6   General conclusions and future perspectives

In the previous chapters results are presented on the occurrence of aerosol nitrate in Europe, its implications and relative importance compared to other components. The research carried out during the last four years has resulted in many new insights. Below the main conclusions from the previous chapters are briefly repeated with emphasis on the new elements that resulted from this study.

In Chapter 2 and 3 an effort is described to compile aerosol nitrate data and, subsequently, to derive its spatial distribution over Europe. Data on nitrate are sparsely available from routine measurements in European or national monitoring networks. Therefore an extensive search for data has been performed, yielding a few additional data sets. The available measurements are obtained with a host of different methods. Denuder filter combinations are very suitable for the collection of aerosol nitrate. However, application of single filters may cause sampling artefacts. Therefore, the results of three campaigns (INTERCOMP1999, INTERCOMP2000, PIPAPO) were analysed on artefact formation (Chapter 2) and an extensive literature review of the artefacts involving the sampling of nitrate is presented (Chapter 3). The largest campaign was held at Melpitz, where no artefacts were observed due to the low ambient temperature and low nitric acid concentrations. Without artefacts the long term precision of (total) nitrate measurements reported in literature is 15 % or better. A similar precision was determined in Melpitz. However, single data points may be much more uncertain, especially at low concentration levels. Furthermore, it was shown that quartz filters show partial losses in the temperature range between 20 and 25 ºC and almost complete losses above 25 ºC. Below 20 ºC no losses were observed. On the other hand, cellulose filters quantitatively sample total nitrate, the sum of aerosol nitrate and nitric acid. Nitrous acid was shown not to interfere with the sampling of nitrate.

The analysis of the experimental data and the literature review indicated that under the meteorological conditions in Europe the evaporation artefact from quartz filters is negligible during the winter. In this season nitric acid concentrations are so low that reliable estimation of aerosol nitrate from total nitrate data was feasible. Correction for the nitric acid contribution to total nitrate induces a 10-15% uncertainty in the estimated aerosol nitrate levels, assuming an inaccuracy of 100 %. This uncertainty is similar to that found between several samplers for aerosol nitrate. Our confidence in the (estimated) aerosol nitrate levels and the large correlation lengths found in winter allowed us to interpolate between the measurement sites.

For summer, we were not able to derive a spatial distribution for aerosol nitrate. Firstly, ambient temperatures are often above 20 ºC and the application of quartz and Teflon filters to measure nitrate (or PM mass) may result in a severe underestimation. Secondly, the nitric acid concentration in summer is often comparable to that of aerosol nitrate, which makes a reliable estimate of aerosol nitrate concentrations from total nitrate impossible. Finally, the much shorter correlation length in summer compared to winter in combination with the large distances between the sites prevented us to assess the nitrate

concentrations in between the measurement sites.

During winter (Oct-Mar) aerosol nitrate concentrations ranging between 4 and 6 µg/m^3 are found over a large area from southern England over continental western Europe into Poland. Highest levels (>7 µg/m^3) are found in the valleys in Switzerland and northern Italy. In the north, nitrate concentrations range from 2.5 µg/m^3 in southern Sweden to less than 0.5 µg/m^3 in mid-Scandinavia. To the east and west of the central European maximum the nitrate concentration trails off in a more gradual way. It was inferred that the burden of nitrate in winter in Europe north of the Alps is about 60% of that of sulphate. In western Europe and southern Scandinavia, nitrate levels are higher than those of sulphate.

Whether nitrate is present in the coarse or fine aerosol mode has been subject of scientific debate since the size of nitrate largely influences its impact on the radiation balance. The experimental data for western Europe (UK, Germany, Switzerland, the Netherlands) and northern Italy gathered in Chapter 3 show that nitrate is predominantly found in the fine aerosol fraction during the whole year. Fine aerosol nitrate is also observed in other parts of Europe (e.g. Spain and Hungary) during winter. However, nitrate often has a bimodal character, which means that a background level of coarse mode nitrate appears to be present as well. Moreover, when ambient conditions are such that ammonium nitrate formation is negligible, e.g. at high temperatures and low ammonia levels, all particulate nitrate may be in the coarse mode. In arid or coastal areas the high nitric acid levels associated with these conditions may cause substantial amounts of nitrate to be present in the coarse aerosol mode. As such, we speculate that the size of nitrate is a function of season in southern Europe with fine nitrate dominating in winter and coarse nitrate during summer. The instability of ammonium nitrate combined with diminishing ammonia levels and the reaction of nitric acid with sea salt cause a transfer of nitrate from fine to coarse mode when is polluted air is advected from the continent towards the open ocean. Therefore, fine mode ammonium nitrate is a continental phenomenon.

Besides the analysis of experimental data research has been devoted to the development of the LOTOS model to simulate the levels of ammonium nitrate and other aerosol components over Europe. In Chapter 4 the LOTOS model and its results are described. Modelled nitrate concentrations show a significant seasonal cycle with lowest concentrations in summer and highest concentrations in winter and early spring. Except for the summer, nitrate levels are comparable to those of sulphate for large parts of Europe. These results are in accordance with the observations presented in Chapter 3. On an average level the comparison between observations and the simulation is good, albeit that the model does not always represents the amplitude of single events. Wet deposition fluxes are underestimated, which was attributed to the crude representation of clouds in the model. Sea salt should be included in the model to simulate nitrate partitioning in marine areas correctly.

The model addresses the physical and chemical processes that influence the nitrate levels over Europe. It was shown that heterogeneous chemistry plays an important role in the formation of nitric acid and aerosol nitrate. In winter heterogeneous chemistry dominates the formation of nitric acid, which is readily transferred to the aerosol phase due to

the stability of ammonium nitrate at low temperatures and the dominance of ammonia over nitric acid over continental Europe. In summer, appreciable ammonium nitrate concentrations are limited to those areas with high ammonia emissions.

The representation of ammonia emissions is one of the sources for large uncertainties in the model. It was shown that the seasonal variability of ammonia emissions is a key parameter in the model. In addition, neglecting a seasonal variation results in too high ammonia concentrations in winter. Therefore, the seasonality of the ammonia emissions and its controlling processes throughout Europe need to be addressed in more detail in the future.

In summer a decoupling is observed between the responses of aerosol nitrate and those of total nitrate to ammonia availability. The decoupling has consequences for the evaluation of the performance of models. Since total nitrate is the main quantity measured in the European monitoring networks, model evaluation based on these measures makes it difficult to assess the performance for aerosol nitrate in summer. Small deviations between modelled and measured total nitrate concentrations do not necessarily evidence that the aerosol nitrate concentrations are in line with reality. As a consequence, more data on the partitioning of nitrate between the gas and aerosol phase are needed to evaluate and develop models further.

In Chapter 5 a model study dedicated to European PM2.5 levels is presented with special attention to primary emitted particles, e.g. BC. We used the PM emissions from CEPMEIP and combined those with estimated BC fractions to derive a European BC emission inventory on 0.5-0.25º lon-lat for the year 1995. The BC emissions were estimated to be 0.47 Tg in Europe and 0.26 Tg in the Former Soviet Union (FSU). Transport and small combustion sources (households) are the major sources of BC in Europe and cause these emissions to have a very diffuse nature.

The inventory was used to calculate BC fields over Europe. Comparison with experimental data revealed that the model underestimates BC concentrations by about a factor of 2. The underestimation may be explained by measurement uncertainties, local emissions, the representation of the ageing process and unaccounted sources, which are estimated to cause a maximum underestimation of the BC emissions of 15 %. In addition, comparison with available inventories showed that black carbon emission inventories have evolved over the years resulting in much lower emission estimates. The emission factors used in the inventories are still associated with large uncertainties. Especially for traffic, the most important and uncertain source of BC, better emissions estimates are urgently needed.

The calculated distributions of primary particles were combined with those calculated for secondary inorganic components. Sulphate (25-50%) was found to contribute most to the total PM2.5 mass, followed by nitrate (5-35%) and total primary material (10-25%). The BC content of PM2.5 was estimated to range between 4-10%. The modelled PM2.5 concentrations underestimate measured concentrations, which appeared to be strongly correlated with the primary carbonaceous particles.

Overall, both the measurements and the model study indicate that especially in winter (Oct-Mar), large amounts of nitrate contribute to the total aerosol mass in western Europe, where nitrate aerosol mass often exceeds that of sulphate. At continental sites in Northern

Europe nitrate is mainly present in the fine aerosol mode. Consequently, nitrate may at present exert a significant climate forcing over Europe. It was shown that the forcing of nitrate is about 25 % of that by sulphate. During winter the relative importance of the forcing peaks to 47 % of the sulphate forcing. Based on the nitrate field, a similar number was obtained for the ratio between the nitrate and sulphate burdens in winter. Thus, the forcing of nitrate is highly significant over Europe as compared to sulphate and should be taken into account to estimate the impact on regional climate change.

Outlook

The future of aerosol science is challenging. Important issues such as the relations between aerosols and climate, and aerosols and health need to be quantified better. At this moment large gaps in knowledge exist, which prevent to assess these relations with large confidence. For large regions in the world the aerosol load, not to mention its chemical composition, is unknown. Formation routes (e.g. sulphate and secondary organic aerosol) or emission strengths (e.g. soil dust, BC) are associated with large uncertainties. The (optical) properties of these aerosols, being a mixture of components, are poorly known, which severely hampers the assessment of aerosol impacts on the radiation balance. These gaps in knowledge need to be closed. In this thesis we presented work on these subjects, mainly for nitrate but also for primary aerosol components.

Our study, like many others, was hampered by a lack of reliable observational data. The present study on the importance of nitrate focuses on Europe north of the Alps because measurement data could be found there. A follow-up study should also include south western Europe, for which more data are becoming available. However, virtually no data are available for south eastern Europe or the Former Soviet Union. Large gaps also remain in western Europe, e.g. France. To arrive at a more homogeneous coverage over Europe monitoring sites are needed in these regions.

To address key parameters in the models, such as formation routes, data on the diurnal cycle of nitrate in combination with those of its precursor gases are urgently needed under different (European) conditions. At this moment reliable techniques are becoming available for this purpose. For nitrate artefact free methods such as the SJAC or WEDD/AC make it possible to determine its concentration with a high temporal resolution. The mentioned devices are labour intensive and, unfortunately, not yet applicable for monitoring purposes.

Satellites may provide a continuous source of optical measurements with a very high spatial coverage and resolution. Therefore, satellite remote sensing may be the most important future source of data on atmospheric aerosol composition. However, to date the low temporal coverage and cloud interference hamper the usage of these data for model validation purposes. In addition, the satellite provides information on total extinction (absorption and scattering) of an air column. Assumptions on the chemical composition and size distribution are needed to compute the correct AOD. Therefore, satellite data need to be combined with chemistry transport models and ground based observations to obtain information on these variables. Meaningful integration of available information from observations, modelling and remote sensing may be the biggest challenge of all.

LOTOS is positioned as a model of "intermediate complexity". This means that the physics and chemistry in the model is parameterised in such a way that simulations over several years are feasible in a relatively short timeframe. Such models are very useful to perform a set of sensitivity runs to assess the relative importance of model parameters or parameterisations. Key processes as identified by simple models should be studied in more detail by complex models.

The LOTOS model can be further improved as a combined aerosol and oxidant model. LOTOS computes concentrations that are representative for the background level in a grid cell of 0.5° by 0.25° lon-lat. As a consequence, the model will inevitably underestimate the ambient levels of primary components such as particles and ammonia at locations with higher local emissions than the grid average. However, it may be possible to reduce the underestimation of primary components. Especially in summer, the vertical gradient with higher concentration levels than aloft due to surface emissions is not represented well in LOTOS due to the direct mixing of pollutants in the mixing layer. Therefore, the possibility to increase the number of layers combined with a good Kz-parameterisation to better describe the vertical profiles within the boundary layer should be investigated.

Cloud chemistry should be included in LOTOS to adequately describe the formation of sulphate in clouds. Since sulphate formation in clouds is a strongly non-linear process, depending on the pH of cloud droplets, inclusion is necessary to perform scenario calculations for the future. At the same time, in-cloud scavenging should be taken into account. To improve LOTOS as a combined aerosol and oxidant model it may be worthwhile to include the influence of aerosols on photolysis rates as well.

To address fine and coarse nitrate levels in arid and marine areas, the inclusion of sea salt and dust are necessary. To address the size distribution of nitrate inclusion of full aerosol dynamics is possible. However, incorporation of full aerosol dynamics increases CPU time drastically and adds a large source for uncertainties, since dynamical aerosol modelling is still a relatively unexplored research area. In addition, the direct interaction between fine and coarse aerosols, i.e. coagulation, is ineffective. Therefore, it would be advisable to use two fixed size classes with average modal parameters to simulate the concentrations of sea salt, dust and nitrate in the fine and coarse mode.

Emissions have a large influence on modelling results. In this thesis we identified the emissions of ammonia and primary particulate matter, including BC, to be uncertain. In case of ammonia more knowledge is needed on the emissions as function of ambient conditions and season throughout Europe. In addition, adequate and tested parameterisations for the effective ammonia emissions to a grid box in regional models are needed. For BC, we identified a gap between model results and measurements. Among other factors, too low emission estimates may cause the discrepancy. Moreover, we identified large difference between recent BC emission estimates and those of a few years ago. The reasons for these differences should be sought out by separately analysing changes in emission factors and activities.

In this study a very simple method was used to address the relevance of nitrate in respect of climate forcing. The forcing of nitrate is derived relative to that of sulphate, which is widely recognised to exert a considerable forcing. In this way a rough estimate of

the nitrate forcing was obtained by assuming that nitrate and sulphate have the same optical properties. It was concluded that nitrate is relevant over Europe, most notably in winter, spring and fall. However, the forcing estimates can be largely improved. A detailed study with sophisticated radiation schemes, including the effect of nitrate on the aerosol associated water and therefore on the optical properties of sulphate and nitrate, is needed.

Aerosol cloud interactions may potentially exert a larger forcing on climate than the combined direct aerosol forcing. Therefore, a shift in future research towards the indirect effect may be expected. Ammonium nitrate, being a hygroscopic compound, could play an important role in cloud droplet formation.

Ammonium nitrate plays already an important role in present aerosol formation. This importance will only increase in the future.