

Summary

The central theme of this thesis is the nitrate content of aerosols (or particulate matter, PM). Aerosols play an important role in the climate system. The earth absorbs short-wave radiation from the sun, mostly at the surface but also in the atmosphere. Averaged over the year and for the earth as a whole, the incoming radiation energy is balanced by outgoing terrestrial, long wave, radiation. Any factor that changes the energy received from the sun or lost to space, or alters the redistribution of the energy over the earth may effect climate. Such a factor is called a climate forcing and is expressed in Watts per square metre (W/m^2). Aerosols have a direct effect on the radiation balance of Earth by scattering or, to a lesser extent, absorbing sunlight. In addition, aerosols influence the lifetime and reflective properties of clouds. Besides climate change, aerosols play a crucial role in acidification and eutrophication issues and are associated with adverse health effects.

Aerosols have a lifetime in the atmosphere of about a week. In contrast, greenhouse gases remain in the atmosphere for (tens of) years. The effects of aerosols therefore have a strong regional perspective, where greenhouse gases are distributed homogeneously over the globe. Since the 1980s much research has been devoted to quantify the climate forcing of several aerosol components. Traditionally, most attention was devoted to the secondary component sulphate. In polluted regions sulphate may exert a similar forcing compared to that of the combined greenhouse gases, but opposite of sign. However, sulphate only contributes 30-40% to the aerosol load over these areas. Therefore, more and more research has been performed to quantify the effects of other aerosol components. Most important are black and organic carbon, which are emitted during combustion, (soil) dust and nitrate. Every five years the results of scientific work are assessed by the IPCC (International Panel on Climate Change). Except for nitrate the IPCC estimates the forcing of the above mentioned aerosol components.

In the Third Assessment Report (TAR) the IPCC states that an estimate of the nitrate forcing is not possible due to a lack of reliable data. Sampling aerosol nitrate is subject to evaporation losses and adsorption of nitric acid. In addition, the few available model studies on the influence of nitrate show contradicting results, which is caused by the model assumptions on the size of nitrate and the complex processes involving the formation of nitrate.

For the Netherlands it has been shown experimentally that nitrate exerts a comparable forcing as sulphate. However, similar experimental results are not available for other parts of Europe or the globe. Therefore, the high nitrate forcing has been called a “typically Dutch” phenomenon. In this thesis a study devoted to assess the importance of nitrate for the radiation balance over Europe is presented.

The following activities were employed to assess the importance of nitrate:

- Assessment of the artefacts occurring during sampling of nitrate with different filter types

- Construction of the spatial concentration distribution of nitrate over Europe using available experimental data and correcting for known artefacts
- Development of a chemistry-transport model (CTM) to describe the formation, dispersion and removal of nitrate and other aerosol components in the atmosphere

In Chapter 2 a series of experiments is presented in which measurement methods for aerosol nitrate were compared under different conditions. A major two-week field campaign was held at the rural site, Melpitz, near Leipzig in the east of Germany, with samplers containing the most common filter types in use in Europe. The concentration of nitrate, present as ammonium nitrate, was on average $4 \mu\text{g}/\text{m}^3$. The concentrations determined using the samplers agreed very well with relative differences at the average level of 10 % and less for higher concentrations. This is evidence that the influence of artefacts was negligible. The absence is explained by extrapolation of results obtained in a laboratory setting. It was found there that the loss of ammonium nitrate from Teflon and quartz filters is only substantial when temperatures are much higher than those encountered during the field campaign. Cellulose and cellulose-acetate filters quantitatively collected both ammonium nitrate and gaseous nitric acid in the laboratory study, but in Melpitz measured nitric acid concentrations were too low to identify its adsorption. None of the filters adsorbs gaseous nitrous acid, which was present at substantial levels. We also used the laboratory information to evaluate the results of an intercomparison in the Po-Valley, performed at much higher temperatures than at Melpitz. We found evidence of adsorption of nitric acid by cellulose filters and of evaporation losses of aerosol-nitrate from quartz filters. We parameterised the extent of the evaporation artefact in a general way as a function of temperature. Complete evaporation occurs at temperatures exceeding $25 \text{ }^\circ\text{C}$ and full retention at temperatures less than $20 \text{ }^\circ\text{C}$. At temperatures between 20 and $25 \text{ }^\circ\text{C}$ the retention is on average 50 %, but with high variability. A main conclusion from this study is that quartz is a suitable filter material for sampling nitrate as long as the temperature does not exceed $20 \text{ }^\circ\text{C}$. Cellulose type filters quantitatively collect nitric acid, but negligible amounts of nitrous acid.

In chapter 3 the construction of the aerosol nitrate concentration field in Europe from interpolation of data is described. The first step was an active search for and a subsequent quality assessment of (long term) data for this semi-volatile component, which is subject to a range of artefacts during sampling. Therefore first an overview of (filter) sampling methods in use in Europe and the associated sampling artefacts is presented. Denuder filter pack combinations have very minor artefacts and data obtained with this technique were therefore used as the starting point. Because of the paucity of data from these denuder filter packs, values obtained with simple filter sampling were also considered after a critical analysis. Data from inert filters (Teflon and Quartz) were interpreted as lower limits due to possible evaporation of ammonium nitrate. Next, data from "total-nitrate" filters were evaluated. Such filters collect both aerosol nitrate and nitric acid gas and the contribution of the gaseous compound was corrected for. The distance over which nitrate concentrations correlate was then analysed and it was found that in the winter half-year the correlation length was sufficiently long to warrant interpolation of the point data. The

nitrate concentration field as obtained from interpolation of nitrate-data in the period 1994-1997 was successfully validated with intermediate point data from shorter lasting campaigns. Concentrations of nitrate exceeding $5 \mu\text{g m}^{-3}$ are found over a large area ranging from southern England over continental western Europe into Poland. Experimental data indicate that the nitrate is predominantly present in the fine aerosol fraction (PM_{2.5}). In the north nitrate concentrations range from $2.5 \mu\text{g m}^{-3}$ in Southern Sweden to less than $0.5 \mu\text{g m}^{-3}$ 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, with the exception of France from which country no data could be found, is about 60% of that of sulphate. It should further be mentioned that in the Po-Valley ammonium nitrate levels are as high as those in north western Europe.

In chapter 4 we present the results of a model study to the ammonium nitrate field over Europe for 1995. LOTOS, a chemistry-transport model of intermediate complexity, was extended with a thermodynamic equilibrium module and additional relevant processes to account for aerosol (nitrate) formation and deposition. Our analysis of data on (ammonium) nitrate in Europe was used for model evaluation.

During winter, fall and especially spring high nitrate levels are projected over north western, central and eastern Europe. During winter nitrate concentrations are highest in the Po valley, Italy. These results are in accordance with the field that was constructed from the experimental data. In winter nitric acid, the precursor for aerosol nitrate, is formed through heterogeneous reactions on the surface of aerosols. Appreciable ammonium nitrate concentrations in summer are limited to those areas with high ammonia emissions, e.g. the Netherlands, since high ammonia concentrations are necessary to stabilise this aerosol component at high temperatures. Over large parts of eastern and southern Europe low ammonium nitrate concentrations are modelled. Averaged over all stations the model reproduces the measured concentrations for NO_3 , SO_4 , NH_4 , TNO_3 , TNH_4 and SO_2 within 20%. The daily variation is captured well, albeit that the model does not always represent the amplitude of single events. The model underestimates wet deposition, which was attributed to the crude representation of cloud processes. Also, inclusion of sea salt is necessary to properly assess the nitrate and nitric acid levels in marine areas.

Additional attention has been devoted to the sensitivity of the modelled nitrate levels towards ammonia emissions. Large differences between the modelled nitrate levels were found using different seasonal emission variations. The sensitivity of modelled nitrate concentrations towards ammonia availability shows an inverse relationship with its absolute concentration, since at high nitrate levels nitric acid and not ammonia limits the nitrate formation. We could conclude that neglecting the seasonal variation in ammonia emissions results in too high emissions in winter. The sensitivity of aerosol nitrate and total nitrate to ammonia availability was decoupled in summer, when nitric acid levels are as high or higher than those of particulate nitrate. Therefore, data on the gas/aerosol partitioning of nitrate are necessary for further model development and verification of the model results.

In chapter 5 we present a model simulation for the year 1995 in which we account for

primary aerosols. For this purpose we have developed a new emission inventory for BC, based on the CEPMEIP emission inventory for PM. For Europe and the Former Soviet Union we estimated an annual emission in 1995 of 0.47 Tg and 0.26 Tg, respectively. Transport (off and on-road) and households are the most important sources for BC in Europe. Distributions of BC and additional primary material were calculated using the LOTOS model. Modelled BC concentrations range from 0.05 $\mu\text{g}/\text{m}^3$ and lower in remote regions to more than 0.5 $\mu\text{g}/\text{m}^3$ in central Europe. Peak levels above 1 $\mu\text{g}/\text{m}^3$ are calculated over large urban areas. Comparison with experimental data revealed that the model underestimates BC concentrations by about a factor of 2. The underestimate may be explained by (a combination of) local emissions, measurement uncertainties or the representation of wet deposition. In addition, the uncertainties associated with the emission inventory play a role. Unaccounted sources contribute at most 15 % to the total BC emission. Emission factors, most notably those for traffic, probably cause the largest uncertainty in the BC emission estimates.

The primary aerosol fields were combined with those of the secondary inorganic aerosol components to obtain an estimate of the anthropogenic fine aerosol distribution. Modelled BC levels contribute only 4-10 % to the total fine aerosol mass. Sulphate (25-50%) contributes most to the fine aerosol mass over Europe, followed by nitrate (5-35%) and total primary material (10-25%), respectively. Comparison with experimental data revealed that the model underestimates PM_{2.5} levels, which could be related to the underestimation of the primary components.

The aerosol nitrate concentration fields over Europe, determined within this thesis, enable to estimate the radiative forcing by nitrate in Europe. Based on our simulations the annual forcing by nitrate is calculated to be 25 % of that by sulphate. In summer nitrate is found to be only regionally important, e.g. in the Netherlands, where the forcing of nitrate equals that by sulphate. In winter the nitrate forcing over Europe is about half the sulphate forcing. Over north western Europe and the alpine region the forcing by nitrate was calculated to be similar to that of sulphate. Our calculation for the winter agrees with the derived ratio of the nitrate to sulphate burden. Overall, nitrate forcing is significant and should be taken into account to estimate the impact of regional climate change in Europe.