraction both in cities and in the countryside, was not included in the model.

Figure 1.8 compares calculated and measured hourly time series of PM_{10} and $PM_{2.5}$ concentrations in June-December 2000 at Aspvreten (SE12), Sweden. Both PM_{10} and $PM_{2.5}$ are underestimated by the model from June to September, while in November-December calculated and measured concentrations are very similar. A plausible reason for this could be the inaccuracy of the seasonal variation of emission or the inaccuracy of the model calculation of removal processes. The correlation coefficients are 0.37 for PM_{10} and 0.4 for $PM_{2.5}$, which is regarded to be quite reasonable for hourly PM concentrations. Also here, the model predicts a too small coarse aerosol mass as the model under-prediction for PM_{10} is greater than for $PM_{2.5}$.

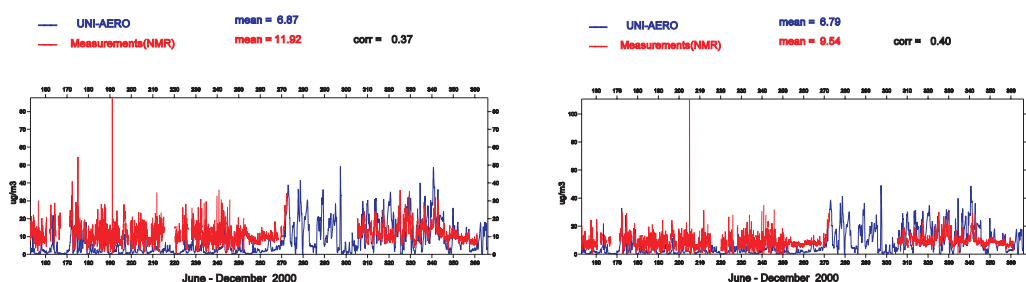


Figure 1.8: Hourly time-series of PM_{10} and $PM_{2.5}$ concentrations: calculated with the aerosol model and measured at Aspvreten, Sweden.

1.3 Comparison of measured and modelled particle number concentrations

Why monitoring and modelling particle number?

Particle mass is mostly determined by accumulation and coarse particles, whereas Aitken and nucleation particles make a negligible contribution to PM_{10} , $PM_{2.5}$, or even PM_1 . On the other hand, coarse particles contribute little to particle number densities. The main contribution to the particle number concentration comes from ultrafine particles (UFP), i.e. nucleation and Aitken particles, and to a lesser extent from accumulation particles. A better characterisation of nucleation and Aitken particles is needed to facilitate our understanding of adverse health effects of aerosols, and of the dynamic growth of Aitken particles to accumulation mode particles by heterogeneous chemical processes. Accurate prediction of the aerosol number is also important for estimating the indirect climate forcing of aerosols.

There is accumulating evidence that UFP with a diameter of less than 100 nm can be highly damaging to lung tissue, and that UFP have a much higher ability to damage the lung than particles of similar chemical composition and larger diameters (see Stone and Donaldson, 1998 and references therein). The alveolar macrophages, which play a key role in removing foreign particles from the lung airways and alveoli, are unable to remove UFP from the lungs as efficiently as larger particles. UFP may even damage macrophage cell function. As a result of the long residence time of UFP in the alveoli inflammatory reactions are caused in the lung, and particles and microbes may enter into the delicate lung tissue, where the damage becomes more severe and prolonged. Thus monitoring and modelling number concentrations, particularly of UFP, seems to be at least equally relevant for studying the negative health effects of aerosols as monitoring particle mass.

Secondly, our ability to accurately model cloud processing of aerosols by heterogeneous chemistry depends on adequate description of the particle number distribution. A much smaller fraction of Aitken particles compared to accumulation particles gets activated, but they gain water becoming interstitial aerosols. Even though the lifetime of interstitial aerosols can be rather short as they get scavenged by the cloud droplets, they contain a significant amount of water thus facilitating aqueous phase reactions. In clouds, this is believed to be the main mechanism of Aitken particles growth to the accumulation mode.

A third important point pertains to the aerosols' ability to act as cloud condensation nuclei. An increase in the number concentration of cloud condensation nuclei results in a larger number of cloud droplets. Given the same amount of water vapour, this results in a shift of the water droplets' size distribution towards smaller sizes. Thus, an increase in the number concentration of cloud condensation nuclei results in more and smaller droplets in the cloud. This change in cloud microphysical properties entails a change in the cloud radiative properties. The characteristic forward-scattering peak in the droplet phase function increases with the droplet size on the expense of side- and backward scattering. Consequently, clouds with smaller droplets show less forward scattering and more side or back scattering and therefore have a larger albedo (i.e. they reflect more visible radiation back into space). An increase in the number concentration of cloud condensation nuclei therefore leads, in general, to an increased negative climate forcing of clouds. This so-called indirect climate

forcing effect of aerosols is one of the largest uncertainties in present climate models. Accurate data and model predictions of aerosol number concentrations, especially for fine particles ($0.1\text{--}1\text{ }\mu\text{m}$), provide the basis for improving our ability to accurately predict the indirect climate forcing effects of aerosols.

Very limited measurement data on particle number concentrations is available. One of the most extensive networks for measuring particle number distributions in Europe is the Nordic network comprising several Swedish, Norwegian, and Finnish stations. As an illustration, Figure 1.9 shows some first results from a newly installed differential mobility particle sizer (DMPS) instrument at the EMEP site in Birkenes. The upper panel shows a time series of the particle number distribution for March 2003. One can clearly see several episodes of Aitken particles growing to accumulation size (f. ex. between day 72 and 75, and again between day 80 and 83), repeatedly fuelled by local nucleation events. Thus DMPS data provide us with valuable information about aerosol dynamical processes.

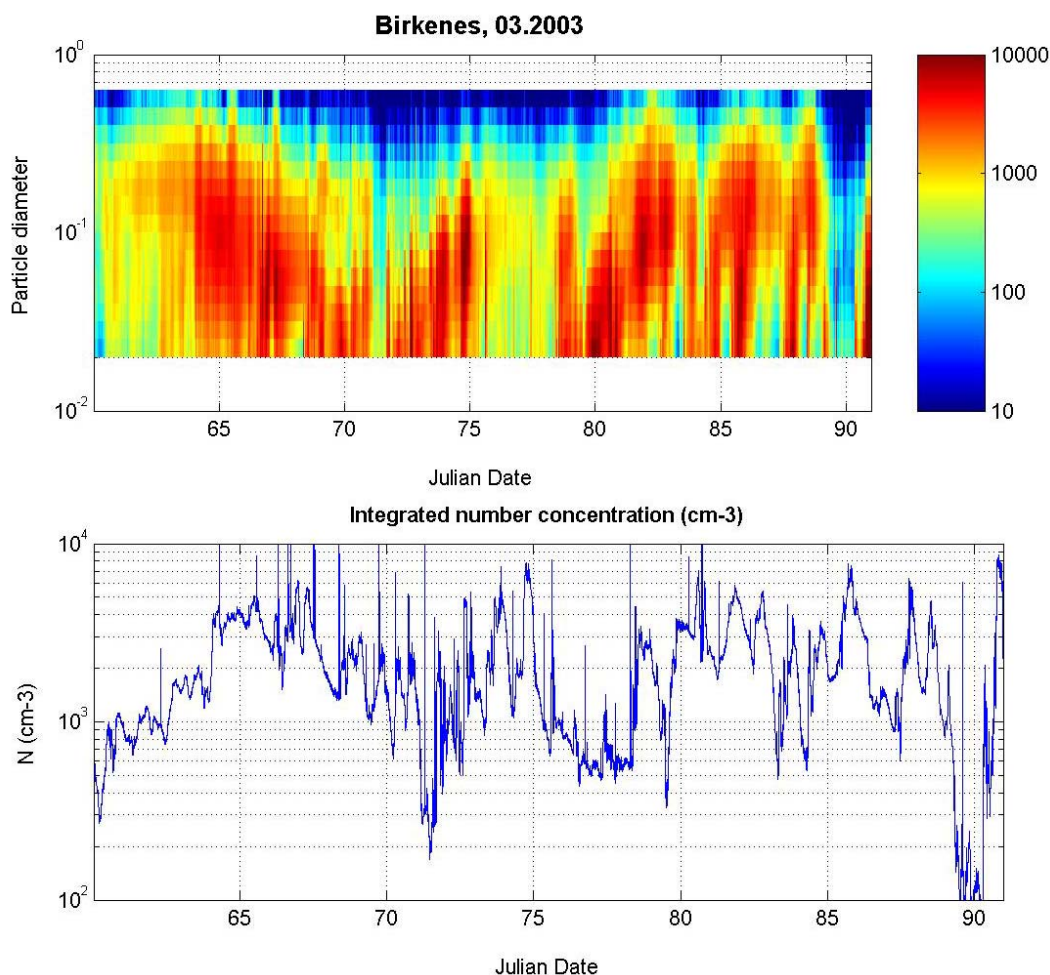


Figure 1.9: Particle number distribution (upper panel) and total particle number concentration at the EMEP site at Birkenes (Norway) in March 2003.

Verification of modelled particle number concentrations

Daily number concentrations

Daily averages of particle number concentrations have been compared with measurements from the Austrian AUPHEP research project. Figure 1.10 compares modelled and measured particle total number concentrations at the site located in a residential area of Wien, somewhat affected by traffic. Modelled particle number concentrations correlate remarkably well with the measurements.

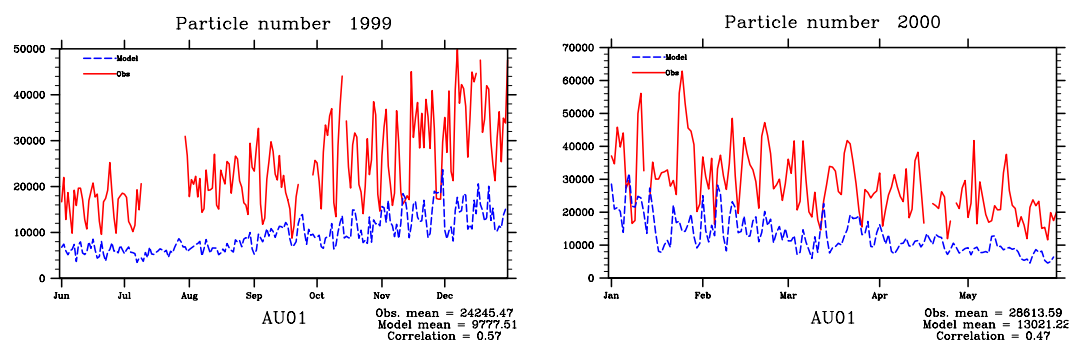


Figure 1.10: Daily time series of particle number concentrations modelled and measured in the residential area in Wien (June 1999 - May 2000).

Figure 1.10 shows that the model underestimates particle numbers and predicts much smaller amplitudes of the diurnal variation. As it was pointed out above, the number concentration is controlled by the number of smallest particles and is therefore strongly affected by aerosol dynamics. The major uncertainties in modelled particle numbers are thought to arise from uncertainties in the size distribution of primary PM emissions. Sensitivity tests have shown the importance of an adequate description of the size distribution of primary PM emissions for obtaining reasonable predictions of particle numbers. On the other hand, a sound parameterisation of the aerosol dynamics is essential for the model to reproduce the observed variations in particle number concentrations.

Hourly particle numbers

Measurement data on the hourly particle number concentrations at four Nordic sites was made available to MSC-W within the framework of a Nordic Council of Ministers aerosol project. A network of Nordic stations running advanced particle measurements was established within the Swedish ASTA research program in close co-operation with University of Helsinki. Since September 2002 NILU/CCC has joined the Nordic network with the DMPS instrument at the Norwegian EMEP site at Birkenes.

The measurements provided to MSC-W were collected during the period 1.06.2000-31.12.2000 at Hyytiälä (a boreal forest site in Central Finland), Pallas and Värriö (north of Finland), and Aspvreten (SE12, Sweden) (Tunved et al., 2003). The data received includes hourly averaged particle number in four size bins from 0.003 to 0.5 μm . Figure 1.11–Figure 1.12 give some examples of comparisons between modelled and measured number concentrations of Aitken

(diameters of 0.02–0.1 μm) and “small” accumulation (diameters of 0.1–0.5 μm) particles.

The comparison shows a rather poor correlation and even anti-correlation between calculated and measured hourly particle numbers for Aitken mode when the whole period is considered. The correlation coefficients between calculated and measured hourly numbers at those four sites are between -0.14 and -0.01 for Aitken particles and between 0.08 and 0.27 for “small” accumulation particles. Figure 1.11 presents the time series of Aitken and accumulation number concentrations at Aspvreten. It has been found however that model comparison with observation in some months is better than in the others. For example, correlation for Aitken number up to 0.4 -0.45 and for accumulation number up to 0.65 can be found.

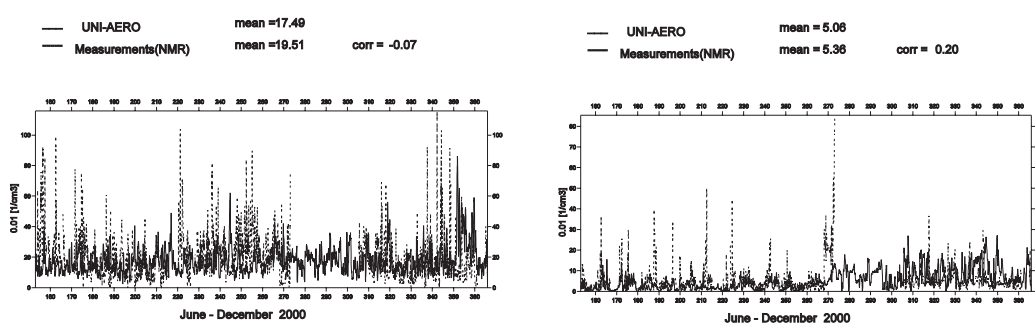


Figure 1.11: Time series of measured and modelled hourly number concentrations of Aitken (diameters 0.02-0.1 μm) and accumulation (diameters 0.1-0.5 μm) particles at Aspvreten, Sweden in June-December 2000.

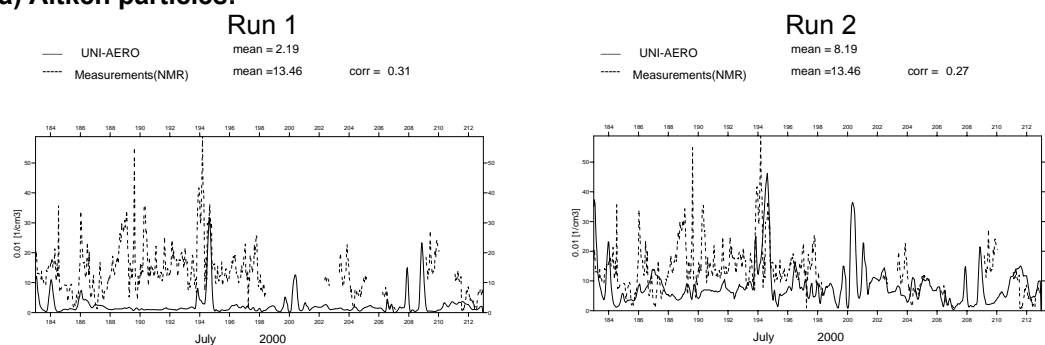
Sensitivity test of calculated particle numbers to the size distribution of PM emissions

No information on the size distribution of primary PM emissions was available to MSC-W. Therefore rough assumptions, the same assumptions for all countries and all types of sources, were made in the aerosol model to distribute $\text{PM}_{2.5}$ mass emissions between the Aitken and the accumulation modes and to derive the number emissions from mass emissions. To study the effect of size distribution of $\text{PM}_{2.5}$ emissions on number concentrations two model runs with different emission size distribution have been performed. The differences in size distribution applied to $\text{PM}_{2.5}$ emissions in run 1 and run 2 are the following:

- $\text{PM}_{2.5}$ mass emissions are distributed between Aitken and accumulation modes as 0.15 to 0.85 in run 1 and as 0.20 to 0.80 in run 2
- the diameter of the emitted Aitken particles is 0.03 μm in run 1 and 0.02 μm in run 2
- the diameter of the emitted accumulation particles is 0.5 μm in run 1 and 0.3 μm in run 2

Thus, more particles in both accumulation and especially Aitken mode were emitted in run 2 than in run 1. The effect of emissions size distribution on the calculated particle numbers can be seen when comparing results presented in Figure 1.12(a) and Figure 1.12(b). Modelled Aitken number concentrations have increased by a factor of 4 and become much closer to the measurements. Modelled accumulation numbers have slightly increased. We can conclude that the size distribution of particle emissions determines the particle number concentrations and therefore should be accurately described in the model. On the other hand, the effect of the size distribution of the particle emissions on PM mass has been found to be insignificant. Recent information on PM emissions specification compiled at the University of Stuttgart reveals that the mass fraction of Aitken particles in PM₁₀ emissions can be for some sources as large as 25% and even 50%. To improve the correlation of model calculated particle numbers, an improvement in the aerosol dynamics parameterisation is needed in addition to an appropriate description of primary particle emissions.

a) Aitken particles:



b) Accumulation particles:

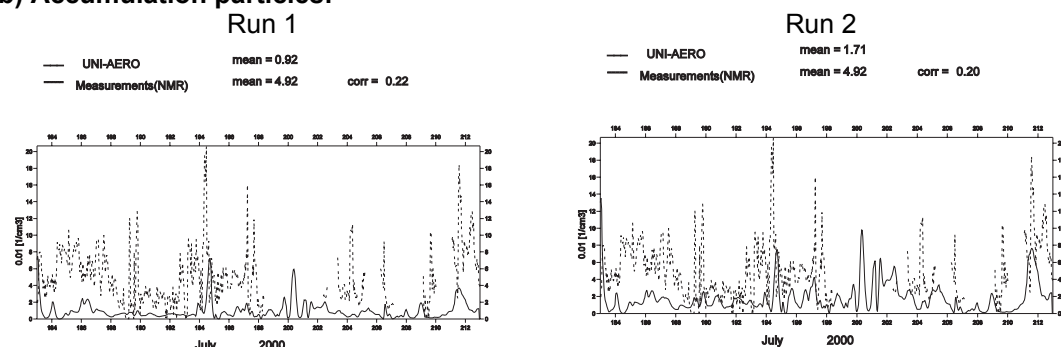


Figure 1.12: Time series of measured and modelled hourly number concentrations of a) Aitken and b) accumulation particles at Hyytiälä in July 2000. Model run 1 and run 2 correspond to different size distributions of primary PM emissions (see explanation in the text).

In addition to primary Aitken particles originating from the direct emissions, new Aitken particles can be produced due to the growth of nucleation particles. Nucleation particles (with diameters less than 0.02 µm), formed by nucleation of H₂SO₄, coagulate very rapidly with Aitken particles, thus increasing the Aitken mass, but not changing the Aitken number. However, newly formed nucleation particles also grow by coagulation with each other and condensation of H₂SO₄ and organic vapours. If there is a sufficient amount of condensable vapours the

nucleation particles can reach the Aitken size, increasing the number of Aitken particles.

Figure 1.13 compares calculated and measured Aitken numbers at Hyytiälä on days with and without nucleation events. In the upper panels, the observed time evolution of particle number size distributions is shown (red to brown colours represent high concentrations). The lower panels present modelled and measured number concentrations of Aitken particles for the same periods.

Figure 1.13(a) shows that the agreement between calculated and measured Aitken numbers is rather poor for the days with nucleation events. High peaks in the measured Aitken number are associated with the nucleation bursts, while the model does not predict those episodes. This could be either because the model fails to predict the nucleation events or because there is too little condensable vapours in the model so that the nucleation particles would not grow fast enough to the Aitken mode, but rather get removed by coagulation. Organic vapour, which can be an important source for new particle growth, was not included in the present version of the aerosol model. Figure 1.13(b) illustrates a period without nucleation events, when particle number is rather determined by emissions and transport. In this case the agreement between the model and the measurements is much better.

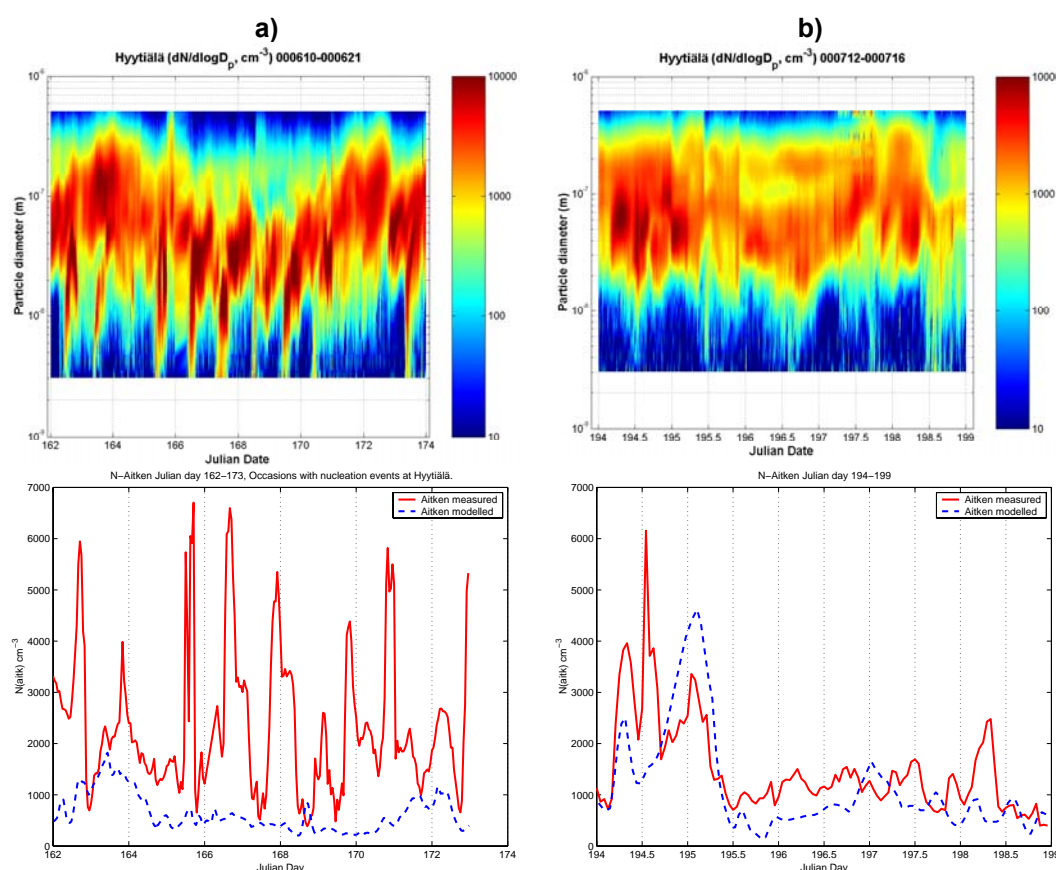


Figure 1.13: Time evolution of particle number size distributions (upper panels) and calculated and measured hourly series of Aitken numbers (lower panels) for periods with and without nucleation events. Hyytiälä, Finland: (a) June 10-22, 2000, (b) July 12-17, 2000.

2. Chemical composition of PM across Europe

by Svetlana Tsyro, Michael Kahnert and Leonor Tarrasón

Monitoring of physical aerosol properties is a relatively recent addition to the EMEP monitoring programme. By contrast, monitoring of inorganic constituents in aerosols has been performed within EMEP for many years. However, these monitoring activities have traditionally been associated with EMEP's classical acidification and eutrophication programme. To make use of these data for monitoring particulate matter poses new challenges. It needs to be assessed if the present monitoring programme of chemical constituents in aerosols is sufficient for fulfilling EMEP's objectives with regard to particulate matter. Available and missing information in the measurement data needs to be identified, and capabilities and weaknesses of EMEP's modelling capacities need to be investigated.

This chapter prepares the basis for these discussions by presenting comparisons of most recent EMEP monitoring data on aerosol chemical composition with results obtained with the EMEP Unified Model. A comparison of EMEP model results on PM₁₀ chemical composition with measurement data from the work by Putaud et al. (2002) is also shown. In addition, first results from a measurement campaign of elemental and organic carbon, which was coordinated by NILU/CCC, are shown.

The modelling and measurement results presented here will serve to illustrate the status quo of EMEP's monitoring activities and predictive capabilities with regard to aerosol chemical composition. The main conclusions are that the model reproduces aerosol inorganic composition reasonably well, but problems still remain in reproducing the organic fraction and in attaining full mass closure. The major error sources are volatile species, water, and, perhaps most importantly, an insufficient characterisation of "elemental" and organic carbon (EC/OC).

More complete information on the EC/OC content of aerosols is required, concerning both primary emissions of the aerosol and air concentrations. Such information is a prerequisite for improving the parameterisation of EC/OC in the EMEP Unified Model.

Building on these results, recommendations on possible improvements of the monitoring programme and of the model will follow in Chapter 3.

2.1 Inter-comparison of the measured and modelled chemical composition of the aerosol

Particulate matter is a complex mixture of pollutants. Therefore, adequate prediction by the model of $PM_{2.5}$ and PM_{10} depends on the accurate calculation of all PM constituents. In the following, a comparison of modelled results with EMEP network observations in 2000 and 2001 is presented.

Concentrations of Secondary Inorganic Aerosol (SIA), i.e. the sum of sulphate, nitrate, and ammonium aerosols, and of primary PM_{10} calculated with the EMEP Unified model in 2000 are shown in Figure 2.1.

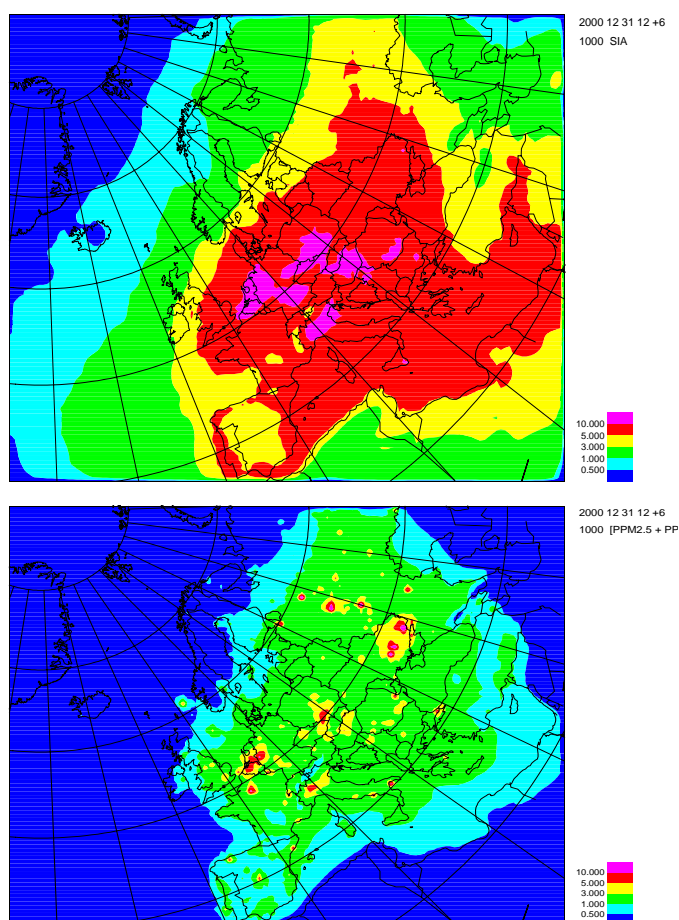


Figure 2.1: Concentrations of secondary inorganic aerosol (SIA, upper panel) and primary PM (lower panel) in 2000 calculated with the EMEP Unified Model.

A more detailed comparison for different chemical components between model results and observations, as far as data are available, is shown in Figure 2.2–Figure 2.6 for the years 2000 and 2001.

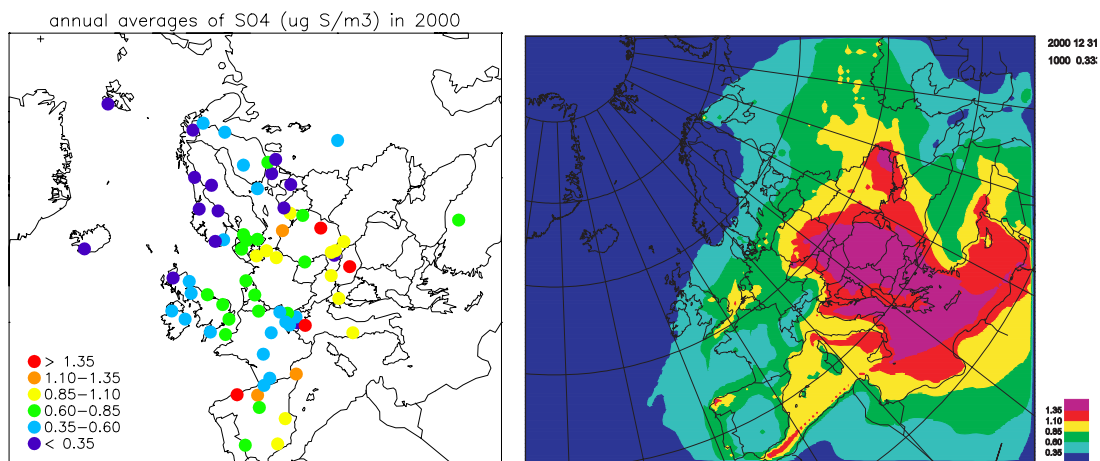


Figure 2.2: Comparison of the annual averages of observed (left) and modelled sulphate mass ($\mu\text{g S/m}^3$) concentrations for 2000.

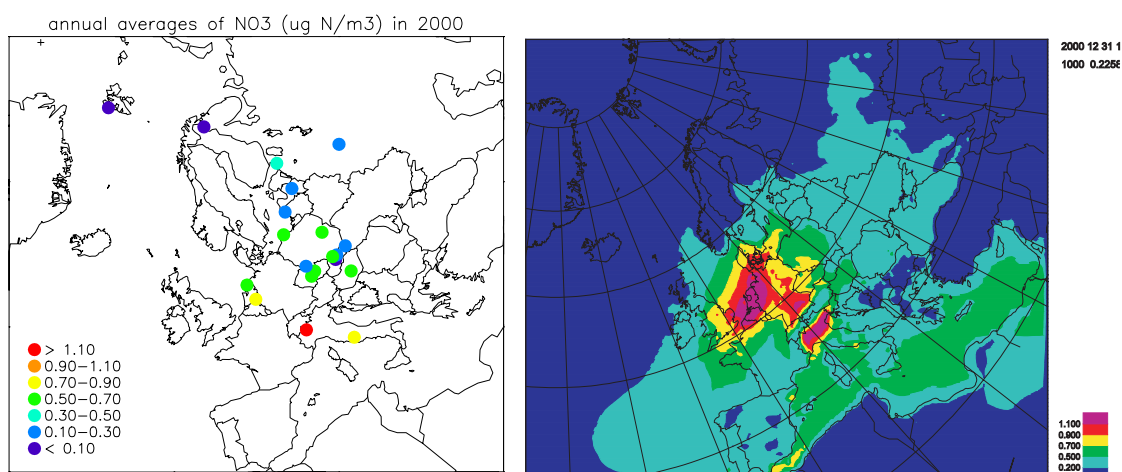


Figure 2.3: As Figure 2.2 (2000), but for nitrate ($\mu\text{g N/m}^3$).

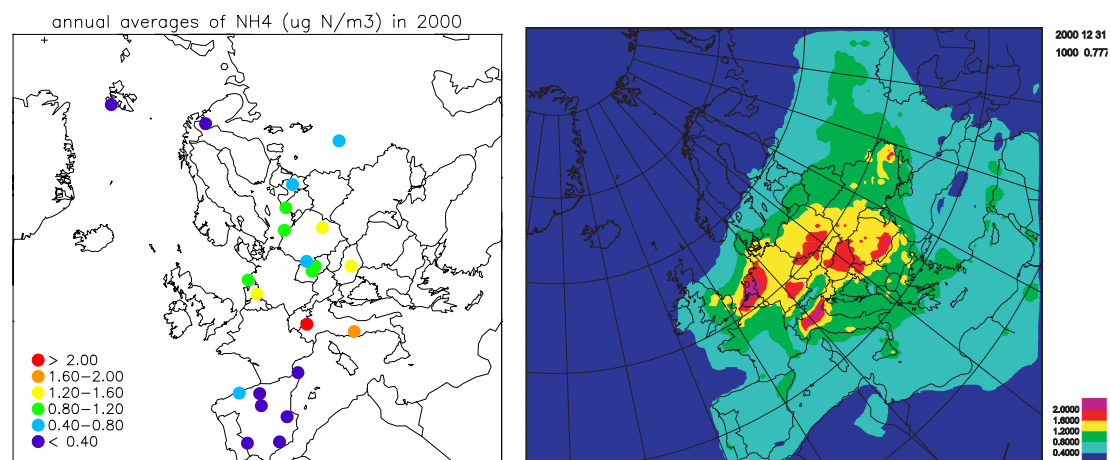


Figure 2.4: As Figure 2.2 (2000), but for ammonium ($\mu\text{g N/m}^3$).

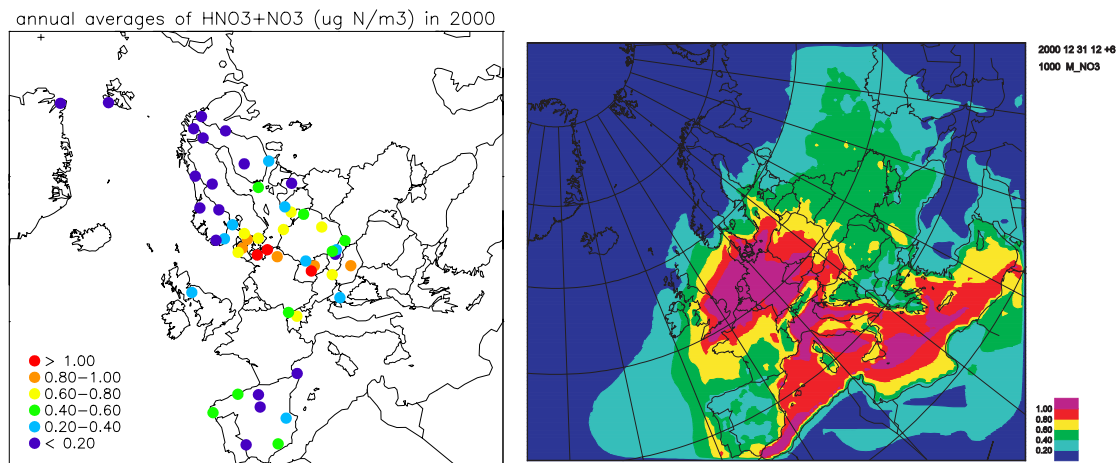


Figure 2.5: As Figure 2.2 (2000), but for sum of nitric acid and nitrate mass concentration ($\mu\text{g N/m}^3$) for 2000.

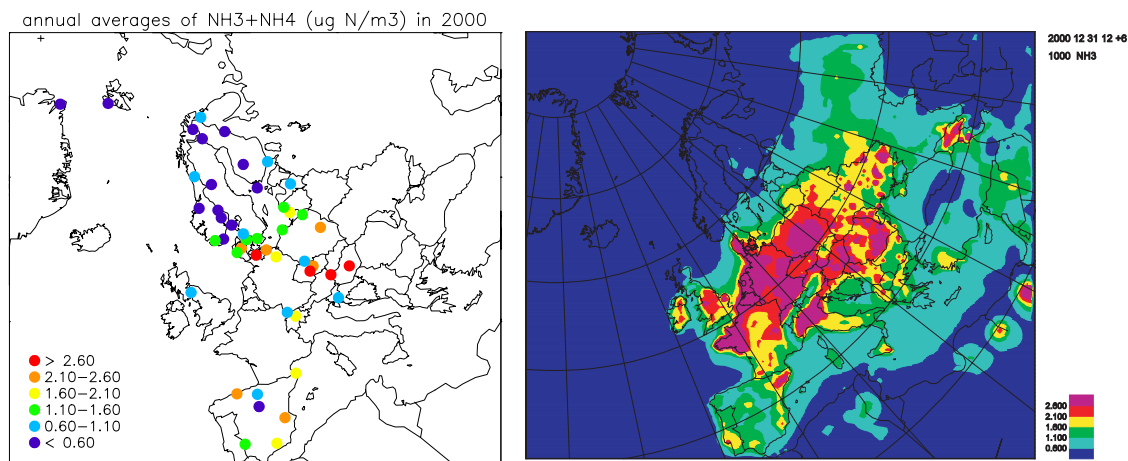


Figure 2.6: As Figure 2.2 (2000), but for the sum of ammonia and ammonium ($\mu\text{g N/m}^3$).

Model calculated concentrations of sulphate, nitrate and ammonium aerosols are generally in a good agreement with observations. Figure 2.2 reveals that the model underestimates SO_4 in Spain and overestimates SO_4 in some central European regions (German-Czech border, Slovakia, and Hungary). There is a rather limited number of filterpack or combined denuder/filterpack measurements available, which allow for a separation of ammonium and ammonia, and of nitric acid and nitrate. Based on these data for nitrate and ammonium, the model calculates larger than observed NO_3 at Dutch sites and NH_4 at Czech and Hungarian sites. The model's overestimation of NH_4 in Spain despite its underestimation of SO_4 is difficult to explain. It is plausible that part of the SO_4 measured at Spanish sites was not bound in ammonium sulphate, but bound with Na from sea salt spray or with Ca and Mg from mineral dust. On the other hand, it could be due to measurement artefacts. The model somewhat overestimates the sum of nitrate and nitric acid ($\text{NO}_3 + \text{HNO}_3$), except for two sites in the north of Spain. For the sum of ammonia and ammonium ($\text{NH}_3 + \text{NH}_4$), both overestimations

of the measured concentrations (e.g. in Central and Eastern Europe and at part of the Spanish sites) and underestimations (e.g. at some Spanish stations and in the Baltic republics) are found.

In Figure 2.7–Figure 2.11 we show the newest observational data and model results for the year 2001. Note that in Figure 2.2–Figure 2.11 only those observation sites are shown that had data coverage over 50 %.

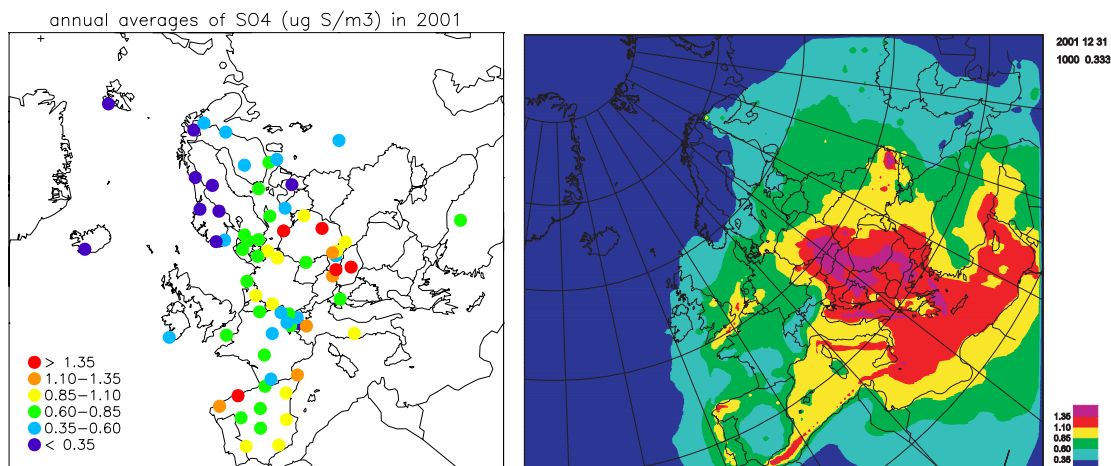


Figure 2.7: Annual averages of observed and modelled sulphate mass concentrations in 2001 ($\mu\text{g S/m}^3$).

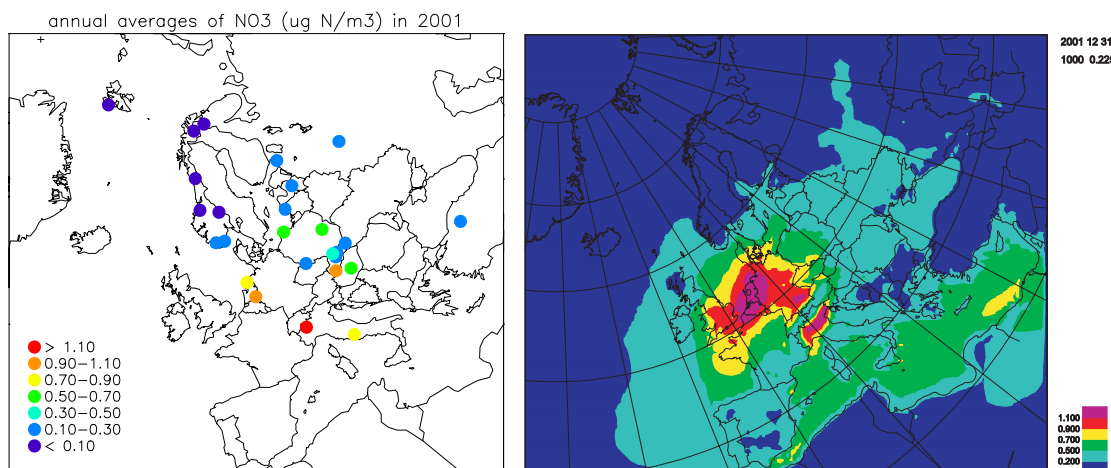


Figure 2.8: As Figure 2.7 (2001), but for nitrate ($\mu\text{g N/m}^3$).

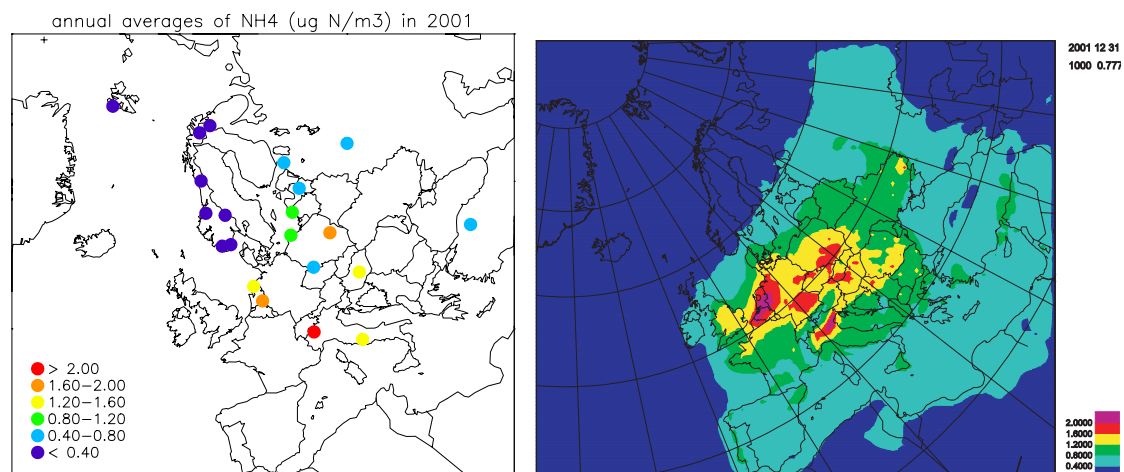


Figure 2.9: As Figure 2.7 (2001), but for ammonium ($\mu\text{g N}/\text{m}^3$).

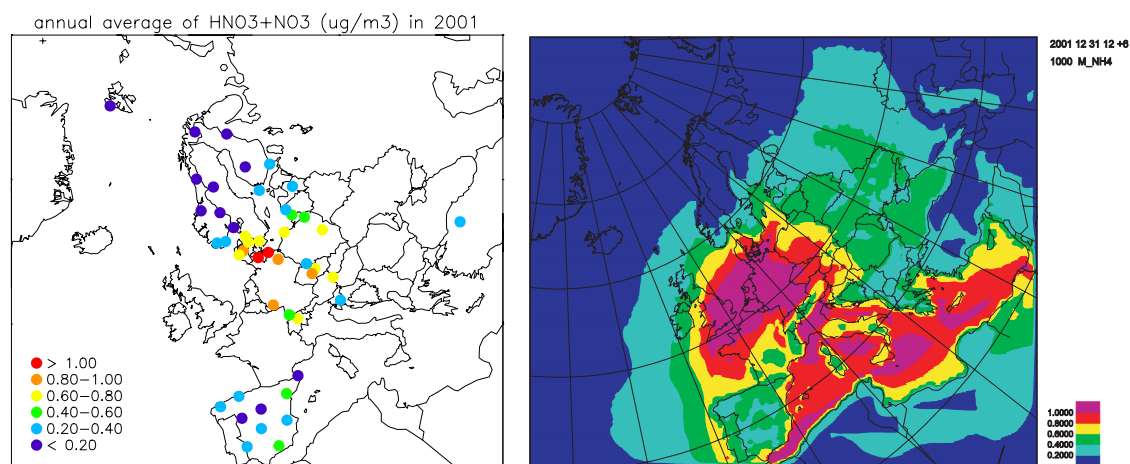


Figure 2.10: As Figure 2.7 (2001), for sum of nitric acid and nitrate mass concentration ($\mu\text{g N}/\text{m}^3$).

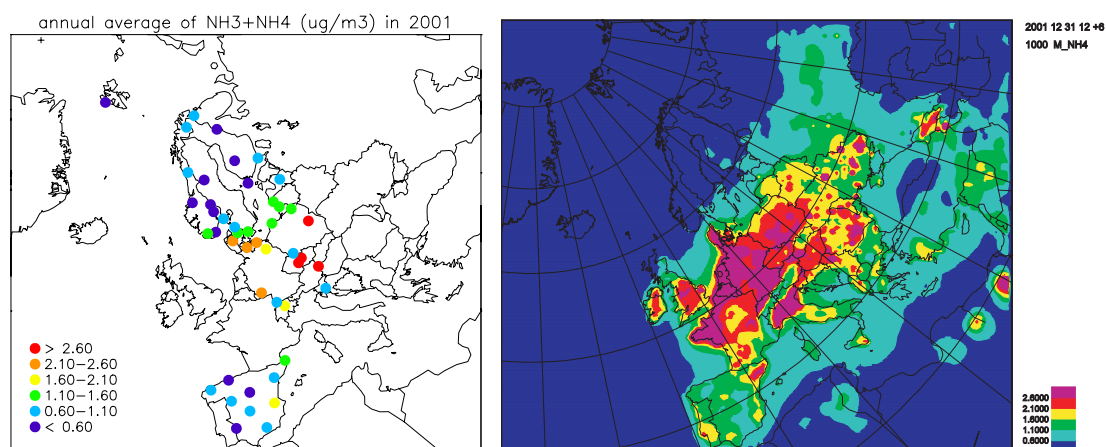


Figure 2.11: As Figure 2.7 (2001), for the sum of ammonia and ammonium ($\mu\text{g N}/\text{m}^3$).

Ammonium, nitrate, and sulphate are those inorganic constituents that are most relevant for gaining a better understanding of the chemical processes in the atmosphere leading to the formation of SIA from precursor gases. At several observation sites masses of ammonia, nitrate, and sulphate in aerosols have changed little from 2000 to 2001. However, a consistent increase of all three species is observed in The Netherlands. Also, there are clearly more stations at which an increase of sulphate concentrations has been observed than stations that have shown a decrease of sulphate concentrations. Also in 2001, the model underestimates SO_4 at Spanish stations. Otherwise, overall model results for SO_4 , NO_3 and NH_4 , as well as for $(\text{HNO}_3+\text{NO}_3)$ and for $(\text{NH}_3+\text{NH}_4)$ appear to compare better with measurements in 2001 than in 2000.

Annual mean concentrations in 2001 of primary anthropogenic OC and EC calculated with the aerosol model are shown in Figure 2.12.

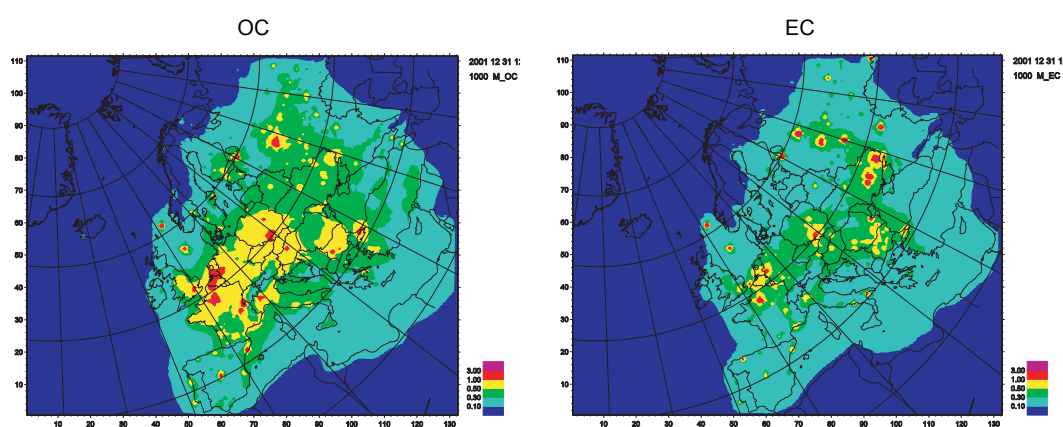


Figure 2.12: Model calculated annual mean concentrations of OC (primary anthropogenic) and EC in 2001.

Comparison with aerosol chemical composition data from networks other than EMEP

In this section, model calculated chemical composition of PM_{10} in 2000 is compared with the results from work by Putaud et al. (2002). In this work, aerosol measurement data from various research projects collected in Europe during the last 10 years were synthesized and analysed. The data was collected in different years and during different time periods. The sampling technique and the methods of chemical analyses applied in different campaigns can also differ. Uncertainties in comparing the datasets arising from all those differences are discussed in Putaud et al. (2002). Measurement sites (Figure 2.13) were classified as natural background, rural, near-city, urban, and kerbside. Uncertainties in the determination of major inorganic species and total carbon was estimated to be within $\pm 10\%$, in the determination of OC – within $\pm 25\%$, and uncertainties in mineral dust concentrations was as large as 100% .

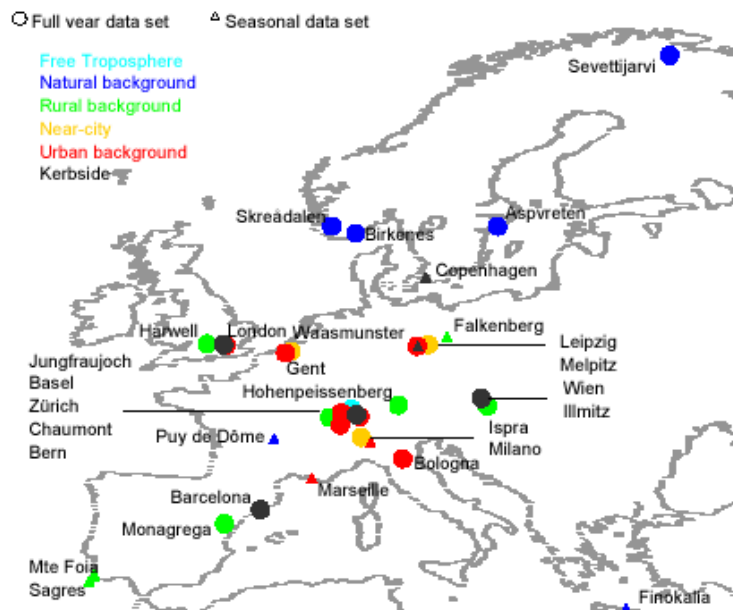


Figure 2.13: The location and classification of measurement sites (from Putaud et al., 2002).

Figure 2.14 shows the annual average of the contributions of the individual aerosol components to the PM_{10} mass from Putaud et al. (2002), and calculated values for 2000 with the EMEP aerosol dynamics model. Kerbsites stations have not been considered, as the model is not expected to resolve PM variability at such small scale. To provide a consistent comparison, we have only considered sites at which all identified chemical components have been measured. The unaccounted mass of the aerosol, that is, the part of aerosol mass that is not chemically identified in the measurements, has not been considered in this comparison. In this way, the percentage contribution to PM_{10} mass from the different chemical components presented in Figure 2.14 is calculated consistently both for model and measurements.

Conclusions are similar as for comparison with EMEP stations. The modelled contribution of sulphate and ammonium to PM_{10} mass is generally in good agreement with the observations at rural and urban background sites, with some overestimation of the relative contribution of nitrate to PM_{10} . The agreement is also good for the mineral dust contribution except at some southern European sites. The smaller calculated contribution of mineral dust at Monagrega is probably due to a significant source of re-suspended dust in Spain, which has not been accounted for in the model. The same reason, i.e. unaccounted re-suspension of dust from roads, could cause too low calculated dust contributions in Bologna.

More significant discrepancies between modelled and measured chemical composition are seen for the organic and elemental carbon fraction. The EMEP aerosol model generally underestimates the carbon component of aerosols. As a consequence, the relative contribution of different components to PM mass is different from modelled and measured calculations. While measurements show

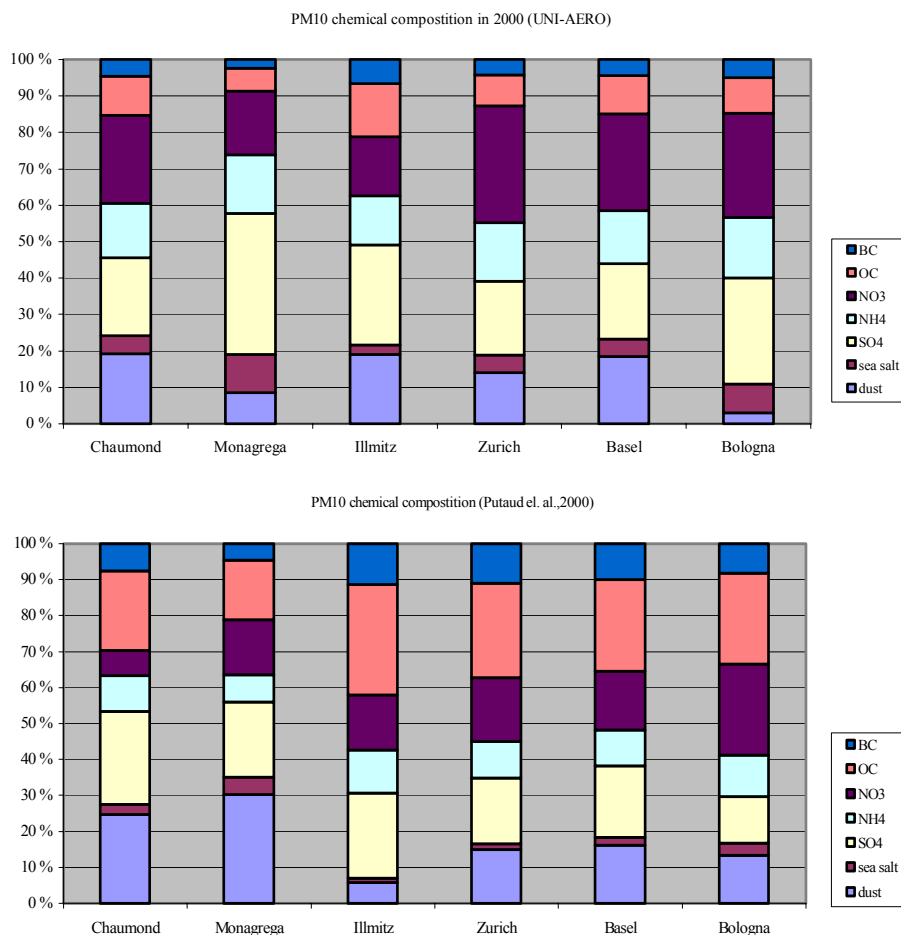


Figure 2.14: Fractional contribution of the aerosol components to PM_{10} as calculated with the aerosol model and constructed by Putaud et al. (2002).

that secondary inorganic aerosols (SIA) contribute about 40% to the total PM_{10} mass, the model indicates that their relative contribution might be up to 60% in some areas. For the sum of organic and elemental carbon, the model indicates only a 15-20% contribution to total PM mass, while the observations indicate a far more significant contribution of about 25-30%.

These discrepancies are, however, mainly related to the systematic underestimation by the model of organic aerosol concentrations. The model considers only primary anthropogenic sources of organic carbon. The present version does not include biogenic organic carbon sources, nor does it account for secondary organic aerosol formation. Discrepancies between modelled and measured contributions of OC, EC and mineral dust may also be due to the uncertainties associated with model assumptions on the chemical composition of primary fine and coarse PM emission, as no information on the chemical speciation of PM emissions was available to MSC-W. Note again that only primary anthropogenic dust is included.

In Figure 2.15 the modelled and measured chemical composition of PM_{10} at natural background, rural, near-city and urban sites is compared. Here, the

different constituents are identified as contributions to total aerosol PM_{10} mass, and not in percentage. Note that the measurements show a varying contribution of aerosol mass of undetermined chemical composition (unaccounted aerosol mass). In addition to not analysed components, the unaccounted mass may contain residual water associated with aerosol or non-C atoms associated with organic aerosol, or it could be due to measurement artifacts (e.g. volatilization of NH_4NO_3 and volatile organic compounds). If all the main aerosol components are measured, they typically account for about 70% or more of the total PM_{10} and $PM_{2.5}$ mass (Putaud et al., 2002).

It is worth noting that the aerosol model did not account for SOA and re-suspended and wind blown mineral dust. Anthropogenic mineral dust, primary OC and EC originate in the model from primary PM emissions. The overall impression from the graphs in Figure 2.15 is that with some exceptions, the chemical composition of aerosol calculated with the EMEP aerosol model agrees reasonably well with the measurements and that the main difficulties are related to the organic component of the aerosol.

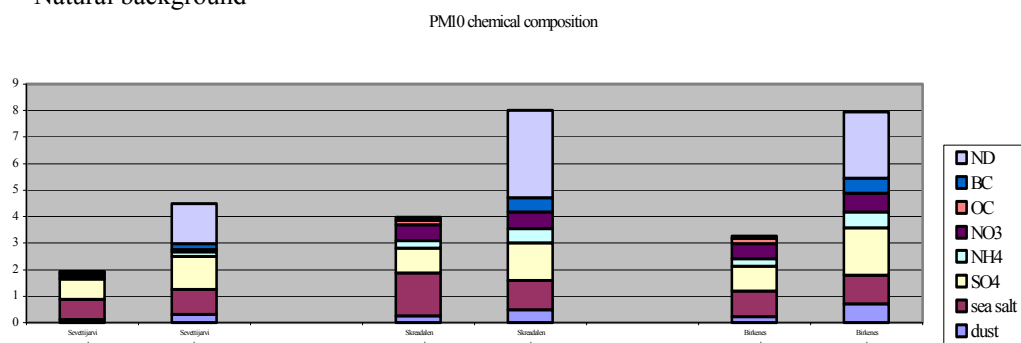
For background sites, the model underestimates anthropogenic aerosols, i.e. SO_4 , NH_4 and BC (OC was not measured at those sites), while calculated and observed NO_3 concentrations are quite close. It should be noted that the measurements at those sites are from the early 1990's, while the model calculations are for 2000. During the late 1990's, SO_x emissions were reduced by ca. 40%, inevitably resulting in lower concentrations of SO_4 and consequently of NH_4 . As expected, concentrations of mineral dust from the model are lower than measurements as only anthropogenic primary dust was included in the calculations.

At rural sites, modelled SIA (except for NO_3 in Chaumont) and sea salt concentrations agree quite well with the measurements. As expected, calculated OC and dust (except for Illmitz) is underestimated. The model's overestimation of mineral dust at Illmitz could be either due to the rather large uncertainties in measurements of mineral dust or due to the assumptions concerning the chemical composition of primary PM emissions.

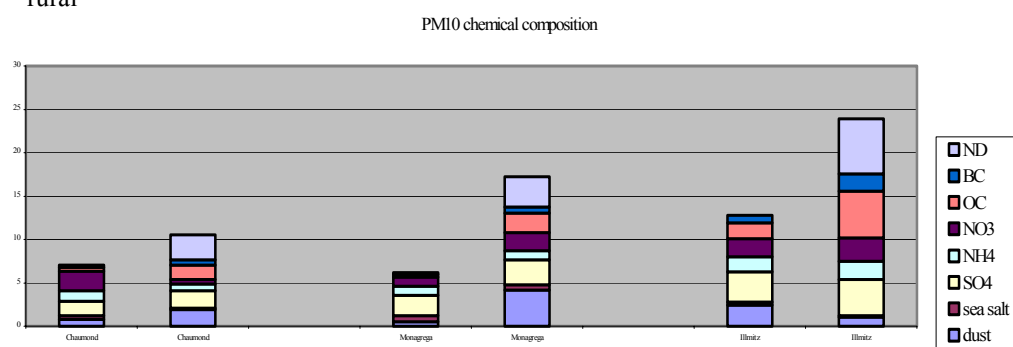
At near-city sites, the chemical characterisation of measured aerosol is incomplete. Lower calculated concentrations of SO_4 at Wassmunster compared with the measurements is probably due to the fact that measurements were taken in 1994-1995, when the European SO_2 emissions were 20-25% larger than in 2000. Relatively much mineral dust calculated by the model at Wassmunster could be a joint effect of the uncertainties in chemical speciation of PM emissions in UNI-AERO and measurements. Calculated SIA, BC and dust is in good agreement with the observations at Melpitz and Ispra. Rather high concentrations of organic matter measured in Ispra could be due to SOA or biogenic aerosols not being included in the model.

At the urban sites Zürich and Basel the model predicts quite accurately concentrations of SIA, which is controlled largely by long-range transport. However, the model systematically underestimates BC and especially OC. The latter is probably because the contribution of SOA, which can be considerable in cities, was not considered in the model.

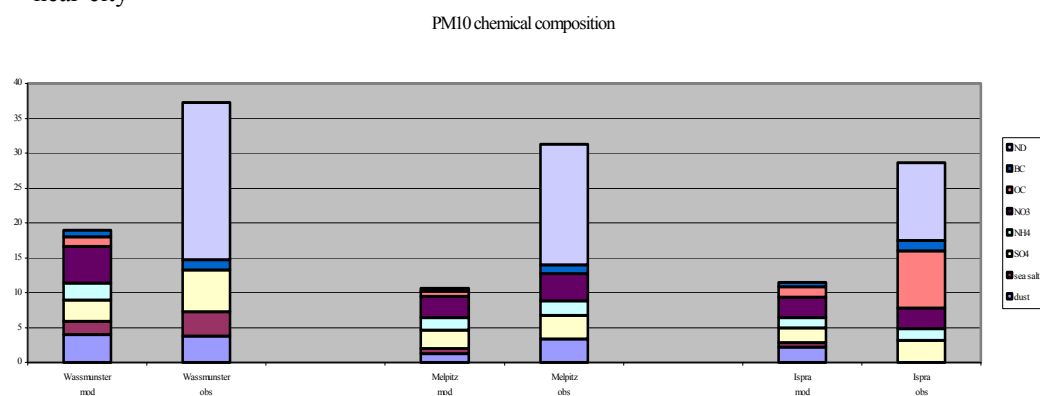
Natural background



rural



near-city



urban

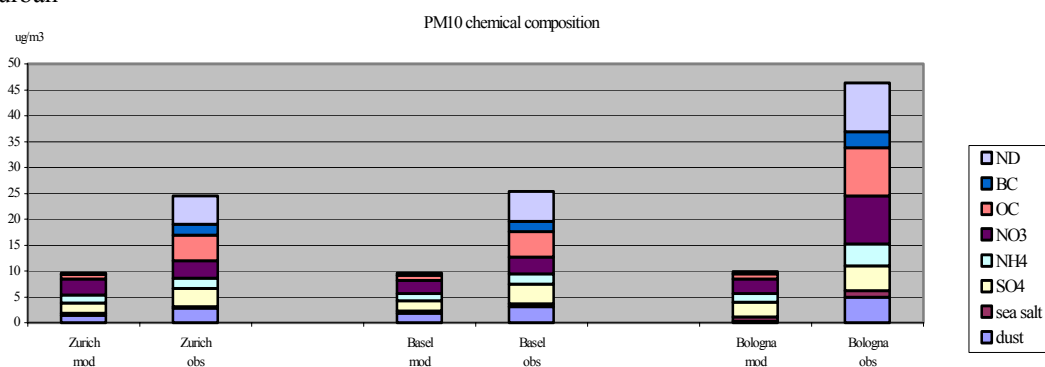


Figure 2.15: Chemical composition of PM_{10} calculated with the EMEP aerosol model and presented by Putaud et al. (2002).

Figure 2.16 presents the seasonal average relative contributions of various aerosol components to PM₁₀ as calculated with the aerosol model. These diagrams can be compared with measurements from Putaud et al. (2002) available at <http://ies.jrc.cec.eu.int/Download/cc>.

At most sites, the model predicts the smallest SO₄ contributions to PM₁₀ in winter and the largest in summer, which, in general, agrees with observations. The largest calculated NO₃ contributions are often found in spring (except for the natural-background sites), while the measurements from Putaud et al. (2002) show maximum contributions of NO₃ in winter. Both model and measurements agree in that NO₃ contributes least in summer, but the differences between winter and summer contributions of NO₃ predicted with the model are sometimes smaller than the observed differences. The reason could be that in summer the observed PM₁₀ concentrations are higher than the corresponding modelled values. This is due to the fact that organic aerosols and dust are only partially accounted for in the model (e.g. at Chaumont, Monagrega, urban sites). It can also be due to the large fraction of unaccounted mass. Putaud et al. (2002) suspect that the large differences between observed winter and summer NO₃ contributions might partially be due to sampling artefacts. Modelled contributions of OC exhibit similar seasonal variations as NO₃, but only primary OC was included in the model. Calculated and measured seasonal average contributions of EC vary relatively little, with a minimum in spring/summer, reflecting the seasonal variation of primary PM emissions. The largest discrepancy between model results and measurements is found for the contribution of mineral dust to PM₁₀. While measurements show the highest dust contribution in spring-summer related to farming activities or desert dust episodes, the model calculates the largest fractions of dust in PM₁₀ in summer-autumn. As it was said above, the model presently accounts only for anthropogenic mineral dust, so that the variability of dust is determined primarily by the seasonal variation of PM emissions. Accounting for re-suspended and wind eroded dust should improve model concentrations of dust in summer.

In summary, compared with aerosol measurements from Putaud et al. (2002) the EMEP aerosol model gives a reasonable description of the aerosol chemical composition. The main discrepancies are found to be related with carbonaceous and mineral dust constituents and the unaccounted part of the aerosol. The main reasons for these discrepancies are most likely due to:

- measurement artefacts: evaporation of volatile organic compounds, volatile NH₄NO₃, and of water in aerosols
- model limitations: SOA and re-suspended and wind eroded mineral dust are not yet included in the model calculations, mostly due to a lack of reliable measurement information to parameterise these processes.
- Emission assumptions on the chemical composition of PM anthropogenic emissions in the model; appropriate information on the chemical speciation of PM emissions is crucial for adequate modelling of the aerosol chemical composition

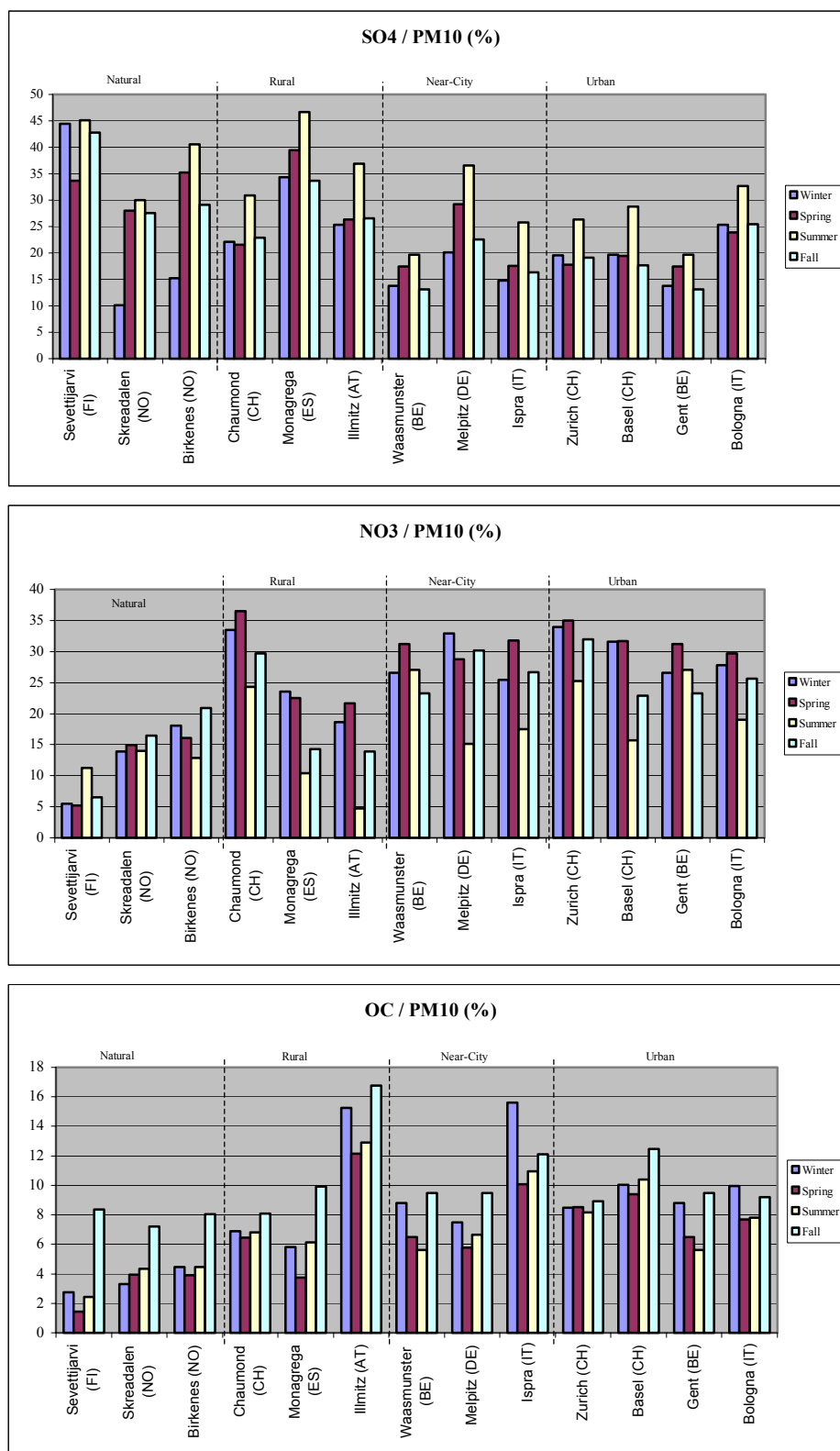


Figure 2.16: Seasonal average contributions of the aerosol components to PM₁₀ calculated with the EMEP aerosol model.

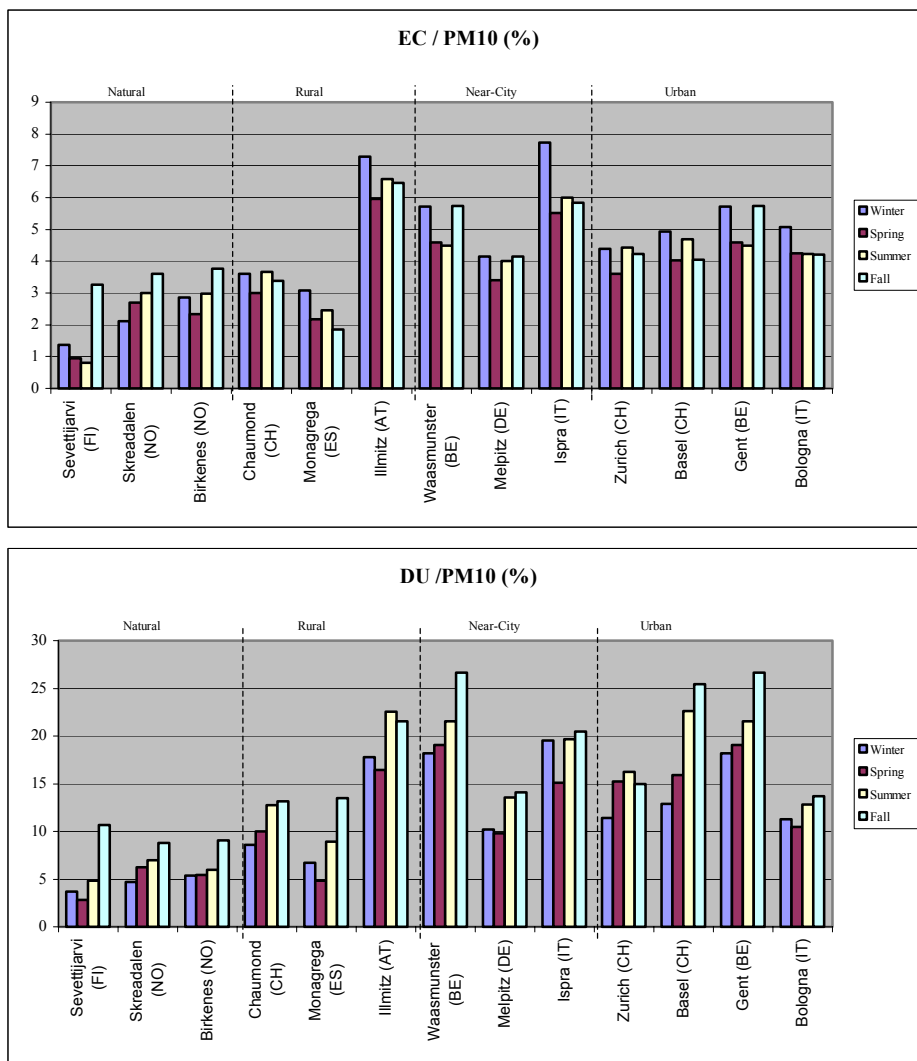


Figure 2.16, cont.

2.2 Measurement campaign of elemental and organic carbon

As indicated in the previous section, more accurate information on the EC/OC content of aerosols will be critical for making further progress in the analysis of the chemical composition of the aerosol. This type of analysis will provide further insight to allocate the unaccounted component to PM₁₀ mass and contribute to the development of aerosol models.

To illustrate the significance of organic and “elemental” carbon, Figure 2.17 shows a comparison of the chemical constituents measured at Birkenes in 2001 with corresponding data for particle mass. One can see that sulphate, nitrate, and ammonium account for roughly 75% of the inorganic mass, and for 1/3 of the total mass. Thus monitoring of at least sodium and chloride in addition to SO₄, NO₃, and NH₄ is important at Birkenes. A high contribution of sea salt is to be expected at monitoring sites in close proximity to the ocean. Even more strikingly, the data from Birkenes reveals that the sum of all inorganic components only accounts for 50% of the total PM₁₀ mass, and that organic carbon (OC) and “elemental carbon” (EC, originating from combustion processes) contribute significantly to the total particle mass. Therefore it is important to supplement the monitoring of PM₁₀, PM_{2.5}/PM₁, and the main inorganic components with EC/OC measurements. CCC, in cooperation with 13 different countries, therefore undertook an EC/OC measurement campaign that lasted for one year. First results from this campaign are presented in this section.

Figure 2.17 also shows that we are missing about 20% to obtain a full mass closure from the chemical constituents. This reflects several uncertainties in the measurements, some of which were already mentioned in the previous section. In addition to the problems caused by volatile components and by water, thermo-optical measurements of OC capture only the mass of the carbon atoms. Correction factors to account for other atoms vary between 1.2 (for species mainly containing hydrogen) to 1.8 (for water soluble organic species with a large portion of oxygen, nitrogen, and other heavier elements) (Matta et al., 2003). Even higher correction factors have been suggested. In Figure 2.17 a factor of 1.5 was used. Clearly, the relatively large range for the OC correction factor introduces a significant uncertainty in the OC mass. EC/OC measurements therefore need to be supplemented in the future by more detailed organic speciations, e.g. by means of liquid chromatography/high resolution mass spectroscopy analysis of aerosol samples from selected sites, and/or by classifications of the organic fraction by solubility classes. We also note that Cl is often difficult to measure. Experience showed that for Norwegian stations more accurate Cl concentrations can be derived from Na measurements by multiplying Na mass concentration with a factor of 1.8. Thus annual averages of Cl concentrations at Birkenes could be as high as 0.5 µg/m³.

The EMEP EC/OC campaign was initiated and coordinated by CCC, and it was, to a large extent, funded by NILU. Sampling of PM₁₀ (and in Birkenes also PM_{2.5}) started in summer 2002 and continued until summer 2003. 15 stations from 13 different European countries participated in the campaign (see Table 2.1). Samples were taken on one day per week. All filters were preconditioned at CCC and sent to the participants. After sampling the filters were sent back to CCC, where they were post-conditioned. The pre- and post-conditioning of the quartz

filters was in accordance with the new EMEP quality assurance guidelines for PM₁₀ sampling as defined in the EMEP manual for Sampling and Chemical Analysis. Subsequently, EC and OC masses are determined by thermo-optical analysis (EMEP/CCC, 2002). Analysis of the filters is still in progress. We will present some first results for the EC/OC data here. A thorough analysis of the data will be conducted soon.

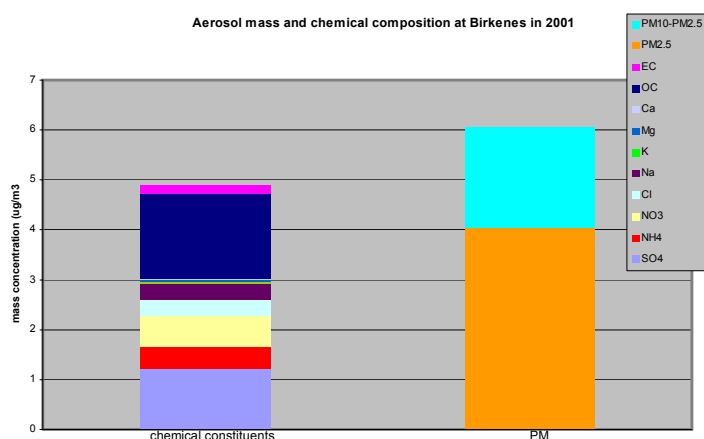


Figure 2.17: Annual averages of chemical composition and particle mass measured at Birkenes (Norway) in 2001.

Table 2.1: Stations that participated in the EC/OC campaign and their sampling equipment.

Stations		Instrument/ Impactor	Filter size	Flow rate
AT02	Illmitz	Partisol	47 mm	16.7 l/min
CZ03	Košetice	FH 95 SEQ	47 mm	38 l/min
BE	Ghent	Gent	47 mm	17 l/min
FI 17	Virolahti		47 mm	38 l/min
DE 02	Langenbrügge	HiVol (Digitel)	150 mm	500 l/min
IE 31	Mace Head	KFG	47 mm	38 l/min
IT 04	Ispra	KFG	47 mm	38 l/min
IT	San Pietro Capofiume	Gent	47mm	17 l/min
NL 09	Kollumerwaard	KFG	47 mm	38 l/min
NO 01	Birkenes	KFG	47 mm	38 l/min
NO 42	Zeppelin	HiVol	8x10 inch	1133 l/min
PT 01	Braganza	HiVol (Sierra)	8x10 inch	1133 l/min
SK 04	Stara Lesna	Partisol	47 mm	16.7 l/min
SE 12	Aspvreten	Gent	47 mm	15-18 l/min
GB	Penicuik	Partisol	47 mm	16.7 l/min

Methodology of EC/OC analysis

Thermal/optical EC/OC analysis is performed using an instrument from Sunset Laboratory Inc. (see Figure 2.18). A standard sized punch is taken from the exposed filters and placed in a quartz oven. The oven is purged with helium, and a stepped temperature ramp increases the oven temperature to 870°C, thermally desorbing organic compounds and pyrolysis products into an oxidizing oven. The organic carbon is quantitatively oxidized to carbon dioxide gas. The carbon dioxide gas is mixed with hydrogen and the mixture subsequently flows through a heated nickel catalyst where it is quantitatively converted to methane. The methane is quantified using a flame ionisation detector (FID). After cooling the oven to 600°C a second temperature ramp is initiated and the elemental carbon is oxidized off the filter by introducing a mixture of helium and oxygen into the oxidizing oven. The elemental carbon is detected in the same manner as the organic carbon (Birch et al., 1996; NIOSH, 1994). A schematic view of the observed thermogram is shown in Figure 2.19.

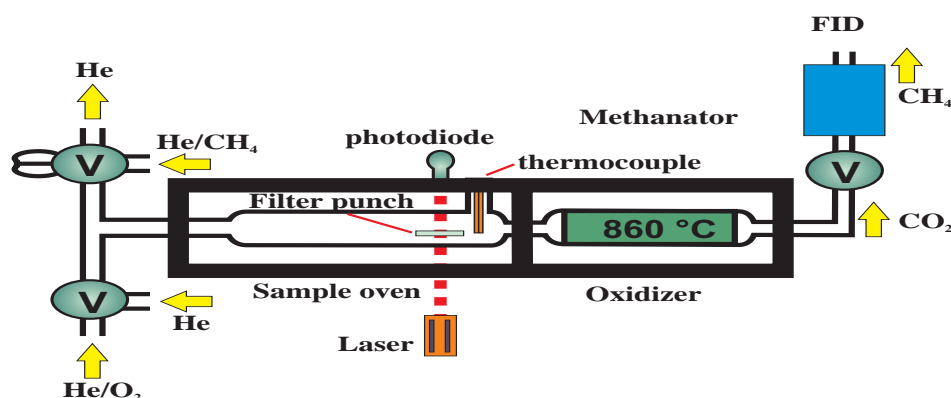


Figure 2.18: Schematic diagram of the Thermal-Optical Instrument (V=valve) (Sunset laboratory).

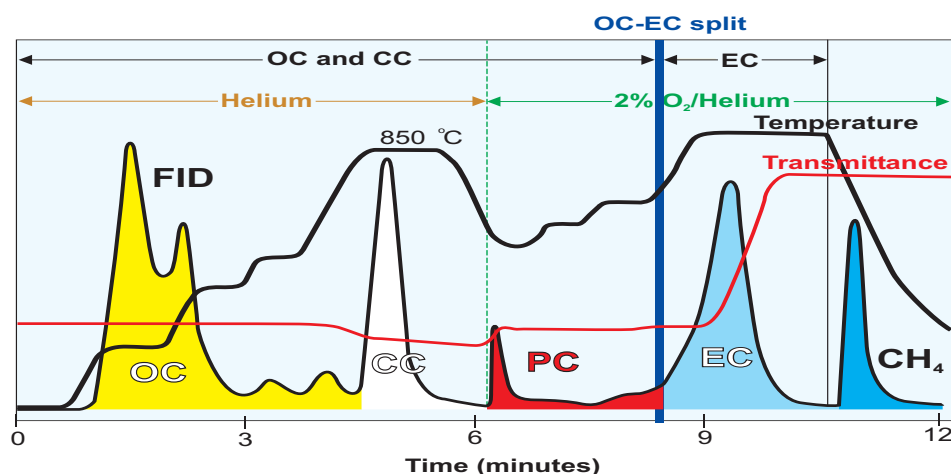


Figure 2.19: Thermogram for filter sample containing organic carbon (OC), carbonate (CC), and elemental carbon (EC). PC is pyrolytically generated carbon or 'char.' The final peak is the methane calibration peak. Carbon sources: pulverized beet pulp, rock dust (carbonate), and diesel particulate (Sunset Laboratory).

Results

Figure 2.20–Figure 2.23 show time series of PM_{10} , EC, and OC mass concentrations (upper panels) and the mass concentration ratios OC/PM_{10} and EC/PM_{10} (lower panels) for a selection of four different sites that participated in the campaign. Note that the OC mass concentrations given in the figures pertain to carbon atoms only. No correction factor has been applied yet to account for other elements in the organic compounds. Thus the OC data shown represent most likely a lower bound for the true OC mass concentration.

Clearly, OC concentrations fluctuate considerably at most measurement sites. Even though peak concentrations of PM_{10} are often accompanied by elevated OC concentrations, the mass ratio OC/PM_{10} is by no means a constant but varies at most stations over a large range. We find episodes during which the (uncorrected) OC mass concentration can account for as little as 3% or for as much as 70% of the PM_{10} mass concentration, with an average of roughly 20%. For large contributions of water-soluble organic species, this can amount to a corrected average OC mass fraction of almost 40%, which is quite substantial. Peak values can even lie significantly higher than this. A particularly high variability is observed at Birkenes in Southern Norway. The high variability of OC and its high average and peak contributions to the total PM_{10} mass concentration underline the need to extend OC monitoring with a reasonably high time resolution. The high fluctuations of the OC/PM_{10} mass ratio reflect the complex nature of the organic fraction, consisting of several thousand individual components originating from different natural and anthropogenic sources. However, they also reflect the measurement uncertainties associated with OC quantification. On the other hand, EC concentrations seem to be less variable, accounting on average for roughly 5% of the total PM_{10} mass.

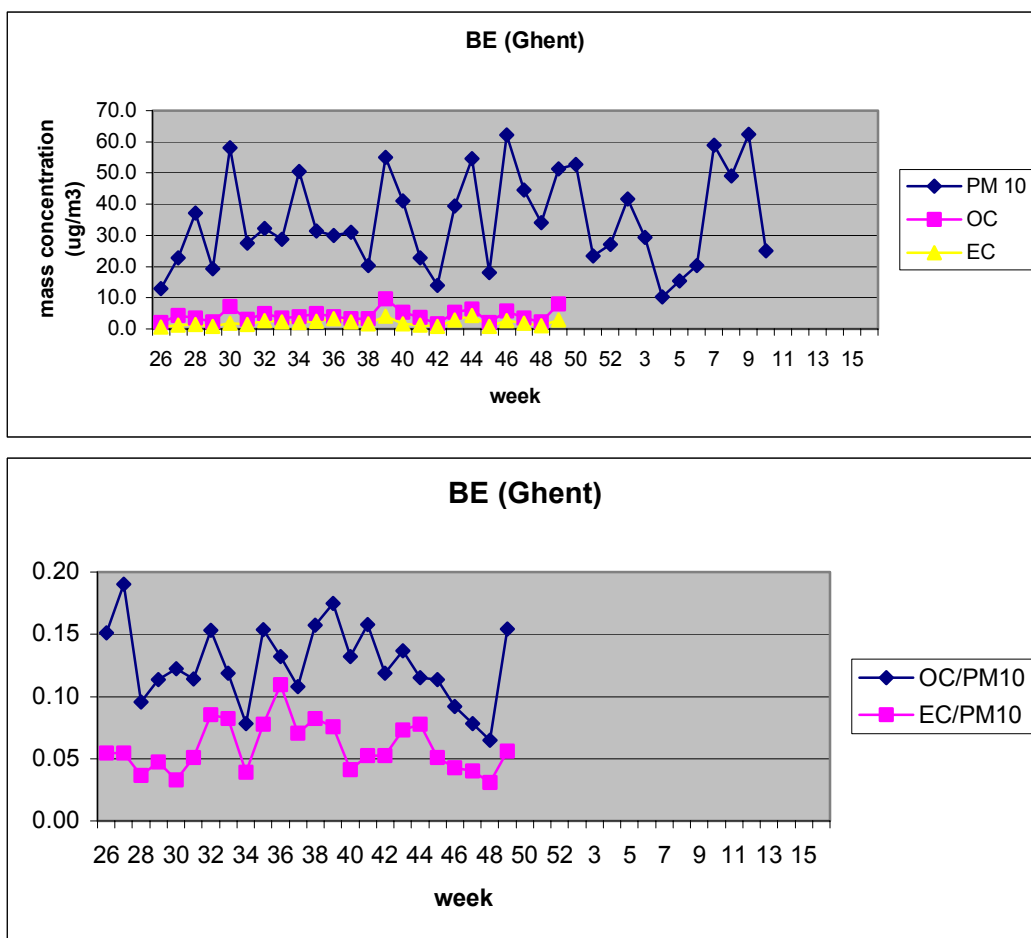


Figure 2.20: EC/OC results for the period of June 2002-April 2003 at Ghent (Belgium): mass concentrations in PM_{10} (upper panel); mass ratios OC/PM_{10} and EC/PM_{10} (lower panel).

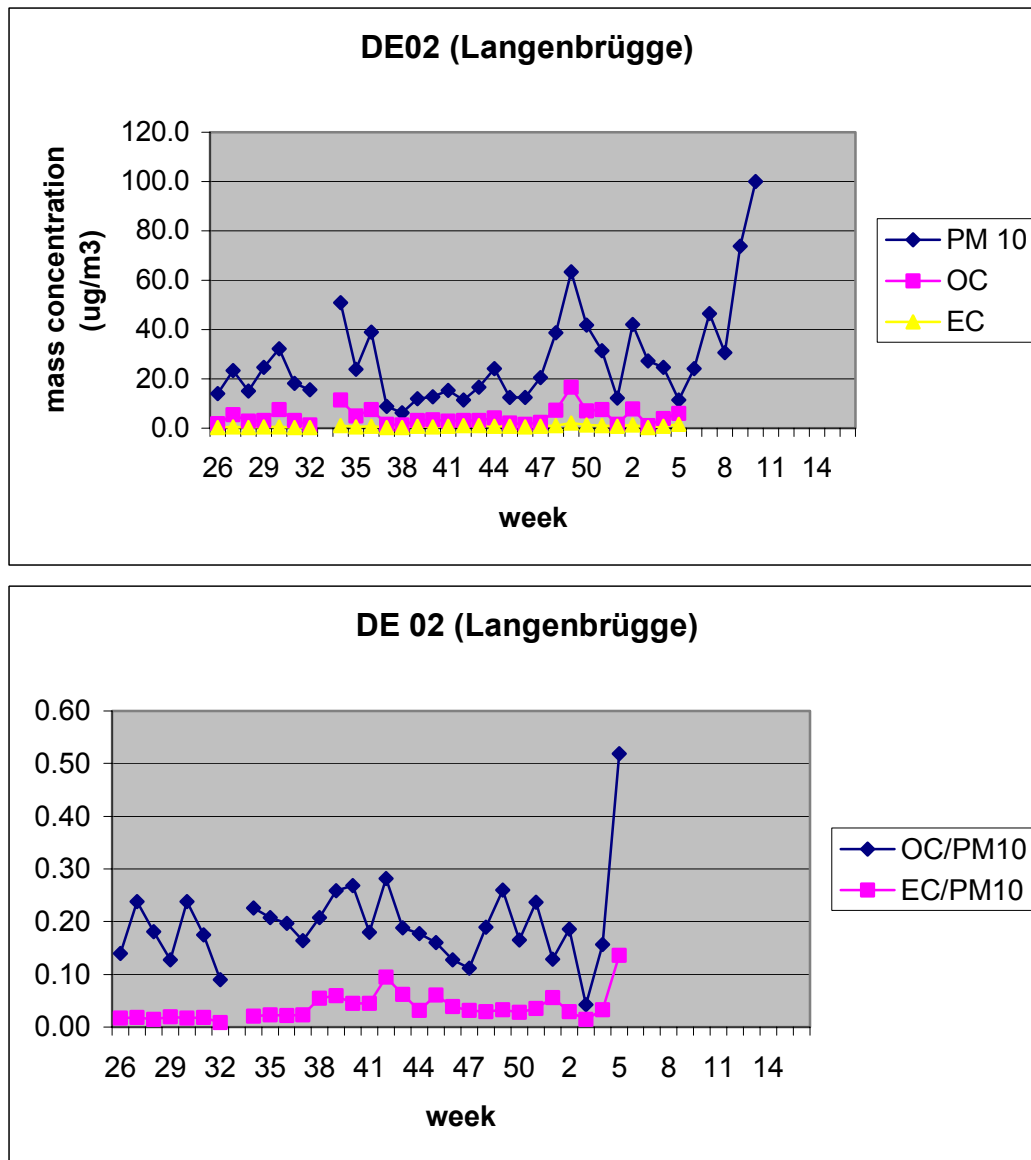


Figure 2.21: As Figure 2.20, but for Langenbrügge (Germany).

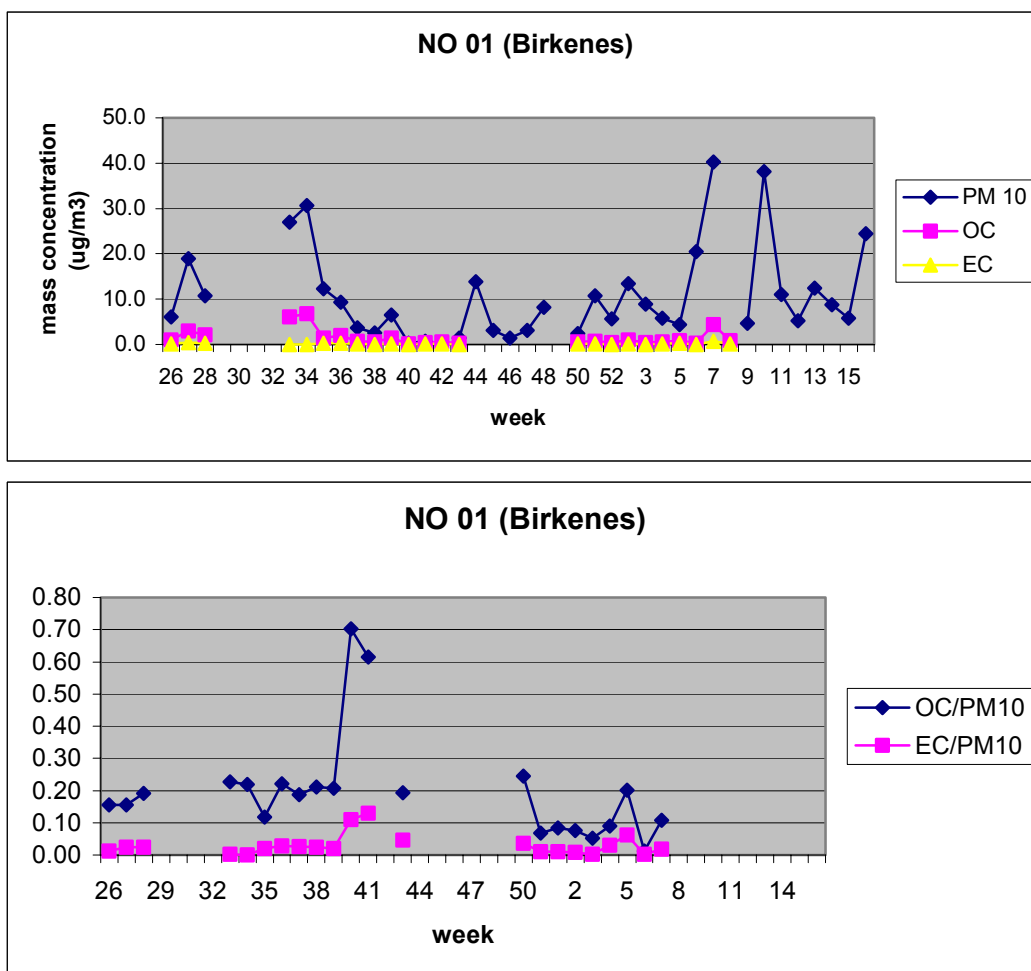


Figure 2.22: As Figure 2.20, but for Birkenes (Norway).

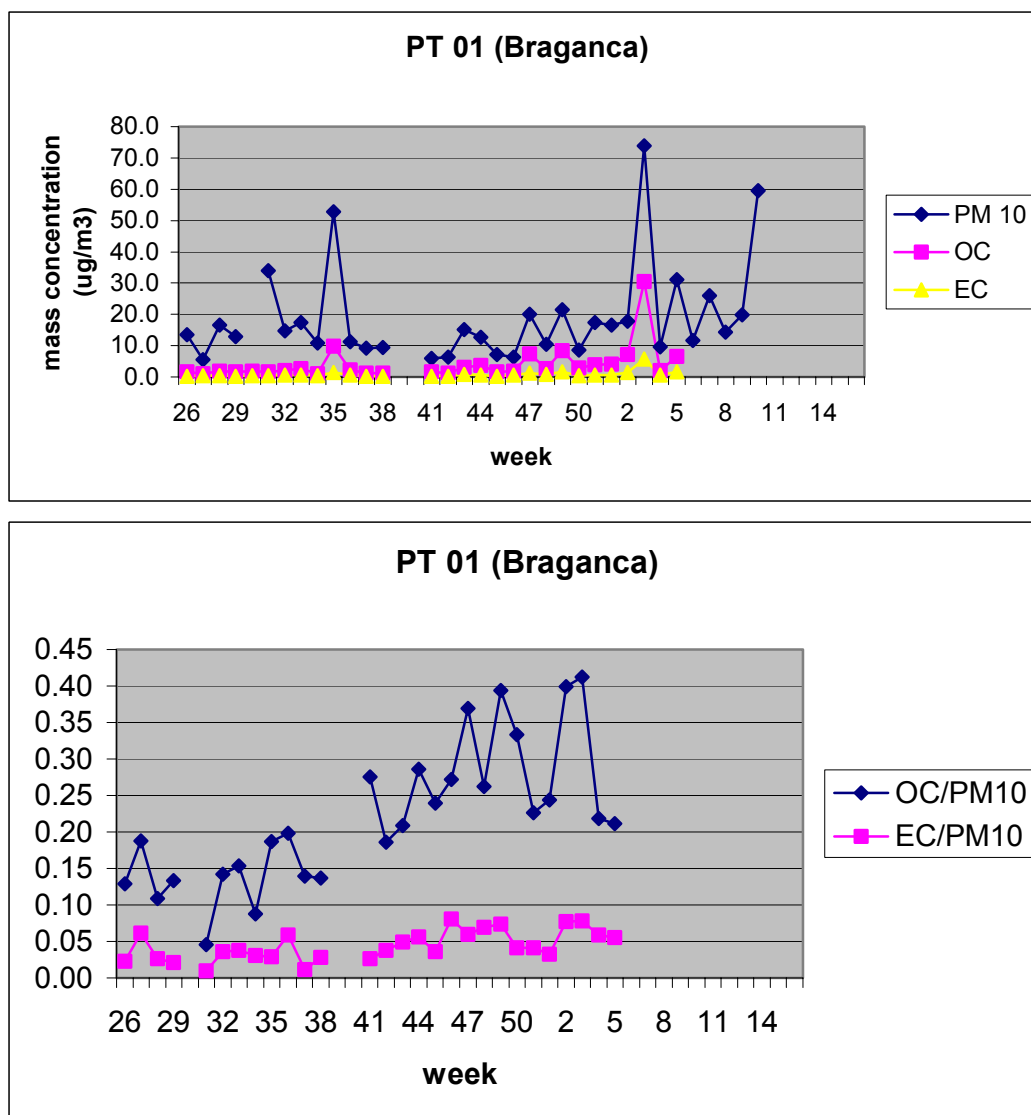


Figure 2.23: As Figure 2.20, but for Braganca (Portugal).

2.3 Conclusions

Modeling results and measurements for the main inorganic constituents have been found to agree, in general, reasonably well. Remaining issues are to clarify the unaccounted mass in aerosols and to improve the observational characterisation of EC/OC. Water, volatile species, and uncertainties in the OC contribution are most likely the main sources of uncertainty. The data material available on the partitioning of NH_3 and NH_4 and of HNO_3 and NO_3 is insufficient. Very little is known about the artifacts associated with volatile organic carbon. EC/OC data are currently available on a campaign basis only, which does not provide enough data material for improving the parameterisation of EC/OC in the model. Also, artifacts connected to sampling and analysis of the EC/OC content need to be carefully assessed. A major source of uncertainty is the correction factor that needs to be applied to OC mass concentrations in order to account for elements other than carbon. More detailed research is needed to reduce this uncertainty. OC speciations and/or a fractioning of OC species into solubility classes are needed for selected sites in order to learn more about the contents of the OC fraction and its spatial and temporal variability. Information on the characterization of OC/EC should also be provided for emission data. More observational information on the EC/OC fraction in aerosols will be of great help for implementing secondary organic aerosols in the EMEP model, which can be expected to significantly improve the agreement between model predictions and observations.

3. Main information available from EMEP

by Michael Kahnert, Leonor Tarrasón, Svetlana Tsyro, Markus Amann, Chris Heyes, Zbigniew Klimont, Vigdis Vestreng, Jan Schaag and Kjetil Tørseth

3.1 Status and future requirements for PM monitoring

Observations are fundamental for achieving a better understanding of the chemical and physical processes relevant for the long-range trans-boundary transport and deposition of particulate pollutants. It is therefore important to develop the monitoring capacity for particulate matter and to sustain it with stable and reliable resources. EMEP is the main framework for establishing a monitoring network on a regional scale for particulate pollutants in Europe. There exists a partial overlap between EMEP and Airbase monitoring stations for PM₁₀, and it is important that both networks make use of relevant data and exchange information. However, measurements of policy-relevant quantities (PM₁₀, PM_{2.5}) under the EC-requirements for PM monitoring are not sufficient to meet EMEP's objectives. More detailed information on chemical and physical properties of aerosols is needed in order to understand and correctly predict long-range trans-boundary transport of aerosols, their deposition, and their effects on human health. EMEP therefore needs to pursue a dual strategy of extending its own aerosol monitoring programme of particulate matter and of obtaining supplemental information from external data providers. In particular, for obtaining information from advanced and resource-intensive measurement techniques it is essential to intensify cooperation with the research community.

EMEP's dual focus on policy/abatement strategies and on process studies puts EMEP in a highly favourable position to provide a link between the policy and the research community. EMEP is also intensifying its cooperation with GAW. Joint supersites are being established, and a harmonisation of the data flow in both networks is currently being implemented.

One focus of this section will be to evaluate the information that can be obtained from the current PM monitoring network, to give recommendations for possible improvements, and to present some case studies to illustrate the information obtainable from comprehensive physical, chemical, and optical aerosol measurements. Fulfilling EMEP's objectives poses a significantly larger challenge for particulate matter than for many other single-component pollutants due to the highly complex and variable nature of particles in air. A critical inventory of the current EMEP monitoring programme for aerosols is therefore in order. EMEP's monitoring network for PM mass concentrations is relatively young and still expanding. This offers the opportunity for designing the network such that it is well coordinated with existing EMEP observations on selected or individual aerosol components. A good coordination is important for obtaining an as complete as possible characterisation of particulate pollutants.

The EMEP database contains a large number of chemical and physical parameters of aerosols observed at various European sites. Table 3.1 provides an overview over the various components reported by different countries in 2001. For some of these components concentration maps showing the measurement sites have been

given in Chapter 2 (see Figure 2.2–Figure 2.11). As can be seen in these figures, the sampling sites are in general distributed quite inhomogeneously, and there are regions with insufficient spatial data coverage. One purpose of this section is to discuss the issue of site density for chemical and physical aerosol observations and the coordination between measurements for different aerosol parameters.

Table 3.1: Number of EMEP stations in different countries reporting different chemical and physical aerosol parameters in 2001.

	AT	CH	CZ	DE	DK	ES	FI	FR	HU	IE	IS	IT	LT	LV	NL	NO	PL	RU	SE	SI	SK	TR	total
Acidity												1											1
Al											1												1
NH4									1			2		2	2	7	3	3				1	21
NH3+NH4	1	1	2	5	3	10	4						1	2		7	4		3	1			44
As				4	2		1				1				1	1							10
Cd	3		2	8	3	2	1				1		1	2	1	1					5		30
Ca															1	7							8
Cl																7							7
Cr					3		1				1					1					5		11
Co																1							1
Cu				8	3	2	1				1		1	2		1					5		24
Fe				2	3		1				1												7
Pb	3		2	8	3	2	1				1		1	2	1	1					5		30
Mg																7							7
Mn				8	2		1				1					1					5		18
Hg											1					1							2
Ni				8	3		1				1			2		1					5		21
NO3									1			2		2	2	7	3	3			5	1	26
HNO3+NO3	1	1	2	6	4	10	4						1	2		10	4		3	1		1	50
K																7							7
Na					3											7							10
SO4	1	3	2	5	3	10	4	8	1	3	1	2		2	2	7	4	3	4	1	5	1	72
V							1				1					1							3
Zn					3		1				1		1	2	1	1					5		15
TSP		1				10						1							4				16
PM10	3	4		8		10						1				2							28
PM2.5	1	2		3		10						1				2							19
Total	13	12	10	73	38	66	22	8	3	3	13	10	6	20	11	88	18	9	14	3	45	4	489

Particle mass concentrations

An important part of the uncertainties encountered in the comparison between the EMEP model and the EMEP/AIRBASE observations of PM mass concentrations derives from uncertainties in re-suspended or eroded wind-blown dust, which is mainly contained in the coarse fraction of particles between 1-10 µm. Also contained in this fraction is a large contribution from natural sea salt particles. Although sodium sulphate and nitrate are also encountered in the coarse fraction, a large contribution to the coarse mode comes from natural sources. By contrast, fine particles usually contain a significant fraction of aged secondary aerosols formed from anthropogenic precursor gases. Also, fine particles are removed

much less efficiently by dry or wet deposition processes than coarse particles and therefore play the most important role in long-range transport processes. It is necessary to complement PM₁₀ monitoring by additional data that allows us to separate fine, aged, long-range transported aerosols with an often large portion of anthropogenic constituents from relatively short-lived coarse aerosols consisting of predominantly natural constituents. This will greatly facilitate the verification of EMEP model results on fine and coarse particles with observations and thus contribute to the improvement of our understanding of the origin of PM.

EMEP is establishing and extending monitoring of fine particles in order to complement PM₁₀ measurements. The metric currently used is the integrated mass of particles up to 2.5 µm (PM_{2.5}). A recent WHO review recommended to use PM_{2.5} as the indicator for health effects induced by particulate pollution, such as increased risk of mortality in Europe (WHO, 2003). Most studies on health effects of fine particles are based on using PM_{2.5}. However, it should be noted that from a scientific standpoint PM₁ is likely to be a better metric, since in a typical aerosol size distribution the minimum between the fine and the coarse mode lies around 1 µm. The concentrations of fine and coarse aerosols are controlled by different processes, and there is no significant mass transfer between the fine and the coarse mode fraction. Thus the PM₁ metric in conjunction with the PM₁₀ metric allows us to better separate the fine and coarse mode aerosols. PM₁ should therefore be seriously considered as an alternative to PM_{2.5} in monitoring of fine particles and in health effect studies.

Particle chemical composition

As can be seen in Figure 2.2 and Figure 2.5, the spatial data coverage for sulphate is quite good in Europe, although more data from Eastern Europe would be desirable. Also, in some countries, such as Germany, the measurement sites are not very evenly distributed. We clearly see in Figure 2.1 that the EMEP model predicts particularly high concentrations of SIA in these regions. Sulphate measurements are reasonably well coordinated with particle mass monitoring. Thus almost all stations from which PM_{2.5} data were available in 2001 also reported sulphate concentrations in aerosols (with the exception of Chaumont in Switzerland, Langenbrügge in Germany, and Lista in Norway). 20 out of 28 stations from which PM₁₀ data were available in 2001 also reported sulphate concentrations in aerosols.

The spatial data coverage of filterpack and denuder/filterpack measurements for distinguishing between ammonia and ammonium and between nitric acid and nitrate is less satisfactory and not sufficiently coordinated with particle mass measurements. Only two stations (Birkenes in Norway and Ispra in Italy) from which PM_{2.5} and PM₁₀ data were available in 2001 also reported separate data for NH₃ and NH₄⁺ and for HNO₃ and NO₃⁺. The other stations performing denuder measurements of ammonium and nitrate did not perform PM mass measurements. For most other stations measuring PM we have only data for the sum of ammonium and ammonia and for the sum of nitric acid and nitrate. A reasonably complete data set of all relevant inorganic components coordinated with monitoring of particle mass has been reported from only one EMEP site in 2001, namely from Birkenes in Southern Norway. (We note that in different geographical regions there are different inorganic components that, in addition to

sulphate, nitrate, and ammonium, may be important. At Birkenes, for instance, sea salt is usually more important than mineral dust, whereas in Southern Europe mineral dust can be more important than sea salt.) Thus a better coordination between PM mass observations and the chemical characterisation of aerosols within EMEP, and in fact an extension of chemical measurements, is needed.

First results from the EC/OC campaign 2002/03 coordinated by CCC strongly confirm that elemental carbon and, even more so, organic carbon make a large contribution to the total mass of particles throughout Europe. This agrees well with recent findings by Putaud et al. (2002). High priority has to be placed on obtaining a better characterisation of the EC/OC fraction both in the monitoring programme and in the further development of the EMEP model. Weekly EC/OC determinations for the coarse and the fine fraction are desirable for a reasonably high number of sites. In addition, OC speciation of individual compounds and/or fractioning into different solubility classes (water soluble, water insoluble, other solvents) should be performed for a limited number of sites.

Particle number concentrations

The high significance of obtaining more information on particle number concentrations for reaching a better understanding of health effects, aerosol dynamical processes, and indirect climate forcing has been discussed in some detail in Chapter 1. One can conclude that it would be highly desirable to supplement the aerosol monitoring programme, focusing on particle mass, with more detailed information about particle number distributions. However, measurements of particle size distributions are more expensive and technically more demanding. A revision of EMEP's monitoring programme is currently being discussed. A three-level approach has been suggested for the monitoring programme, with a large number of level 1 sites performing the "classical" monitoring activities of PM₁₀ and inorganic aerosol chemistry, a somewhat smaller number of level 2 sites providing, in addition, PM_{2.5} or PM₁ measurements, elemental and organic carbon monitoring, mineral dust analysis, etc., and a selected number of level 3 sites performing more advanced and demanding monitoring activities. Monitoring of particle number distributions could fall under such level 3 activities. The recent addition of a DMPS instrument to the EMEP site in Birkenes (Norway) for monitoring size distributions is a step in the right direction. More such data are needed throughout Europe.

It would also be conceivable to recruit more researchers to provide their data into EMEP's database. The CREATE project under the 5th framework programme, in which NILU/CCC leads a work package on building an aerosol database, offers an opportunity to complement EMEP's monitoring database by more advanced and otherwise unavailable research data. This also is an important step in a new direction. Such an extension of EMEP's aerosol database will expand the relevance of EMEP's monitoring programme, which is a predominantly policy-driven activity with a main focus on issues related to health and ecosystems. A more comprehensive data set on aerosol chemical composition and number densities will also provide valuable information for climate research and thus strengthen EMEP's role as an environmental monitoring programme.

Optical particle measurements

Modelling long-range transport of aerosols requires computations in a model atmosphere consisting of multiple layers. Mass and number concentrations of particles on the ground and in upper layers influence each other in various ways. A comprehensive validation of the EMEP unified model should therefore aim in the future at taking information on vertical distributions of particles into account. Ground measurements can provide us with a very detailed physical and chemical characterisation of particulate matter. However, they do not provide us with information about the vertical distribution of particles in the boundary layer and in the free troposphere. Mass and particle concentrations and chemical composition of aerosols measured on the ground are in general not representative for the corresponding particle characteristics at higher altitudes. Additional data are therefore needed. In situ measurements from airborne instruments are expensive and only available on a campaign basis. However, various kinds of optical measurements can serve to retrieve information on the distribution and temporal evolution of particles at higher altitudes.

As an illustration Figure 3.1 shows a time series of the Ångström exponent α (upper panel) retrieved from sun photometer data at the Zeppelin EMEP site at Ny-Ålesund on Spitzbergen (Norway). This sun photometer is part of the global network AERONET (<http://aeronet.gsfc.nasa.gov>). Low values of α , such as those observed on September 16 2002, indicate a higher abundance of larger particles in the atmospheric column above the measurement site.

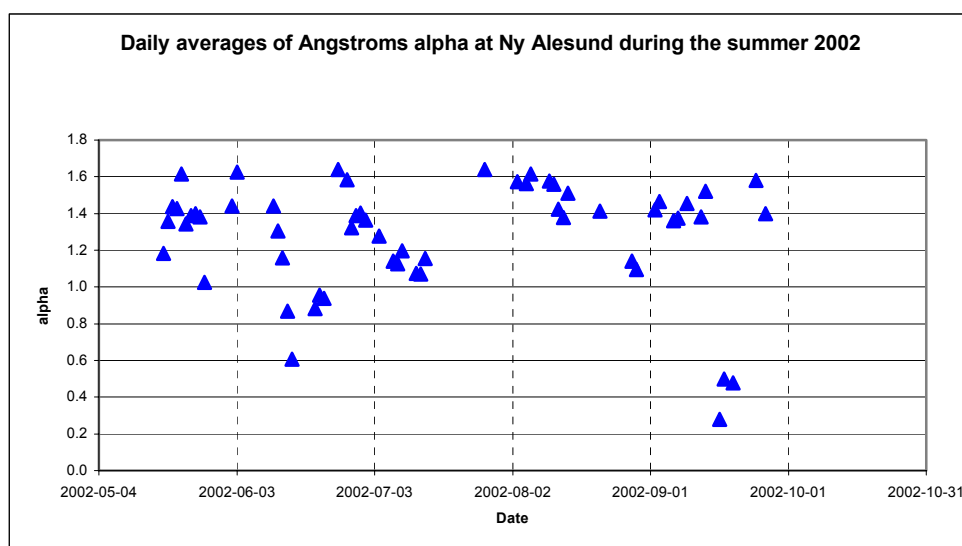


Figure 3.1: Daily averages of the Ångström exponent α at Ny-Ålesund during summer 2002.

Figure 3.2 shows a time series of the aerosol optical depth (AOD) on September 16 retrieved from the same photometer data. Larger particles scatter mainly the longer wavelengths. One can clearly see how the low α values on September 16 in Figure 3.1 coincide with a strong increase in the AOD during the

morning hours in the long-wave channel at 863 nm. Thus we can deduce from the sun photometer data that the size distribution of the particles passing the column shifts to larger particles during the morning hours of September 16.

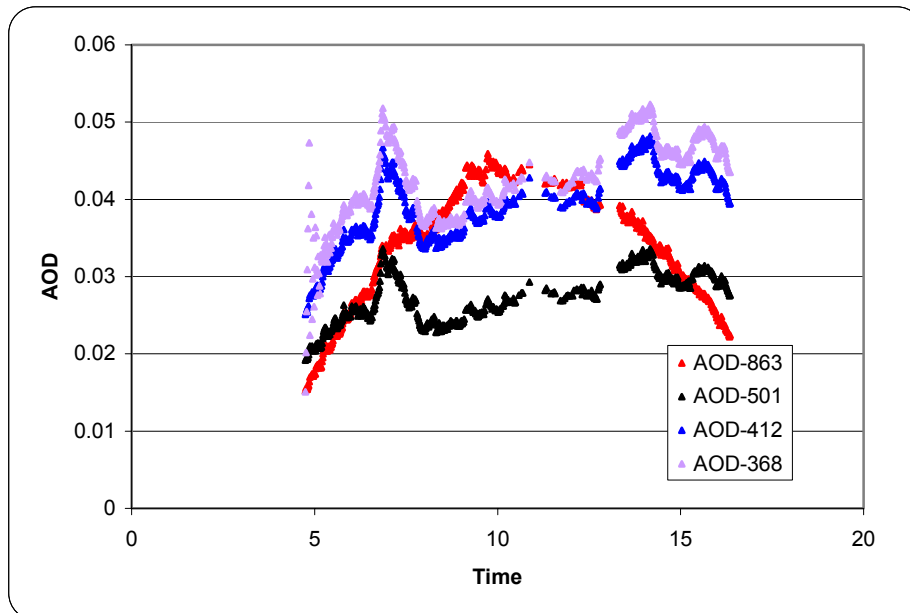


Figure 3.2: AOD at Ny-Ålesund during 16th September 2002.

Another illustration of the high potentials of optical measurements is given in Figure 3.3–Figure 3.4. The plots show Raman lidar measurements performed at the Southern Great Plains site of the US Atmospheric Radiation Measurement (ARM) programme and are taken from the ARM website (<http://www.nsd.arm.gov/cgi-bin/quicklook/frame.pl>). Lidar backscattering data provide us with a unique range-resolved picture of the vertical distribution of aerosols in the atmosphere and their temporal evolution. In Figure 3.3, especially in the upper panel, one can clearly discern a high concentration of aerosols in the boundary layer, which expresses itself by a higher scattering ratio in the boundary layer than in the upper tropospheric layers, in which Rayleigh scattering by molecules dominates. The variation of the vertical extent of the aerosol layer over the two-day period as well as an increase in aerosol concentrations is clearly seen. The high scattering ratios starting to occur at around 0200 UTC on April 21 indicate cloud formation. Also, the variation of the cloud base and the cloud top can be clearly observed in the data visualisation.

The instrument sends out polarised laser light and measures the backscattered light in two perpendicularly polarised channels, thus allowing for the determination of the depolarisation ratio. Since nonspherical particles depolarise light much more strongly than spherical particles, this allows us to discriminate between water and ice clouds. Figure 3.4 (note the larger vertical scale compared to Figure 3.3) shows that the clouds forming early on April 21 above the boundary layer have a rather low depolarisation ratio, whereas clouds observed throughout

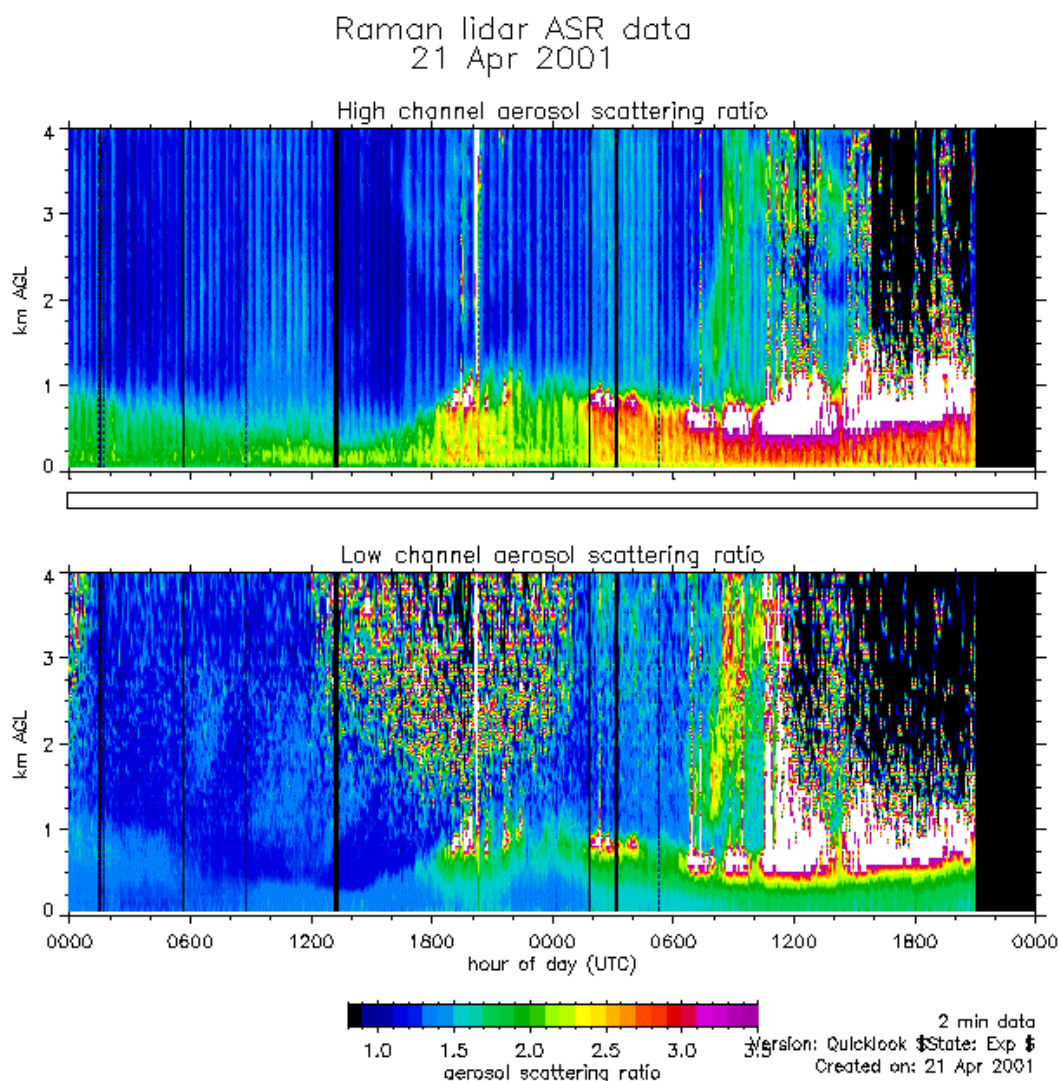


Figure 3.3: Aerosol backscattering ratio during a two-day period at the SGP ARM site.

the two days near the tropopause have a high depolarisation ratio. One can conclude that the low-altitude clouds consist of liquid water, whereas the higher clouds are ice or mixed-phase clouds.

The above examples are meant to illustrate the wealth of information contained in optical measurements, both from ground-based and from satellite-borne instruments. A lot can be learnt from these data about the transport and evolution of aerosols in the atmosphere. A lot can also be learnt about the aerosols' interaction with clouds, which is important for wet deposition of aerosols, for cloud processing of particles, and not least for climate studies. Optical data would also provide useful information on aerosol loads in the boundary layer and the free troposphere for future model validation studies. It should therefore be considered to include a selected number of optical monitoring data into EMEP's aerosol database, or even to recruit new sites performing continuous optical aerosol monitoring as EMEP "level 3 sites".

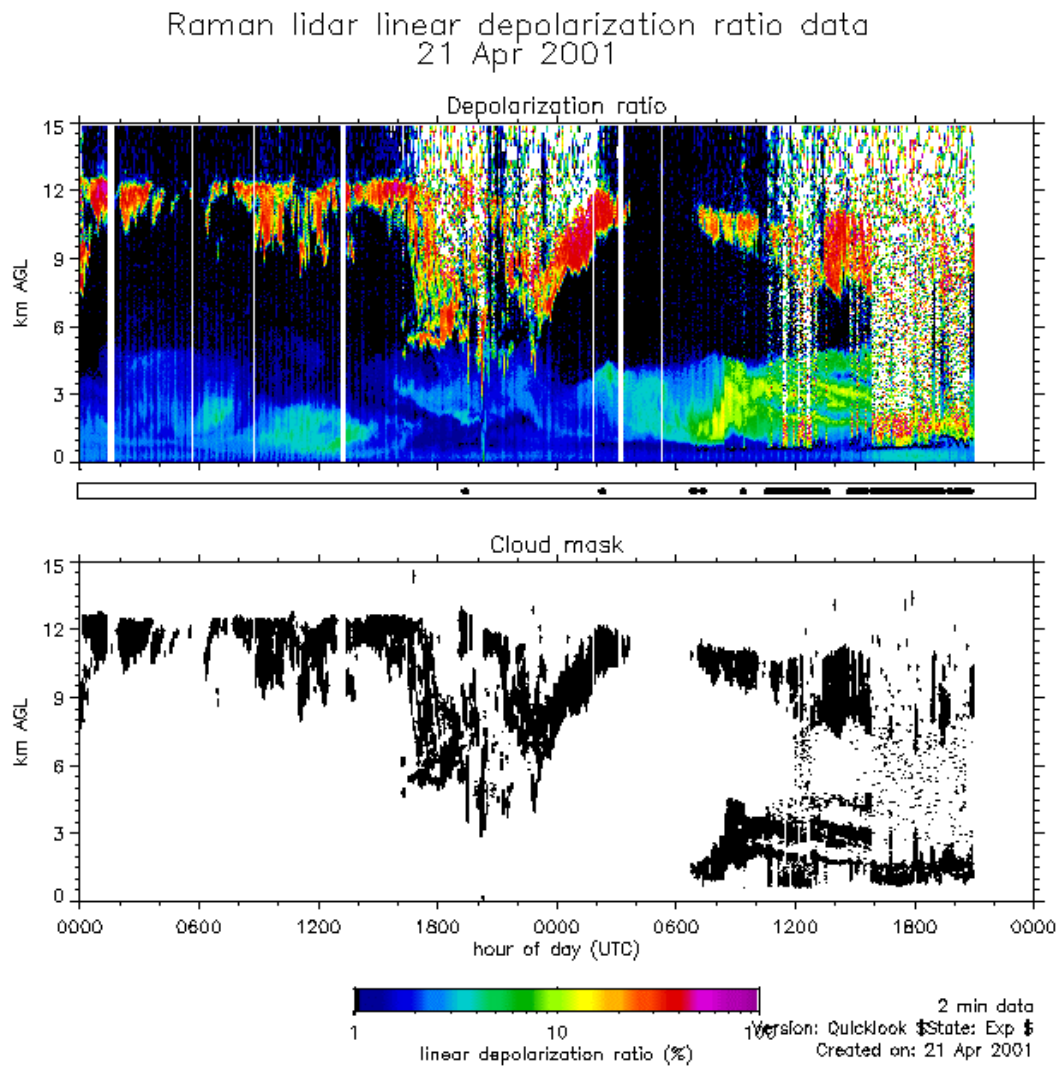


Figure 3.4: As Figure 3.3, but for the backscatter depolarisation ratio (upper panel) and for a cloud mask (lower panel).

3.2 Status and further development of EMEP Aerosol Modelling

Two models of different purpose and complexity level are presently operated at EMEP/MSC-W, for calculating long-range transport of particulate matter. These are:

- the Eulerian Unified EMEP model, and
- the EMEP research aerosol model (UNI-AERO).

The EMEP Unified model is a mass model that deals with bulk aerosol and does not account for aerosol dynamics. The EMEP research aerosol model, UNI-AERO, resolves the particle size distribution with four mono-disperse modes and accounts for aerosol dynamics.

Differences between the two models are justified by their different purposes. The Unified EMEP model mass model is used for calculation of source-receptor relationships of aerosol mass concentrations (EMEP, 2003c). The EMEP research aerosol model, UNI-AERO is used for testing new parameterisations, studying the effect of different aerosol processes on aerosol concentrations, and analysing the sensitivity of results to main uncertainties in input parameters and assumptions.

Results from the comparison of the two models with observations justify the use of the Unified mass model for calculation of mass concentrations of $PM_{2.5}$ and PM_{10} over Europe. The introduction of aerosol dynamic processes implies differences in the calculated concentrations within 10% for $PM_{2.5}$ and 20% for PM_{10} . These are relatively small differences compared to the systematic underestimation of the model results against observations of PM_{10} (35-44%) and $PM_{2.5}$ (20-30%).

The model underestimation of observed values is found to be related with carbonaceous and mineral dust constituents and the unaccounted part of the observed aerosol (mainly water and volatile species). Consequently, the OC contribution to aerosol mass is considered to be a main source of uncertainty in the modelled anthropogenic results.

3.2.1 Main differences in model formulation

The EMEP Unified model describes the emission, chemical transformation, transport and dry and wet removal of about 69 photochemical species. The aerosol components in the Unified model are Secondary Inorganic Aerosols (SIA), i.e. sulphate (SO_4), nitrate (NO_3) and ammonium (NH_4), and primary anthropogenic fine and coarse particles, respectively $PPM_{2.5}$ and coarse PPM. The model calculates mass concentrations of all these individual aerosol components and $PM_{2.5}$ and PM_{10} .

The EMEP research aerosol model, UNI-AERO, describes 14 different chemical components including 7 aerosol components in 4 monodisperse modes: SIA (SO_4 , NO_3 and NH_4), primary anthropogenic aerosols, including organic carbon (OC), elemental carbon (EC) and mineral dust, and natural aerosol in the form of sea salt. UNI-AERO calculates particle number, size distribution and aerosol chemical composition in addition to PM mass. Presently, UNI-AERO calculates

PM_{2.5} and PM₁₀, but it can also calculate other PM concentrations, e.g. PM₁, if desired. The aerosol dynamics module implemented in UNI-AERO is still under development.

The main differences in model formulations include:

Emissions: Emissions of gaseous precursors (SO₂, NO_x, NH₃) are treated in the same way in both models, while PM_{2.5} and coarse PM emissions in UNI-AERO are further distributed according to their chemical speciation and size distribution. Information on the emission share of OC, EC and mineral dust between three different size modes is therefore necessary.

Chemistry: The EMEP Unified model includes the full photochemistry with 69 components and about 170 reactions, while UNI-AERO is presently built up on the simplified SO_x-NO_x-NH_y chemistry of the Acid deposition model (UNI-ACID). For model comparison, the same equilibrium model EQSAM for aerosol/gas fractioning of nitrate and ammonium was used in both models. In UNI-AERO, EQSAM also calculated the mass of water associated with aerosol. The results presented in Chapters 1 and 2 in this report are obtained with the aerosol model using a new EQSAM version, which also accounts for Na and Cl from sea salt spray.

Dry and wet deposition: The same scheme for dry deposition and wet scavenging was used in the Unified and the aerosol dynamics model. The only differences in the calculated dry deposition velocities and scavenging rates for aerosols result from different description of the aerosol size distribution by the models. The parameter choices in the Unified model have been made to achieve as similar calculations of aerosol dry and wet deposition as possible in the two models.

Sea salt: Prior implementation in the Unified model, a parameterisation for sea salt spray generation was included and tested in the aerosol model. Sea salt contributes to fine and coarse aerosol mass, and its importance is largest in coastal areas, especially in cold seasons. After further verification with the aerosol model, sea salt aerosol will also be implemented in the Unified model.

In both models, PM_{2.5} and PM₁₀ mass concentrations are calculated as sum of the following individual mass components:

$$PM_{2.5} = SO_4 + \text{fine } NO_3 + NH_4 + \text{primary } PM_{2.5} (+ \text{fine sea salt in UNI-AERO})$$

$$PM_{10} = PM_{2.5} + \text{coarse } NO_3 + \text{primary coarse PM} (+ \text{coarse sea salt in UNI-AERO})$$

A detailed description of both models is given in EMEP Status Report 1/2003 Part I (EMEP, 2003a).

The effect of the differences in model formulation, and thus the effect of different processes on calculated PM₁₀ is visualised in Figure 3.5. The red curve shows the monthly variation of PM₁₀ from the EMEP Unified model (UNIF), the mass model, over a series of German and Swiss EMEP stations. Analogous results from the aerosol model are given in the blue curve (AERO). To understand better the

origin of differences between the two curves, results from two sensitivity tests are shown. The green curve shows PM_{10} as calculated by the aerosol model without sea salt (AER-SS). The diamonds show the results from a mass model run with the same chemistry as used in the aerosol research model (ACID).

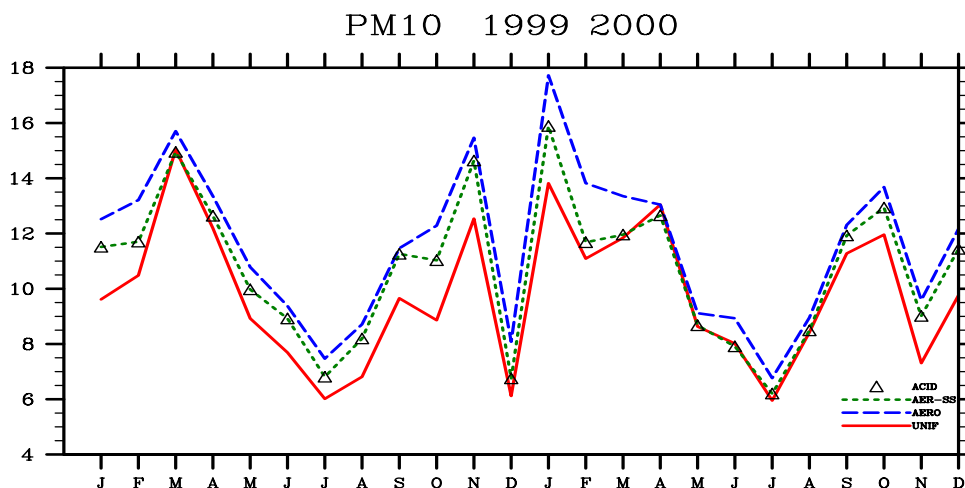


Figure 3.5: Monthly series of PM_{10} concentrations in 1999-2000 calculated with the Unified model (UNI, in red), aerosol dynamics model (AERO, in blue) and acid deposition model (ACID, in diamonds) and PM_{10} with subtracted sea salt mass from the aerosol model (AER-SS, in green). See text for discussion.

The largest differences between the models are due to differences on the chemistry and to the inclusion of sea salt. The green curve (AER-SS) shows that the effect of sea salt is particularly important in winter and spring. Differences between the blue curve, PM_{10} from the Unified model (UNIF), and the green curve (AER-SS) show the effect of chemistry. The close coincidence between (AER-SS) and (ACID) indicates that the effect of aerosol dynamics in the PM_{10} concentrations is rather small.

Comparison of calculated PM distributions over Europe from both models is shown in Figure 3.6. The main conclusions from the comparison of the two models are:

- The largest differences in the resulting PM concentrations are due to chemistry and accounting for sea salt, while aerosol dynamics has much smaller effect on the aerosol mass
- The differences in $PM_{2.5}$ concentrations are largely within 10% and in PM_{10} concentrations are largely within 20%. Along the Atlantic coast, the differences can reach 20 and 50% respectively due to the effect of sea salt.

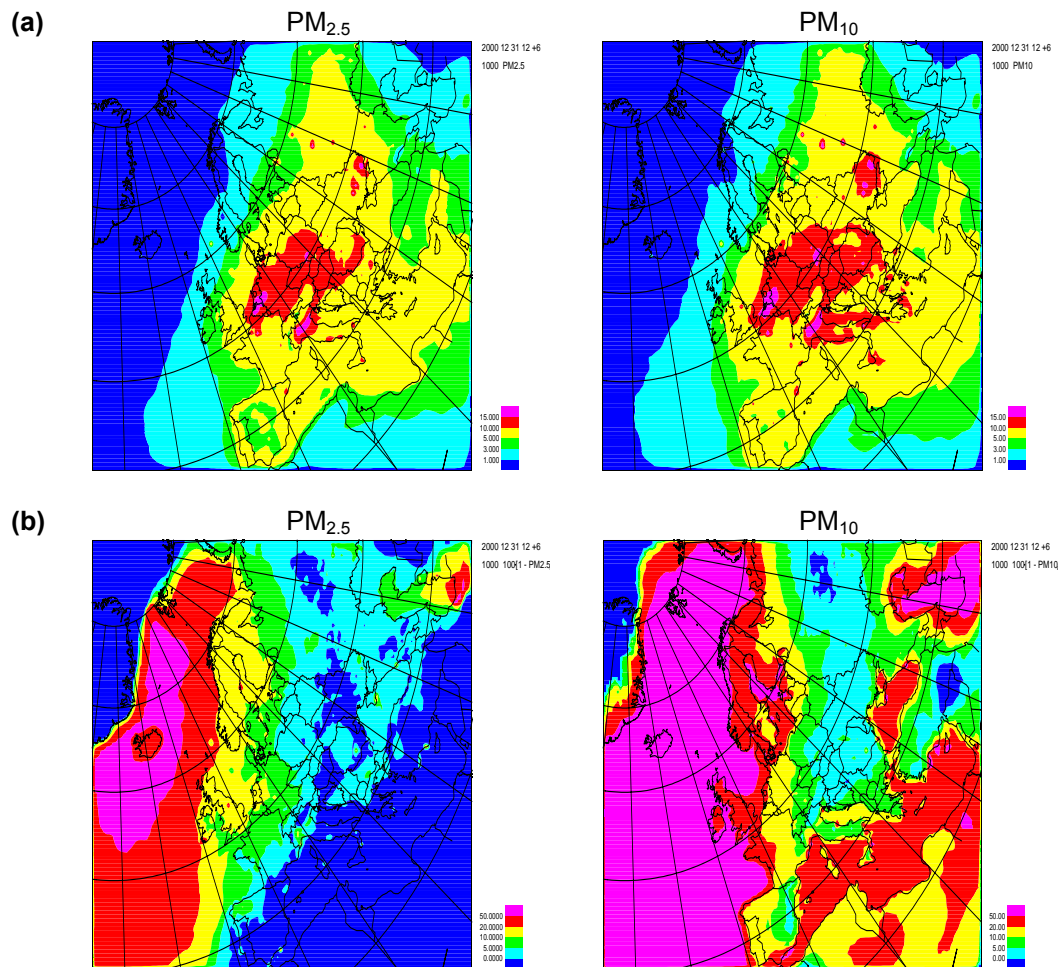


Figure 3.6: Upper panel (a): $PM_{2.5}$ and PM_{10} mass concentrations in 2000 calculated with the Unified model ($\mu g/m^3$). Lower panel (b): Relative differences in percent (%) in PM_{10} and $PM_{2.5}$ mass concentrations with respect to calculations with the research aerosol model (UNI-AEREO).

3.2.2 Summary of model performance

The model results were verified with available measurements from the EMEP monitoring network and the AIRBASE data system operated by ETC/ACC. Comparison of the Unified mass model and the aerosol research model and validation with available measurements for the years 1999 and 2000 is presented in EMEP Status Report 1/2003 Part II (EMEP, 2003b).

The spatial and temporal correlation between calculated and measured concentrations of the individual secondary inorganic aerosols and their sum, SIA, is quite high (0.5-0.7) for both models. PM_{10} concentrations from the Unified model correlate better with the measurements in polluted areas due to a better description of chemistry in the model. On the other hand, the correlation between PM_{10} from UNI-AERO and measurements is better in the regions affected by sea salt.

Both models show similar correlations with observations of PM_{10} (0.4-0.5) and a general underestimation of the observed PM_{10} mass. The underestimation of PM_{10} mass (30-50%) by the Unified model is larger than with UNI-AERO (20-30%) because of the introduction of sea salt in UNI-AERO (ref. Tsyro (2003) in EMEP Status Report 1/2003 Part II).

The seasonal model performance is also presented in EMEP Status Report 1/2003 Part II (EMEP, 2003b). The main difference with the results presented in this report is related to the implementation of an upgraded version of the equilibrium model EQSAM for gas/aerosol partitioning in the system SO_4 - NO_3 - NH_4 -Na-Cl- H_2O . A new version of EQSAM, extended to include Na and Cl from sea salt spray and allow the formation of coarse NO_3 on sea salt aerosols, was recently implemented both in UNI-AERO and the Unified mass model. The new EQSAM version also includes the improved parameterisations for calculation of the aerosol molalities and the solute activity coefficients. First results for NO_3 and NH_4 look quite promising (Figure 3.7 and Figure 3.8), but further testing is still in progress.

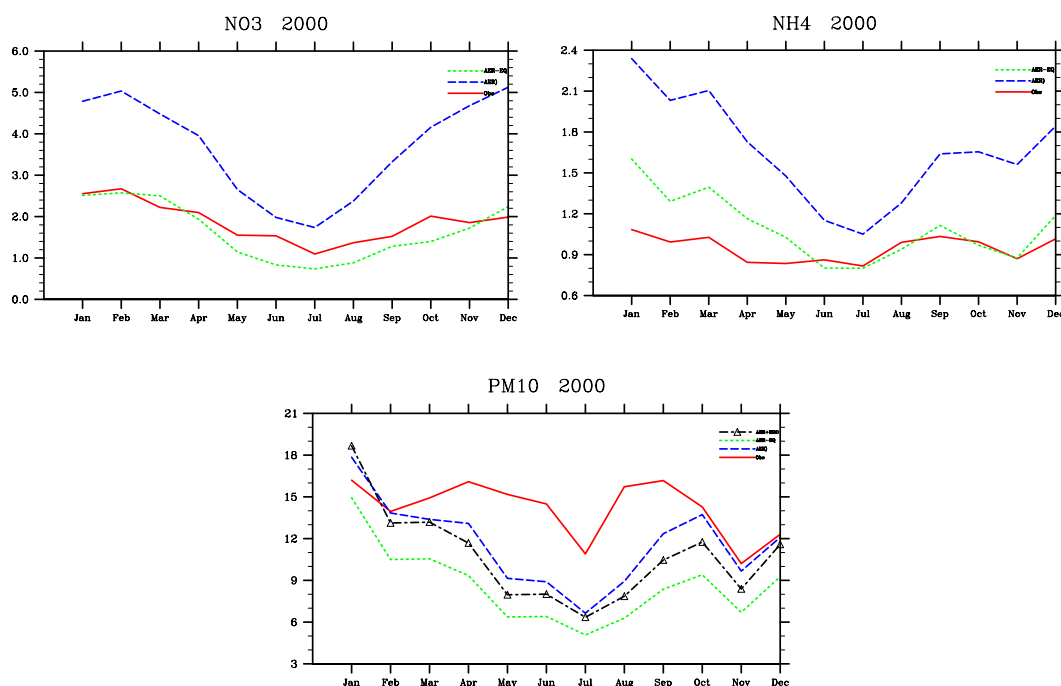


Figure 3.7: Monthly time-series in 2000 of NO_3 , NH_4 and PM_{10} calculated with different versions of the aerosol model and observed at EMEP sites (averaged over 20 sites for NO_3 , 27 sites for NH_4 and 13 sites for PM_{10}). Here, measurements – red curve, UNI-AERO with the previous EQSAM version – blue curve, UNI-AERO with the new EQSAM – green, PM_{10} including 25 % aerosol water – black curve.

The improved results in NO_3 and NH_4 concentrations obtained with the aerosol model have resulted in further under-prediction of PM_{10} (Figure 3.7), changing from “better results for wrong reasons” to “worse results for good reason”. This shows how important is the chemical characterisation of the aerosol when interpreting results from PM mass calculations against observations.

The comparison modelled aerosol chemical composition with observations so far has shown rather encouraging results (ref. Chapter 2 of this report). The main reasons for discrepancies between predicted and observed aerosol chemical composition are:

- 1) not accounting for SOA and re-suspended mineral dust in the model,
- 2) assumptions made on the chemical speciation of primary PM emissions,
- 3) measurement artefacts mainly related to water and volatile species

It is important to note that the comparison of PM₁₀ mass with observations is masked by measurement artefacts and the presence of an unknown amount of residual aerosol water in the samples. All calculated PM₁₀ concentrations presented in this report are dry PM₁₀ mass. The black curve in Figure 3.7 represents the calculated “wet” PM₁₀ where the retaining aerosol water is assumed to be 25 % of the dry mass.

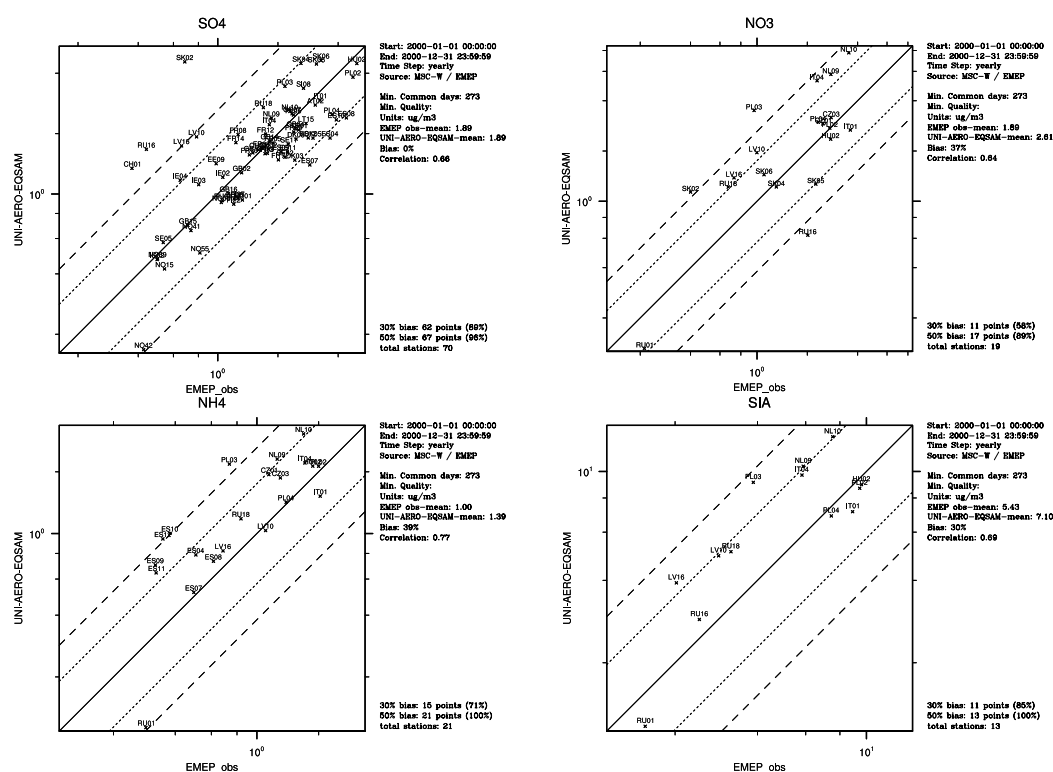


Figure 3.8: Scatter plots of SO₄, NO₃, NH₄ and the sum of SIA calculated with the EMEP aerosol model with the new EQSAM versus EMEP observations in 2000 (the scatter-plot for PM₁₀ is presented in Chapter 1). The relative bias here is calculated as (Model-Obs)/Obs.

Additional testing of model performance for the research aerosol model UNI-AERO involves also the analysis of particle number concentrations. Correlations with daily number concentrations are reasonably good (0.4-0.6) while the correlations of modelled values with hourly particle number concentrations have low values (0.2) and not surprisingly sometimes even anti-correlations. It is not

expected at this moment that the research aerosol model should reproduce hourly variations of particle number. Further testing of aerosol dynamics parameterisations and process analyses are needed to assure improvement in the model performance with respect to particle number concentrations. Sound parameterisation of the aerosol dynamics is an essential prerequisite for the model to capture the observed variations in particle number concentrations, and would be of importance for cloud processes and analysis of climate effects.

3.2.3 Requirements for further model development

The comparison between the Unified and aerosol model and verification of results with observations justifies the use of the EMEP Unified model for calculating PM mass. The Unified model was used this year for calculating the source-receptor relationship for SIA, PM_{2.5} (EMEP, 2003c). For calculations of particle number concentrations as well the size distribution of aerosol mass and number the aerosol research model should be used.

The aerosol model is also a useful tool for performing process studies and for testing new aerosol parameterisations prior to implementation in the Unified model. This implies that further Unified model development concerning aerosols will be first tested in the research module and then incorporated to the mass model.

Further model development is determined by the status of its performance against observation and by the requirements for the models further use. The status of model performance is given by results from model comparison with observations of the physical and chemical characteristics of the aerosol. These have shown that the modelled underestimation of observed values is related with carbonaceous and mineral dust constituents and the unaccounted part of the observed aerosol (mainly water and volatile species). The Unified model is requested to provide reliable data on the anthropogenic PM_{2.5} concentrations at background areas across Europe for use in health impact assessment.

Consequently, model development should be addressed to the introduction of anthropogenic carbon components and mineral dust in to the model. This requires appropriate information on the chemical composition and the size distribution of primary PM emissions and the introduction of tested parameterisations of the formation of secondary organic aerosols (Andersson-Sköld and Simpson, 2001).

Although the focus is mostly on anthropogenic part of the aerosol, there is a significant natural contribution in PM_{2.5} mass concentrations. In order to validate the model results for PM₁₀ and PM_{2.5} efforts have also been addressed to the inclusion of natural sea salt and wind blown dust sources in the Unified model. The implementation of generation of sea salt spray (Monahan et al., 1986; Mårtensson et al., 2003) has already been tested in the aerosol research model. Mineral dust is believed to be an important PM₁₀ constituent in spring and summer, and work on implementing re-suspended and wind blown dust in the aerosol model is in progress. After the necessary testing and verification of sea salt and mineral dust with the aerosol model these aerosols will also be included in the Unified model.

Finally, we would like to emphasize that there is an urgent need for appropriate information on the chemical composition and the size distribution of primary PM emissions. For model validation, more PM measurements covering different geographical regions are required. Since many sources contribute to the PM mass, measurements of PM_{2.5} and PM₁₀ should, as far as possible, be supplemented with analyses of the aerosol chemical composition. The importance of measurements of particle number concentrations was already advocated above and in Chapter 1. These are essential requests in order to facilitate further model development, verification and improvement.

3.3 Information of PM emissions

Emission information on PM precursor gases (SO₂, NO₂ and NH₃) and primary PM emissions are requested every year to the Parties to the Convention. The emission reporting requirements have been widely revised and extended resulting new Guidelines for Estimating and Reporting Emission data (EB.AIR/GE.1/2002/7) that were implemented for the first time this year. It is encouraging to see that reporting of particulate matter primary mass emissions has increased considerably in the last two years, reaching now a reached a level of reporting comparable to that of HMs and POPs.

Still, the requirements for PM emission data are only concerned with PM mass, namely, TSP, PM₁₀ and PM_{2.5}. Important information concerning the chemical speciation and size distribution of the primary emissions is not explicitly requested, which reduces the possibility of reviewing and verifying such data.

Given the identified uncertainties in the characterisation of the carbonaceous and mineral part of the aerosol, information on the share of elemental to organic carbon in PM emissions becomes an important prerequisite to improve our description of the origin of PM air concentrations. It is recommended to support dedicated expert studies in order to analyse the actual share of mineral components, black or elemental carbon and organic carbon components at different size ranges of PM primary emissions.

3.3.1 *PM emission data reported in 2003*

More than fifty percent of the Parties to the Convention on Long-Range Transboundary Air Pollution (CLRTAP) have already implemented the new Guidelines for Estimating and Reporting Emission data (EB.AIR/GE.1/2002/7). The timeliness, the amount of data, the completeness and the internal consistency of this year's submissions have increased compared to previous years.

It is for the second time that Parties to the Convention on Long Range Transboundary Air Pollution (CLRTAP) were requested to report particulate matter (PM) emissions according to the Draft Guidelines for Estimating and Reporting Emission data (EB.AIR/GE.1/2001/6 and Add.1).

A total of 24 Parties to the Convention submitted PM emission data to the UNECE. As many as 19 Parties (39%) submitted national total TSP emissions, 15 (30%) Parties submitted sector PM₁₀ emissions and 13 Parties (25%) reported of fine fraction of aerosol mass emissions (PM_{2.5}).

Actual emission PM data for 2000 and 2001 is available via the Internet at <http://webdab.emep.int>. Reported annual totals can be found in Vestreng (2003). An overview of officially reported PM data available from the UNECE/EMEP database can be found in Table 3.2.

The spatial distribution of PM₁₀ and PM_{2.5} emissions for use in model assessments at MSC-W for year 2001 model runs are shown in Figure 3.9 and Figure 3.10.

Table 3.2: Overview of 2000 and 2001 emissions for PM gaseous precursors and primary PM emissions. All values as Gg. (Data used for chemical transport modelling.)

	2000					2001				
	SO ₂ ^a	NO _x ^a	NH ₃ ^a	PM _{2.5} ^b	PM ₁₀ ^b	SO _x ^a	NO _x ^a	NH ₃ ^a	PM _{2.5} ^b	PM ₁₀ ^b
Albany	58	29	32	5	8	58	29	32	5	8
Armenia	8	10	25	5	7	4	13	25	5	7
Austria	38	196	54	27	47	37	199	54	28	48
Azerbaijan	15	43	25	19	30	15	43	25	19	30
Belarus	143	135	142	39	62	151	135	137	39	62
Belgium	165	329	81	36	65	162	317	81	36	66
Bosnia and Herzegovina	419	55	23	19	46	419	55	23	19	46
Bulgaria	982	185	56	74	132	846	164	54	74	132
Croatia	58	77	23	16	25	58	77	23	16	25
Cyprus	50	23	4	2	1	48	18	4	2	1
Czech Republic	264	321	74	63	104	251	332	77	63	43
Denmark	28	209	104	13	20	25	204	102	13	20
Estonia	95	41	9	17	37	92	38	9	17	37
Finland	74	236	33	38	48	85	222	33	38	54
France	654	1441	784	299	545	610	1411	779	303	550
Georgia	9	30	97	8	12	9	30	97	8	12
Germany	638	1584	596	156	239	650	1592	607	156	239
Greece	483	321	73	40	57	485	331	73	40	57
Hungary	486	185	71	26	47	400	185	66	24	43
Iceland	27	28	3	3	3	27	28	3	3	3
Ireland	131	125	122	11	14	131	125	122	11	14
Italy	758	1372	437	150	213	758	1372	437	150	213
Kazakhstan	237	50	18			237	50	18		
Latvia	17	35	12	7	11	13	42	12	7	11
Lithuania	43	48	50	9	1	49	55	50	9	1
Luxembourg	3	17	7	3	4	3	17	7	3	4
Netherlands	92	413	152	37	62	89	410	148	37	61
Norway	27	224	25	56	66	25	221	25	54	64
Poland	1511	838	322	135	282	1564	805	309	142	305
Portugal	274	385	102	32	44	286	377	102	32	44
Rep. of Moldova	12	17	25	13	28	12	17	25	13	28
Romania	912	319	221	118	187	912	319	221	118	187
Russian Federation	1997	2357	650	692	1129	1997	2357	650	692	1129
Serbia and Montenegro	387	158	79	39	86	394	158	79	39	86
Slovakia	124	106	30	24	44	129	106	28	24	44
Slovenia	96	58	19	8	13	96	58	19	8	13
Spain	1484	1335	386	145	209	1394	1303	380	145	209
Sweden	57	252	57	45	66	57	248	54	48	69
Switzerland	19	96	68	12	26	21	92	68	12	24
TFYR of Macedonia	105	30	16	9	20	137	32	16	9	20
Turkey	2112	951	321	223	420	2112	951	321	223	420
Ukraine	1029	561	358	269	463	1029	561	378	269	463
United Kingdom	1188	1737	297	108	178	1125	1680	290	108	178
North Africa	413	96	235			413	96	235		
Remaining Asian areas ^c	854	169	278			854	169	278		
Baltic Sea	228	352	0		7	228	352	0		7
Black Sea ^d	57	86	0		1	57	86	0		1
Mediterranean Sea	1189	1639	0		1	1189	1639	0		1
North Sea	454	648	0		43	454	648	0		43
Remaining North-East Atlantic Ocean	901	1266	0		63	901	1266	0		63
Natural marine emissions	743	0	0			743	0	0		
Volcanic emissions ^e	2000	0	0			2000	0	0		
TOTAL	24146	21218	6598	3097	5217	23841	21033	6578	3108	5186

^a All emission figures are for the part of countries within the EMEP domain of calculation. Emission figures displayed without shading are officially reported to the CLRTAP. Emissions figures in grey shaded cells are expert estimates (see text). Emission figures in bold have changed from last year's emission report

^b Figures in bold in grey shaded cells are expert estimates from IASIA. Other figures in grey shaded cells are expert estimates from TNO. Figures without shading are officially reported emission values.

^c "Remaining Asian areas" refers to Syria, Lebanon, Israel and parts of Uzbekistan, Turkmenistan, Iran, Iraq and Jordan.

^d PM₁₀: Based on gridded data from ENTEC.

^e Volcanic emissions reported by Italy.

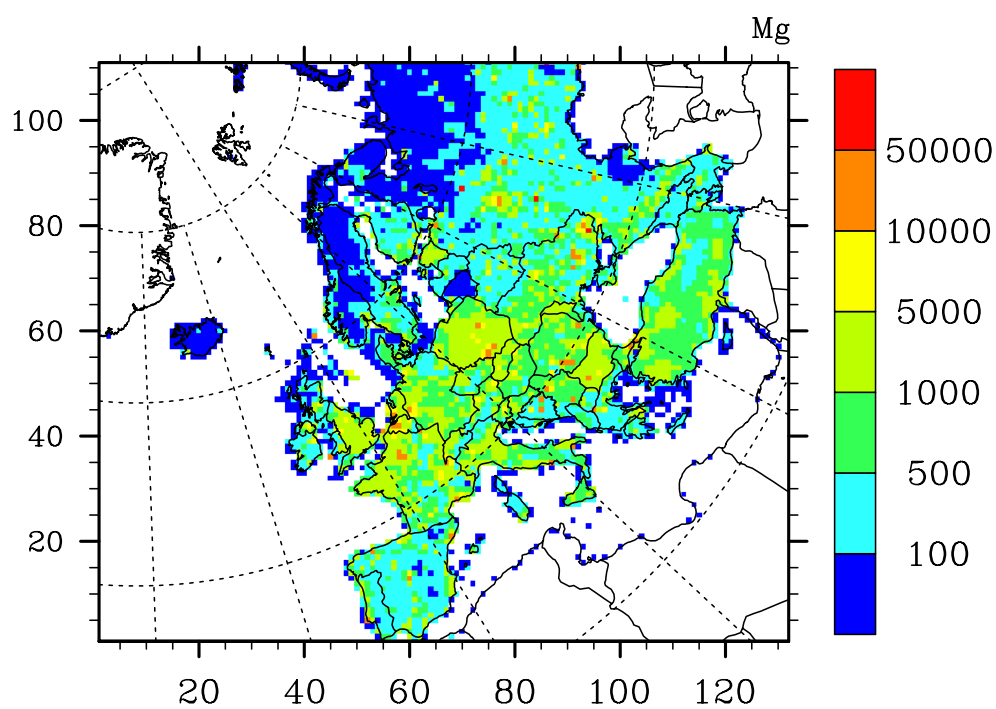


Figure 3.9: Emissions of PM_{10} in 2001 at 50 km resolution (Mg).

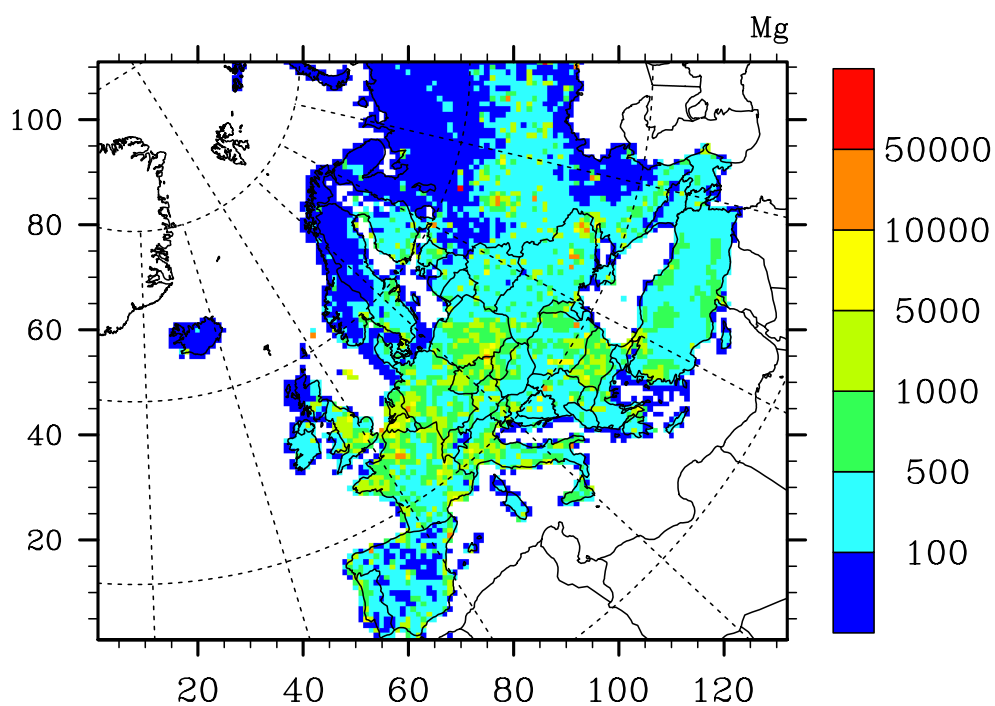


Figure 3.10: Emissions of $PM_{2.5}$ in 2001 at 50 km resolution (Mg).

3.3.2 *A comparison of the officially reported emission inventories with CIAM estimates for the year 2000*

Table 3.3 compares the national total emissions reported to UNECE in 2003 with the estimates of the RAINS model. All model estimates are for the year 2000, while national submissions relate to 2000 or 2001, because not all countries have reported data for the year 2000. In total, 24 Parties submitted data on PM emissions, of which 10 provided data for all size fractions. The comparison with the RAINS model is possible for 17 countries. Considering national totals of PM_{2.5} and PM₁₀, the differences between the RAINS estimates and the national submissions are less than 10 percent for six countries (Austria, Belgium, Hungary, Netherlands, Poland, United Kingdom). By contrast, the agreement is typically poor for TSP (with the exception of a few countries like Austria, Estonia, and Poland), mainly because of differences in the estimates of fugitive emissions from sources such as construction, open mining, agricultural operations, re-suspension of road dust, etc., or dramatically different assumptions about emission factors for particles larger than 10 µm. In some cases, the national submissions report only a few sectors and can therefore not be compared with the national totals estimated by RAINS.

A closer analysis was conducted for five countries, namely, for Belgium, the Czech Republic, France, Slovakia, and Sweden. While in many cases the estimates of national total emissions agree reasonably well, there are important discrepancies in the estimates for individual sectors and activities. In some cases it is possible to track the differences to different assumptions on emission factors, the efficiency of control equipment in place, and differences in underlying fuel statistics. However, in many other cases the documentation supplied by countries on the methodology and assumptions used for deriving their national emission estimates was insufficient to identify the sources of the inconsistencies. Thus, it will be crucial that for the planned validation process countries make available their supporting information in order to reach a common understanding of the sources of PM emissions.

A general feature is that estimates for PM_{2.5} and PM₁₀ agree much better than for TSP. Since the further integrated assessment analysis will focus on the health impacts of particulate matter, priority should be given to PM_{2.5} and to a lesser extent to PM₁₀, while TSP is of minor relevance for health impacts. Thus further work should focus on the understanding of the sources of PM_{2.5} emissions in Europe.

While some estimates differ greatly even for national totals, it is possible to identify one or two single assumptions as the major source for the differences. Thus clarifying a very limited number of aspects could greatly improve the emission inventories and their representation in the RAINS model.

Detailed results from this inter-comparison are available at CIAM and will be used to guide bilateral discussions between CIAM and national experts. CIAM will report the outcome of these meetings to the Task Force on Emission Inventories and Projections.

Table 3.3: National total 2000/2001 particulate matter emissions in Gg reported in 2003, and RAINS model estimates for the year 2000.

Party	Year	UNECE			CIAM (RAINS)		
		PM _{2.5}	PM ₁₀	TSP	PM _{2.5}	PM ₁₀	TSP
Albania	-	-	-	-	5	8	16
Armenia	-	-	-	-	-	-	-
Austria	2000	27	47	78	30	43	79
Azerbaijan	-	-	-	-	-	-	-
Belarus	-	-	-	-	39	62	124
Belgium	2000	36	65	277	37	59	125
Bosnia and Herzegovina	-	-	-	-	19	46	95
Bulgaria	-	-	-	-	74	132	303
Canada	2000	989	5122	16613	-	-	-
Croatia	-	-	-	-	16	25	54
Cyprus	2001	-	0.6	-	-	-	-
Czech Republic	2001	-	46	75	63	104	162
Denmark	2000	13	20	42	18	29	53
Estonia	2001	-	-	77	17	37	69
Finland	2001	38	54	80	23	30	49
France	2000	299	545	1486	171	251	481
Georgia	-	-	-	-	-	-	-
Germany	2000	-	-	250	156	239	463
Greece	-	-	-	-	40	57	91
Holy See	-	-	-	-	-	-	-
Hungary	2000	26	47	129	27	43	83
Iceland	-	-	-	-	-	-	-
Ireland	-	-	-	-	11	19	38
Italy	-	-	-	-	150	213	386
Kazakhstan	-	-	-	-	-	-	-
Kyrgyzstan	-	-	-	-	-	-	-
Latvia	2000	-	-	10	7	11	23
Liechtenstein	2001	-	0.05	-	-	-	-
Lithuania	2001	-	0.6	11	9	14	32
Luxembourg	-	-	-	-	3	4	7
Malta	-	-	-	-	-	-	-
Monaco	2001	-	-	0.01	-	-	-
Netherlands	2000	37	62	72	33	55	107
Norway	2001	54	64	80	43	48	61
Poland	2001	142	305	496	160	281	475
Portugal	-	-	-	-	32	44	74
Romania	-	-	-	-	118	187	351
Republic of Moldova	-	-	-	-	13	28	92
San Marino	-	-	-	-	-	-	-
Russian Federation	-	-	-	-	692	1129	2754
Serbia & Montenegro	-	-	-	-	39	86	181
Slovakia	2000	-	-	52	24	44	82
Slovenia	-	-	-	-	8	13	21
Spain	-	-	-	-	145	209	358
Sweden	2000	45	66	86	21	31	62
Switzerland	2001	-	24	-	12	17	32
TFYR of Macedonia	-	-	-	-	9	20	40
Turkey	2001	-	-	143	-	-	-
Ukraine	-	-	-	-	269	463	1065
United Kingdom	2000	108	187	-	121	200	412
United States	2001	6154	21266	-	-	-	-
European Community	-	-	-	-	991	1483	2786

3.3.3 Emissions of black carbon in Europe

While recent assessments of health impact theories suggest total PM_{2.5} mass to be the most robust metric that can be associated with observed health impacts (WHO, 2003), there is growing attention on the carbonaceous fraction of fine particulate matter. In addition, recent advances in climate research point out that the critical role of carbonaceous aerosols on radiative forcing is suspected to be a significant factor warming the climate. Especially airborne black carbon absorbs solar radiation and contributes to global warming (Hansen et al., 2000; Andreae, 2001; Jacobson, 2001).

Carbonaceous particles, i.e., black carbon and organic carbon particles, constitute a certain fraction of primary PM_{2.5} emissions. Their shares in total PM_{2.5} emissions depend on the emission source, fuel type and control measure applied.

An attempt was made to estimate, based on the RAINS database for primary PM_{2.5} emissions, emissions of black carbon in Europe and their likely development in the coming decades. While this work is not fully completed, the following paragraphs present first preliminary results.

The current RAINS PM module (Klimont et al., 2002) was further developed to distinguish black carbon, organic carbon and PM₁ emissions from anthropogenic sources. This includes more than 300 different activities in different economic sectors, taking into account the various emission control measures that are applied. Emission factors for these three species were derived from the literature and checked for consistency with the RAINS database. The present estimates focus on the combustion of fossil fuels and do not include emissions from biomass burning, industrial processes, cigarette smoking and barbecuing.

Table 3.4 presents initial estimates of the emissions of black carbon for 1990, 1995, 2000 and 2010 for selected groups of countries. Overall, black carbon (BC) constituted about 8 percent of the PM_{2.5} emissions in 1990, although a stark difference between Western Europe and other countries can be observed, i.e., the contribution varies between 14 and about 5 percent, respectively. (Here and in the following, “Western Europe” denotes EU-15 plus Switzerland and Norway.) This share increased by the year 2000 to about 12 percent (about 20 and 9 percent for Western Europe and other countries, respectively); however, it is expected to decline in the future. While there was no big change in the black carbon emissions of Western Europe between 1990 and 2000, the implementation of tighter emission controls for mobile sources is expected to lead to a decline in black carbon emissions by the year 2010. By contrast, the decline of coal consumption in households after 1990 led to a significant decrease in the central and eastern European countries. While the adoption of EU legislation will further decrease BC emissions in the accession countries, emissions are expected to increase again in other countries due to the expected increase in traffic volumes.

Figure 3.11 shows the sectoral origin of black carbon emissions. In Western Europe, black carbon emissions originate predominantly from road transport, mainly from diesel vehicles. By contrast, residential combustion was responsible for the major share in Eastern Europe in the past, and it is expected to remain a significant source also in the future.

Table 3.4: Initial estimates of emissions of black carbon in Gg for 1990, 1995, 2000, and 2010, assuming full implementation of current legislation. Western Europe denotes EU-15, CH, and NO.

	1990	1995	2000	2010
Western Europe	229	226	195	105
Accession countries	54	44	44	28
Other countries	121	76	76	83
Total	404	346	315	216

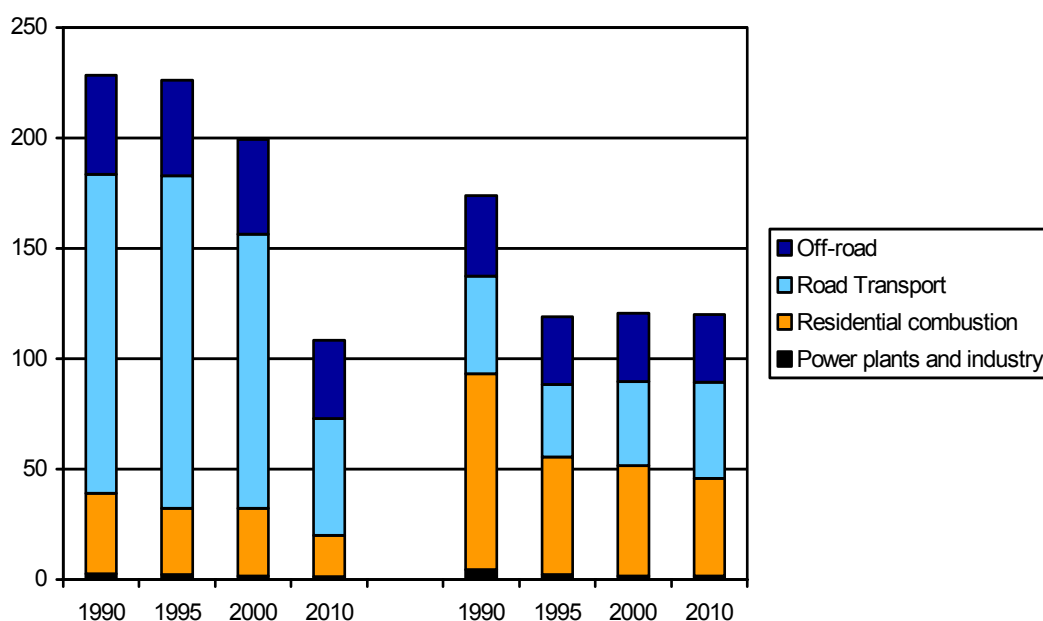


Figure 3.11: Sectoral origin of black carbon emissions in Gg in Western Europe (left) and the other countries (right).

The preliminary analysis indicates that emission trends of BC do not always parallel those of PM_{2.5} emissions. This is caused by stringent PM controls for sectors that have low BC emissions due to well-controlled combustion (e.g., large power stations) or industrial non-combustion sources. In contrast, BC emissions are high from small combustion sources (e.g., in the domestic sector), where only little PM control is installed.

In the future, BC emissions might be higher than projected in the analysis above due to possible spill-over of other policies. In particular, attempts to meet greenhouse gas reduction targets might lead to a larger use of bio-mass in the residential sector than projected in the “business as usual” scenario, that underlies the emission projection. Also a larger share of diesel vehicles and more rapid introduction of gasoline direct injection (GDI) engines could potentially lead to higher BC emissions than calculated above. Other important factors that could increase BC emissions are delayed replacement of inefficient stoves in the

domestic sector and delayed introduction of legislation for off-road machinery (especially for two-stroke gasoline engines and shipping).

In the absence of other inventories of BC for Europe, these preliminary results were compared with published global estimates of BC (Cooke et al., 1999; Bond et al., 2003). RAINS estimates for Europe are significantly lower than Cooke et al. (1999). Part of the observed difference can be explained by differences in activity data, i.e., Cooke et al. (1999) estimates are based on 1984 fuel consumption. Even after accounting for this, however, a large discrepancy in emission estimates remains, i.e., a factor of five, indicating great differences in emission factors being employed. More recent global work (Bond et al., 2003) also reports much lower emissions of BC for Europe than Cooke et al. (1999). RAINS results and results reported by Bond et al. (2003) for 1995 and 1996, respectively, are similar for several important sectors (transport, residential combustion). However, RAINS calculates smaller BC emissions from, primarily, power plants and industry, leading to about 30 percent lower overall BC estimates for Europe than those reported by Bond et al. (2003). More work is needed to explain the differences and include all BC sources.

4. Projections for 2010 and 2020

by Chris Heyes, Markus Amann and Leonor Tarrasón

4.1 Projections of PM emissions up to 2020

The projections for the years 2010 and 2020 considered here assume full implementation of the current emission control legislation (CLE), e.g., the EURO-IV emission standards for cars and trucks, and the stricter emission limit values for large combustion plants resulting from the recent revision of the Large Combustion Plant Directive.

Table 4.1 lists the recent RAINS estimates of the total European emissions of PM for the years 1990, 2000, 2010 and 2020. Results are provided for TSP, PM₁₀ and PM_{2.5}. Major reductions in PM emissions occurred between 1990 and 2000, mainly because of the economic restructuring in Eastern Europe where old and obsolete plants in the power sector and in industry were either closed or rehabilitated. The emissions in the European Union have also decreased, mainly due to switching to cleaner fuels and implementation of better control equipment on existing plants. Between 1990 and 2000, TSP emissions in Europe declined by 56 percent; for 2010 and 2020 reductions of 60 and 61 percent are projected, respectively. Since the emission reductions are more difficult for smaller particles, the PM_{2.5} emissions decrease less, i.e. by 48 percent. Consequently, the fine fraction (PM_{2.5}) will be relatively more important in the future (27 percent of TSP in 2010 compared to 25 percent in 1990).

Table 4.1: Changes in “Current legislation” (CLE) PM emissions in Gg in Europe, 1990 – 2020.

	TSP				PM ₁₀				PM _{2.5}			
	1990	2000	2010	2020	1990	2000	2010	2020	1990	2000	2010	2020
EU-15	5187	2786	2371	2420	2655	1483	1151	1114	1593	991	726	669
Non-EU	15165	6113	5714	5575	6381	2798	2456	2457	3468	1661	1448	1481
Total Europe	20352	8899	8085	7995	9036	4280	3607	3571	5061	2652	2173	2150

It is interesting to note that the trends in reduction of coarse and fine particles in the periods 1990 – 2000 and 2000 – 2010 are different. The fine fraction is reduced more than the coarse after 2000. PM_{2.5} and PM₁₀ are calculated to decline by 18 and 16 percent, respectively, while the total PM emissions are reduced by only 9 percent between 2000 and 2010. This is due to a number of sources that emit mostly ‘large’ particles but for which the control possibilities are limited. Examples of such sources include construction activities, arable farming, storage and handling of bulk products, etc.

The sectoral origins of PM emissions in Europe (by SNAP code) are presented in Table 4.2 and Table 4.3. In 2000 the major sources of TSP emissions in EU-15 were mobile sources (road- and off-road vehicles), contributing 29 percent, and

stationary combustion with a share of 27 percent, followed by industrial production processes (20 percent), and agriculture (16 percent). Since the estimates did not include any reductions of non-exhaust emissions from transport, the contribution of that sector in 2010 increases to 34 percent, making it by far the most important source of particulate emissions in the EU. The relative contribution of combustion processes decreases to 18 percent, while industrial processes and agriculture remain important, contributing about 19 and 18 percent, respectively. It is characteristic that the relative importance of individual sectors and the development of emissions are different for fine particles ($PM_{2.5}$). In this case, the role of transport is even more pronounced (40 percent of emissions in 2000). However, because of strict controls on exhaust emissions (first of all from road transport and, to a lesser extent, from the off-road sector), the share of mobile sources in total $PM_{2.5}$ emissions decreases in 2010 to 34 percent of the total. The relative contributions of all other sectors either remain similar (stationary combustion, about 32 percent) or increase compared to 2000.

The situation looks different for non-EU countries. In this case, the emissions are dominated by stationary combustion and industrial processes, representing together 76 percent of total emitted PM. The share of mobile sources in 2000 is six percent for TSP and 13 percent for $PM_{2.5}$. Although the relative importance of transport emissions increases in the future for all PM size classes, it is calculated that even for fine particles its share will not exceed 15 percent in 2010. In 2010, the largest source of PM in non-EU countries remains stationary combustion (61 and 44 percent share for TSP and $PM_{2.5}$, respectively).

Table 4.4 presents the change in PM emissions by country between 1990 and 2020, assuming full implementation of current legislation (CLE). Reductions are expected for all countries and for all size fractions. They are particularly large for accession countries owing to continuation of economic restructuring and adoption of EU emission standards. The simulations done with the RAINS model demonstrate that the combination of these two factors will cause a substantial decrease in environmental pressures caused by PM emissions in those countries.

Table 4.2: *PM emissions in Gg in the EU-15 countries by SNAP 1 sectors.*

SNAP 1 sector	TSP			PM ₁₀			PM _{2.5}		
	2000	2010	2020	2000	2010	2020	2000	2010	2020
1: Combustion in energy industries	203	110	136	135	82	89	82	54	55
2: Non-industrial combustion plants	272	150	114	171	116	100	138	102	92
3: Combustion in manufacturing industry	272	177	171	158	99	98	114	77	78
4: Production processes	543	451	447	244	216	216	130	114	113
5: Extraction and distribution	60	38	29	30	20	15	4	2	2
7: Road transport	662	680	750	325	209	189	259	125	90
8: Other mobile sources and machinery	149	135	122	141	128	115	133	121	108
9: Waste treatment	45	44	42	34	33	32	32	31	30
10: Agriculture	435	426	426	137	134	134	26	26	26
12: Other (not included in CORINAIR)	145	160	183	107	115	126	73	74	75
TOTAL	2786	2371	2420	1483	1151	1114	991	726	669

Table 4.3: *PM emissions in Gg in the non-EU countries by SNAP 1 sectors.*

SNAP 1 sector	TSP			PM ₁₀			PM _{2.5}		
	2000	2010	2020	2000	2010	2020	2000	2010	2020
1: Combustion in energy industries	928	669	627	517	394	368	244	195	182
2: Non-industrial combustion plants	2253	2429	2151	664	645	575	322	305	279
3: Combustion in manufacturing industry	429	372	413	219	204	225	141	134	147
4: Production processes	1033	739	787	717	520	561	519	375	409
5: Extraction and distribution	200	129	129	89	68	68	9	8	8
7: Road transport	232	286	369	129	134	162	108	106	124
8: Other mobile sources and machinery	121	124	134	115	117	127	109	111	120
9: Waste treatment	221	221	221	166	166	166	150	150	150
10: Agriculture	641	691	691	136	163	163	23	29	29
12: Other (not included in CORINAIR)	56	54	53	46	44	43	37	35	34
TOTAL	6113	5714	5575	2798	2456	2457	1661	1448	1481

Table 4.4: Estimates of PM emissions in Gg by country for the years 1990, 2000, 2010, and 2020, assuming full implementation of current legislation¹.

Party	TSP				PM ₁₀				PM _{2.5}			
	1990	2000	2010	2020	1990	2000	2010	2020	1990	2000	2010	2020
Albania	46	16	11	12	18	8	6	7	10	5	5	5
Austria	95	79	76	77	53	43	38	36	37	30	25	24
Belarus	242	124	111	99	119	62	60	56	75	39	40	38
Belgium	196	125	91	87	92	59	42	40	56	37	26	23
Bosnia and Herzegovina	133	95	68	62	63	46	36	34	25	19	16	15
Bulgaria	672	303	316	329	286	132	132	134	134	74	72	72
Croatia	92	54	35	37	45	25	20	20	26	16	14	14
Czech Republic	851	162	117	107	349	104	66	58	171	63	39	34
Denmark	58	53	49	48	33	29	25	23	22	18	15	13
Estonia	211	69	24	14	102	37	17	8	40	17	11	5
Finland	59	49	46	47	38	30	25	25	29	23	19	18
France	581	481	425	454	308	251	201	201	214	171	127	117
Germany	2069	463	415	425	1007	239	196	189	513	156	120	112
Greece	137	91	96	101	87	57	60	60	58	40	40	39
Hungary	365	83	65	68	142	43	32	32	67	26	19	19
Ireland	62	38	36	35	30	19	16	15	15	11	9	7
Italy	483	386	309	305	273	213	147	136	193	150	94	82
Latvia	55	23	15	16	22	11	7	7	12	7	4	4
Lithuania	86	32	26	27	33	14	12	12	18	9	7	7
Luxembourg	15	7	8	9	6	4	3	3	4	3	2	2
Netherlands	135	107	103	109	75	55	49	50	47	33	28	28
Norway	71	61	58	59	55	48	45	44	48	43	40	39
Poland	1622	475	387	371	624	281	221	209	271	160	128	124
Portugal	72	74	62	69	43	44	34	36	31	32	24	24
Romania	734	351	301	291	374	187	168	166	208	118	106	104
Republic of Moldova	150	92	85	51	45	28	25	18	20	13	12	10
Russian Federation	5841	2754	2866	2784	2567	1129	1063	1091	1547	692	629	668
Serbia & Montenegro	299	181	140	149	142	86	74	81	63	39	37	40
Slovakia	184	82	64	55	98	44	34	28	52	24	19	16
Slovenia	75	20	14	13	32	13	10	8	14	8	6	5
Spain	408	358	292	298	218	209	145	139	141	145	94	86
Sweden	96	62	58	59	60	31	27	26	47	21	17	16
Switzerland	34	32	32	33	20	17	16	16	14	12	10	10
TFYR of Macedonia	67	40	30	28	32	20	16	15	14	9	8	7
Ukraine	3333	1065	948	972	1213	463	397	413	638	269	227	242
United Kingdom	722	412	304	296	330	200	141	133	184	121	85	79

¹ Note that the following countries are missing in this overview: Armenia, Azerbaijan, Canada, Cyprus, Georgia, Holy See, Iceland, Kazakhstan, Liechtenstein, Malta, Monaco, San Marino, Turkey, United States and European Community.

4.2 Model estimates of PM concentrations

Modelled projections for surface air concentrations of PM in 2010 and 2020 rely on the accuracy of the emission projections and on the capability of the model to reproduce observed PM mass concentrations from present emission and meteorological transport information.

Future meteorological conditions have taken into account in EMEP projections with the basic assumption that meteorological variability in a span of 20 years would be the same as for the present situation. Under this assumption, characterising the meteorological variability during the present decade would be sufficient to provide an estimate of the meteorological variability in 2010 and 2020. Although it would be interesting to take into account future meteorological variability in view of new information available from climate research modelling in EMEP's PM concentration projections, this is not the most crucial factor for the reliability of the projection data.

The calculations presented here should not be considered as projections for 2010 and 2010. They are to be considered only as an illustration of the effect of anthropogenic emission changes to PM levels. They are the result of a sensitivity tests for anthropogenic emissions in 2010 and 2020, using the meteorological conditions of year 2000.

The emission projections used for the model calculations are given in Table 4.5 both for gaseous precursors and primary emissions of PM. All emission figures are for the part of countries within the EMEP domain of calculation. Emission figures displayed without shading are officially reported to the CLRTAP. Emission figures in bold have changed from last year's emission report (Vestreng and Klein, 2002). Grey shaded cells contain emission projections expert estimates provided by IIASA/CIAM as presented in the previous section and correspond to CLE (Current Legislation Projections). As no other information was given, the same size and chemical speciation assumptions used in 2000 for primary PM emissions have been used in 2010 and 2020.

The Secondary Inorganic Concentrations (SIA) presented in the upper panels of Figure 4.1 are more reliable from the point of view of model performance than the PM₁₀ projection data presented in the lower panels. This is because the model is known to underestimate PM₁₀ concentrations in Europe by 35-45%. On the other hand, a significant part of this PM₁₀ underestimation is believed to be related to the fact that natural mineral dust sources are not represented by the model. For projections of the effect of anthropogenic emission reductions, analysis of PM_{2.5} air concentrations (even more so for PM₁) are more significant, because the natural component is less important for PM_{2.5}. The underestimation of the EMEP model calculations with respect to the few available measurements of PM_{2.5} concentrations is estimated to be 20-30%.

Table 4.5: Emissions projections for 2010 and 2020 for PM gaseous precursors and primary Pm emissions. All values as Gg. (Data used for chemical transport modelling).

	2010					2020				
	SO _x	NO _x	NH ₃	PM _{2.5}	PM ₁₀	SO _x	NO _x	NH ₃	PM _{2.5}	PM ₁₀
Albany	55	36	35	5	6	48	42	35	5	7
Armenia	4	13	25	5	7	4	13	25	5	7
Austria	39	103	70	25	38	29	96	70	24	36
Azerbaijan	49	90	25	19	30	27	113	25	19	30
Belarus	480	255	163	40	60	360	322	163	38	56
Belgium	106	181	97	26	42	92	176	97	23	40
Bosnia and Herzegovina	415	60	23	16	36	388	68	23	15	34
Bulgaria	846	266	127	72	132	468	169	101	72	134
Croatia	70	87	37	14	20	68	101	37	14	20
Cyprus	39	23	9	2	1	30	20	8	2	1
Czech Republic	283	286	110	39	66	201	198	57	34	58
Denmark	55	127	73	15	25	23	114	83	13	23
Estonia	175	73	29	11	17	22	20	29	5	8
Finland	116	153	34	19	25	79	110	34	18	25
France	400	858	791	127	201	430	871	791	117	201
Georgia	9	30	97	8	12	9	30	97	8	12
Germany	550	1081	589	120	196	497	830	589	112	189
Greece	546	334	77	40	60	113	280	77	39	60
Hungary	546	198	139	19	32	51	106	90	19	32
Iceland	29	30	3	3	3	29	30	3	3	3
Ireland	42	65	131	9	16	27	64	131	7	15
Italy	500	1000	443	94	147	225	765	443	82	136
Kazakhstan	237	50	18			237	50	18		
Latvia	104	84	35	4	7	44	29	14	4	7
Lithuania	107	110	81	7	12	77	60	81	7	12
Luxembourg	4	10	9	2	3	2	17	9	2	3
Netherlands	50	266	194	28	49	74	249	194	28	50
Norway	22	156	22	40	45	23	189	22	39	44
Poland	1397	879	561	128	221	715	482	561	124	209
Portugal	170	255	75	24	34	130	250	75	24	36
Rep. of Moldova	117	66	49	12	25	102	64	49	10	18
Romania	594	437	304	106	168	350	273	304	104	166
Russian Federation	2343	2653	913	629	1063	1887	3128	913	668	1091
Serbia and Montenegro	269	152	82	37	74	159	167	82	40	81
Slovakia	110	130	49	19	34	72	68	37	16	28
Slovenia	27	45	22	6	10	17	21	22	5	8
Spain	774	847	390	94	145	394	835	390	86	139
Sweden	67	148	66	17	27	65	159	66	16	26
Switzerland	26	79	68	10	16	26	63	66	10	16
TFYR of Macedonia	81	29	16	8	16	70	33	16	7	15
Turkey	1821	951	321	223	420	1821	951	321	223	420
Ukraine	1476	1222	665	227	397	945	1400	665	242	413
United Kingdom	625	1181	302	85	141	301	988	288	79	133
North Africa	413	96	235			413	96	235		
Remaining Asian areas	805	79	278			805	79	278		63
Baltic Sea	228	352	0		7	228	352			7
Black Sea	57	86	0		1	57	86			1
Mediterranean Sea	1189	1639	0		1	1189	1639			1
North Sea	454	648	0		43	743				
Remaining North-East Atlantic Ocean	901	1266	0		63	901	1266			
Natural marine emissions	743	0	0			454	648			43
Volcanic emissions	2000	0	0			2000				
TOTAL	22304	19263	7882	2481	4197	17521	18181	7712	2409	4160

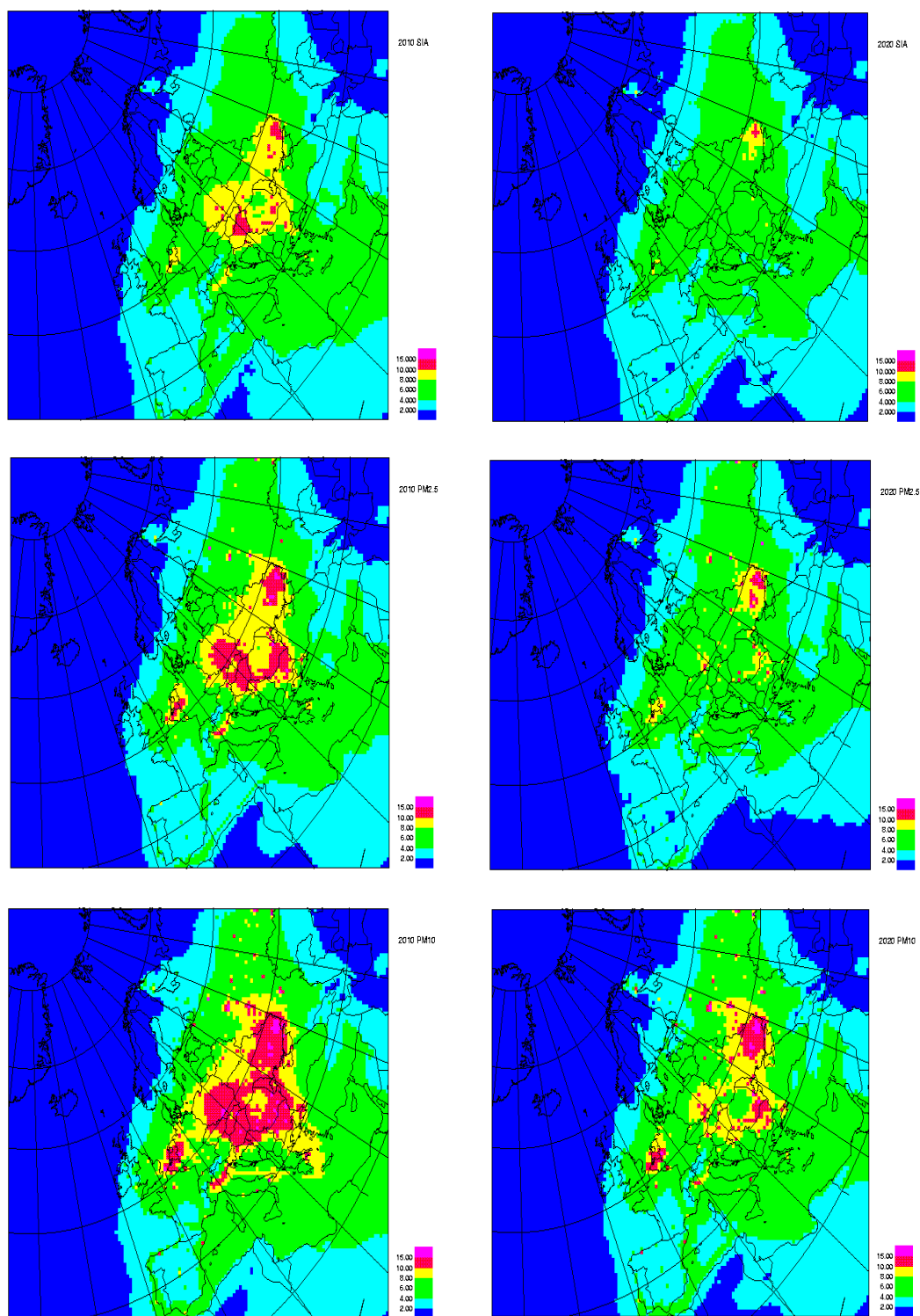


Figure 4.1: Projections of SIA (upper panels), $PM_{2.5}$ (middle panels) and PM_{10} (lower panels) air concentrations for 2010 (left) and 2020 (right). All concentrations in $\mu g/m^3$.

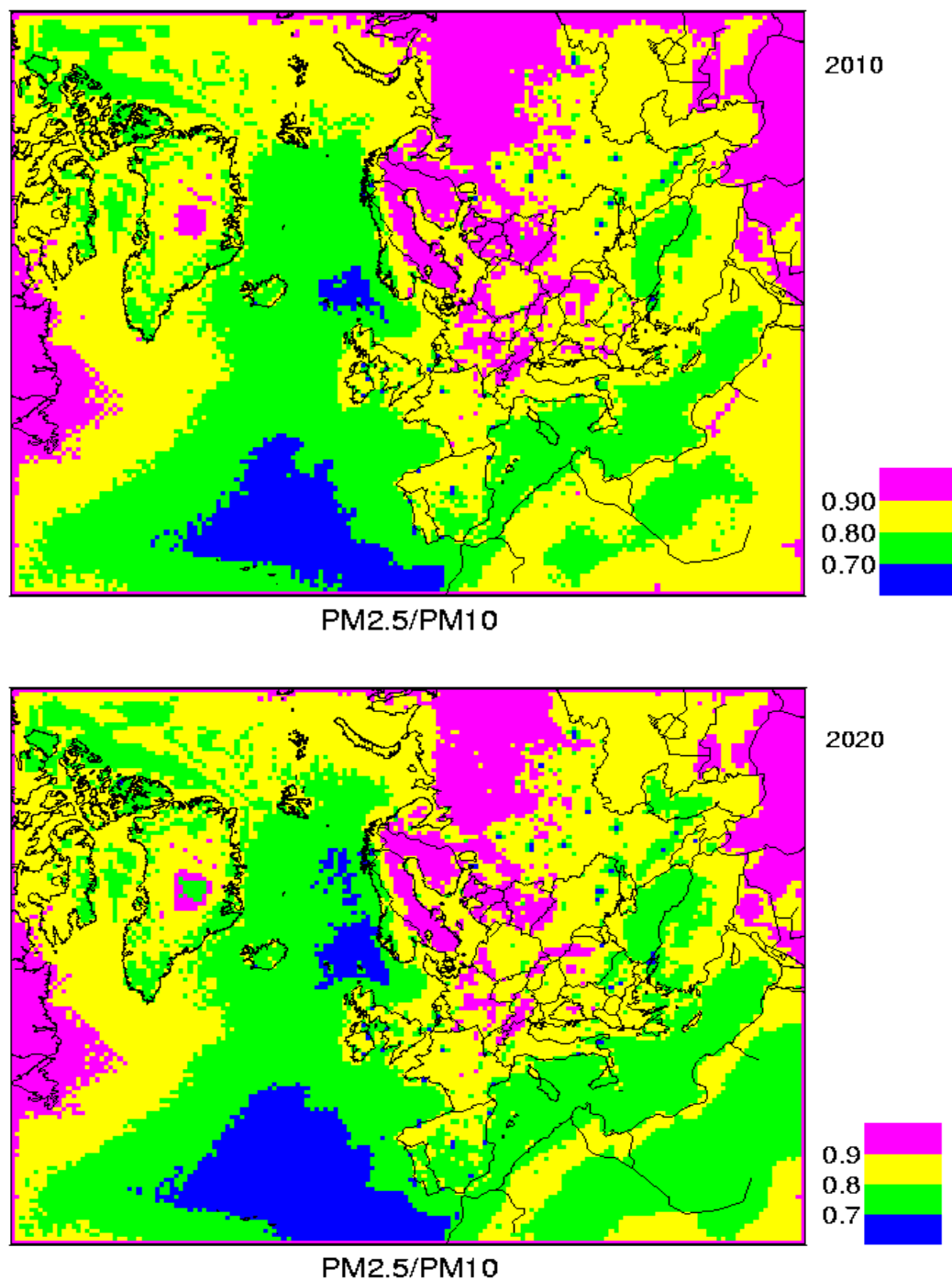


Figure 4.2: Relative contribution of $PM_{2.5}$ to PM_{10} concentrations in 2010 (upper panel) and 2020 (lower panel). Note that the relative importance of $PM_{2.5}$ decreases somewhat in 2020.

5. References

- Andersson-Sköld, I. and Simpson, D. (2001) Secondary organic aerosol formation in northern Europe: A model study. *J. Geophys. Res.*, 106, No. D7, 7357-7374.
- Andreae, M.O. (2001) The dark side of aerosols. *Nature*, 409, 671-672.
- Birch, M.E. and Cary, R.A. (1996) Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. *Aerosol Sci. Technol.*, 23, 221-241.
- Bond, T.C., Streets, D.G., Yarber, K.F., Nelson, S.M., Woo, J.-H., Klimont, Z. (2003) A technology-based global inventory of black and organic carbon emissions from combustion. Submitted to *J. Geophys. Res.*
- Cooke, W.F., Lioussé, C., Cachier, H. and Feichter, J. (1999) Construction of a 1° x 1° fossil fuel emission data set for carbonaceous aerosol and implementation and radiative impact in the ECHAM4 model. *J. Geophys. Res.*, 104 (D18), 22137-22162.
- EMEP (2003a) EMEP Status Report 1/2003 - Part I: Transboundary acidification, eutrophication and ground level ozone in Europe: Unified EMEP model description. Oslo, Norwegian Meteorological Institute (MSC-W & MSC-E report 2003 Part I). <http://www.emep.int>.
- EMEP (2003b) EMEP Status Report 1/2003 – Part II: Transboundary acidification, eutrophication and ground ozone level: Unified EMEP Model Performance. Oslo, Norwegian Meteorological Institute (EMEP/MSC-W & MSC-E Status report 1/2003 Part II). <http://www.emep.int>.
- EMEP (2003c) EMEP Status Report 1/2003 - Part III: Transboundary acidification, eutrophication and ground level ozone in Europe: Source-receptor relationships. Oslo, Norwegian Meteorological Institute (MSC-W & MSC-E report 1/2003 Part III). <http://www.emep.int>.
- EMEP/CCC (2002) Measurements of particulate matter: status report 2002. Ed. by M. Kahnert. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 4/2002).
- Hansen, J. et al. (2000) Global warming in the twenty-first century: an alternative scenario. *Proc. Natl. Acad. Sci. USA*, 97(18), 9875-9880.
- Jacobson, D. (2001) Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols. *Nature*, 409, 695-697.
- Klimont, Z., Cofala, J., Bertok, I., Amann, M., Heyes, C. and Gyarfas, F. (2002) Modelling particulate emissions in Europe a framework to estimate reduction potential and control costs. Laxenburg, Austria, International Institute for Applied Systems Analysis (IIASA) (Interim Report IR-02-076).

- Matta, E., Facchini, M.C., Decesari, S., Mircea, M., Cavalli, F., Fuzzi, S., Putaud, J.-P., and Dell'Acqua, A. (2003) Mass closure on the chemical species in size-segregated atmospheric aerosol collected in an urban area of the Po Valley, Italy. *Atmos. Chem. Phys.*, 3, 623-637.
- Monahan, E.C., Spiel, D.E., Davidson, K.L. (1986) A model of marine aerosol generation via white caps and wave disruption. In: *Oceanic Whitecaps*. Ed. by E.C. Monahan and G. MacNiocchail. Dordrecht, Reidel. pp. 167-193,
- Mårtensson, E.M., Nilsson, E.D., de Leeuw, G., Cohen, L.H., and Hansson, H.-C. (2003) Laboratory simulations and parameterisation of the primary marine aerosol production. *J. Geophys. Res.*, 108 (D9), 10.1029/2002 JD002263.
- NIOSH (1994) NIOSH manual of analytical methods (NMAM), 4th ed., method 5040. Cincinnati, National Institute for Occupational Safety and Health.
- Putaud, J.-P., Van Dingenen, R., Baltensperger, U., Brüggemann, E., Charron, A., Faccini, M.-C., Decesari, S., Fuzzi, S., Gehrig, R., Hansson, H.-C., Harrison, R.M., Jones, A.M., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N., Müller, K., Palmgren, F.K., Querol, X., Rodriguez, S., Schneider, J., Spindler, G., ten Brink, H., Tunved, P., Tørseth, K., Weingartner, E., Wiedensohler, A., Wählin, P. and Raes, F. (2002) European Aerosol Phenomenology. Physical and chemical characteristics of particulate matter at kerbside, urban, rural, and background sites in Europe. Ispra, European Commission, Joint Research Centre (EUR 20114 EN).
<http://ies.jrc.cec.eu.int/Download/cc>.
- Stone, V. and Donaldson, K. (1998) Small particles – big problem. *Aerosol Soc. Newsletter*, 33, 12-14.
- Tsyro, S. (2003) Model performance for particulate matter. In: *EMEP Status report 1/2003. Transboundary acidification, eutrophication and ground ozone level, Part II: Unified EMEP model performance*. Oslo, Norwegian Meteorological Institute (EMEP/MSC-W & MSC-E Status report 1/2003 Part II). <http://www.emep.int>.
- Tunved, P., Hansson, H.-C., Kulmala, M., Aalto, P., Viisanen, Y., Karlsson, H., Kristensson, A., Swietlicki, E., Dal Maso, M., Ström, J., and Komppula, M. (2003) A one-year study of the Nordic aerosol. *Atmos. Chem. Phys. Discuss.*, 3, 2783-2833.
- Vestreng, V. (2003) Review and revision. Emission data reported to CRTAP. Oslo, Norwegian Meteorological Institute (EMEP Status Report 2003. Technical Report 2003, Meteorological Synthesizing Centre – West).
- Vestreng, V. and Klein, H. (2002) Emission data reported to UNECE/EMEP: Quality assurance and trend analysis - Presentation of WebDab. Oslo, Norwegian Meteorological Institute (EMEP/MSC-W Note 1/2002).
<http://www.emep.int>.

WHO (2003) Health aspects of air pollution with particulate matter, ozone and nitrogen dioxide. Bonn, WHO ECEH.
<http://www.euro.who.int/document/e79097.pdf>.