On the importance of aerosol nitrate over Europe

Data analysis and modelling

Martijn Schaap

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Het belang van aerosol nitraat over Europa:

Data-analyse en modelleren

(met een samenvatting in het Nederlands)

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Contents

5   Anthropogenic Fine Aerosol Distribution over Europe with special emphasis on primary PM$_{2.5}$ and Black Carbon   5-115

6   General conclusions and future perspectives   6-144

Summary   150

Nederlandse Samenvatting   154

Dankwoord   158

List of Publications   159

Curriculum Vitae   160

1 Introduction

Since the industrial revolution mankind releases more and more compounds into the atmosphere. Some of these emitted compounds are widely acknowledged to have negative and undesirable effects on human welbeing and ecosystems. An evident form in which air pollution is visible in common life is winter smog. Under stable fair weather conditions the atmosphere becomes hazy and visibility is reduced. The haziness can be attributed to the presence of aerosols, which are the subject of the thesis presented here. Aerosols play an important role in climate change, acidification, eutrophication and atmospheric chemistry. In addition, aerosols are associated with adverse health effects.

An aerosol is generally defined as a system of liquid or solid particles in gaseous suspension. In atmospheric chemistry and physics the term aerosol is used to indicate the aerosol particles only. The aerosol size, commonly given as a diameter, spans several orders of magnitude from several nanometres, e.g. clusters of molecules, to pollen as large as 100 micrometers. In addition, aerosols are composed of many different compounds causing aerosols to be heterogeneous in respect of chemical composition as well as size. In this thesis we focus primarily on the nitrate component of aerosols and assess its importance over Europe. Relatively little is known of this aerosol component, mostly due to the difficulties encountered to measure the nitrate concentration reliably.

1.1 The role of aerosols in the atmosphere

1.1.1 Climate change

The earth system absorbs radiation from the sun, mainly at the surface but also a smaller amount in the atmosphere. For the annual mean and the Earth as a whole the incoming short wave radiation energy is almost entirely balanced by outgoing terrestrial, long wave, radiation energy. Any factor that changes the energy received from the sun or lost to space, or that alters the redistribution of energy over the earth may affect climate. Such factor is termed a radiative forcing and is expressed in Watts per square meter (W/m^2). The Earth receives short wave and emits long wave radiation. Greenhouse gases absorb the long wave terrestrial radiation. Increasing concentrations of these long-lived gases retain more energy in the lower atmosphere, which tends to warm the lower troposphere and the surface.

In the last decennia it has been established that aerosols play a crucial but complex role in climate change. Aerosols may exert a significant forcing; directly through interaction with light and indirectly due to interactions with clouds. The direct effect is the scattering and absorption of incoming solar radiation by aerosols. The direct effect, which represent a negative forcing may regionally counterbalance the positive forcing by greenhouse gases (e.g. Kiehl and Briegleb, 1993; IPCC, 2001). Indirectly, aerosols act as cloud condensation nuclei for cloud and fog droplets. Number, size and composition of the aerosols affect the droplet concentration, optical properties and lifetime of clouds. The knowledge on

these aerosol effects in the climate system is still relatively poor.

1.1.2   Acidification and eutrophication

The inorganic aerosol species sulphate, nitrate and ammonium and their precursor gases sulphur dioxide, nitric acid and ammonia cause acidification when deposited to the earths surface. Ammonia acts as a base in the atmosphere and therefore it may appear strange that it acts as an acidifying compound in the soil. However, in the soil ammonia is oxidised by bacteria to nitrate in which acid is formed according to the stoechimetric reaction: $NH_3 + 2\ O_2 \rightarrow NO_3^- + H_3O^+$. The aerosol compounds have a longer lifetime then their precursor gases and thus provide a vehicle for long-range transport of these compounds (Seinfeld and Pandis, 1998). Effects have therefore also been observed in (vulnerable) ecosystems, far away from the major source areas. Besides severely damaged forests in central Europe (SEI, 1998) large fish death was observed in southern Scandinavia during the 1980s (SEI, 1998).

Besides their role in acidification the mentioned nitrogen species also act as nutrients. Atmospheric input of nitrogen may disturb the nutrient balance of ecosystems. Nutrient poor ecosystems are especially sensitive to eutrophication. Increasing nutrient loads may cause species adapted to nitrogen deficiency to be out-competed by species with a higher nitrogen demand, which results in a loss of biodiversity (Krupa, 2003). Atmospheric and fluvial input are sources of nutrients to the oceans, each probably similar in magnitude (Cornell et al., 1995, Seitzinger et al., 2002). There, exceeding nutrient loads may lead to the growth of toxic algae. In addition, it has been suggested that input of nutrients may effect marine productivity in oceanic and coastal areas (Spokes et al., 2000).

1.1.3   Health effects

Since the London smog events it became apparent that aerosols are harmful for human health (Brimblecomb, 1987). In the last decade numerous studies have found relations between aerosol concentrations in the air and mortality, hospital admissions and respiratory symptoms (Dockery et al., 1993; Pope et al., 1995). Inhalation is the only route of exposure that is of concern in relation to the direct effects of suspended particulate matter on human health. Most of these associations are found with PM10 and PM2.5 concentrations, which approximately covers the inhalable or thoracic size fraction of PM. PM10 or PM2.5 is the mass of the aerosols with a diameter less than 10 or 2.5 µm and contains a large number of components. It is yet unclear which component or size fraction of aerosols is responsible for their health effects. However, some studies direct to the particles derived from combustion of fossil fuels (e.g. Hoek et al. 2002).

1.1.4   Atmospheric chemistry

Aerosols play a role in atmospheric chemistry. Aerosols affect the amount of radiation and therewith photolysis rates of chemical species due to scattering and absorption of light (He and Carmichael, 1999). In addition, aerosols provide a surface on which reactions may occur, which do not occur or are very slow in the gas phase. In this way aerosols act as a
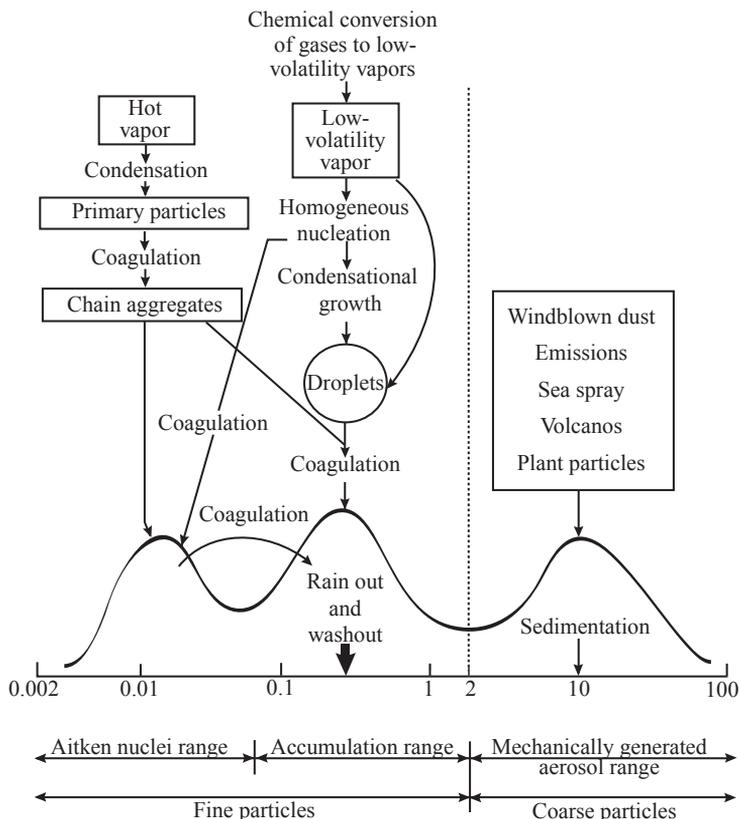
Figure 1.1 Schematic of the aerosol size distribution and the most important processes governing the size distribution

mediator for reactions to occur. Also, aerosols affect atmospheric chemistry by transport of semi-volatile compounds, which may be released into the gas phase at a different location. Aerosols may even act as a source for gases. An example is the reaction of N_2O_5 and nitric acid with sea salt. In this reaction reactive chlorine is liberated, which may have important implications for the halogen cycle and oxidation processes in the marine atmosphere (Andreae and Crutzen, 1997). Finally, aerosols play an important role in cloud chemistry by affecting the pH of cloud water.

1.2 Aerosol size distribution

In the previous section it is pointed out that aerosols play an important role in several environmental issues. The impact of aerosols is a function of size and chemical composition. The composition and size of aerosols are controlled by their sources and the physical and chemical processes, which they undergo in the atmosphere. The size of aerosols spans several orders of magnitude, ranging from several nanometres to hundreds of micrometers (Seinfeld and Pandis, 1998).

The residence time of a particle in the atmosphere is strongly determined by the size

and therewith the mass of a particle. The aerosol size distribution is controlled by a complex system of physical processes, see Figure 1.1. New particles in the atmosphere originate from emissions, mostly at the earth's surface, and through (homogeneous) nucleation of low vapour pressure gases, for example sulphuric acid. These processes are the main source for particles in the nucleation and aitken mode, i.e. those particles smaller than 0.1 nm. Low vapour pressure gases may also condense on existing aerosols, which grow in size. Condensation and nucleation compete for the available amount of the gases. In the polluted lower atmosphere most of the gaseous material is transferred to the aerosol phase by condensation due to the large available surface area of pre-existing particles, which does not mean that nucleation does not occur.

Coagulation is the main sink for nucleation and aitken mode particles and a source of material for the accumulation mode particles. In this mode, 0.1 - 1.0 _m, the life time of aerosols is largest. Coagulation with larger particles from the coarse mode is due to their limited mobility very unlikely to occur and is therefore a negligible sink. The removal of particles by dry deposition is also inefficient in this size range, causing the accumulation of mass in this mode. The main loss for these aerosols is rain out, which causes the particles to have a lifetime of several days to weeks.

Particles in the coarse mode are mainly emitted from the earth's surface and consist mostly of natural components with a crustal, marine or volcanic origin. Also biological sources contribute to this mode, e.g. pollen. Emissions are caused by the natural forces, e.g. the wind, or by anthropogenic activities such as traffic entrainment of paved and unpaved roads, agricultural operations, construction etc. Particles from this mode are effectively removed by sedimentation; they are heavy and "fall" through the atmosphere to the surface.

1.3   Aerosol composition and its sources

Besides the size of aerosols the composition plays a crucial role in the potential effects of aerosols. The composition of aerosols is controlled by their origin and the physical and chemical processing, which they undergo in the atmosphere. A distinction can be made between primary and secondary aerosols. Primary aerosols are emitted directly into the atmosphere, whereas secondary aerosols are products of chemical reactions in the atmosphere. Due to processes as condensation and coagulation these primary and secondary aerosols will partially or completely be mixed in the atmosphere, which makes it difficult to classify aerosol according to this definition. In this study, when primary or secondary aerosols are mentioned we mean the primary and secondary components of the aerosol. Another important distinction is made between natural and anthropogenic origin of aerosol components. This distinction is made because the anthropogenic part of the aerosols can be subject to regulation.

Helsinki (Finland)

PM10 = 7.8 µg/m^3

Voerde (Germany)



Barcelona (Spain)

PM10 = 49.5 µg/m^3
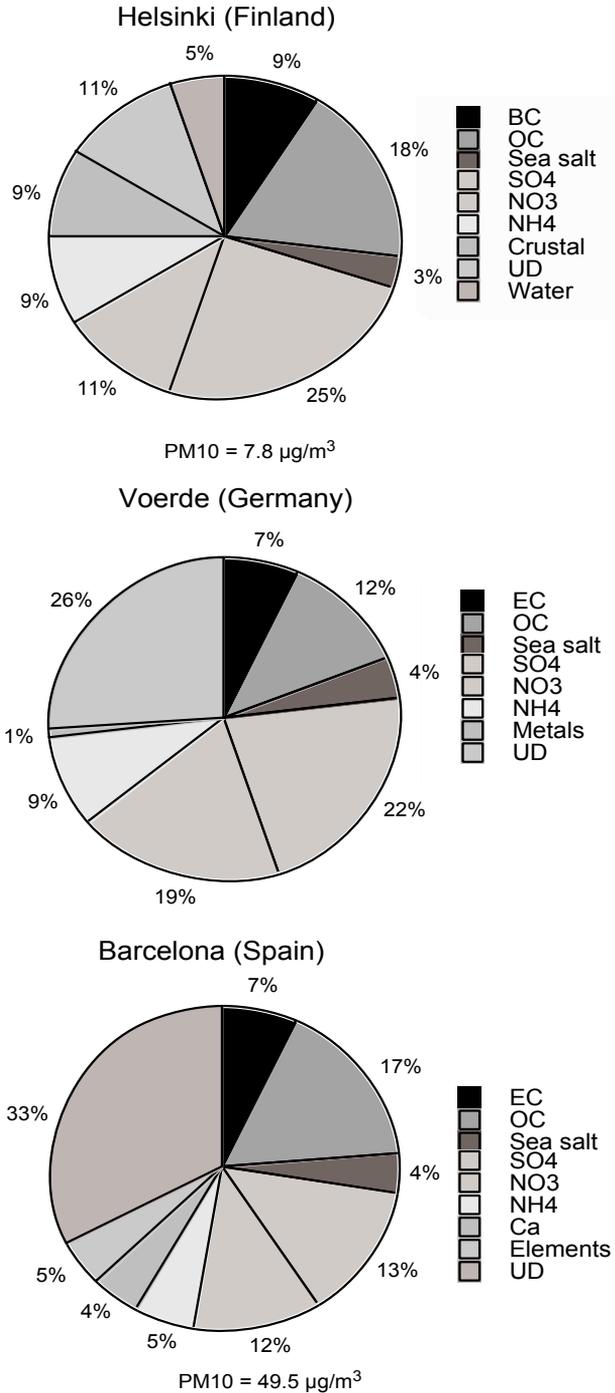
Figure 1.2 Overview of aerosol composition at several sites in Europe, including the unidentified (UD) fraction. Data from Pakkanen et al. (1999), Kuhlbush et al., 2000) and Rodriquez et al. (2002)
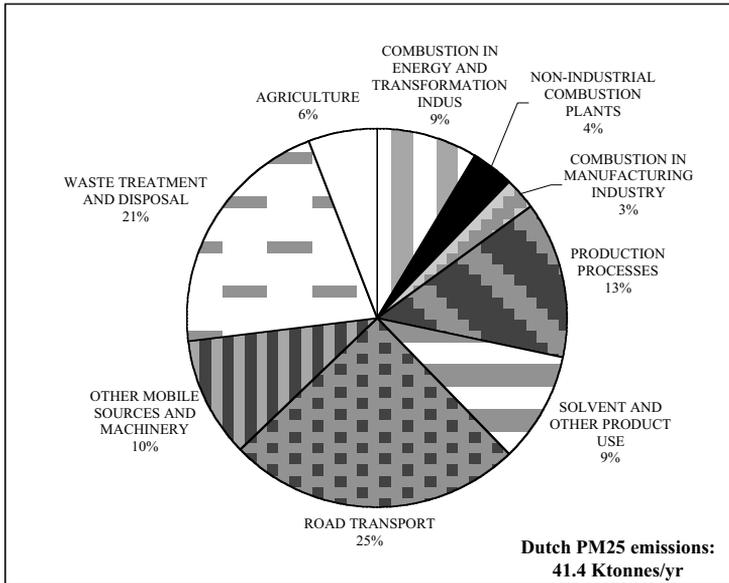
Figure 1.3 Dutch particulate matter emissions for 1995 (TNO,2001)

In figure 1.2 the results of a few mass balance studies of aerosols are shown. These studies are sparse due to the large amount of work and the difficulties associated with the sampling and subsequent analysis of the aerosol composition. Aerosol components can be grouped in carbonaceous, inorganic and crustal and marine material. Striking is that quite a large portion of the mass (11-33%) is not identified. This fraction may contain a considerable amount of water, as shown for Helsinki (Pakkanen et al., 1999).

In climate research traditionally sulphate has been given most attention. Although sulphate is a major component it comprises only a part of total mass. Sulphate, nitrate and ammonium are secondary components and their precursors are sulphur dioxide, nitrogen oxides and ammonia. Over Europe the emissions of these compounds are largely due to human activities. Together these components comprise about 25-50 % of the total mass of PM10. Carbonaceous species also contribute a large fraction to aerosol mass. Total carbon can be divided in elemental or black carbon (EC/BC) and organic (OC) carbon. Elemental carbon is graphitic carbon. Organic carbon is composed of an enormous variety of organic compounds, from which only a small part has been identified. Carbonaceous aerosols are mainly emitted by combustion processes, which are largely due to mankind. Natural emissions are biomass burning (e.g. natural forest fires) and volcanoes. Organic carbon has also a secondary origin. Reaction products of terpenes, emitted by vegetation, may contribute significantly in remote areas.

Primary emitted particles also contain metals. Some metals are very specific for certain activities and are therefore used to assess the sources of the aerosol. Approaches combining activity data with emission factors have also been undertaken to assess the sources of primary aerosols. In Figure 1.3 an estimate of the Dutch PM2.5 emissions is given (TNO,2001). Although the inventory is not complete it gives a good impression of the

major source categories. Transport, waste incineration and combustion processes contribute more than 70 % to the total emission.

The oceans are a large natural source of aerosols. Due to evaporation of little drops of sea water sea salt particles are emitted to the atmosphere. The emission strength is a strong function of the wind speed, the higher the wind speed the higher the emission. Most of the mass is emitted in the coarse aerosol fraction, PM10-2.5. Another, large source of aerosols is (re)suspended dust, which is a semi-natural emission source since mankind influences the state of the soils. This source, also largely induced by wind, is especially important in arid regions as the African deserts and the Mediterranean area. Especially, deserts are a large source of dust particles, which may be transported over thousands of kilometres (Prospero et al., 2001). Dust emissions also occur due to anthropogenic activities. Traffic, for instance, induces the updraft of dust, causing elevated concentrations of crustal material near roads. This is illustrated for Barcelona, where the mass of crustal components is higher than outside the city in the arid Ebro valley (Rodriguez et al., 2002).

Crustal elements and sea salt are mostly found in the PM10-2.5 size range, whereas carbonaceous and secondary inorganic components are mainly found in the PM2.5 size range. This indicates that the contribution of anthropogenic induced aerosol mass in the latter size fraction is large.

1.4   Overview direct aerosol forcing

Greenhouse gases absorb the long wave terrestrial radiation and retain energy in the lower atmosphere, which tends to warm the lower troposphere and the surface. These gases have always been present in our atmosphere causing a natural greenhouse effect. However, since the industrial revolution the levels of greenhouse gases are rising and the additional human induced loading exerts a positive forcing on climate. Due to their long life time the radiative forcing of these gases is rather uniformly distributed over the globe. Greenhouse gases are thought to exert a human induced forcing of +2.43 W/m^2, which is associated with a high level of scientific understanding (IPCC, 2001). Assessment of the radiative forcing of aerosols is more complicated than that of greenhouse gases because of the temporal and spatial highly variable aerosol mass, number concentration and chemical composition. The high variability of the aerosol burden is illustrated in Figure 1.4, which displays a satellite derived composite of the aerosol optical depth (AOD) for August 1997 (Robles-Gonzales et al., 2000). The AOD is a measure for the total extinction of an aerosol column.

The radiative forcing of aerosols is a function of the column burden of the aerosol mass, the light scattering efficiency, scattering as function of relative humidity and the upward scattered fraction. These properties are determined by the chemical composition and size distribution of the aerosol. The scattering efficiency as function of the aerosol size shows that aerosols with a diameter of 0.1-1 µm are most effective in scattering solar (UV-VIS) light (Seinfeld and Pandis, 1998). Smaller and larger particles scatter light much less effective.
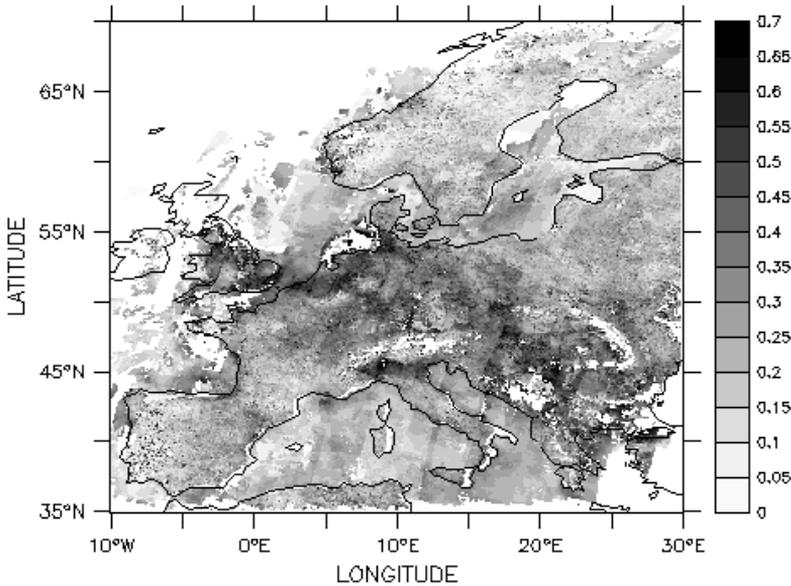
Figure 1.4 Aerosol optical depth over Europe for August, 1997 (Robles-Gonzalez et al., 2000)

The present knowledge on the direct forcing of aerosols is summarized in figure 1.5 (IPCC, 2001). Sulphate is the most studied aerosol component with an estimated forcing of -0.4 W/m^2. Note the high uncertainty of a factor of two in this estimate. In Figure 1.6 the spatial distribution of the forcing is shown. Due to the short life time the forcing of sulphate peaks in the industrialized regions of the earth, e.g. Europe, the USA and south eastern Asia. Over these areas the forcing offsets the forcing by green house gasses (+ 2.43 W/m^2).

Carbonaceous aerosols originate from fossil fuel burning and from biomass burning. The forcing of the absorbing, and thus warming, fossil fuel black carbon is estimated to off set the purely scattering organic carbon. Model calculations arrive at +0.2 and -0.1 W/m^2, respectively. The spatial distribution of the forcing is similar to that of sulphate due their common origin. For carbonaceous aerosol originating from biomass burning the net forcing effect is negative. Although some efforts have been made to address the contribution of BC and OC separately, a combined estimate of -0.2 W/m^2 is given by IPCC. Biomass emissions are mainly found in tropical regions and the distribution of their forcing differs significantly from that of fossil fuel combustion aerosols. The uncertainty in the estimates for carbonaceous aerosols is at least a factor of three.

Recent studies indicate that a significant fraction (~30 %) of dust may be of anthropo-genic origin (Tegen and Fung, 1995; Sokolik and Toon, 1996). This fraction exerts a short wave forcing by the scattering and partial absorption of short wave radiation and a positive long wave radiative forcing by absorption of long wave radiation. The latter is
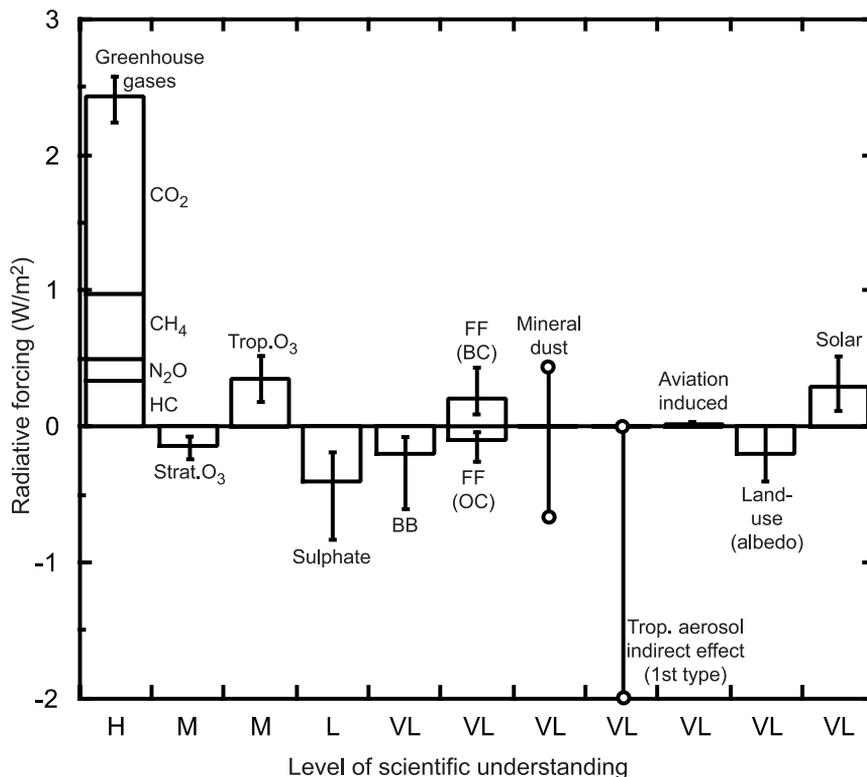
Figure 1.5 Overview of radiative forcing estimates by IPCC(2001). Confidence levels are indicated as: H=High, M=Medium, L=Low and Vl=Very Low. Further: HC = Halocarbons, BB = Biomass burning, FF = Fossil Fuel

caused by the relatively large size of these particles and the relatively high altitude to which these particles are transported. Many uncertainties remain in the estimation of the forcing of mineral dust and therefore only a range is given. The available studies suggest that the short wave negative effect is most likely to be larger than the positive long wave forcing. However, a net positive forcing can not be ruled out.

In the previous section nitrate was found to be a significant contributor to the total aerosol mass in Europe. However, the IPCC (2001) does not give a best estimate of it's radiative forcing. In section 1.6 the reasoning of the IPCC is discussed and an overview of the studies on nitrate is given.

1.5   Formation of nitrate in aerosols

Aerosol nitrate is mainly formed from the reaction of nitric acid with alkaline gas and aerosol species in the atmosphere, e.g. ammonia, sea salt or dust. The precursors of nitric acid are nitrogen oxides, which are for a large fraction emitted by fossil fuel combustion. Together with volatile organic compounds (VOC) nitrogen oxides control the photochemical ozone formation, in which they act as catalysts. NO and NO_2 are poorly soluble and not very reactive towards the earths surface, which dwarves wet and dry deposition as
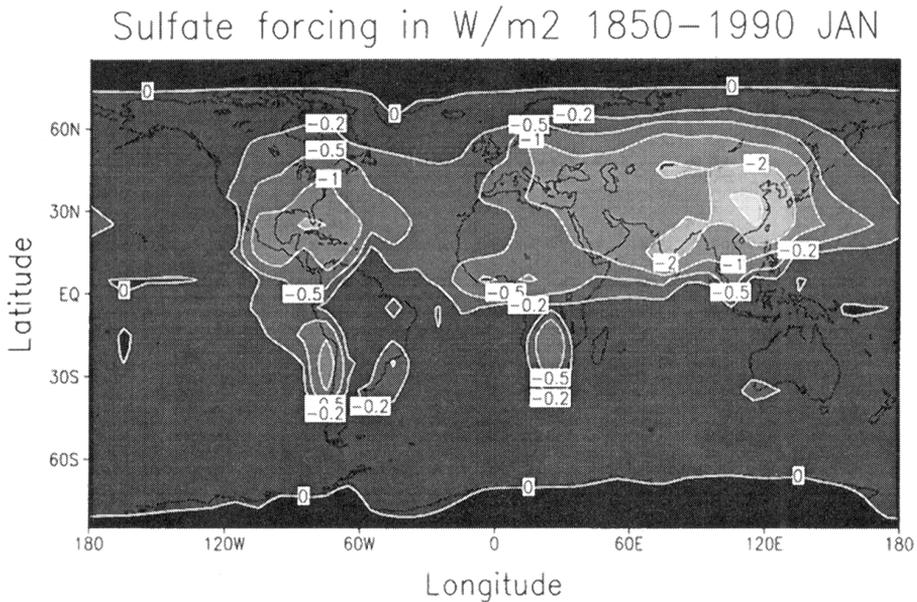
Figure 1.6 Sulphate radiative forcing (W/m^2) for January (Source: Van Dorland et al., 1997)

a significant sink for these species. The most important removal process of NO_x is the formation of nitric acid.

Nitric acid is formed via several chemical pathways. During the day, NO_2 may react with the OH radical:

$$NO_2 + OH \rightarrow HNO_3$$
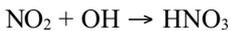
During the night another important formation pathway occurs via N_2O_5 and involves the following reactions:

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_3 + NO_2 \leftrightarrow N_2O_5$$

$$N_2O_5 + H_2O \rightarrow 2\ HNO_3$$
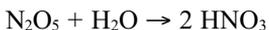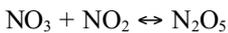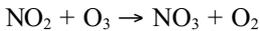
Hydrolysis of N_2O_5 takes place on the surface of aerosols yields two equivalents of nitric acid. This process is not important during the day, since the NO_3 radical is readily photodissociated:

$$NO_3 + h\nu \rightarrow NO + O_2$$
$$NO_3 + h\nu \rightarrow NO_2 + O$$
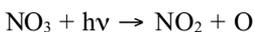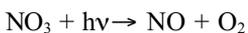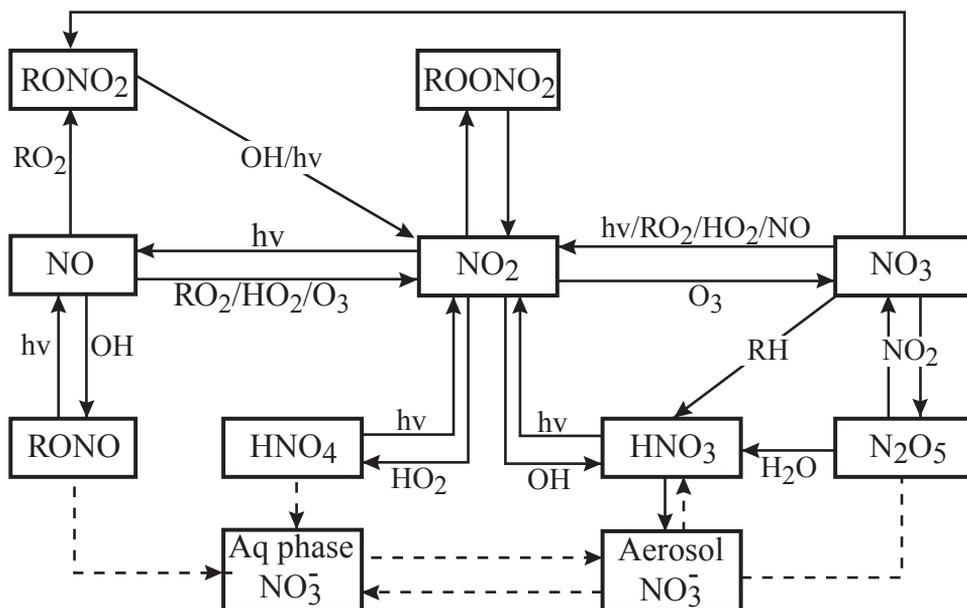
Figure 1.7 Overview of tropospheric chemistry of oxidized nitrogen. Hydrocarbon branches are denoted as R.

Furthermore, N_2O_5 can photolytically and thermally dissociate:

$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$
$N_2O_5 (+M) \rightarrow NO_2 + NO_3 + (M)$

These two pathways account for the largest part the formation of nitric acid (see Chapter 4). However, additional mechanisms as the reaction of the nitrate radical with organic compounds may also yield nitric acid and/or organic nitrates. During day time part of the nitric acid may be photolysed to reproduce NO_x. However, in the boundary layer the reaction is so slow that most nitric acid is removed by wet and dry deposition or transferred to the particulate phase. The complete tropospheric chemistry of nitrogen species is summarized in Figure 1.7.

Nitric acid in the atmosphere may react with ammonia to form ammonium nitrate:

$HNO_3 + NH_3 \leftrightarrow NH_4NO_3$
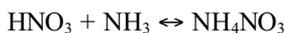
Particulate ammonium nitrate is a semi-volatile compound, which will maintain an equilibrium with its gaseous counterparts. Due to its low vapour pressure ammonium nitrate will condense on pre-existing aerosol, where the largest surface is available. Ammonium nitrate is therefore predominantly found in the sub-micron size fraction. Under atmospheric conditions aerosols are most likely to be a liquid droplet. In such aerosols ammonium nitrate is dissolved in a mixture of components, such as ammonium sulphate. Dissolution of nitric acid and ammonia in such highly concentrated solutions is
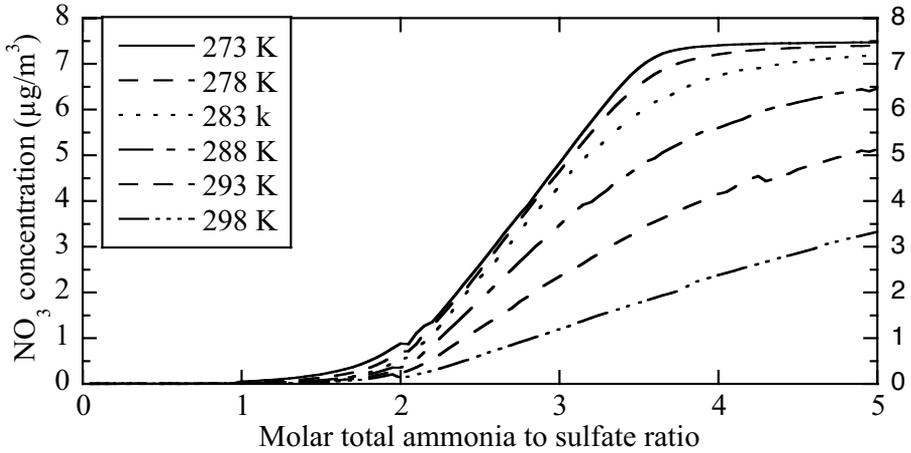
Figure 1.8 The nitrate concentration as function of ammonia availability for different temperatures at 80 % relative humidity. The available amount of both nitrate and sulphate was 7.5 μg/m³.

complex and a strong function of the composition, relative humidity and temperature (Mozurkewich, 1993; Ansari and Pandis, 1998). Nitric acid for example will hardly dissolve in a solution of sulphuric acid. Only when ammonia neutralizes the sulphuric acid, nitric acid can dissolve into the aerosol. Ammonium nitrate is only efficiently formed when the ammonia to sulphate ratio exceeds 2, e.g. all the sulphate is present as ammonium sulphate. This behaviour of ammonium nitrate is illustrated in Figure 1.8, where the amount of nitrate in the aerosol is shown as function of temperature and ammonia availability. At high temperatures, e.g. in summer, much more ammonia is needed to arrive at a certain ammonium nitrate concentration as compared to the winter. Therefore, ammonium nitrate is likely to have a strong seasonal signature.

Sea salt acts as a sink for nitric acid and may provide a surface on which N_2O_5 may hydrolyse. Reaction with nitric acid causes HCl to be liberated:

$NaCl + HNO_3 \rightarrow NaNO_3 + HCl$
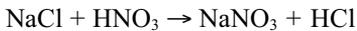
In contrast to ammonium nitrate sodium nitrate is a non-volatile compound under atmospheric conditions. Partitioning of nitric acid in to sea salt is therefore irreversible. Most of the sea salt mass and surface, and therefore the resulting nitrate, is located in the coarse aerosol mode (Vignati et al., 1999). Reaction of nitric acid with mineral dust also yields a stable product, e.g. $Ca(NO_3)_2$, which is also mostly found in the coarse aerosol fraction.

Nitrate may be present in the fine and coarse aerosol mode, where it is associated with ammonium and, sea salt and dust, respectively. For its climate effect it is important to know its chemical form and size distribution. The size distribution of nitrate is a complex function of the ambient conditions and the concentrations of bases involved. This may result is a seasonal variation in the size of the nitrate as has been observed in Spain (Rodriquez et al., 2002).

1.6   Measurement artefacts

Traditionally, aerosols have been collected by filtration methods and subsequently analysed for the chemical composition. This is a straightforward procedure, but the volatile character of ammonium nitrate and the reactivity of gaseous nitric acid make these filtration methods sensitive to artefacts (Slanina et al., 2001). Evaporation of ammonium nitrate from inert filters has been reported in a host of studies (e.g. Hering and Cass, 1999 and references therein). Evaporation of the sampled ammonium nitrate can occur when it becomes unstable due to e.g. changing ambient conditions during sampling, differences between ambient conditions and those inside the sampler or a pressure fall over the filter (pack). Evaporation of ammonium nitrate may lead to a severe underestimation of the nitrate concentration in aerosols. Evaporation artefacts not only occur during sampling but are also observed during storage (Witz, 1985).

Additional artefacts may be caused by nitric acid, which is a very reactive and adsorptive gas. Reactions of nitric acid with previously collected aerosol material or filter substrate have been reported (Spicer and Schumacher, 1979). Adsorption of nitric acid may lead to an overestimation of the nitrate concentration in aerosols.

The optimum method to collect the semi-volatile nitrate is to stabilise it after collection against evaporation, by impregnating filters with a reagent or to use a reactive type of filter. However, such substrates also collect gaseous nitric acid. Gas-denuders are therefore applied to remove the interfering nitric acid. Over twenty years of experience has shown that these denuder filter combinations are very suitable for aerosol nitrate collection (e.g. Harrison and Kitto, 1990 and references therein). However, applying such relatively complicated systems is expensive and labour intensive. Therefore, in Europe monitoring is almost exclusively done by means of filter methods.

To overcome sampling artefacts and the coarse temporal resolution associated with filters the Steam Jet Aerosol Collector has been devised (SJAC) (Slanina et al., 2001), which enables to sample and analyse the inorganic aerosol composition on a 20 minute basis. The sampling of this device is based on droplet formation. After passage through two (wet) denuders to strip nitric acid and ammonia, steam is injected in the air. Due to the supersaturation the aerosols will grow to droplets, which are subsequently removed from the air stream by a cyclone. The resulting solution is analysed for their ion concentrations. However, application of the SJAC for long term monitoring is still difficult.

1.7   Nitrate climate forcing

Only a few studies on the climate forcing by the nitrate component of aerosols have been performed. The first estimate has been published by Van Dorland et al. (1997). These authors assumed a gas aerosol partitioning for their nitric acid field calculated with a global model and speculated that the nitrate forcing is approximately -0.03 W/m^2. Adams et al. (2001) and Jacobson (2001) derive a forcing of -0.22 and -0.02 W/m^2, respectively, on basis of very similar burdens. The large discrepancy between these studies can be explained by the model set-up/assumptions. Jacobson (2001) assumes 90 % of the nitrate burden to be in the coarse aerosol mode, which has a low scattering efficiency. In contrast,

Adams et al. (2001) calculated global ammonium nitrate fields, which were assumed to have a size distribution similar to sulphate. In the study by Adams et al. (2001) off-line monthly averaged fields of nitric acid were used for the calculation of the gas-aerosol partitioning. The calculated seasonal variation in the nitrate concentrations was tuned towards few available measured data by adapting the ammonia emission strength. Recently, Metzger et al. (2002) presented a global modelling study on nitrate fields. This is the first global study which interactively calculates the nitric acid formation and the gas aerosol partitioning. The computations by Metzger et al. (2002) also show that nitrate is an important component of aerosols over large (continental) areas in the world.

Measurement studies show that nitrate is an important contributor to the aerosol forcing on the regional scale. Ten Brink et al. (1997) and Veefkind et al. (1996) show that during summer in the Netherlands the sub-micron nitrate mass and therewith its forcing is comparable to that of sulphate. Unfortunately, comparable studies have not been performed elsewhere. Therefore, it is unclear to which extent this finding applies to other parts of Europe.

Clearly, the model results described above are very uncertain and large discrepancies remain between the different models. The models differ in basic assumptions on the nitrate size distribution and the degree of model complexity. All authors mention the need to verify their model results against reliable data on aerosol nitrate. For this reason and the lack of experimental evidence the IPCC (2001) did not attempt to estimate the direct forcing of nitrate.

1.8   Research aims and thesis outline

In the previous sections it was shown that aerosols play an important role in several environmental issues. Aerosols may locally cool or, in case of BC, sometimes even warm climate, and modelling efforts have been made to describe the role of different aerosol components in the climate system. In the case of nitrate, large uncertainties in modelling studies and the lack of experimental evidence for an important role of nitrate prevented the IPCC to quantify the forcing by nitrate. These factors can be directly linked to a lack of reliable data on the ambient concentration of nitrate and its precursors. In this thesis we would like to strengthen the knowledge on aerosol nitrate in the climate issue. For this purpose we focus on Europe, which has been identified as a region where nitrate is potentially important. We would like to address the following questions:

- Is nitrate an important component of aerosols over Europe? E.g. what are the nitrate concentrations over Europe? How do these compare to other aerosol constituents?

- How accurate can nitrate be measured? What are the artefacts in nitrate sampling procedures under different conditions? Can we use indirect data to obtain information on the aerosol nitrate concentration?

- What is the size distribution and chemical composition of the nitrate particles? E.g. is nitrate present as ammonium nitrate, sodium nitrate or calcium nitrate?

- What are the most important processes that lead to nitrate formation? Which factors control the partitioning of nitrate between the aerosol and gas phase?

- Can we estimate the forcing of nitrate, and what is its relevance in comparison with other aerosol components, e.g. sulphate?

To answer the first question data on nitrate were gathered throughout Europe. However, the quality of most of the data was unknown. Therefore, Chapter 2 describes the analysis of a series of experiments conducted to investigate artefact formation. One of those experiments is a full field comparison conducted at the research site, Melpitz. Special attention will be given to the evaporation artefact as function of temperature. In Chapter 3 the findings from these experiments and other studies were used to construct a nitrate distribution solely based on quality controlled measurements over Europe. In conjunction with the analysis of the experimental data, the LOTOS model has been developed to calculate inorganic aerosols and is fully described in Chapter 4. The model has been applied to the whole year of 1995 and the results are discussed. In addition, the impact of nitrate on the radiation balance over Europe is assessed. In the appendices of Chapter 4 we briefly present additional simulations in which the influence of a few uncertain model parameters on the modelling results is explored. Subsequently, the model system has been applied to calculate the fine aerosol distribution over Europe due to anthropogenic sources. For this purpose, a newly developed inventory for primary particles, including black carbon, has been used. As a result, the nitrate levels are placed in perspective. The chapters mentioned above are presented in the form of papers. These papers have been published in or are submitted to peer reviewed journals. This thesis is then concluded with a general discussion of the results in framework of the research questions given above and with an outline for further research.

References

Adams, P.J., Seinfeld, J.H., Koch, D.M., Mickley, L., Jacob, D. (2001), General circulation model assessment of direct radiative forcing by the sulphate-nitrate-ammonium-water inorganic aerosol system, J. Geophys. Res., 102 (D1), 1097-1111

Andreae, M.O., Crutzen, P.J. (1997), Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry, Science, 276, 1052-1058

Ansari, A.S., Pandis, S.N. (1998), Response of Inorganic PM to Precursor Concentrations, Environ. Sci. Technol., 32, 2706-2714

Brimblecombe, P. (1987), The Big Smoke, Methuen, London, UK

Cornell, S., Rendell, A., Jickells, T. (1995), Atmospheric inputs of dissolved organic nitrogen to the oceans, Nature, 376, 243-246

Dockery, D.W., Pope, C.A., Xu, X., Spengler, J.D., Ware, J.H., Fay, M.E., Ferris, B.G., Speizer, F.E. (1993), An association between air pollution and mortality in six US cities, N. Engl. J. Med., 329, 1753–1759

He, S., Carmichael, G. R., (1999), Sensitivies of photolysis rates and ozone production

in the troposphere to aerosol properties, J. Geophys. Res., 103, 26307-26324

Harrison, M.R., and Kitto, A.M.N. (1990), Filed intercomparison of filter pack and denuder sampling methods for reactive gaseous and particulate pollutants, Atmos. Envir., 24A, 2633-2640

Hering, S., and Cass, G. (1999), The magnitude of bias in the measurement of PM2.5 arising from volatilisation of particulate nitrate from Teflon filters, J. Air & Waste Manage. Assoc., 49, 725-733

Hoek, G., B. Brunekreef, S. Goldbohm, P. Fischer and P.A. van den Brandt (2002), Association between mortality and indicators of traffic-related air pollution in the Netherlands: a cohort study, The lancet, 360, 1203-1209

IPCC (2001), Climate Change 2001: The Scientific Basis, Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change (IPCC), Cambridge University Press, Cambridge, UK

Jacobson, M.Z. (2001), Global direct radiative forcing due to multicomponent anthropo-genic and natural aerosols, J. Geophys. Res., 196, 1551–1568

Kiehl, J.T., and Briegleb, B.P. (1993), The relative roles of sulphate and greenhouse gases in climate forcing, Science, 260, 311-314

Krupa, S.V. (2003), Effects of atmospheric ammonia (NH_3) on terrestial vegetation: a review, Environmental pollution, 124, 179-221

Kuhlbusch, T.A.J., John, A.C., Fissan, H., Schmidt, K.-G., Schmidt, F., Pfeffer, H.-U, Gladtke, D. (1999), Pm10 and Pm2.5 mass concentration, chemical composition, and size distribution measurements at three different sites in the Ruht-area, Germany, J. Aerosol Sci., 30, S45-S46

Metzger, S.M., Dentener, F.J., Jeuken, A., Krol, M., Lelieveld, J. (2002), Gas/aerosol partitioning II: Global modelling results, J Geophys. Res., 107 (D16), doi:0.1029/2001JD001103

Mozurkewich M. (1993), The dissociation constant of ammonium nitrate and its depend-ence on temperature, relative humidity and particle size, Atmos. Environ., 27A, 261-270

Pakkanen, T.A., Hillamo, R.E., Aurela, M., Andersen, H.V., Grundahl, L., Ferm, M., Persson, K., Karlsson, V., Reissell, A., Royset, O., Floisand, I., Oyola, P. and Ganko, Y. (1999), Nordic intercomparison for measurement of major atmospheric nitrogen compounds, J. Aerosol Sci., 30, 247-263

Pope, C.A. III, Thun, M.J., Namboodiri, M.M., Dockery, D.W., Evans, J.S., Speizer, F.E., Heath, C.W. (1995), Particulate air pollution as a predictor of mortality in a prospective study of US adults, Am. J. Respir. Crit. Care Med., 151, 669–674

Prospero, J.M., Olmez, I. and Ames, M. (2001), Al and Fe in PM 2.5 and PM 10 suspended particles in South-Central Florida: The impact of the long range transport of African mineral dust, Water, Air, and Soil Pollution, 125, 291-317

Robles Gonzalez C., Veefkind, J.P., de Leeuw, G. (2000), Aerosol optical depth over Europe in August 1997 derived from ATSR-2 data, GRL, 27, 955-958

Rodriguez, S., Querol, X., Alastuey, A., Plana, F. (2002), Sources and processes affecting levels and composition of atmospheric aerosol in the western Mediterranean,

J. Geophys. Res-A, 107 (D24), art no: 4777

SEI (Stockholm Environment Institute) (1998), Regional air pollution in Africa, http://www.sei.sk

Seinfeld, J.H. and Pandis, S.N. (1998), Atmospheric chemistry and physics: From air pollution to climate change, John Wiley & Sons, Inc., New York, USA

Seitzinger, S.P., Kroeze, C., Bouwman, A.F., Caraco, N., Dentener, F., Styles, R.V. (2002), Global patterns of dissolved inorganic and particulate nitrogen inputs to coastal systems: Recent conditions and future projections, Estuaries, 25 (4B), 640-655

Slanina, J., ten Brink, H.M., Otjes, R.P., Even, A., Jongejan, P., Khlystov, A., Waijers-Ijpelaan, A., Hu, M., Lu, Y. (2001), Continuous analysis of nitrate and ammonium in aerosols by the Steam Jet Aerosol Collector (SJAC), Atmos. Environ., 35, 2319-2330

Sokolik, I.N., Toon, O.B. (1996), Direct radiative forcing by anthropogenic airborne mineral aerosols, Nature, 381, 681-683

Spicer, C.W, and Schumacher, P.M. (1979), Particulate nitrate: Laboratory and field studies of major sampling interferences, Atmos. Environ., 13, 543-552

Spokes, L.J., Yeatman, S.G., Cornell, S.E. and Jickells, T.D. (2000), Nitrogen deposition to the eastern Atlantic Ocean: The importance of south-easterly flow, Tellus, 52, 37-49

Tegen, I., Fung, I. (1995), Contribution to the atmospheric mineral aerosol load from land-surface modification, J. Geophys. Res., 100 (D9), 18707-18726

Ten Brink, H.M, Kruisz, C., Kos, G.P.A., Berner, A. (1997), Composition/size of the light-scattering aerosol in the Netherlands, Atmos. Environ., 31, 3955-3962

TNO (2001), The CEPMEIP emission database, http://www.air.sk/tno/cepmeip

Van Dorland, R., Dentener, F.J., Lelieveld, J. (1997), Radiative forcing due to tropospheric ozone and sulphate aerosols, J. Geophys. Res., 102 (D23), 28079-28100

Veefkind J. P., van der Hage, J.C.H., and ten Brink, H.M. (1996), Nephelometer derived and directly measured aerosol optical depth of the atmospheric boundary layer, Atmos. Res., 41, 217-228

Vignati, E., de Leeuw, G., Schulz, M., Plate, E. (1999), Characterization of aerosols at a coastal site near Vindeby (Denmark), J. Geophys. Res.,104, 3277-3287

Witz, S. (1985), Effect of environmental factors of filter alkalinity and artifact formation, Envir. Sci. Technol., 19, 831-835

2   Artefacts in the sampling of nitrate studied in the "INTERCOMP" campaigns of EUROTRAC-AEROSOL

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Abstract

Sampling of aerosol-nitrate can be problematic because of evaporative loss of the semi-volatile ammonium nitrate or adsorption of nitric acid gas. Such artefacts, which depend on filter type and ambient conditions, are not well documented for the filters in use in Europe and this was the reason to study these in a series of intercomparison trials. The trials were performed within the "INTERCOMP" programme of the AEROSOL subproject of EUROTRAC-2.

The major effort was a two-week field campaign at the rural site, Melpitz, near Leipzig in eastern 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 $\mu g/m^3$. The concentrations stemming from 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 the mentioned artefacts was negligible. The absence is explained by extrapolation of results of tests on the artefacts 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 during the field campaign. Cellulose and cellulose-acetate filters quantitatively collected both ammonium nitrate and 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 evaporation losses of aerosol-nitrate from quartz filters. We parameterised the extend of the evaporation in a general way as a function of temperature. There is complete evaporation at temperatures exceeding 25 °C and full retention at temperatures less than 20 °C. At temperatures between 20 and 25 °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 °C during sampling. Cellu-lose type filters quantitatively collect nitric acid, but negligible amounts of nitrous acid.

2.1 Introduction

Nitrate is a dominant component of fine particulate mass in western and central Europe (Schaap et al., 2002). In summer, nitrate concentrations are consistently lower than in winter. This may be a real phenomenon but it can also be due to evaporation during sampling of the semi-volatile ammonium nitrate, the most dominant form in which nitrate is present in this part of Europe (Ten Brink et al., 1997; Schaap et al., 2002). The volatilisation artefact depends on the filter material and ambient meteorological conditions like temperature and relative humidity (Chow, 1995; Hering and Cass, 1999). There is a higher evaporative loss in summer, the reason being a larger evaporative tendency of ammonium nitrate with increasing temperatures and with drier air. The evaporation artefact leads to serious underestimation of the true values, as illustrated in measurements in the Po valley (Putaud, et al., 2002), which will be further evaluated below.

Despite of the evaporation artefact, the actual nitrate concentration can also be overestimated depending on the filter type. Cellulose type aerosol filters, commonly used in Europe, may adsorb nitric acid and possibly nitrous acid gas which are thus assigned to aerosol nitrate (Spicer and Schumacher, 1979; Savoie and Prospero, 1982).

In the past several studies were performed to investigate sampling artefacts by the use of different filter types and samplers (Appel et al., 1979; Eatough et al., 1988; Dasch et al., 1989; Harrison and Kitto, 1990; Hering and Cass, 1999; and others). Most of these studies have been performed in the US, where other filters are in use than in Europe. Those performed in northern Europe (Pakkanen et al., 1999) are of less relevance because the nitrate found there is mainly present in the form of stable compounds, like $NaNO_3$ (Pakkanen et al., 1999).

In the study reported here we investigated the mentioned artefacts occurring during sampling of aerosol-nitrate. In the framework of the extensive INTERCOMP2000 campaign for comparison of aerosol sampling and establishing proper sampling tools a field intercomparison took place in Melpitz, near Leipzig. Melpitz is of particular interest because the station has a long record of nitrate data. The series shows a rapidly increasing importance of nitrate relative to sulphate concentrations in the course of the last decade (Spindler et al., 1999). Quartz filters are in use at the site. The campaign provided an opportunity to compare the data as obtained within the long term record with those measured by the participants. Full details of the INTERCOMP2000 set-up and meteorology can be found in Müller et al., (2003). We will only discuss the experimental set-up relevant for the nitrate sampling.

As a preparation for the field campaign a wind-tunnel study was performed in 1999. Here conditions like temperature, relative humidity and concentration of aerosol nitrate and related gases could be controlled. Furthermore, the results of the already mentioned Po-Valley study will be discussed in this paper. All of the campaigns were organised in the framework of the EUROTRAC-2 AEROSOL programme.

Table 2.1 Overview of samplers used

Size	Nr	Sampler	Filter/Foil type	Flow (l/min)	Extraction	Analysis
PM10	1	IFT_HV_2	Quartz	1000	Water	IC
	2	IFT_LV_2	Teflon	16.7	Water	IC
	3	Ugent_1[a]	Nuclepore	16.7	Water	IC
	4	Ugent_2[a]	Nuclepore	16.7	Water	IC
	5	Ugent_3[a]	Nuclepore	16.7	Water	IC
	6	IFT_SJAC	-		Water	IC
PM2.5	7	BTU_HV	Quartz	500	Water	IC
	8	IFT_HV_1	Quartz	500	Water	IC
	9	IFT_LV_1	Teflon	16.7	Water	IC
	3	Ugent_1[b]	Teflon	16.7	Water	IC
	4	Ugent_2[b]	Mix. Cell. ester	16.7	Water	IC
	5	Ugent_3[bc]	Whatman 41	16.7	Water	IC
PM1	10	IFT_LV	Teflon	16.7	Water	IC
Impactor	11	IFT_I	TEDLAR	75	Water	IC
	12	TUV_I	Aluminium	30	Water	IC

[a] PM2.0, [b] coarse filter, for PM10 the concentration derived from the fine and coarse filter have to be added up, [c] with additional W41 backup filter during the latter half of the campaign

2.2   Experimental

2.2.1   INTERCOMP2000

Site description and meteorological conditions

In the period of 4 to 13 April 2000 a field experiment was conducted at the Melpitz research station (latitude 51°32'N, longitude 12°54'E, altitude 87 m), located in the downstream plume of the Leipzig conurbation. A detailed description of the site and the meteorological situation during the campaign can be found in Müller et al. (2003). Conditions during the campaign were quite cool and humid for the time of the year. The maximum temperature did not exceed 15 °C. Daily average temperatures were all below 10 °C and the average relative humidity ranged between 67 and 88 %.

Sampling methods

During the campaign four institutes used twelve different samplers to collect aerosol samples for nitrate analysis or directly measured the nitrate content of the aerosol. The samplers, their acronyms and main features of the sampling methods are listed in Table 2.1 and described in detail below. As indicated most of these were filter samplers with a PM2.5 and a PM10 pre-selector. In addition, three "stacked" filter-units (SFU) and two

low pressure Berner impactors were operated. The filters were either inert (Teflon, Quartz fibre or polycarbonate) or of a cellulose-based material (cellulose or a mixed cellulose ester). A Steam Jet Aerosol Collector (SJAC) (Slanina et al., 2001) was used to measure nitrate with a one-hour time resolution. The filters and impactors were operated with a 12 or 24-hour time resolution, starting at 8:00 a.m. for 24-hour sampling and additionally at 8:00 p.m. for 12-hour sampling. All available data were aggregated to 24-hour values.

The IFT_HV_1 is a High Volume Digitel (DHA80) sampler. The second high volume sampler operated by IFT (IFT_HV_2) is a modified Sierra Anderssen-PM10 sampler, which has been used for monitoring purposes since 1992 (Spindler et al. 1999). Both systems were equipped with quartz fibre filters (25.4 x 20.3 cm, Type MK 360, Munktell Filter, Sweden). The low volume sampler is the Partisol 2000 Air Sampler (Rupprecht and Patashnik Co. Inc., USA) (Spindler et al., 2002). Daily samples of PM10, PM2.5 and PM1 were collected on Teflon filters (Millipore, Eschborn, Germany, Type 4700, 3 µm pore size). A 5-stage Berner low pressure cascade impactor (IFT_I) was also operated (Berner et al., 1979). A Steam Jet Aerosol Collector (SJAC) (Slanina et al., 2001), operated offline, was used to measure nitrate with a one-hour time resolution. The aerosol nitrate content was determined from a quarter of the HV filters or a half of the LV filters, respectively, by standard ion chromatography procedure (Brüggemann et al., 2000).

The BTU_HV sampler and sample analysis was identical to IFT_HV_1 (Wieprecht et al., 2001).

The TUV_I instrument is a nine-stage low-pressure cascade impactor, type LPI 30 (Berner et al., 1979). The experimental and analysis procedures are described in Berner et al. (1998).

The three samplers used by Ugent were Gent PM10 stacked filter unit (SFU) samplers (Maenhaut et al., 1994; Hopke et al., 1997). They were equipped with a Gent PM10 inlet (Hopke et al., 1997), the aerosol was separated into two size fractions (PM2.0 and PM2-10) by sequential filtration through two 47-mm diameter filters. The coarse filter was for all three samplers an 8 micron pore size, Apiezon-coated, Nuclepore polycarbonate filter. The fine filter was a Gelman Teflon filter (2 micron pore size) in Ugent_1; a Millipore mixed cellulose ester filter (acetate + nitrate), type SSWP04700 (3 micron pore size), in Ugent_2; and a Whatman 41 cellulose filter in Ugent_3. From April 7 on, an additional Whatman 41 filter was used in the latter. Besides the actual samples, also 6 field blanks were collected with each of the three Ugent samplers. Air was drawn through the field blanks for about 30 seconds. All samples were analysed for nitrate by ion chromatography (IC). Each sample was placed in a 15 mL polystyrene tube and extracted with 10 mL Milli-Q water in an ultrasonic bath (60 min). The IC analyses were done with a DIONEX 4500i chromatograph, with a conductometric detector, an AG12A guard column, an AS12A analytical column, an ASRS auto-suppressor with external water mode and a PC-based AutoIon (AI-450) data acquisition and analysis system. The eluent was 2.7 mM sodium carbonate / 0.3 mM sodium bicarbonate (isocratic). Injection of the samples was done manually using a 100-µL sample loop.

Table 2.2 Experiment matrix and results in the wind-tunnel tests.
The abbreviations used for the different methods are:
"Paper": Whatman-41 cellulose
"Qrz": Quartz fiber
"CA": Cellulose acetate membrane
"DD": Denuder difference method
The detection limit for the various samplers is reflected in blank run 5. In runs 3,4,6-9 the measured nitric acid gas concentration was very similar to the design value of 10 $\mu g\ m^{-3}$.

Experiment design			Measured nitrate NO3 ($\mu g\ m^{-3}$)					
			DD	Paper	CA	Qrz	Teflon	SJAC
	1	KNO_3 10 $\mu g/m^3$	9.2	6.8	12.2	11.8	9.2	9.2
duplo	2	KNO_3 10 $\mu g/m^3$	8.7	7.9	8.7		8.5	8.5
	3	$NH_4NO_3+HNO_3$	12.1	23.5	24.9	22.2	12.3	7.0
duplo	4	$NH_4NO_3+HNO_3$	11.7	22.6	21.3		11.6	6.6
	5	overnight aerosol-free	-0.3	0.1	0.1	0.1	-0.0	<0.1
	6	HNO_3	2.3	13.5	12.2	11.6	2.0	<0.1
duplo	7	HNO_3	2.7	16.1	14.4		2.8	<0.1
	8	HNO_2	0.4	0.8	0.5	0.6	0.0	<0.1
duplo	9	HNO_2	0.5	1.3	0.5		-0.0	<0.1
	10	NH_4NO_3 20$\mu g/m^3$	21.0	16.6	20.1	21.2	15.1	16.6
duplo	11	NH_4NO_3 20$\mu g/m^3$	20.4	17.0	20.9		14.4	16.4
	12	NH_4NO_3 5$\mu g/m^3$	1.4	4.9	5.8	5.4	0.3	3.4
	13	NH_4NO_3 7$\mu g/m^3$ (35°C)	12.9	14.3	16.0	1.9	0.1	8.9
	14	NH_4NO_3 20$\mu g/m^3$ (35°C)	32.3	34.5	35.8	10.5	1.2	26.2
duplo	15	NH_4NO_3 20$\mu g/m^3$ (35°C)	30.9	33.9	33.0		1.0	25.7
15+ night	16	NH_4NO_3 20$\mu g/m^3$ (35°C)	36.6	40.7	40.8	0.7	0.1	
	17	KNO_3 20$\mu g/m^3$	32.3	33.9	34.9	35.0	32.3	27.4
duplo	18	KNO_3 20$\mu g/m^3$	34.7	34.2	36.9		34.7	28.1

2.2.2 Laboratory intercomparison

The tests in the laboratory-based INTERCOMP99 have been described elsewhere (Ten Brink et al., 2001), and the relevant parameters are summarised here (Table 2.2). Tests were performed in a wind tunnel behind a large holding chamber in which the aerosol was generated. A series of filter samplers with different filter types were compared. Non-volatile potassium nitrate was used as a reference material. The sampling efficiency of pure ammonium nitrate and a combination of ammonium nitrate and nitric acid gas were tested, at various concentrations and temperatures. In addition, the adsorption of gaseous nitric and nitrous acid (HONO) was investigated. The typical sampling time was 2 hours to allow for duplicate tests.

Samplers

Filters of the same type as in INTERCOMP2000 were used, but were placed in open-face filter holders without inlet tubing to prevent losses of nitric acid in this tubing. A denuder difference method (Behlen, 1996) served as the reference (artefact-free) collection method. The first filter in the filter pack was Teflon, which allowed for the assessment of the sampling characteristics of this material. The filter pack further consisted of a nylon back up filter and was used in combination with a separate sodium chloride coated denuder. The SJAC was also present. This served two purposes: first the SJAC was tested against the other methods and, secondly, it was used to follow, on-line, the concentration of nitrate and ammonium and to check the concentration of the associated gases in the set-up phase of the test.

Comparability of the analysis procedures was good, and "field" blanks were negligible compared to values obtained with actual sampling of aerosol-nitrate.

Aerosol and gas generation

Particle-free ambient air, which was typically at temperature of 21 °C and a relative humidity between 50 and 60 %, was pumped through the chamber and wind-tunnel at a flow of 15 m^3/min. This rate allows for the use of a variety of samplers in parallel. Aerosol nitrate and nitric acid were produced by nebulizing nitrate and nitric acid solutions, respectively. The generated droplets rapidly dried when the small aerosol stream was added to the main flow. The resulting particles had a size and a mass concentration comparable to those in the atmosphere. Stability in the generation is an important parameter because evaporative loss of ammonium nitrate is also a function of filter loading (Chow, 1995). The concentration of the aerosol during a run was therefore followed with a time resolution of one minute with both an optical sizer (LAS-X) and an integrating nephelometer (Ten Brink et al., 2000) and it was found that short-time volume/mass fluctuations were less than 5 %.

The nitric acid production was tested with an automated wet-denuder (Slanina et al., 2001). Wall losses of nitric acid in the large system appeared to be negligible. It was also checked that the concentration of nitric acid and the aerosols was homogeneous over the inner central half of the exit plane where the samplers were placed.

HONO was generated by a method developed at MPI, Hamburg (Behlen, 1996). The concentration and the stability of HONO generation were followed by a NO_x-monitor. The concentration of this gas decreased with some 25 % over time, but there were no short-time fluctuations.

2.2.3   Po-valley

The experimental set-up, analysis procedures and site description are extensively described by Putaud et al. (2002) and Baltensperger et al. (2002).
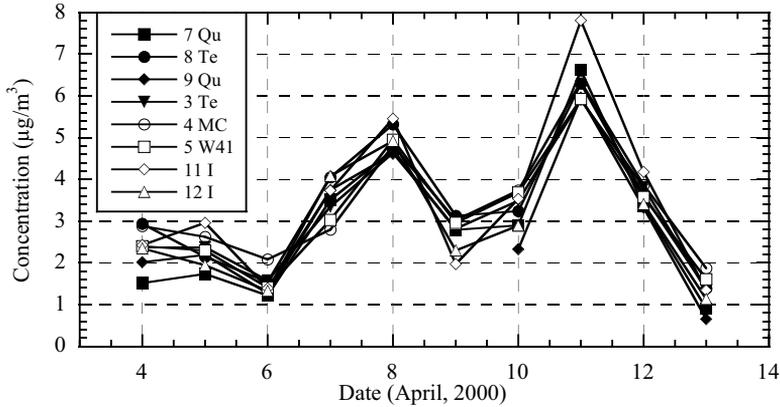
Figure 2.1 Nitrate content of PM2.5 during INTERCOMP2000. The numbers indicate the individual samplers (see Table 2.1) where the abbreviations denote its main feature: Te = Teflon, Qu = Quartz, MC = Mixed Cellulose ester, W41 = Whatman41, and I = Impactor.

2.3   Results and discussion

2.3.1   INTERCOMP2000

In the analysis of the (nitrate) data from INTERCOMP2000 sulphate was considered to be the most conservative species. For comparison purposes the same procedure was followed for sulphate as for nitrate. In Figure 2.1, the nitrate content of PM2.5 at Melpitz is shown as obtained with the indicated samplers. The data show elevated concentrations from the 7th to the 12th of April, with maxima on the 8th and 11th. The average concentration of nitrate in PM10, 4 $\mu g/m^3$, was close to the annual average at the site. During the campaign nitrate was mainly, at 81 %, found in the PM2.5 size range. Average nitrate concentrations in PM2.5 and PM10 were calculated from all filter and impactor data and served as reference values. The average nitrate concentration over the whole sampling period calculated from the averages of each sampler was 4.0 $\mu g/m^3$ with a 6 % relative

Table 2.3 Ratio of the average concentration of nitrate and sulphate in PM10 over the campaign to the mean of all samplers, # without the 11th

PM10	IFT_LV	IFT_HV	Ugent_1	Ugent_2	Ugent_3	TUV_I	IFT_I[#]	SJAC
NO3	1.02	0.89	1.01	1.06	1.01	1.01	0.97	1.14
SO4	1.10	0.95	1.06	1.01	0.98	1.01	1.02	1.18

*Table 2.4 Ratio of the average concentration of nitrate and sulphate in PM2.5 over the campaign to the mean of all samplers, * without the 9th, # without the 11th*

PM2.5	IFT_LV	BTU_HV	IFT_HV[*]	Ugent_1	Ugent_2	Ugent_3	TUV_I	IFT_I[#]
NO3	1.03	0.90	0.88	0.97	1.04	0.98	1.07	0.94
SO4	1.04	1.14	1.03	0.97	0.93	0.88	1.04	0.92

standard deviation and 3.3 µg/m^3 with a 6 % relative standard deviation for PM10 and PM2.5, respectively. In Table 2.3 and 2.4 the relative ratios between the samplers are shown. All samplers are within 15 % of the average. Figure 2.2 compares the data for PM10 and PM2.5 from the individual samplers to the reference values. The relative standard deviation of the average values for a single day ranges between 4 % and 28 % for PM10 and between 6 % and 30 % for PM2.5. The highest standard deviations are found for the lowest concentrations, as a result of a quite constant absolute difference of about 0.5 µg/m^3 between samplers (see Fig 2.3). Differences in the levels obtained with PM2.5 samplers were slightly higher, which may be explained by the different cut-offs used ranging from 2.0 to 3.5 µm. The data obtained with cellulose or mixed cellulose ester filters fall well within the range of the data from the inert filters (Teflon and quartz). From the laboratory experiments, discussed below, we know that nitric acid gas is fully adsorbed by cellulose type filters. However, the concentration of nitric acid was so low relative to that of aerosol nitrate during the present campaign (Acker et al., 2003) that its interference is small. Therefore, nitric acid does not give rise to significantly different values from those obtained with the inert filters on which nitric acid does not adsorb.

On average the SJAC data for PM10 seem to be slightly higher than the other data. Because the non-volatile sulphate shows the same feature (see Fig. 1b), we conclude that this finding can not be interpreted as a loss of nitrate by evaporation from the filters. Additionally, an absence of volatilisation is in good agreement with the comparability of the data from the inert and cellulose filters. The laboratory intercomparison showed that no volatilisation occurred from the latter, and we conclude that evaporation from the inert filters was not significant.

Ferm et al. (1988) compared different total nitrate samplers. For daily average total nitrate concentrations relative standard deviations were found to be lower than 15 % for different laboratories using the same sampling technique. At the low end of the concentration range (< 2 µg/m^3) standard deviations were significantly higher. When each laboratory used their own technique very similar results were found. These findings are in good agreement with the data in our study. The same applies for a study by Harrison and Kitto (1990).
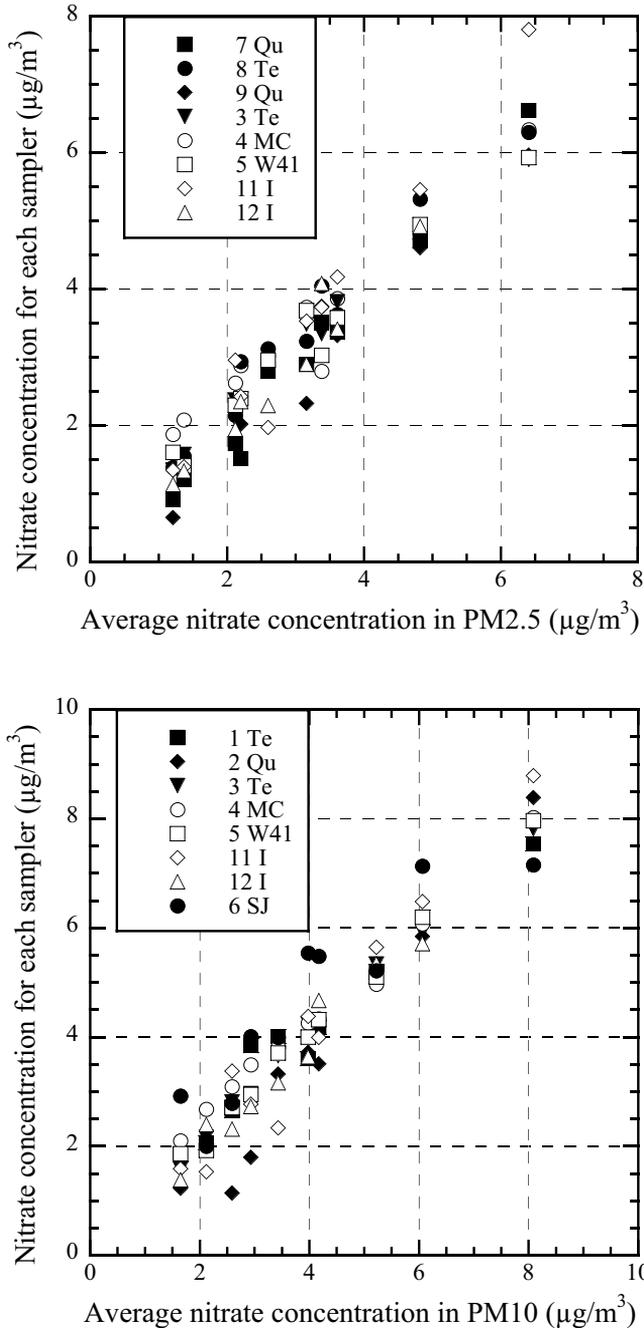
Figure 2.2 Comparison between the nitrate concentrations obtained from the individual samplers and the average nitrate concentration in PM2.5 (upper panel) and PM10 (lower panel). The numbers indicate the individual samplers (see Table 2.1) where the abbreviations denote its main feature: Te = Teflon, Qu = Quartz, MC = Mixed Cellulose ester, W41 = Whatman41, I = Impactor and SJ = SJAC.
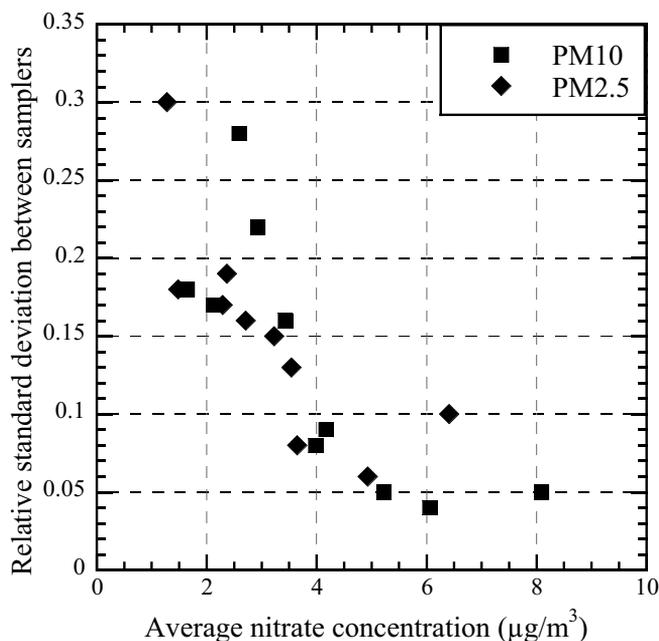
Figure 2.3 Relative standard deviation in the average of all samplers for PM2.5 and PM10 per day

2.3.2   *Laboratory study*

In the laboratory study the first step was to test the collection efficiency of the filters for sub-micron aerosol with stable potassium nitrate. It was found that even the Whatman 41 filter sampled close to 100 %.

With the semi-volatile ammonium nitrate, sampled at an air temperature of 24 °C, the quartz filter sampled as much as the reference sampler. However, only 75 % of the nitrate was collected on the front Teflon filter of the reference sampler. At an elevated air tempera-ture of 35 °C, less than 30 % of the nitrate was sampled on the quartz and almost none on the Teflon filter. These differences are due to evaporation of ammonium nitrate after collection. The reason is that the aerosol sampled on the filters is not in equilibrium with the associated gases because the time between generation and arrival at the filters is too short to establish this equilibrium (under equilibrium conditions at 35°C, 46 $\mu g/m^3$ of ammonium nitrate will be present in the gas phase as ammonia and nitric acid (Seinfeld and Pandis, 1998)). The presence of this dis-equilibrium is indicated by the low concen-trations of nitric acid, which were less than 10 % of the equilibrium value. In contrast to the inert-type filters the cellulose type filters quantitatively retained the nitrate.

In the interference test with nitric acid gas, the nitrate concentrations found on the cellulose-type filters were similar to the nitric acid concentration measured with the gas-denuders. This shows that these filter types quantitatively collect nitric acid. The retention appeared to be in the form of ammonium nitrate. This is probably due to neutralization of the nitrate on the filter by NH_3, which was present at a continuous background level.
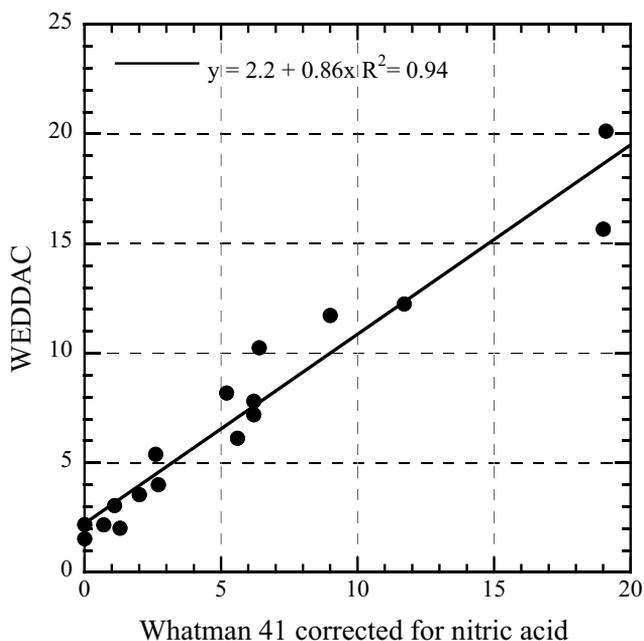
Figure 2.4 Concentration of nitrate as sampled on a Whatman 41 filter (corrected for HNO3) compared to the WEDDAC

Additional tests at a later date showed that on cellulose filters nitric acid is also retained in the absence of ammonia. A marginal amount of nitrate was found on the Teflon filter. In contrast, the other inert material, quartz, quantitatively collected the nitric acid, in the form of ammonium nitrate. This ammonium nitrate was apparently formed on the filter in a reaction of the nitric acid and the mentioned free ammonia in the system. In the runs with both ammonium nitrate and nitric acid the Teflon filters only collected ammonium nitrate, whereas the quartz sampled also nitric acid, showing the very complex behaviour of quartz towards nitrate. HONO gave an almost negligible interference.

A crucial test was that to measure the retention of ammonium nitrate in loaded filters when aerosol-free air of 35 °C was passed through the filters for an extended period. No evaporation was observed from the cellulose-type filters. The nitrate was retained as ammonium nitrate. The quartz and teflon filters showed virtually complete evaporation, see Table 2.2.

2.3.3　Po-Valley

During the late spring of 1998 an intercomparison of three samplers took place in the Po-Valley in a larger field campaign (PIPAPO). Some results of this campaign have already been reported (Putaud et al., 2002; Baltensperger et al., 2002). We provide here an evaluation of the nitrate concentrations as obtained with quartz filters, the Whatman 41 cellulose filters and the artefact free on-line method. Figure 2.4 compares the results of the cellulose filter measurements (Putaud et al., 2002) with those obtained by the WEDD/AC

Table 2.5 Po-Valley: ratio of nitrate on Quartz to Whatman41 filters, with and without correction for nitric acid absorption by the Whatman 41 filter.

Temperature (°C)	raw data	HNO3 corrected
< 20	0.58	0.93
20 – 25	0.29	0.41
> 25	0.07	0.08

system (Baltensperger et al., 2002). For this purpose, the measurements from the WEDD/AC system (20 minute resolution) were integrated for comparison with the longer sampling time of filters (4 - 7 hour resolution), correcting the filter data for the HNO_3 artefact (by subtracting the HNO_3 data as measured with the WEDD/AC from the filter data). Both methods show good agreement with respect to the nitrate concentration and exhibit a correlation coefficient $R^2 = 0.94$, with 6% more nitrate determined on the filters. This confirms the ability of cellulose filters to quantitatively sample ammonium nitrate even at elevated temperature (temperatures ranged between 18° and 30°C).

Using this information, we analysed the evaporation artefact of quartz filters as a function of (average) temperature during the sampling period, by classifying the temperature into three regimes. We corrected the Whatman 41 data for the contribution of nitric acid to obtain the actual aerosol nitrate concentration using measured concentrations of nitric acid (Baltensperger et al., 2002). In Figure 2.5 the nitrate concentrations obtained with the quartz filters are compared with those obtained with the cellulose filters. It can be clearly observed that the differences between the two samplers were highest for the highest temperatures. The average concentration ratios between the samplers are given in Table 2.5 for these intervals (we excluded one obvious outlier). It was found that at temperatures higher than 20 °C substantial or complete loss of ammonium nitrate occurs from the quartz filters.

2.4   General discussion and implications for monitoring

2.4.1   Cellulose type filters and adsorption artefact

In Europe cellulose filters are in use in the EMEP network. From the present study we conclude that these filters are samplers of total nitrate. This conclusion, viz., that cellulose based filters quantitatively collect nitric acid, is substantiated by earlier studies by Appel et al. (1979), Spicer and Schumacher (1979) and Mehlmann (1986), who showed that the capacity of retaining nitric acid on cellulose filters is limited. However, the loads measured in the laboratory and in the field experiment are (much) lower than the saturation limit.
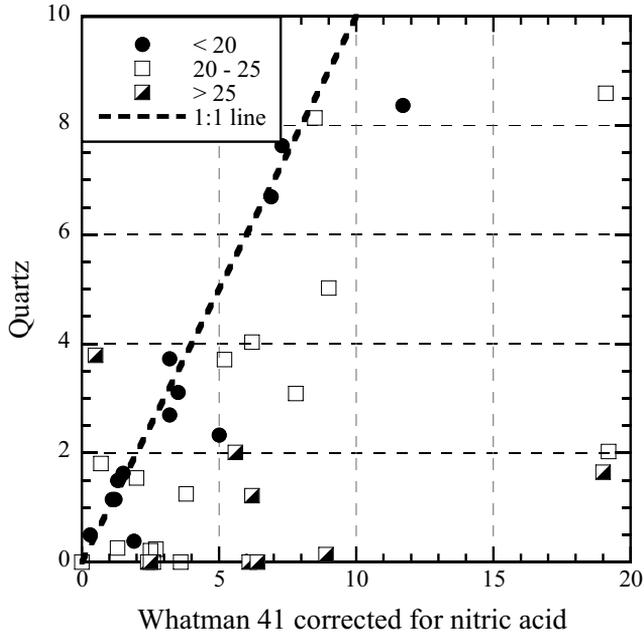
Figure 2.5 Concentration of nitrate as sampled on a quartz filter compared to that on a Whatman 41 filter (corrected for HNO₃)

2.4.2 Evaporation artefact

Underestimation of the nitrate concentration with Teflon filters is a well-documented phenomenon (Appel et al., 1979; Chow, 1995; Hering and Cass, 1999), but less so with quartz for which few data exist on the temperature dependence of the evaporation artefact. In Figure 2.5 we summarize the information on the evaporation artefact with quartz filters obtained in this study. In INTERCOMP2000 we did not find a measurable evaporation artefact. Its absence was explained by the relatively low temperature and high relative humidity encountered during the campaign. These conditions should be associated with very low concentrations of the gases associated with the semi-volatile ammonium nitrate. Indeed, the measured nitric acid concentrations were low (Acker et al., 2003). At tempera-tures exceeding 25 °C during the Po Valley campaign and in the wind tunnel, complete loss of nitrate was observed, whereas a partial loss was observed between 20 and 25 °C. These results are in agreement with those of Eatough et al. (1988), who also observed considerable losses in the afternoon, with temperatures exceeding 20 °C. Below 20 °C no significant evaporation was observed.

Losses during a 24-hour sampling period are not only a function of ambient conditions and sampling apparatus, but also of the sampling strategy. When filters are changed in the morning, losses may occur at the higher temperatures in the afternoon of the previous day but nitrate sampled at night is sampled quantitatively. When filters are changed in the afternoon or evening, nitrate sampled during the night might be lost when temperatures

rise during the day. Such seemingly minor details, together with the type of filter material used and length of sampling lining in which nitric acid may be lost, should in reality be spelled out when nitrate measurements are being reported.

2.5   Conclusions

In this study we report on the comparability of nitrate measurements as studied in three intercomparison campaigns. During the campaign in Melpitz the nitrate concentrations obtained from the different samplers compared well. Evaporation artefacts were not identified, which was attributed to the stability of ammonium nitrate at the low ambient temperatures and high relative humidity. Adsorption of nitric acid to cellulose filters could not be identified, although it was found in the wind tunnel intercomparison experiment. There it was established that cellulose type filters sample the sum of particulate nitrate and nitric acid. Artefacts in the sampling of ammonium nitrate with quartz filters were complex. Evaporation only occurred at the higher temperature of 35 °C. Using this laboratory knowledge the data from a third intercomparison campaign in the Po-Valley, in 1998, were evaluated. We found clear evidence of adsorption of nitric acid by cellulose filters and evaporation losses of aerosol-nitrate from the quartz filters used. We could parameterise the extend of the evaporation artefact as a function of temperature. There is complete evaporation at temperatures exceeding 25 °C and full retention at temperatures less than 20 °C. Between 20 and 25 °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 °C during sampling. Cellulose type filters quantitatively collect nitric acid and particulate ammonium nitrate, but negligible amounts of nitrous acid. A final remark is that seemingly minor details like the time of filter change, type of filter material and length of the sampling line, should in reality be spelled out and tested with respect to effect on the sampling before nitrate measurements are being made and reported.

References

Acker, K., Spindler, G., Brüggemann, E. (2003), Nitrous and nitric acid measurements during the INTERCOMP2000 campaign in Melpitz, Atmos. Envir., Submitted to Atmos. Env.

Appel, B.R., Wall, S.M., Tokiwa, Y., Haik, M. (1979), Interference effects in sampling particulate nitrate in ambient air, Atmos. Environ., 13, 319-325

Baltensperger, U., Streit, N., Weingartner, E., Nyeki, S., Prévôt, A.S.H., van Dingenen, R., Virkkula, A., Putaud, J.-P., Even, A., ten Brink, H., Blatter, A., Neftel, A., Gäggeler, H.W., Urban and rural aerosol characterization of summer smog events during the PIPAPO field campaign in Milan, Italy, J. Geophys. Res., 107, 10.1029/2001JD001292

Behlen, A. (1996), Reactive Stickstoffverbindungen in der Atmosphäre: Konzentrationsbestimmung und trockene Deposition auf Natursteine, Schriftenreihe Angewandte

Analytik, 29, Institut fur Anorganische und Angewandte Chemie der Universität Hamburg

Berner A., Lürzer C., Pohl, F., Preining O., Wagner P (1979), The size distribution of the urban atmospheric aerosol in Vienna, The Science of the Total Environment 13, 245-261.

Berner A., Dusek U., Galambos Z., Kruisz C. (1998), Sampling of fog droplets by cascade impactors, Contributions to Atmospheric Physics, 71, 101-114.

Brüggemann, E., Frank, U., Gnauk, Th, Herrmann,H., Müller, K., Neusüß, Ch., Plewka, A., Spindler, G., Stärk, H.-J., Wennrich, R. (2000) Korngrößendifferenzierte Identifikation der Anteile verschiedener Quellgruppen an der Feinstaubbelastung. Abschlußbericht zum FE-Vorhaben Sächsisches Landesamt für Umwelt und Geologie (SLUG) 13-8802.3521/46

Chow, J.C. (1995), Measurement Methods to Determine Compliance with Ambient Air Quality Standards for Suspended Particles, J. Air & Waste Manage. Assoc., 45, 320-382

Dasch, J.M., Cadle, S.H., Kennedy, K.G., Mulawa, P.A. (1989), Comparison of annular denuders and filter packs for atmospheric sampling, Atmos. Environ., 23, 2775-2782

Eatough, N.L., McGregor, S., Lewis, E.A., Eatough, D.J., Huang, A.A. and Ellis, E.C. (1988), Comparison of sic denuder methods and a filter pack for the collection of ambient HNO3 (g), HNO2 (g) and SO2 (g) in the 1985 NSMC study, Atmos. Environ., 22, 1601-1618

Ferm, M., Areskoug, H., Hanssen, J.-E., Hilbert, G., Lattila, H. (1988), Field intercomparison of measurement techniques for total NH4+ and total NO3- in ambient air, Atmos. Environ., 22,2275-2281.

Harrison, R.M., and Kitto, A.M.N. (1990), Field intercomparison of filter pack and denuder sampling methods for reactive gaseous and particulate pollutants, Atmos. Envir., 24A, 2633-2640

Hering, S., and Cass, G. (1999), The magnitude of bias in the measurement of PM2.5 arising from volatilisation of particulate nitrate from Teflon filters, J. Air & Waste Manage. Assoc., 49, 725-733

Hopke, P.K., Xie, Y., Raunemaa, T., Biegalski, S., Landsberger, S., Maenhaut, W., Artaxo, P., and Cohen, D. (1997), Characterization of the Gent stacked filter unit PM10 sampler, Aerosol Science and Technology, 27, 726-735.

Maenhaut, W., Francois, F., and Cafmeyer, J. (1994), The "Gent" stacked filter unit (SFU) sampler for the collection of aerosols in two size fractions: Description and instructions for installation and use. In: Applied Research on Air Pollution using Nuclear-Related Analytical Techniques, Report on the First Research Co-ordination Meeting, Vienna, Austria, 30 March - 2 April 1993, NAHRES-19, IAEA, Vienna, pp. 249-263.

Mehlmann, A. (1986), Grössenverteilung des Aerosolnitrats und seine Beziehung zur gasförmigen Salpetersäure, PhD thesis, Johannes Gutenberg University, Mainz.

Müller, K., Spindler, G., Baltensperger, U., Hitzenberger, R., Maenhaut, W., Wieprecht, W., ten Brink, H.M. (2003), INTERCOMP 2000, a campaign to assess the compara-

bility of methods in use in Europe for measuring aerosol composition, Submitted to Atmos. Env.

Pakkanen, T.A., Hillamo, R.E., Aurela, M., Andersen, H.V., Grundahl, L., Ferm, M., Persson, K., Karlsson, V., Reissell, A., Royset, O., Floisand, I., Oyola, P., and Ganko, T. (1999), Nordic intercomparison for measurement of major atmospheric nitrogen species, J. Aerosol Sci, 30, 247-263

Putaud, J.P., Van Dingenen, R., Raes, F. (2002), Submicron aerosol mass balance at urban and conurban sites in the Milan area (Italy), J. Geophys. Res., 107, 10.1029/2000JD000111.

Schaap, M., Müller, K., ten Brink, H.M. (2002), Constructing the European aerosol nitrate concentration field from quality analysed data, Atmos. Environ, 36, 1323-1335

Savoie, D.L., Prospero, J.M. (1982), Particle size distribution of nitrate and sulphate in the marine atmosphere, Geophys. Res. Lett., 9, 1207-1210

Slanina, J., ten Brink, H.M., Otjes, R.P., Even, A., Jongejan, P., Khlystov, A., Waijers-Ijpelaan, A., Hu, M., Lu, Y. (2001), Continuous analysis of nitrate and ammonium in aerosols by the Steam Jet Aerosol Collector (SJAC), Atmos. Environ., 35, 2319-2330

Seinfeld, J.H. and Pandis, S.N. (1998), Atmospheric chemistry and physics: From air pollution to climate change, John Wiley & Sons, Inc., New York, USA

Spicer, C.W, and Schumacher, P.M. (1979), Particulate nitrate: Laboratory and field studies of major sampling interferences, Atmos. Environ., 13, 543-552

Spindler, G. Müller, K., Herrmann, H. (1999), Main particulate matter components in Saxony (Germany); Trends and sampling aspects, Environ. Sci. & Pollut. Res., 6, 89-94

Spindler, G. Müller, K., Brüggemann, E., Herrmann, H. (2002), Integration of the field experiment INTERCOMP2000 in the long-term particle concentration observation at the Melpitz site, Proceedings of the EUROTRAC-2 Symposium 2002, P. M. Midgley and M. Reuther (eds), Margraf Verlag, Weikersheim

Ten Brink, H.M, C. Kruisz, G.P.A. Kos and A. Berner (1997), Composition/size of the light-scattering aerosol in the Netherlands, *Atmospheric Environment*, 31, 3955-3962

Ten Brink, H.M, Khlystov, A., Kos, G.P.A., Tuch, T., Roth, C., Kreyling, W. (2000), A high-flow humidograph for testing the water uptake by ambient aerosol, Atmos. Envir., 34, 4291-4300

Ten Brink M. Schulz, J.-P. Putaud, P. Jongejan, E. Plate (2001), Comparison of the collection of ammonium nitrate by various sampling methods, Proceedings of the EUROTRAC Symposium 2000, P. M. Midgley, M. Reuther and M. Williams (eds), Springer Verlag, Berlin

Wieprecht, W., Acker, K., Auel, R., Müller, K. (2001), INTERCOMP2000 Melpitz: Intercomparison of PM2.5 high volume sampler, J. Aerosol Sci, 32, S1019-1020

3   Constructing the European aerosol nitrate concentration field from quality analysed data

Abstract

We report on the construction of the aerosol nitrate concentration field in Europe from an interpolation of data. The first step was an active search for and a subsequent quality assessment of the (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 are therefore used as the starting point. Because of the paucity of data from these devices, values obtained with simple filter sampling were also considered after a critical analysis. We found that the largest artefact associated with inert filters (Teflon and Quartz) is evaporation of ammonium nitrate. Hence, concentrations obtained with the use of inert filters are lower values. 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 distances 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 validated with intermediate point data from shorter lasting campaigns. The field has a large area of high nitrate concentrations ranging from southern England over continental western Europe into Poland, with concentrations of nitrate exceeding 5 µg m^{-3}. Strong arguments are provided that the nitrate is predominantly present in the fine aerosol fraction (PM2.5). To the north nitrate concentrations range from 2.5 µg m^{-3} in S-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 concentration of nitrate in winter in Europe north of the Alps, with the exception of France from which country no data could be found, is 60% or more of that of sulphate. It should further be mentioned that in the Po-Valley ammonium nitrate levels are as high as those in western Europe.

3.1   Introduction

Nitrate could be an important component of the mass of the fine particles, PM2.5, in Europe (Heintzenberg 1998, Kuhlbusch et al., 1999; EMEP, 1998; Chung, 2000). The reason for a growing interest in PM2.5 is the discussion on a regulatory guideline for the maximum concentration of this parameter in the EU. The importance of the various components, and thus of nitrate, for the health hazard associated with PM2.5 has yet to be established; for the time being regulation only considers total aerosol mass and nitrate is possibly an important contributor to this mass. However the region in Europe where this applies has not been identified. Nitrate is also an acidifying component and a nutrient and the extent of the nitrate field is thus also of interest for the environmental topic of acid deposition and eutrophication.

Apart from the mentioned issues, fine aerosol particles play a major role in climate change, by reflecting solar radiation. In the central IPCC-report on this effect (IPCC, 1996) only sulphate and carbon are considered, but in the Netherlands nitrate appears to be as important as the indicated aerosol components (Khlystov, 1998; ten Brink et al., 1997). For other locations in Europe no data are available on the contribution of nitrate to the light-reflecting aerosol. Recently, modelling studies of the global nitrate field were made by Adams et al. (1999) and Jeuken et al. (2000) and the influence on reflection of solar radiation (Van Dorland et al., 1997; Adams et al., 2001). These indicate a rather small contribution by nitrate on a global scale, but the results of the studies are highly uncertain due to the complexity of the formation mechanism and assumptions in the models. In addition, verification of the model results is seriously hampered by the lack of reliable data, specifically in Europe (Adams et al., 1999). The lack of reliable data was the incentive for the present study in which we made use of measured concentration data to construct the nitrate field in Europe.

At present, available long-term data are obtained with the standard 24 hour sampling of aerosol by filtration and subsequent chemical analysis of the nitrate content. This is a straightforward procedure, however, the volatile character of ammonium nitrate and the reactivity of gaseous nitric acid make these filtration methods prone to artefacts (Slanina et al., 2001). The quality of the data is therefore unknown. Artefacts not only occur during sampling but are also observed during storage (Witz, 1985). In view of the artefact problem we will start the study with an overview of measurement methods in Europe, and the associated artefacts. It will be shown what the magnitude of the artefacts are and how they can be corrected for. The selection of data is based on this pre-evaluation. The specific corrections performed for the respective data are discussed in a special section after providing the general results first.

3.2   Filter types in use in Europe

Before we turn to a detailed overview we will briefly tabulate the artefacts occurring with the main filter types in use in Europe and introduce the denuder-filter pack technique in which the same type of filters are applied.

- inert material, Teflon and quartz: loss of ammonium nitrate by evaporation
- impregnated material and nylon: deliberate collection of nitric acid but possibly also other gaseous nitrogen oxide derivatives
- alkaline filters, cellulose (paper), cellulose-acetate: collection of nitric acid and possibly nitrous acid (HONO)

3.2.1   *Denuder filter packs*

The optimum method to collect the semi-volatile nitrate is to stabilise it after collection against evaporation, by impregnating filters with a reagent or to use a reactive type of filter. However, such substrates also collect gaseous nitric acid. Gas-denuders are therefore applied to remove the interfering nitric acid. Over twenty years of experience have shown that these devices are very suitable for aerosol nitrate collection (e.g. Harrison and Kitto, 1990 and references therein). However relatively little attention has been given to a possible interference by nitrous acid (HONO) which is easily absorbed by alkaline substrates and could subsequently be oxidised (Pakkanen et al., 1999). An own analysis of the extent of this effect, see section 2.3 for details, shows that such an artefact is small. The long-term precision of the DF (Denuder Filter) technique is 15 % or better (Sickles et al., 1999).

In the Netherlands (RIVM-network) a modified denuder-filter technique combination has been in use since 1989. Here a high-capacity active carbon denuder is employed to remove nitric acid and a cellulose filter for aerosol collection. It has been consistently shown that the method is equivalent with the (reference) denuder filter pack method (Mennen et al., 1992; van Putten and Mennen, 1998, ten Brink et al., 2001).

3.2.2   *Inert filters*

With filters made of the chemically inert materials Teflon and quartz, volatilisation of collected ammonium nitrate and reaction of nitric acid gas with collected alkaline aerosol particles are well-known artefacts. In southern California the loss of nitrate has been extensively studied (e.g. Hering and Cass, 1999 and references therein). It was found that the extent of the loss varies, which could not be related to simple parameters and thus a generalisation was not possible. However, we extracted from the data that at temperatures less than 10 °C, the loss is small. Especially this aspect is of interest for the much cooler climatic conditions in Europe.

A "positive" artefact is reaction of nitric acid with co-sampled alkaline aerosol. However, in the area for which we assessed the nitrate concentration field evaporation dominates adsorption, as is evidenced from a comparison of data obtained with inert filter and reference methods (Putaud et al., 2001; Pakkanen et al., 1999; Behlen, 1996).

Therefore it is almost certain that nitrate data obtained with inert filters (IF) are lower values. Especially during summer ambient nitrate concentrations can be largely underestimated (Putaud et al., 2001; Pakkanen et al., 1999; Hering and Cass, 1999).

3.2.3   Total Nitrate

Impregnated filters, filter packs and nylon filters are often referred to as "total nitrate" filters (TN), since they sample both aerosol nitrate and gaseous nitric acid. In a filter pack, the first filter collects the aerosol while the second traps the volatilised nitrate and ambient nitric acid. Nitric acid is quantitatively collected in the range of concentrations occurring in Europe (Matsumoto and Okita, 1998). The nitrate reported is the total nitrate of the two filters combined. The long term precision of the sampling procedure is better than 15% (EMEP, 1998; Harrison and Kitto, 1990, Pakkanen et al., 1999).

A potential artefact is the absorption of nitrous acid and subsequent oxidation to nitrate. This artefact is negligible when NaCl is used for impregnation, since it does not absorb HONO (Matsumoto and Okita, 1998, Pakkanen et al., 1999). When this artefact would be important more alkaline impregnated filters should contain substantially more total nitrate than denuder filter packs. This has not been observed for a series of different total filters in campaigns of Ferm et al. (1988), Krieg (1997b) and EMEP (1998). Analysis of the data from Perrino et al. (2001) shows that interference on NaF coatings is negligible. We thus conclude that the HONO absorption artefact is negligibly small.

3.2.4   Cellulose filters

At a number of sites cellulose (paper) filters are used. Recently, it was shown that ammonium nitrate is fully retained on such filters (ten Brink et al., 2001), even at such elevated temperatures that evaporation should have been complete. The adsorption of nitrous acid was negligibly small. Cellulose filters quantitatively adsorb nitric acid: Appel et al. (1979) and Spicer et al. (1979) in the US and Mehlmann (1986) in Germany show that the capacity for retaining of nitric acid is much higher than the amounts sampled in Europe. Summarising, cellulose filters act as Total Nitrate filters and because of absence of preparation the precision in the nitrate values is most probably even better than that for the TN filter data given above. When a cellulose filter is used as the front-filter in a filter pack very little nitrate is expected on the back-up filter and, more importantly, the data from this second filter can not be used to assess the nitric acid concentration.
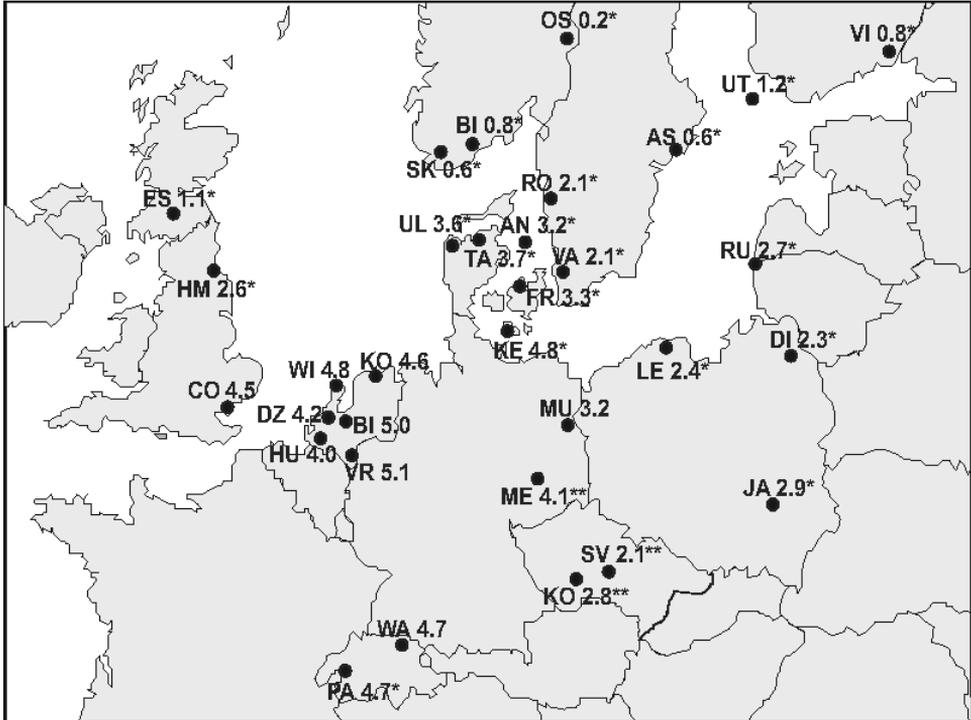
Figure 3.1 Geographical location of the sites indicated with the codes as listed in table 3.1. Also presented the annual average nitrate concentrations (µg m⁻³) (* data corrected for nitric acid, ** data acquired with inert particle filters)

3.3   Data acquisition and criteria for selection and correction

3.3.1   Site selection and time span

The aim of the present study is to construct the (average) nitrate concentration field in Europe. For a climatological average at least a ten-year record would be required, but only in the Netherlands such a long data set exists. For the other sites the records are of a shorter duration. For consistency, data from the same period of four   1994 to 1997) were used, provided that the data completeness was 66% or better.

We used some data from other years to check for consistency. Among these data are our own DF-results from the period 1987 to 1994, reported here for the first time. Most of the other DF-data were made available by the institutes approached. Data were, obviously, also taken from the public EMEP database. For the research on the spatial and temporal correlation of the nitrate concentration at the various sites use was made of the (yet unpublished) data provided by RIVM for the Netherlands and NERI for Denmark, for which we are particularly grateful. The number of data for a site in the southern UK (Colchester) was insufficient. However, in the years prior to the design period data were gathered in the area (Harrison and Allen, 1990) which fully support the values obtained in the design period. Therefore the Colchester data were included.

Data stemming from measuring locations which are more than 400 m above the sur-rounding plain were not considered here, because these are above the boundary layer in winter and thus not representative for the regional surface concentration, see e.g. Arends et al. (1997). It should be realised that artefacts, specifically a loss of nitrate by volatilisa-tion, can occur during storage of the filter prior to analysis (Witz, 1985). Precautions to avoid losses are often not being made in monitoring programs: we only used data in the present study, which came from filters that were properly handled. The sites that meet these requirements are tabulated in Table 3.1 and shown in Figure 3.1.

It appears that at only one location in S-Europe (Montelibretti near Rome, Italy) a long-term nitrate record, acquired with a DF system, exists. However, apart from this site only one other site with a long-time record is present in S-Europe. Therefore the southern limit of the area in which we made an analysis of data was at 47.5° N. A similar reasoning confines the area between 10° west and 30° east. Within this domain long-term data, fulfilling the criteria mentioned above, could not be found in Belgium, France and the western part of Germany.

3.3.2   *Correction of Total Nitrate data*

As mentioned above, data on total nitrate have to be corrected by subtracting the amount of nitric acid to obtain values for aerosol nitrate. At some sites measurements of nitric acid concentrations are available for such extended periods that confidence in their average values is high. At other sites we used concentrations of nitric acid as measured at sites in the vicinity. In some regions extended data sets on nitric acid data are absent and nitric acid concentrations had to be estimated. The method by which this was done and the corrections are discussed in detail below. In table 3.1 the concentrations of aerosol nitrate, obtained after correction for nitric acid, are being tabulated along with those of the (uncorrected) total nitrate.

3.4   Construction of the nitrate concentration field

3.4.1   *Data points*

The average nitrate concentrations at the sites selected here are shown in Figure 3.1. These are compiled from data in the time period from 1994 to 1997 (Table 3.1). The data are for a rather short time span in a climatological sense and thus only semi-quantitative conclusions are in place. Concentrations in the Netherlands, of 5 µg m^{-3} and of 4 µg m^{-3} Germany and Switzerland respectively, are not significantly different. Similar values come from the shorter data record in Colchester, southern England. The values at Melpitz and the Czech Republic (Cz) are minimum values because inert filters were used.

Table 3.1 Overview of the average annual nitrate concentrations at the indicated sites and for the winter season (Oct-Mar) only. Averages over the period 1994-97 unless otherwise indicated. The codes by which the locations are identified in the figures are given in the second column. Cn denotes country. Where appropriate "total nitrate" concentrations are tabulated, as well as the aerosol nitrate concentrations after correction for nitric acid. Methods / filter-types are indicated as: DF = Denuder Filter pack, IF = Inert Filter, TN = Total Nitrate method.

Note: * Data for Muncheberg are for 1995-98 ** Data from Colchester originate from a shorter time series, see text.

| Station	Code	Cn	Method	Year		Winter		Reference
				TNO_3	aNO_3	TNO_3	aNO_3	
Kolummerwaard	KO	NL	DF	-	4.6	-	4.9	RIVM, 1999
Bilthoven	BI	NL	DF	-	5.0	-	5.4	RIVM, 1999
Vredepeel	VR	NL	DF	-	5.1	-	4.4	RIVM, 1999
De Zilk	DZ	NL	DF	-	4.2	-	4.6	RIVM, 1999
Wieringerwerf	WI	NL	DF	-	4.8	-	4.9	RIVM, 1999
Huijbergen	HU	NL	DF	-	4.0	-	3.9	RIVM, 1999
Muncheberg[*]	MU	DE	DF	-	3.2	-	4.7	Zimmerling et al., 2000
Wallisellen	WA	CH	DF	-	4.7	-	7.1	Thoni et al., 2000
Colchester[**]	CO	GB	DF	-	4.5	-	4.6	Chung, 2000
Melpitz	ME	DE	IF	-	4.1	-	5.4	This study
Kocetice	KO	CZ	IF	-	2.8	-	3.4	EMEP, 2000
Svratouch	SV	CZ	IF	-	2.1	-	2.1	EMEP, 2000
Keldsnor	KE	DK	TN	5.5	4.8	5.9	5.5	Frohn et al. 1998
Anholt	AN	DK	TN	3.9	3.2	4.0	3.6	Frohn et al. 1998
Tange	TA	DK	TN	4.4	3.7	4.8	4.4	Frohn et al. 1998
Ulborg	UL	DK	TN	4.3	3.6	4.6	4.2	Frohn et al. 1998
Fredriksborg	FR	DK	TN	4.0	3.3	4.5	4.1	Frohn et al. 1998
Payerne	PA	CH	TN	5.3	4.7	6.7	6.4	EMEP, 2000
Eskdalemuir	ES	GB	TN	1.7	1.1	1.9	1.5	EMEP, 2000
High Muffles	HM	GB	TN	3.2	2.6	-	-	EMEP, 2000
Leba	LE	PL	TN	3	2.4	3.7	3.3	EMEP, 2000
Diabla Gora	DI	PL	TN	2.9	2.3	4.0	3.6	EMEP, 2000
Jarczew	JA	PL	TN	3.9	2.9	5.0	4.4	EMEP, 2000
Rucava	RU	LV	TN	3.3	2.7	3.7	3.3	EMEP, 2000
Birkenes	BI	NO	TN	1.2	0.8	1.1	0.9	EMEP, 2000
Skreadalen	SK	NO	TN	1.0	0.6	0.7	0.5	EMEP, 2000
Osen	OS	NO	TN	0.6	0.2	0.6	0.4	EMEP, 2000
Vavihill	VA	SE	TN	2.7	2.1	2.9	2.5	EMEP, 2000
Roervik	RO	SE	TN	2.7	2.1	2.8	2.4	EMEP, 2000
Aspvreten	AS	SE	TN	1.2	0.6	1.3	0.9	EMEP, 2000
Uto	UT	FI	TN	1.8	1.2	1.8	1.4	EMEP, 2000
Virolahti	VI	FI	TN	1.4	0.8	1.5	1.1	EMEP, 2000
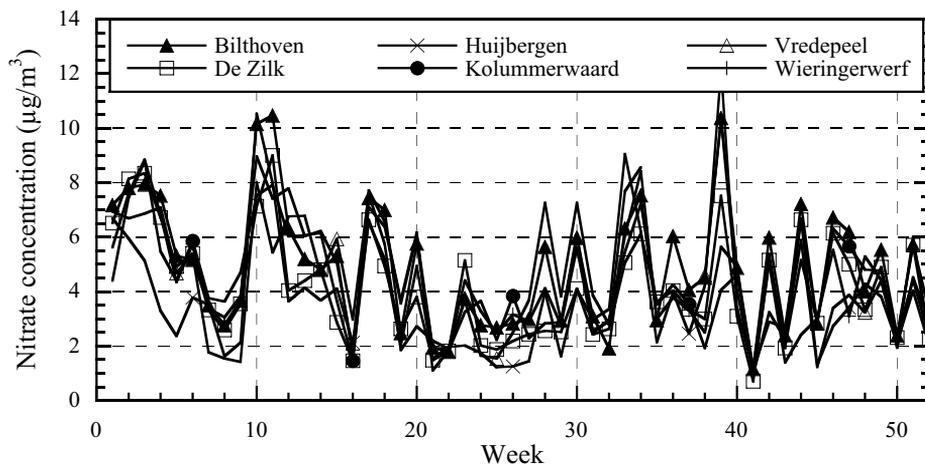
Figure 3.2 Weekly mean nitrate concentrations in 1997 at six monitoring stations in the Netherlands.

Table 3.2 Coefficients of correlation for nitrate at the indicated sites in the winter period (Oct-Mar), calculated from weekly averaged concentrations.

Site	BI	KO	VR	DZ	HU	WI	AN	FR	UL	TA	KE	MU	ME
BI	1.0	0.90	0.78	0.92	0.80	0.92	0.37	0.45	0.61	0.55	0.65	0.53	0.78
KO	0.90	1.0	0.73	0.89	0.72	0.95	0.42	0.54	0.75	0.64	0.78	0.56	0.72
VR	0.78	0.73	1.0	0.67	0.80	0.78	0.20	0.25	0.49	0.34	0.52	0.51	0.67
DZ	0.92	0.89	0.67	1.0	0.74	0.91	0.39	0.53	0.65	0.63	0.67	0.56	0.74
HU	0.80	0.72	0.80	0.74	1.0	0.76	0.12	0.20	0.42	0.31	0.46	0.57	0.70
WI	0.92	0.95	0.78	0.91	0.76	1.0	0.36	0.45	0.73	0.60	0.70	0.61	0.72
AN	0.37	0.42	0.20	0.39	0.12	0.36	1.0	0.81	0.75	0.84	0.75	0.16	0.35
FR	0.45	0.54	0.25	0.53	0.20	0.45	0.81	1.0	0.74	0.83	0.80	0.34	0.49
UL	0.61	0.75	0.49	0.65	0.42	0.73	0.75	0.74	1.0	0.92	0.81	0.47	0.64
TA	0.55	0.64	0.34	0.63	0.31	0.60	0.84	0.83	0.92	1.0	0.83	0.39	0.54
KE	0.65	0.78	0.52	0.67	0.46	0.70	0.75	0.80	0.81	0.83	1.0	0.43	0.77
MU	0.53	0.56	0.51	0.56	0.57	0.61	0.16	0.34	0.47	0.39	0.43	1.0	0.92
ME	0.78	0.72	0.67	0.74	0.70	0.72	0.35	0.49	0.64	0.54	0.77	0.92	1.0

3.4.2 Spatial representativity

Construction of the nitrate concentration field from point data seems warranted when the distance over which the concentrations correlate is sufficiently large. Arends et al. (1997) found, for the dense network in Belgium, that the spatial correlation for sulphate is very high even over distances as large as complete countries. In analogy we use the sites in the Netherlands and Denmark to determine the correlation length for nitrate. The correlation length is defined as the distance between two points over which 50% of the temporal variance is explained by that at the second point, e.g. the correlation coefficient is 0.7. It is then assumed that the correlation and absolute concentrations at points in-
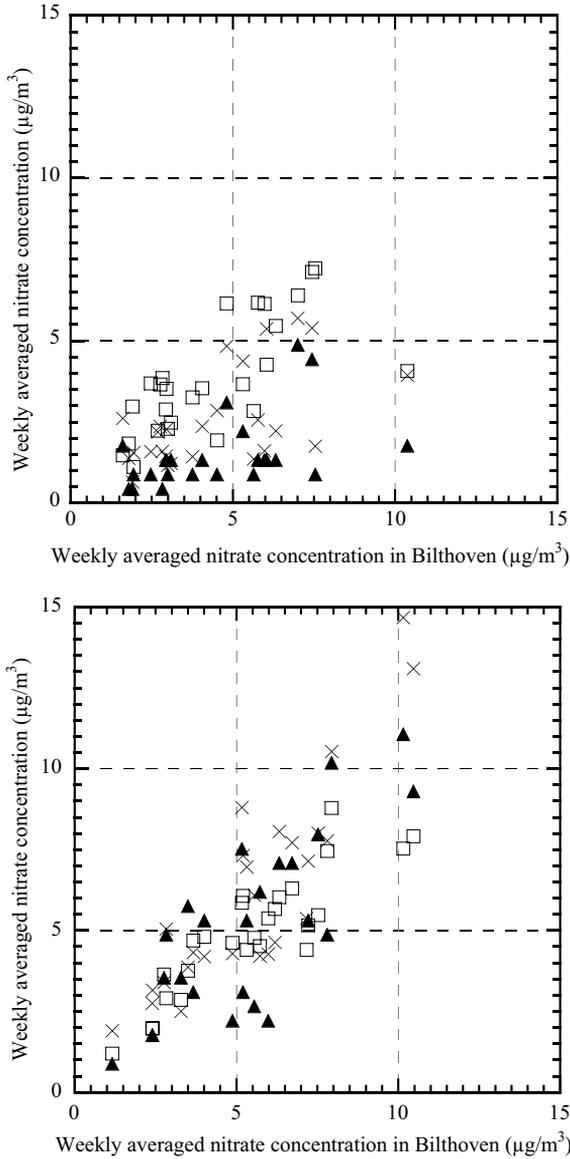
Figure 3.3 Weekly averaged nitrate concentrations in Kolummerwaard (□), Melpitz (x) and Muncheberg (▲) as compared to those at Bilthoven during summer(upper panel) and winter (lower panel), 1997

between the tow are correlated higher.

In Figure 3.2 the weekly mean nitrate concentrations for six Dutch stations are presented for the year 1994. In the summer the correlation coefficient ranges between 0.54 and 0.92 (on basis of data from 1994 to 1999). The best correlation between the stations occurs in the winter half-year. In that period the correlation coefficient ranges from 0.67 to 0.95 between the various stations with the highest correlation for the nearest pair of
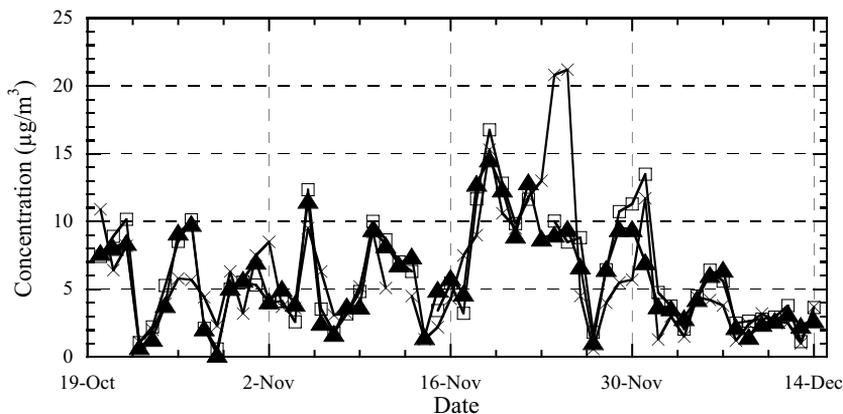
Figure 3.4 Nitrate concentrations at the locations of Melpitz, Leipzig and Halberstadt during fall 1993

sites (see Table 3.2). The maximum distance between the sites is over 200 km. In Denmark correlations with a similar coefficients as those in the Netherlands were found for the winter season. Kolummerwaard, the most northerly Dutch station, is within the correlation range of Keldsnor, the most southerly station in Denmark at a distance of circa 350 Km.

There is also a good correlation between Muncheberg and the Dutch sites in winter. In Figure 3.3 the weekly averaged concentrations in 1997 are compared with those in the Netherlands. In winter the correlation between the sites is reasonable ($0.51 < r < 0.61$. The correlation between Melpitz and Keldsnor and Melpitz and the Dutch sites over distances of ca. 350 and up to 550 Km, respectively, is also good (see Table 3.2 and Figure 3.3). It should be noted that the nitrate concentrations in eastern Germany correlate well both in a relative sense but also in an absolute sense especially in the periods with high concentrations. In summer the correlation is small and not significant ($0.19 < r < 0.42$) and the concentrations are also very different. The correlation of weekly averaged data between Melpitz and Muncheberg is also high.

In addition, data from campaigns were used to establish the correlations on a short-term basis. The values from the German site of Eilsum (Behlen, 1996) correlate well with those in the Netherlands on a day by day basis. Data in Halberstadt, correlated well with those in Melpitz and Leipzig, situated 140 Km to the SE, see figure 3.4, with correlation coefficients of close to 0.70. It is thus concluded that the distances over which nitrate concentrations correlate in Europe is large in the winter half-year, with estimated correlation lengths in the order of 400 Km which are sufficiently long to warrant interpolation of the concentration between measuring locations. In addition the nitrate data are most reliable in this season.
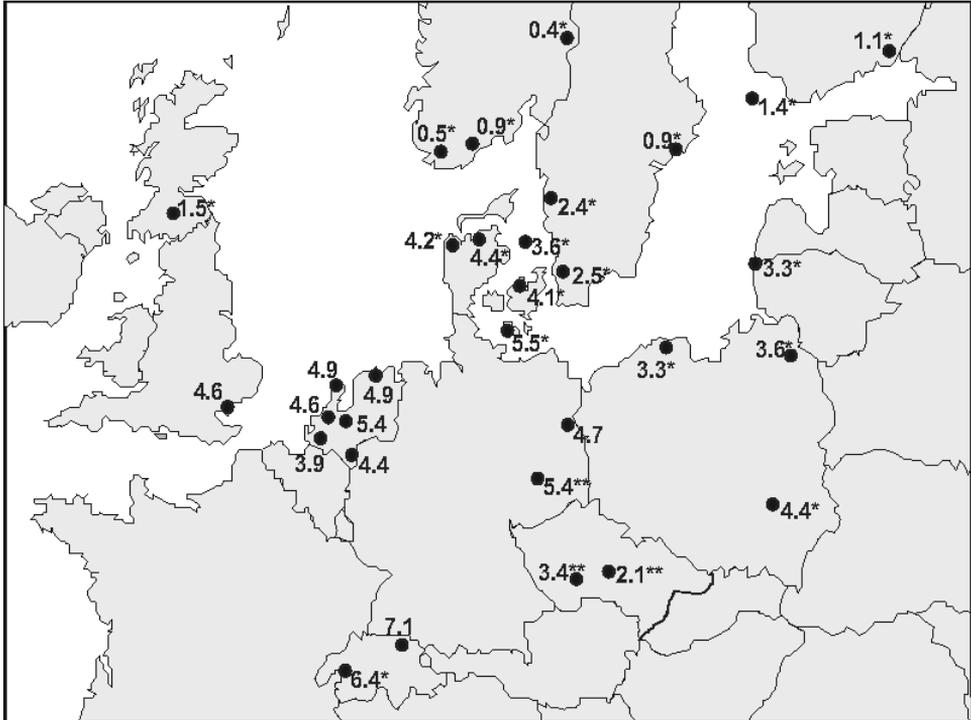
Figure 3.5 Nitrate concentration (µg m^{-3}) during winter (Oct-Mar) (data corrected for nitric acid, ** data acquired with inert particle filters).*

3.4.3   Construction of the nitrate concentration field in Europe

The nitrate concentration field for the winter half year (October-March) was obtained by Delaunay triangulation and subsequent linear interpolation of the point data (see Figure 3.5 and 3.6). A region with nitrate concentrations exceeding 4 µg m^{-3} stretches from southern England over continental western Europe into Poland, with a maximum in Switzerland. Nitrate concentrations exceed 3 µg m^{-3} in central eastern Europe. There is strong gradient from south to north in Scandinavia. To put these concentrations in perspective they are compared with those of sulphate presented in Figure 3.7. It appears that in western Europe the nitrate concentration equals or exceeds that of sulphate. The nitrate to sulphate concentration ratio decreases to ~0.5 in eastern Europe. The lowest ratios are found in northern Scandinavia. The total burden of nitrate, defined as the horizontally integrated concentration in Europe north of the Alps, relative to that of sulphate is therefore close to 0.6.
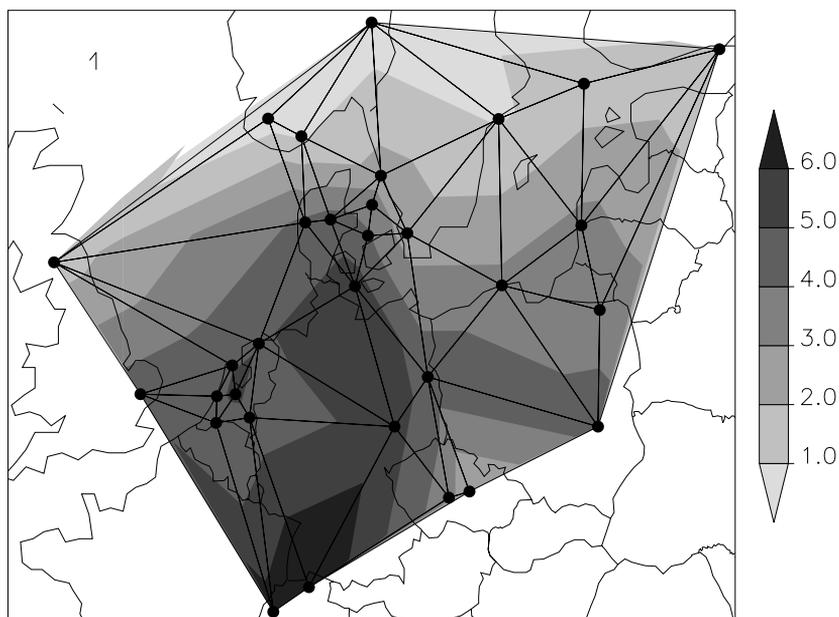
Figure 3.6 Nitrate field (µg m⁻³) obtained by Delaunay triangulation and subsequent interpolation of the data presented in Figure 3.5.

3.5   General discussion

3.5.1   Concentration field

Data quality

Data quality is highest in western Europe because of the use of the reference artefact-free DF-samplers. The inert filters give minimum values in Melpitz and the Czech Republic. The uncertainty in the data inferred from total nitrate needs a more detailed discussion. As an example the correction method for the total nitrate concentration measured at Payerne, Switzerland, is discussed, see also Table 3.3. In the table wintertime nitric acid, total nitrate and aerosol nitrate data are given. In addition, data from sites in the vicinity are provided. From these data the average nitric acid concentration in winter was estimated to be 0.3 µg/m³, which is the value subtracted from the average total nitrate concentration to obtain the value for aerosol nitrate as presented in Table 3.1 and Figure 3.5. A doubling of the nitric acid correction would lead to a 5 % decrease in the aerosol nitrate concentrations, which is insignificant compared to the measuring uncertainties.

For Denmark the correction was based on data from EMEP (1998) and Andersen and Hilbert (1993). In Denmark the nitric acid concentration is small compared to the total nitrate concentration and even a doubling of the nitric acid correction would lead to a mere 10 % change in aerosol nitrate.

In southern Sweden and along the coast of the Baltic Sea few nitric acid data are available and total nitrate data were corrected assuming a nitric acid concentration of 0.4 µg/m^3. This value was obtained by averaging the available wintertime nitric acid data in this region in the range of 0.1 – 0.7 µg/m^3 (Behlen, 1996; Foltescu et al., 1996, EMEP, 1998; Plate, 2000). Using the highest value in this range results in an uncertainty of only 10 % in the aerosol nitrate concentrations. Further to the north in Scandinavia the correction becomes more uncertain, since nitric acid data are absent. However, the absolute values are low so that the real aerosol nitrate concentrations are very low anyhow. An overview of nitric acid data is given in an extended report (Schaap et al., 2001).

For Jarczew (Poland) we assumed a concentration of nitric acid of 0.6 µg/m^3 HNO$_3$, as a conservative maximum that is high compared to the corrections at the other sites. This correction would lead to an uncertainty of 20 % in aerosol nitrate. In Poland (Jarczew, Leba, Diabla Gora) there is an additional complication in that the aerosol nitrate concentration obtained here could be 20 % high, since total nitrate as determined with the local method was systematically 20 % higher than the calibrated reference filter pack (EMEP, 1999). In summary, the corrections for nitric acid in the given areas in winter are (negligibly) small.

The corrections for the annual average data points given in paragraph 3.4 were made using the same method as for the winter data discussed above. However, annual data are more uncertain because of a higher uncertainty in the summer values. The reason is that inert filters are subject to severe evaporation losses due to the lower stability of ammonium nitrate in summer (see above). Additionally, at higher temperatures the concentrations of nitric acid relative to aerosol nitrate are higher (Zimmerling et al., 2000, Thöni et al., 2000), which leads by necessity to a larger uncertainty in the correction of this component in the total nitrate data.

Check of the consistency of the field with data from campaigns

The field as constructed in the previous chapter was checked with data at sites inside the field domain (see also Schaap et al., 2001); these data are either from short-term campaigns or from longer term data from earlier years. Short-term values from sites in eastern Germany and at the north coast of Germany range from 4.8 to 5.9 µg/m^3 (Behlen, 1996; Plate,2000) and sites in the Ruhr area give similar concentrations (Kuhlbusch et al., 1999). These values are in agreement with the concentration projected in the field (Fig. 3.6). Additional data obtained in Basel and Schupfheim (CH) also compare well with the projected data (Thöni and Leuenberger ,1999; Krieg, 1997a).

For data from other time periods than the design period only qualitative conclusions are in place. In Wolkersdorf, Austria, the average aerosol nitrate concentration in the winter of 1990/91 obtained with a DF-method was 6.2 µg/m^3 (Puxbaum et al., 1993). In Erfurt (Germany), west of Leipzig an annual value of 3.7 µg/m^3 was obtained in 1991 (Brauer et al., 1995) which is similar to those projected in paragraph 4.1. In Sokolov (Czech Republic) the nitrate concentration in 1991 was 3.9 µg/m^3 (Brauer et al., 1995), which is substantially higher than that found with the Teflon filters at the Czech sites. This is indicative that the Teflon filters are subject to severe nitrate loss. The apparently

Table 3.3 Total nitrate concentrations as measured in campaigns and the concentrations of nitric acid gas and aerosol nitrate at Payerne (PA), Switzerland, and at sites in the vicinity. Data are for the winter (Jan-March and October-December) of the year indicated or for the period specified. In the lowest row the average wintertime total nitrate for the period 1994-1997 is given. The tabulated average nitric acid concentration, extrapolated from the indicated campaigns, was used to correct the total nitrate to the tabulated aerosol nitrate concentration in the last column.

Site	Period	N	TNO$_3$	HNO$_3$	aNO$_3$	Reference
Payerne	Dec 93	21	5.0	0.2	4.8	Krieg (1997b)
Payerne	Jan 95	20	6.4	0.3	6.1	Krieg (1997b)
Payerne	Okt 95	21	7.6	0.3	7.3	Krieg (1997b)
Wallisellen	1995-97	518	7.3	0.2	7.1	Thoni et al. (2000)
Wallisellen	1999	177	6.9	0.2	6.7	Thoni et al. (2000)
Basel	1998	182	6.9	0.2	6.7	Thöni and Leuenberger (1999)
Schupfheim	1996	168	5.9	0.2	5.7	Krieg (1997a)
Payerne	1994-97	686	6.7	0.3	6.4	This study

larger nitrate loss from Teflon in the Czech Republic than those from the quartz filters near Leipzig are in line with observations by Eatough et al. (1988) and ten Brink et al. (2001) in intercomparison tests.

Addendum. Due to the lack of data from southern Europe the nitrate field could not be assessed there. However, for the Po region in northern Italy sufficient nitrate data are available to allow the conclusion that the area with high maximum nitrate concentrations during winter includes northern Italy (Krieg, 1994; EMEP, 1998; Putaud, 2001). Applying the same correction procedure for Ispra as for the sites north of the Alps with nitric acid data from Krieg (1997b) and EMEP (1998) winter time aerosol nitrate concentrations of 7.2 µg/m^3 are obtained with an associated uncertainty of 15%.

Size fraction

The size of the particles in which nitrate is contained is of special environmental interest, as indicated in the introduction. In the Netherlands, measurements have been made with cascade-impactors in which the aerosol is size-fractionated into several size-classes. It appears that sampling artefacts in cascade impactors are rather small, see Hering and Cass (1999) or ten Brink et al. (1997). In measuring campaigns in almost every second year since 1979 it has been consistently found that the nitrate in the Netherlands (ten Brink et al., 1997) is preferentially present in the fine aerosol fraction (particles smaller than 2.5 µm). In the UK and at Melpitz the same applies (Heintzenberg et al., 1998; Colbeck, 2000). In Muncheberg only the fine aerosol was collected and hence, the high, nitrate concentrations tabulated pertain to fine aerosol nitrate. Another more indirect indication that the nitrate is in the fine aerosol-mode is its presence in the form of the ammonium compound. In Europe, ammonium nitrate has consistently been observed in the fine aerosol fraction. The reason for this is that ammonium nitrate is formed in a heterogene-
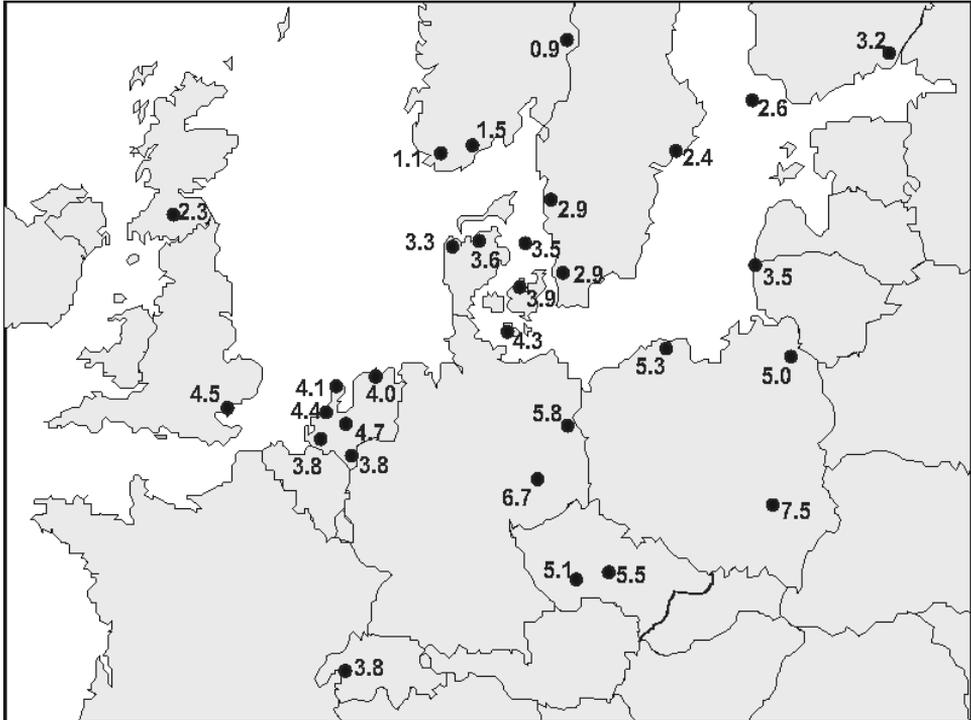
Figure 3.7 Sulphate concentration (µg m^{-3}) during winter (Oct-Mar) at the sites where also nitrate data were available

ous reaction at the surface of existing aerosol which is concentrated in the fine aerosol (Seinfeld and Pandis, 1997). A dominant presence of ammonium nitrate is therefore taken as evidence that the nitrate is in the fine aerosol fraction. Nitrate is indeed mainly present as ammonium nitrate in the Netherlands, Denmark, Germany and Switzerland and thus most likely in the whole of western Europe. In Hungary the winter nitrate is also the fine mode (Meszaros et al., 1997). Therefore, we expect that also in central Europe the nitrate in winter is present as fine nitrate and that the projected field can be interpreted accordingly.

3.6   Conclusions and implications

In this study an attempt was made to construct the average nitrate concentration field for Europe for the period 1994-1997. For this purpose we actively searched for data. We show that sampling artefacts with the denuder filter-packs used in Europe is small and that data obtained with such devices can serve as reference data. It was shown that values data acquired with inert filters are lower limits. Total nitrate concentrations were corrected for the contribution by nitric acid for which separate information was analysed.

To assess the spatial representativity we assessed the correlation length, which was found to be approximately 400 km in winter. This finding warranted interpolation of data at stations at distances of that order or smaller. The field constructed in this way was

successfully validated with data from measuring campaigns. It is found that in winter large areas in Europe have nitrate concentrations exceeding 4 µg m^{-3}, with a possible maximum of 7 µg m^{-3} in Switzerland. In western Europe nitrate concentrations are equal to or even exceed those of sulphate, while sulphate concentrations are higher in eastern and northern Europe. Overall, north of the Alps the nitrate concentration burden in the boundary layer is about 60% of that of sulphate.

It is shown that nitrate is in the fine aerosol (particles smaller than 2.5 micrometer in diameter). We identified a large area in Europe where the volatile ammonium nitrate contributes 5 µg m^{-3} or more to regional PM2.5. This is a large proportion of the proposed particulate standards for PM2.5 in Europe: 20 µg m^{-3}. For regulatory purposes it is therefore important to sample PM with an appropriate method without (large) nitrate artefacts.

The presence of nitrate in the fine aerosol mode is of specific relevance for the reflection of radiation. The scattering of visible light gives rise to visibility impairment. Nitrate must therefore be a key component in regional haze in Europe, which has already been demonstrated to be the case in the Netherlands (Diederen et al., 1985; ten Brink et al., 1997). In addition, nitrate reflects solar radiation and the associated cooling could be similar in magnitude as that by sulphate over the area mentioned. Locally such an effect was already identified in the Netherlands (Khlystov, 1998).

References

Adams, P.J., Seinfeld, J.H., Koch, D.M. (1999), Global concentrations of tropospheric sulfate, nitrate, and ammonium aerosol simulated in a general circulation model, J. Geophys. Res., 104 (D11), 13791-13823

Adams, P.J., Seinfeld, J.H., Koch, D.M., Mickley, L., Jacob, D. (2001), General circulation model assessment of direct radiative forcing by the sulfate-nitrate-ammonium-water inorganic aerosol system, J. Geophys. Res., 102 (D1), 1097-1111

Andersen, H.V., and Hilbert, G. (1993), Measurements of NH3/NH4 and HNO3/NO3 by denuder and filter pack, NERI Technical Report No. 73, National Environmental Research Institute, Roskilde, Denmark

Appel, B.R., Wall, S.M., Tokiwa, Y., Haik, M. (1979), Interference effects in sampling particulate nitrate in ambient air, Atmos. Environ., 13, 319-325

Arends, B.G., Baard, J.H., ten Brink, H.M. (1997), Trends in summer sulphate in Europe, Atmos. Environ., 31, 4063-4072

Behlen, A. (1996), Reactive Stickstoffverbindungen in der Atmosphäre – Konzentrationsbestimmung und trockene Deposition auf Natursteine, Schriftenreihe Angewandte Analytik, 29, Institut fur Anorganische und Angewandte Chemie der Universität Hamburg

Brauer, M., Dumyahn, T.S., Spengler, J.D., Gutschmidt, K., Heinrich, J., Wichmann, H.-E. (1995), Measurement of Acidic Aerosol Species in Eastern Europe: Implications for Air pollution Epidemiology, Environ. Health Perspect,103, 482-488

Chung, M.-C. (2000), Chemical composition and transport of ambient aerosols, PhD thesis, University of Essex, Colchester, UK.

Colbeck, I. (2000), personal communication

Diederen, H.S.M.A., Guicherit, R., Hollander, J.C.T. (1985), Visibility reduction by air pollution in the Netherlands, Atmos. Environ., 28, 2623-2637

Eatough, N.L., McGregor, S., Lewis, E.A., Eatough, D.J., Huang, A.A. and Ellis, E.C. (1988), Comparison of sic denuder methods and a filter pack for the collection of ambient HNO3 (g), HNO2 (g) and SO2 (g) in the 1985 NSMC study, Atmos. Environ., 22, 1601-1618

EMEP (1998), Pilot measurements of nitrogen containing species in air, EMEP/CCC-Report 5/98, NILU, Oslo, Norway

EMEP (1999), Data quality 1997, quality assurance, and field comparisons, EMEP/CCC-Report 6/99, NILU, Oslo, Norway

EMEP (2000), EMEP home page, http://www.nilu.no/projects/ccc/index.html

Ferm, M., Areskoug, H., Hanssen, J.-E., Hilbert, G., Lattila, H. (1988), Field intercomparison of measurement techniques for total NH4+ and total NO3- in ambient air, Atmos. Environ., 22,2275-2281.

Foltescu, V.L., Selin Lindgren, E., Isakson, J., Oblad, M., Tiede, R., Sommar, J., Pacyna, J.M., Toerseth, K. (1996), Airborne concentrations and deposition fluxes of major and trace species at marine stations in southern Scandinavia, Atmos. Environ., 30, 3857-3872

Frohn, L., Skov, H., Hertel, O. (1998): Atmosfærisk deposition af kvælstof, Vandmiljøplanens Overvågningsprogram 1997 (in English: Atmospheric deposition of nitrogen, The Aquatic Nationwide Monitoring Program 1997), NERI Technical Report No. 255, National Environmental Research Institute, Roskilde, Denmark

Harrison, M.R., and Kitto, A.M.N. (1990), Filed intercomparison of filter pack and denuder sampling methods for reactive gaseous and particulate pollutants, Atmos. Envir., 24A, 2633-2640

Harrison, R. M. and Allen, A.G. (1990), Measurements of atmospheric HNO3, HCl and associated species on a small network in eastern England, Atmos. Environ., 24A, 369-376

Hering, S., and Cass, G. (1999), The magnitude of bias in the measurement of PM2.5 arising from volatilisation of particulate nitrate from Teflon filters, J. Air & Waste Manage. Assoc., 49, 725-733

Heintzenberg, J., Müller, K., Birmili, W., Spindler, G., Wiedensohler, A. (1998), Mass related aerosol properties over the Leipzig Basin, J. Geophys. Res, 103, 13125-13135

IPCC (1996), Climate Change 1995, The Science of Climate Change, Cambridge University Press, Cambridge, UK

Jeuken, A. (2000), Evaluation of chemistry and climate models using measurements and data assimilation, Ph.D. thesis, University of Technology Eindhoven, The Netherlands

Khlystov (1998) Cloud forming properties of the ambient aerosol in the Netherlands and resultant shortwave radiative forcing of climate, PhD Thesis, Wageningen University, The Netherlands

Kuhlbusch, T.A.J., John, A.C., Fissan, H., Schmidt, K.-G., Schmidt, F., Pfeffer, H.-U,

Gladtke, D. (1999), Pm10 and Pm2.5 mass concentration, chemical composition, and size distribution measurements at three different sites in the Ruht-area, Germany, J. Aerosol Sci., 30, S45-S46

Krieg , F. (1994), Stickstoffhaltige Gas- und Aerosolkomponenten in Payerne und Lugano 1993, Umwelt-Materialien, 76 (Luft), Buwal, Bern, Switzerland

Krieg, F. (1997a), Atmosphärische Stickstoffkomponenten in Schüpfheim (Kt. Luzern): Resultate 1996, FUB-report, FUB, Rapperswill, Switzerland

Krieg, F. (1997b) Stickstoffhaltige Gas- und Aerosolkomponenten in Payerne 1995, Umwelt-Materialien, 76 (Luft), Buwal, Bern, Switzerland

Matsumoto, M., and Okita, T. (1998), long term measurements of atmospheric gaseous and aerosol species using an annular denuder system in Nara, Japan, Atmos. Environ., 32, 1419-1425

Mehlmann, A. (1986), Grossenverteilung des Aerosolnitrats und seine Beziehung zur gasformigen Salpetersaure, PhD thesis, Johannes Gutenberg University, Mainz

Mennen, M.G., van Elzakker, B.G., van Hellemaon, J., Eisen, I., van der Meulen, A. (1992), Evaluation of a two-and-a-half year study of acidic pollutants using Annular Denuder Systems, RIVM Report 222702003, National Institute of Public Health and the Environment, Bilthoven, the Netherlands

Meszaros, E., T. Barcza, A. Gelencser, J. Hlavay, Gy. Kiss, Z. Krivacsy, A. Molnar, K. Polyak (1997), Size distributions of inorganic and organic species in the atmospheric aerosol in Hungary, J. Aerosol Sci., 28, 1163-1175.

Pakkanen, T.A., Hillamo, R.E., Aurela, M., Andersen, H.V., Grundahl, L., Ferm, M., Persson, K., Karlsson, V., Reissell, A., Royset, O., Floisand, I., Oyola, P., and Ganko, T. (1999), Nordic intercomparison for measurement of major atmospheric nitrogen species, J. Aerosol Sci, 30, 247-263

Perrino, C., Ramirez, D., Allegrini, I. (2001), Monitoring acidic air pollutants near Rome by means of diffusion lines: development of a specific quality control procedure, Atmos. Environ., 35, 331-341

Plate, E. (2000), Variabilität de Zusammensetzung anorganischer Aerosole – insbesondere der reaktiven Stickstoffverbindungen – in küstennahen Gebieten der Nordsee und Ostsee, PhD thesis, University of Hamburg, Hamburg, Germany

Puteaud, J.P., Van Dingenen, R., Raes, F. (2001), Submicron aerosol mass balance at urban and conurban sites in the Milan area (Italy), submitted to J. Geophys. Res.

Puxbaum, H., Haumer, G., Moser, K., and Ellinger, R. (1993), Seasonal variation of HNO_3, HCl, SO_2, NH_3 and particulate matter at a rural site in northeastern Austria (Wolkersdorf, 240 m a.s.l.), Atmos. Environ., 27A, 2445-2447.

RIVM (1999), Luchtkwaliteit. Jaaroverzicht 1997 (in English: Airquality. 1997 Results, RIVM Rapport 725301001, RIVM, Bilthoven, the Netherlands

Schaap, M., Muller, K., ten Brink, H.M. (2001), Constructing the European aerosol nitrate concentration field from experimental data, ECN-report RX--01-033, ECN, Petten, the Netherlands

Seinfeld, J.H. and Pandis, S.N. (1997), Atmospheric chemistry and physics: From air pollution to climate change, John Wiley & Sons, Inc., New York, USA

Sickels, J.E., Hodson, L.L., Vorburger, L.M. (1999), Evaluation of the filter pack for long-duration sampling of ambient air, Atmos. Environ., 33, 2187-2202

Slanina, J., ten Brink, H.M., Otjes, R.P., Even, A., Jongejan, P., Khlystov, A., Waijers-Ijpelaan, A., Hu, M., Lu, Y. (2001), Continuous analysis of nitrate and ammonium in aerosols by the Steam Jet Aerosol Collector (SJAC), Atmos. Environ., 35, 2319-2330

Spicer, C.W, and Schumacher, P.M. (1979), Particulate nitrate: Laboratory and field studies of major sampling interferences, Atmos. Environ., 13, 543-552

Ten Brink, H.M, C. Kruisz, G.P.A. Kos and A. Berner (1997), Composition/size of the light-scattering aerosol in the Netherlands, *Atmospheric Environment*, 31, 3955-3962

Ten Brink, H.M., Schulz, M., Putead, J.-P., Jongejan, P., Plate, E. (2001), Comparison of the collection of ammonium nitrate by various sampling methods, Proc. Eurotrac-Symposium 2000, in press

Thöni, L., and Leuenberger, C. (1999), Abschätzung der Stickstoffdeposition mittels Immissionsmessungen und Modellrechnungen in der Kantonen Basel-Stadt und –Land, FUB-report, FUB, Rapperswill, Switzerland

Thöni, L. Seitler, E., Schnyder, N., Künzli, B., Marti, S. (2000), Depositionsunter-suchungen im Kanton Zürich - Wallisellen: Resultate 1999, Wallisellen und Bachtel: Entwicklung über die Jahre. FUB-report, FUB, Rapperswill, Switzerland

Van Dorland, R., Dentener, F.J., Lelieveld, J. (1997), Radiative forcing due to tropo-spheric ozone and sulfate aerosols, J. Geophys. Res., 102 (D23), 28079-28100

Van Putten, E.M. and Mennen, M.G. (1998), Laboratory study of five methods for measuring ambient ammonium aerosol, RIVM Report 722601004, National Institute of Public Health and the Environment, Bilthoven, the Netherlands

Witz, S. (1985), Effect of environmental factors of filter alkalinity and artifact formation, Envir. Sci. Technol., 19, 831-835

Zimmerling, R., Dammgen, U., Behrend, U. (2000), Konzentrationen versauernd und eutrophierend wirkender Spurengase und Aerosol-Bestandteile in Nordost-Brandenburg, Wissenschaftliche Mitteilungen der Bundesforschungsanstalt für Land-wirtschaft, Sonderheft 213, Landbauforschung Völkernrode ,Braunschweig, Germany

4 The nitrate aerosol field over Europe: simulations with an atmospheric chemistry-transport model of intermediate complexity

Schaap, M., van Loon, M., ten Brink, H.M. Dentener, F.J. and Builtjes, P.J.H., The nitrate aerosol field over Europe: simulations with an atmospheric chemistry-transport model of intermediate complexity, published in Atmos. Chem. Phys. Disc.

Abstract

Nitrate is an important component of fine aerosols in Europe. We present a model simulation for the year 1995 in which we account for the formation of the ammonium nitrate, a semi volatile component. For this purpose, LOTOS, a chemistry-transport model of intermediate complexity, was extended with a thermodynamic equilibrium module and additional relevant processes to account for aerosol formation and deposition. Our earlier 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. This is in accordance with the field that was constructed from the 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. 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 represents the amplitude of single events. The model underestimates wet deposition which was attributed to the crude representation of cloud processes. The treatment of ammonia was found to be the major source for uncertainties in the model representation of secondary aerosols. Also, inclusion of sea salt is necessary to properly assess the nitrate and nitric acid levels in marine areas.

Over Europe the annual forcing by nitrate is calculated to be 25 % of that by sulphate. In summer nitrate is found to be regionally important, e.g. in the Netherlands, where the forcing of nitrate and sulphate are calculated to be equal. In winter, spring and fall the nitrate forcing over Europe is about half that by sulphate. Over north western Europe and the alpine region the forcing by nitrate was calculated to be similar to that of sulphate. Overall, nitrate forcing is significant and should be taken into account to estimate the impact of regional climate change in Europe.

4.1   Introduction

Aerosols of an anthropogenic origin play a key role in changing the earth's radiation budget. Aerosols directly scatter and/or absorb solar radiation. Indirectly, they influence the micro-physical properties of clouds and therewith their effective albedo. Over polluted continental regions the direct forcing of sulphate alone can be as large as those of the combined greenhouse gases, but opposite of sign (e.g. Charlson et al., 1992; Kiehl and Briegleb, 1993). In the last decade the influence of a number of other aerosol components, like organic carbon, black carbon and (anthropogenic derived) mineral dust, on the radiation budget has also been shown (IPCC, 2001, and references therein). However, IPCC (2001) did not present a best estimate for the direct forcing by nitrate, mostly because of a lack of reliable measurement data on this semi volatile compound.

A recent critical assessment of nitrate observations in Europe showed that nitrate significantly contributes to the aerosol concentration in Northern Europe (Schaap et al., 2002a). Especially in winter (Oct-Mar) large contributions of nitrate to the total aerosol mass were found in western Europe, where nitrate concentrations often exceeded those of sulphate. At continental sites nitrate is mainly present in the fine aerosol mode (Ten Brink et al., 1997; Heintzenberg et al., 1998; Putaud et al., 2003). The aerosols in this size range scatter UV-VIS light most efficiently, which indicates that nitrate could exert a significant climate forcing over continental Europe in winter (Ten Brink and Schaap, 2002) and regionally even during summer (Ten Brink et al., 1997). The latter was also recognised in a comparison of model results with aerosol optical depth obtained from the ATSR2 satellite for August 1997 (Jeuken et al., 2001; Robles-Gonzales et al., 2003).

Sub-micron nitrate is predominantly present in the form of ammonium nitrate (NH_4NO_3), a semi-volatile compound:

$$NH_3 + HNO_3 \leftrightarrow NH_4NO_3$$

The equilibrium between ammonium nitrate and its gaseous precursors is relatively well understood (e.g. Basset and Seinfeld, 1983; Mozurkewich, 1993; Nenes et al., 1998; Zhang et al., 2000). The gas-aerosol partitioning of nitrate depends strongly on the availability of its precursor gasses and on the ambient conditions (Ansari and Pandis, 1998). Atmospheric ammonia is first neutralized by sulphuric acid (H_2SO_4) to form ammonium sulphate (($NH_4)_2SO_4$). Remaining ammonia may then combine with nitric acid to form ammonium nitrate. Model sensitivity studies have shown that under conditions where ammonia limits the formation of nitrate a decline in sulphate concentrations may result in a subsequent rise of the nitrate levels (Ansari and Pandis, 1998; West et al., 1999; Metzger et al., 2002a). This results in a non linear response of fine aerosol mass and aerosol forcing to changes in aerosol precursor concentrations (West et al., 1998). Hence, a thorough knowledge of the processes involved in the formation of nitrate is needed to assess its future role in climate change.

Although nitrate was routinely included in the calculations of regional scale models like the European EMEP model, the results received little attention. Much more emphasis

was drawn to the importance of ammonium nitrate by the global model studies of Metzger et al. (2002b) and Adams et al. (1999) showing that nitrate was an important component of aerosols over large (continental) areas in the world. Moreover, Adams et al. (2001) found nitrate in the year 2100 to be more important than sulphate with respect to aerosol radiative forcing. These studies used a model with a resolution of 2.5 by 2.5 degrees or coarser. However, satellite retrieved aerosol optical depth (AOD) fields over Europe show a large spatial variation and strong gradients around industrialized areas, indicating the influence on AOD of local emissions of primary aerosols and/or precursor gases (Robles Gonzalez et al., 2000). Ammonia is one of such precursors with strong gradients in the emission distribution, which is associated with large concentration gradients of ammonia and associated ammonium nitrate. Therefore, we expect that a model with a higher horizontal resolution is more suitable to assess aerosol and especially ammonium nitrate fields than global models.

We evaluate the aerosol nitrate field over Europe using the three-dimensional (3D), 25 Km resolution, European scale, LOTOS model. In the next section the LOTOS model set-up is introduced. In section 3 the results for the year 1995 are presented and compared to measured data. Section 4 describes the results of AOD and forcing calculations performed in this study. Discussion and conclusions follow in section 5. A detailed study of the sensitivity of the calculated nitrate concentrations to emissions is presented in a separate paper (Schaap et al., 2003a; see also Appendix B).

4.2   Description of the LOTOS model

4.2.1   Background

The model employed in this study is the 3D chemistry-transport model LOTOS that was developed for LOng Term Ozone Simulations. It is of intermediate complexity in the sense that the relevant processes are parameterised in such a way that the computational demands are modest enabling hour-by-hour calculations over extended periods of one or more years within acceptable CPU time, even on a workstation or a PC. LOTOS was originally developed and used as a photo-oxidant model (Builtjes, 1992; Hass et al., 1997; Roemer et al., 2003). Recently, the photochemical module was extended to simulate the inorganic secondary aerosols SO_4, NH_4 and NO_3. The model set-up presented below is LOTOS version 5.2, which was used here to perform calculations for the full year of 1995.

Table 4.1 Total emissions of SO_x, NO_x, VOC, CH_4, CO and NH_3 for 1995 (Ktonnes) for anthropogenic activities in Europe excluding the former USSR

SNAP[a]	Description	SOx	NOx	VOC	CH4	CO	NH3
1	Energy transformation	12,382	3,738	169	111	645	8
2	Small combustion sources	2,147	803	820	496	9,939	2
3	Industrial combustion	2,948	1,617	115	69	3,884	2
4	Industrial process emissions	550	326	1,350	85	2,898	119
5	Extraction of fossil fuels	36	112	1,149	5,811	105	0
6	Solvent and product use	0	0	4,580	0	0	3
7	Road transport	689	6,854	5,931	207	31,988	52
8	Non road transport	296	2,142	775	19	2,837	0
9	Waste handling and disposal	92	105	231	9,297	2,916	92
10	Agriculture	0	26	223	12,052	278	4,344
	Total	19,139	15,721	15,344	28,147	55,489	4,621

[a] *Selected Nomenclature Air Pollution*

4.2.2   Model structure

LOTOS was ran for the region that spans from 10°W to 40°E and from 35°N to 70°N with a spatial resolution of 0.5x0.25 degrees lon-lat, roughly corresponding to 25 by 25 km. The vertical extent of the model is 3.5 km (above sea level). The vertical domain is divided in three layers. The lowest layer represents the variable mixing layer on top of which two layers with equal, but variable, depth are located. Due to the continuously changing mixing height, the grid volumes vary in space and time. The mixing height is part of the meteorological input for 1995, which is diagnostic and derived from ECMWF using procedures developed by the Free University of Berlin. Every hour, the mixing layer height is updated and the mass in the three layers is redistributed by mass conserving linear interpolation. The vertical coverage of the model is considered sufficient for the purpose of this study, since it has been shown that in 80 to 90 % of the time the aerosol load above 3 km is negligible (ten Brink et al., 2001). To compare the calculated concentrations with measurements the concentration of each compound is calculated at a reference height of 2m using vertical profile information derived from the deposition parameterisation.

4.2.3   Emissions

The inventories of the anthropogenic emissions of SO_x, NO_x, NM-VOC, CO, CH_4, NH_3 are based on CORINAIR 1995 data version 2.2 (Builtjes et al., 2003). The country totals have been gridded on the LOTOS grid following the methodology of the CEPMEIP project (TNO, 2001). The inventories use the source categories following the Selected Nomenclature Air Pollution (SNAP). The emission totals for each SNAP level 1 category used in this study are listed in Table 4.1. Only for traffic a further subdivision has been
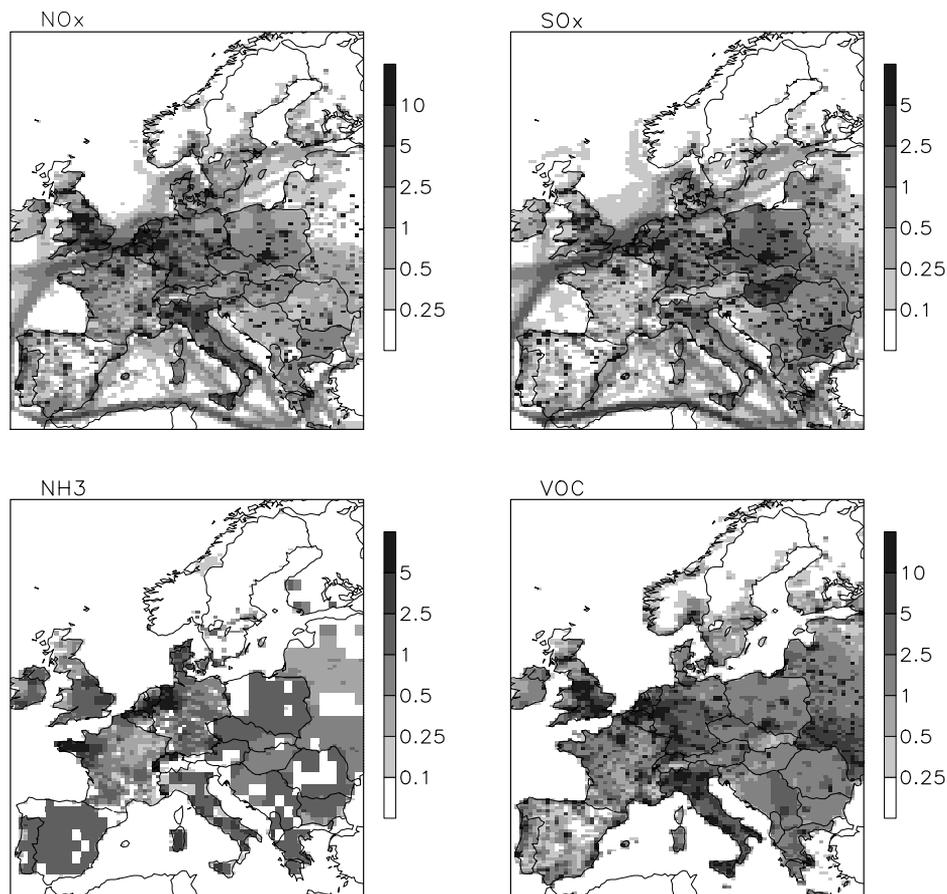
Figure 4.1 Distribution of the emissions (Ktonnes/yr) of NOx (as NO2), SOx (as So2), NH3 and VOC

made into gasoline exhaust, diesel exhaust and fuel evaporation. In Figure 4.1 annual gridded yearly averages are shown of a number of emitted compounds. Note that the ship emissions for 1995 are taken from EMEP (EMEP, 2002).

The temporal variation of the emissions is represented by time factors. For each source category a monthly factor breaks down the annual total into monthly value. This value is divided by a factor for the day of the week (i.e. Monday, Tuesday etc.) and finally by a factor for the hour of the day (local time). Except for ammonia, these factors are obtained from the TROTREP project (Builtjes et al., 2003). In comparison with the emissions of SO_x, NO_x, and VOC, the emission of ammonia is uncertain and not as well understood. Ammonia emissions in Europe are for the largest part (80-95 %) associated with agricultural activities (van der Hoek, 1998). The seasonal variation in ammonia emissions is uncertain and may differ regionally as function of farming procedures and climatic conditions. The seasonal variation in the ammonia emissions is modelled based on experimental data representative for the Netherlands as shown in Figure 4.2 (Bogaard and
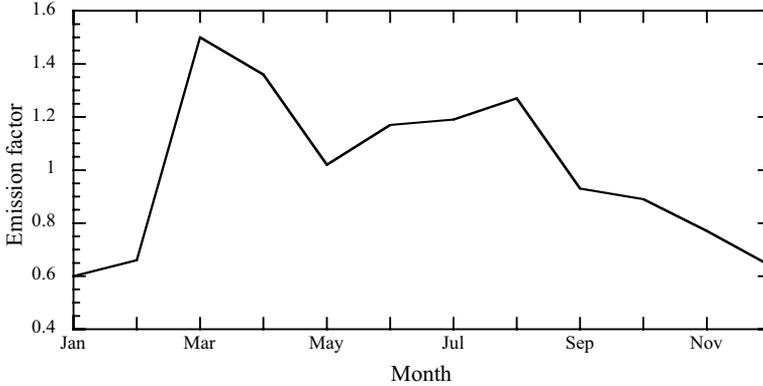
*Figure 4.2 Monthly emission factor for ammonia (source: Bogaard and Duyzer, 1997)*

Duyzer, 1997). The seasonal variation shows a distinct maximum in March and a slight maximum in August due to the application of manure on top of a function that roughly scales with duration of daylight. Following Asman (2001) we assumed a diurnal cycle in the emission with half the average value at midnight and twice the average at noon.

Exchange, emission or deposition, of ammonia depends on the compensation point, which refers to the situation in which the ammonia concentration in air is in equilibrium with the vegetation. Assessing the compensation point of ammonia is not possible for many surfaces (Asman, 2001). In addition, the presence of a compensation point is probably most important in relatively remote regions away from the main sources. Close to sources ammonia exchange will be dominated by deposition. We can therefore safely describe emission and deposition separately.

Due to the emissions there is a large vertical gradient of ammonia concentrations in the source areas with highest concentrations near the ground. However, in our model the emissions are completely vertically mixed over the first mixing layer. We may therefore underestimate the effective dry deposition of ammonia close to the sources. To account for this effect Asman and Janssen (1987) and Dentener and Crutzen (1994) lowered the 'effective' emissions in their model by 25 %, assuming that this part of the emission was removed on sub-grid scales. Janssen and Asman (1988) argued that by uniformly lowering the ammonia emission, ammonium formation could be underestimated and more sophisti-cated correction factors were proposed. These correction factors would be highly variable depending on region, the surface roughness downwind of the sources, availability of acidic precursors, meteorological conditions and the history of the air parcel (e.g. Asman, 1998). Much of this information is not available in our model and therefore no correction factors are used in this study.

The large uncertainty in the ammonia emissions, the seasonal variation and the use of correction factors is further discussed in a separate publication, Schaap et al. (2003a, see also Appendix B).

4.2.4   Chemistry

Gasphase photochemistry in LOTOS is described using a modified version of the CBM-IV mechanism (Whitten et al., 1980). The mechanism was tested against the results of an intercomparison presented by Poppe et al. (1996) and found to be in good agreement with the results presented for the other mechanisms. The photolysis rates are calculated following Poppe et al. (1996). The chemical differential equations are solved using TWOSTEP, (Verwer, 1994). The chemistry scheme further includes gas phase and heterogeneous reactions leading to secondary aerosol formation.

The reaction of N_2O_5 on aerosol surfaces has been proposed to play an important role in tropospheric chemistry (Dentener and Crutzen, 1993). This reaction is a source for nitric acid during night time, whereas during the day the NO_3 radical is readily photolysed. We parameterised this reaction following Dentener and Crutzen (1993). In this parameterisation a Whitby size distribution is assumed for the dry aerosol. The wet aerosol size distribution is calculated using the aerosol associated water obtained from the aerosol thermodynamics module (see below). The reaction probability (γ) of N_2O_5 on the aerosol surface has been determined for various solutions. Reaction probabilities between 0.01 and 0.2 were found (Jacob, 2000 and references therein). A recent study by Mentel et al. (1999) indicates values at the lower part of this range. which is somewhat lower than the generally used recommendation by Jacob (2000). In the polluted lower troposphere of Europe, however, the hydrolysis on the aerosol surfaces is fast, with lifetimes of N_2O_5 less than an hour (Dentener and Crutzen, 1993). Therefore the exact value of γ is not determining the results strongly. Due to the limited availability on cloud information, we neglect the role of clouds on the hydrolysis of N_2O_5, which may also contribute to nitric acid formation. However, due to the very fast reaction of N_2O_5 on aerosol in polluted Europe, the role of clouds on N_2O_5 hydrolysis is probably less important.

The ISORROPIA thermodynamic equilibrium module (Nenes et al., 1998) is used to describe the equilibrium between gaseous nitric acid, ammonia and particulate ammonium nitrate and ammonium sulphate and aerosol water. In this work we assume equilibrium between the aerosol and gas phase at all times. For sub-micron aerosol this equilibrium assumption is valid in most cases, but it may not be valid for coarse fraction aerosol (Meng and Seinfeld, 1996). However, since our model does currently not incorporate sea salt or dust, which are sinks for gaseous nitric acid, the results of our equilibrium calculations over marine and arid regions should not be overinterpreted (Zhang et al., 2000).

Although it is not the focus of this study, it is important to give a good representation of sulphate formation, since sulphate competes for the ammonia available to combine with nitric acid. Most models that represent a direct coupling of sulphur chemistry with photochemistry underestimate sulphate levels in winter in Europe. This feature can probably by explained by a lack of model calculated oxidants or missing reactions (Kasibhatla et al., 1997). Therefore, in addition to the gas phase reaction of OH with SO_2 we represent additional oxidation pathways in clouds with a simple first order reaction constant (Rk), which is calculated as function of relative humidity (%) and cloud cover (c):

Rk = 8.3e-5 * (1 + 2*c) (s^{-1}), for RH < 90 %
Rk = 8.3e-5 * (1 + 2*c) * [1.0 + 0.1*(RH-90.0)] (s^{-1}), for RH ≥ 90 %

This parameterisation is similar to that used by Tarrason and Iversen (1998). It enhances the oxidation rate under cool and humid conditions. With cloud cover and relative humidity of 100% the associated time scale is approximately two hours. Under humid conditions, the relative humidity in the model is frequently higher than 90 % during the night. Model results using this parameterisation agree significantly better with observational data than results calculated using a reaction scheme that considers explicit cloud chemistry.

4.2.5   *Removal processes and boundary conditions*

The dry deposition of gases and aerosols is parameterised by the surface-atmosphere interaction model DEPAC (Erisman et al., 1994). From a 1.1 x 1.1 km^2 resolution land use database the fraction of surface in each grid cell covered by the land use classes used in DEPAC have been calculated (Nijenhuis and Groten, 1999). For each cell the deposition velocity is calculated weighting the surface fractions of every land use class. Surface wetness and snow cover have a large effect on the deposition velocities for a number of species, especially SO_2. Surface wetness is determined as function of the relative humidity at the surface. Wet deposition is calculated using simple coefficients for below cloud scavenging (de Leeuw et al., 1988). Since in-cloud scavenging is not accounted for, calculated concentrations in rainwater will probably be underestimated (see section 3.3).

Boundary conditions for O_3, NO_x and VOC in LOTOS are obtained from the 2D global Isaksen model (Roemer, 1995). For sulphate we use a boundary condition of 0.7 µg/m^3 as deduced from measurements. Measurements show that sulphate is completely neutralized over remote areas in Europe (Kerminen et al., 2001). Therefore, we assume the imported sulphate to be fully neutralized by ammonium. Ammonium nitrate at the model boundaries was assumed to be zero. This assumption is probably valid for the west, north and south boundaries where the nitrate concentrations in air are very low or associated with sea salt and dust (Kerminen et al., 2001, Kouvarakis et al., 2002). At the eastern boundary the assumed boundary conditions and, hence, the model results for both nitrate and sulphate are highly uncertain and we decided to present results only west of 30°E.

4.3 Results and preliminary discussion

In the following section we present modelled seasonal and annual aerosol distributions for the year 1995. Section 4.3.2 describes the formation of nitrate and in section 4.3.3 a detailed comparison with available measured data is made. In our comparison we focus on the concentrations of nitrate, but also present supporting information on sulphate, ammonium and the aerosol precursors.

4.3.1 Aerosol distributions

In Figure 4.3 the annual averaged fields of aerosol nitrate, sulphate, ammonium and their gaseous precursors are presented.

Nitrate

Nitrate, in our model present as ammonium nitrate, is a continental phenomenon, since its concentration rapidly trails off from coast to open sea. Maximum nitrate concentrations are found in an area over The Netherlands, Belgium and north western Germany where modelled concentrations range between 5 and 8 $\mu g/m^3$. Elevated concentrations can also be identified over northern Italy, England, southern Germany and the Czech Republic, where the annual averaged concentrations exceed 4 $\mu g/m^3$. These areas, incidentally, are characterized by high ammonia emissions. Over southern Europe nitrate concentrations do not exceed 2 $\mu g/m^3$, except for northern Italy and a region over former Yugoslavia. Over most of Scandinavia annual average nitrate concentrations are calculated to be lower than 0.5 $\mu g/m^3$, due to the low amounts of nitric acid formed there.

Sulphate

In case of sulphate a band of high concentrations, 3 to 7 $\mu g/m^3$, is calculated over western Europe to the Balkans with maximum concentrations in Germany, Poland and south eastern Europe. Secondary maxima can be observed in northern Spain, central England and the Po valley. In more remote regions the concentration ranges between 2 and 3 $\mu g/m^3$. In northern Scandinavia the modelled concentrations are less than 1 $\mu g/m^3$.

Nitrate to sulphate ratio

To assess the contribution of nitrate we show the nitrate mass ratio ($NO_3/[NO_3+SO_4]$) in Figure 4a. A clear seasonal trend can be observed with the lowest contribution in summer. In this season nitrate is confined to western Europe. Large nitrate contributions can be identified over The Netherlands, northern Italy and England. The ratio ranges between 10 and 30 % for the latitude band between 46°N and 56°N. The ambient conditions, i.e. high temperature and low relative humidity, in eastern and southern Europe do
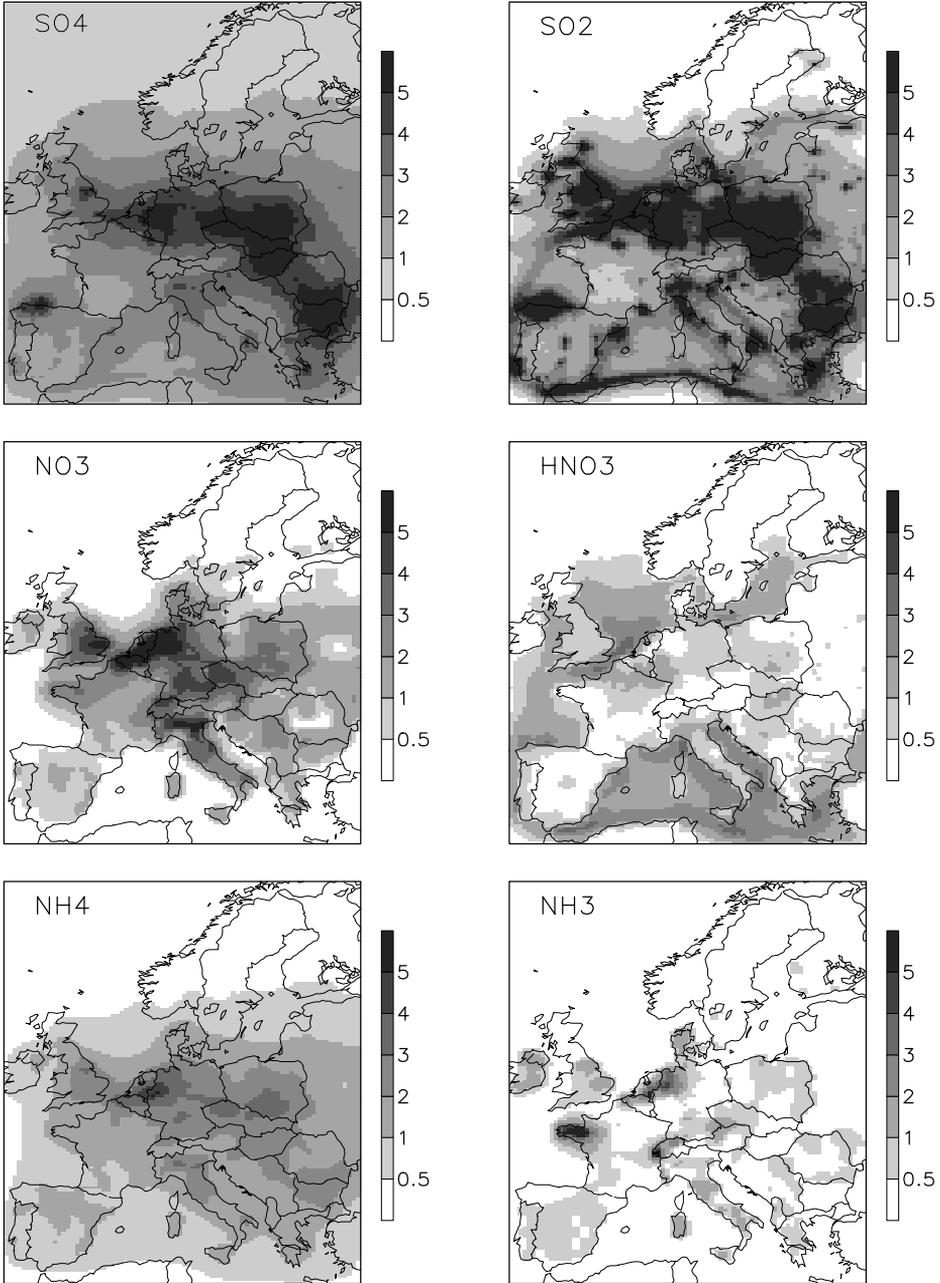
Figure 4.3 Annual average concentrations (μg/m³) of inorganic aerosols and their precursor gases at measuring height.
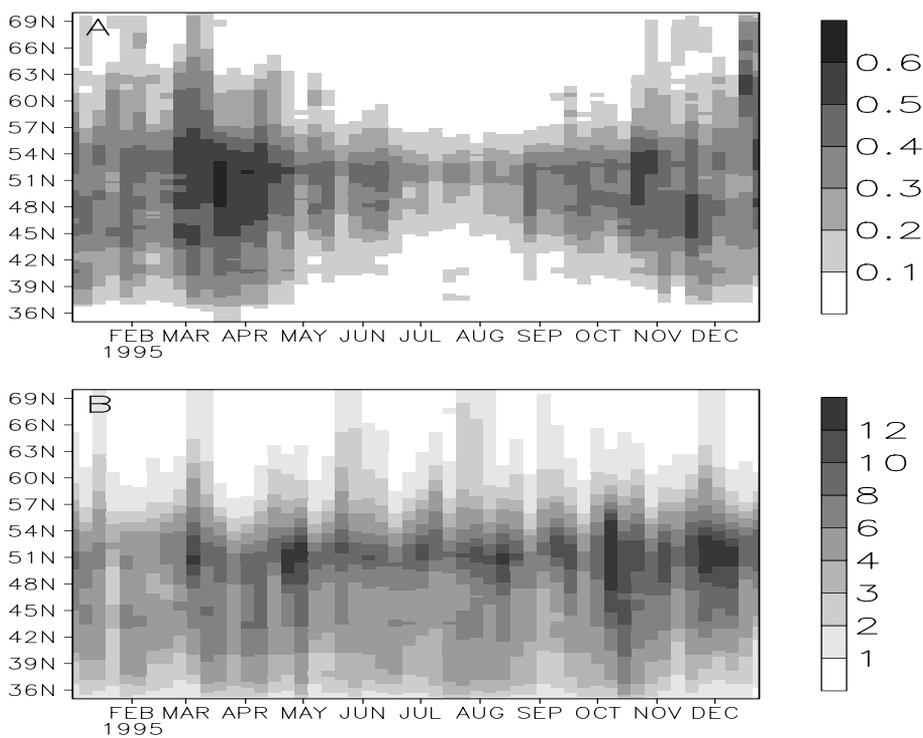
Figure 4.4 Seasonal variation of a) the NO3/(NO3+SO4) ratio and b) the total dry inorganic aerosol mass (µg/m³), averaged over 10W to 30 E on a weekly basis.

not favour ammonium nitrate formation. In summary, in summer concentrations of sulphate are much higher than those of nitrate in most regions.

In the winter, spring and fall nitrate shows a different behaviour than in the summer, despite the fact that the concentrations of sulphate are marginally different in the various seasons. In the mentioned seasons the nitrate concentration field shows a large area of high nitrate concentrations over western and central Europe. High concentrations during winter and early spring are calculated in the Po valley, where they are almost everywhere above 7 µg/m³. The contribution of nitrate ranges between 30 and 60 percent between 40 to 60°N. In western Europe the nitrate concentrations exceed those of sulphate, whereas they are slightly lower than those of sulphate in eastern Europe. The higher nitrate concentrations as compared to the summer can be explained by the much higher stability of ammonium nitrate at low(er) ambient temperatures and higher relative humidities. The maximum contribution of nitrate occurs in spring, which coincides with the maximum ammonia emissions in this season.

Total secondary inorganic mass

In figure 4b the weekly variation of the secondary inorganic mass, the sum of nitrate, sulphate and ammonium, over 1995 is shown as function of latitude. During 1995 maximum concentrations were found in autumn and in early winter, e.g. October to December. Also during spring the inorganic mass concentrations are slightly enhanced. Throughout the whole year the total inorganic mass is highest between 47°N and 54°N, with concentrations exceeding 6 $\mu g/m^3$ on average. Levels decrease strongly going from the European continent towards southern Scandinavia. In the south the gradient trailing off from the central maximum is less steep, which is in line with the higher emissions and population density there as compared to northern Europe.

Precursor gases

At continental regions the annual average nitric acid concentrations are mainly below 1.0 $\mu g/m^3$, see Figure 3. Over sea the concentrations are much higher than those over land. Especially the ship tracks, in which large amounts of NO_x are emitted, are visible in the calculated nitric acid fields. As noted before, in these regions in reality this nitric acid may be associated with sea salt. In winter computed concentrations of nitric acid are much lower then those of nitrate. In summer, only in north western Europe nitric acid concentrations are well below those of nitrate. In other areas they are higher or comparable to those of aerosol nitrate.

Due to the short atmospheric lifetime of ammonia its concentration field strongly resembles its emission distribution (Fig. 3). Maximum concentrations occur in the areas with the highest emissions, such as the Netherlands, southern England and the Po-valley. Only in these areas mixing layer averaged annual concentrations of more than 1 $\mu g/m^3$ are calculated. Outside the source areas the ammonia concentrations decline rapidly.

4.3.2   *Nitric acid formation*

Nitric acid/nitrate is formed via homogeneous gas phase oxidation and heterogeneous reactions. Since photochemistry is inefficient during winter the high ammonium nitrate concentrations modelled for the winter can only be explained by 1) a longer effective lifetime of nitrate in winter as compared to the summer and 2) a substantial production of nitric acid via the heterogeneous pathway. The longer life time of (total) nitrate in winter can be explained by the higher stability of ammonium nitrate in winter, which causes a higher portion of the nitrate to partition to the aerosol, which has a longer lifetime than nitric acid against deposition. In Figure 5 the relative contribution of the heterogeneous hydrolysis of N_2O_5 to the total nitric acid production is shown throughout the year. In the model domain more than 50 % of the nitric acid in winter is formed heterogeneously, especially in the high latitude regions where the days are short and light intensity is low. Photochemical formation is more important during summer, although heterogeneous formation of nitric acid is still significant (~20%). In general, the relative contribution of the heterogeneous reaction increases towards the north, which can be understood from competing effects of temperature, light and OH radical concentrations. The only exception occurs during mid summer when at high latitudes the nights are very short and the OH
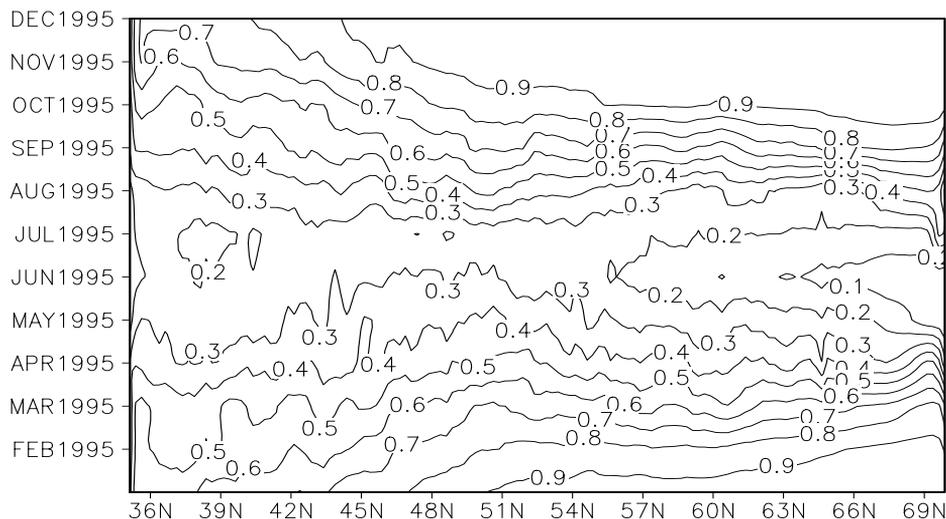
Figure 4.5 The ratio of the heterogeneous to total nitric acid formation as function of latitude (averaged over 10W to 30E) and season.

reaction becomes relatively more important again with increasing latitude.

4.3.3   *Comparison with measured data*

In this section we compare the model results with observations. Verification of model results is only possible when reliable measurement data are available.

Availability of measurements

For sulphate and sulphur dioxide a large database of data exists, e.g. EMEP (EMEP, 1999). Measuring sulphate seems a straightforward procedure. Measurements of particulate nitrate are sparser and moreover most methods are not reliable because of artefacts associated with the volatility of ammonium nitrate, and the reactivity of nitric acid. Schaap et al. (2002a) made a compilation of available aerosol nitrate measurements in Europe and critically assessed their quality. Shortly, reliable data are only obtained with devices that remove nitric acid prior to aerosol sampling and stabilize the collected ammonium nitrate against evaporation, e.g. denuder filter combinations. Field campaigns in Europe indicate that evaporation from quartz filters is significant at temperatures higher than 20°C (Schaap et al., 2003b). Hence, the obtained data for nitrate (and ammonium) are likely to represent lower limits. Teflon filters are more vulnerable to evaporation losses (Eatough et al., 1988; Hering and Cass, 1999) and data obtained with these filters have not been used here. Positive artefacts occur by adsorption of nitric acid on the filter and data from cellulose filters are thus interpreted as total nitrate, the sum of aerosol nitrate and gaseous nitric acid. In winter both evaporation and adsorption of nitric acid is thought to be small due to low ambient temperatures and small nitric acid concentrations. Hence, summertime data were found to be more uncertain than those acquired during winter. Mountain stations

have been excluded for the model to measurement comparison. Most of the stations measuring total nitrate are located along a coastline. Aerosol nitrate data are mostly found at continental sites.

Comparison of modelled and measured aerosol concentrations

The modelled annual average concentrations of the inorganic aerosol species are compared to measured data in Figure 6. The comparison for nitrate and ammonium is presented for each station in Table 4.2 and Table 4.3. In Table 4.4 we show a number of statistical parameters, calculated on a daily basis. Besides the ratio between the modelled and measured average values we show the average correlation coefficient, the residual, the root mean square of the difference (RMSE) and the fraction of modelled concentrations that are within a factor of two of the measured values. The ability of the model to predict the amplitude of the daily variations is analysed using the normalised ratio of standard deviations of the mean concentrations. For a detailed description of the statistical parameters used we refer to the Appendix. A selection of stations, chosen to represent different regions in Europe, was made for which time series of the model to measurement comparison are shown in Figures 4.7 to 4.10.

Nitrate

On average the model simulates slightly higher (10 %) aerosol nitrate concentrations than those measured. However, for single stations the agreement is not as good as indicated by the average RMSE of 3.57 $\mu g/m^3$. The RMSE for nitrate is higher than for sulphate, indicating that the simulated nitrate data deviate more from the measured data. Likewise a smaller fraction (57 vs. 65%) of the modelled values are within a factor of 2 of the measured data. The comparison is biased towards measurements obtained in the Netherlands, since 5 out of 9 stations are located there (see Table 4.2). The measured data do not show a significant gradient over the Netherlands, whereas the model simulates the highest concentrations inland and lowest at the coast. The (different) seasonal variations in the Netherlands and eastern Germany are well reproduced by the model (compare Figure 8a and 8b). In southern Europe only at Monte Libretti, near Rome, aerosol nitrate is measured routinely. Although modelled and measured data compare favourably, strong conclusions on model performance in this part of Europe can not be drawn on basis of a single station.

Table 4.2 Comparison between observed and simulated concentrations (μg/m³) of aerosol nitrate for 1995 * Data for May-Dec. Not included in statistical analysis due to 2 weekly sampling at the site

Station	Lon	Lat	Method	Obs	Sim	Reference
Melpitz	12.9	51.5	IF-Quartz	3.9	3.3	Heintzenberg et al., 1998
Muncheberg	14.1	52.5	DF	2.2	3.3	Zimmerling et al., 2001
De Zilk	4.5	52.3	DF	4.0	3.6	RIVM, 1997
Wieringerwerf	5.0	52.8	DF	4.5	3.2	RIVM, 1997
Bilthoven	5.2	52.1	DF	4.9	6.2	RIVM, 1997
Kolummerwaard	5.3	53.3	DF	4.5	3.7	RIVM, 1997
Vreedepeel	5.9	51.5	DF	4.6	7.9	RIVM, 1997
Monte Libretti	12.6	42.1	DF	2.8	3.3	EMEP, 1997
Wallisellen*	8.6	47.4	DF	3.7	4.7	Thöni et al., 2000

Table 4.3 Comparisonbetween observed and modeled concentrations (μg/m³) of aerosol ammonium for 1995

Station	Lon	Lat	Method	Obs	Sim	Reference
Melpitz	12.9	51.5	IF-Quartz	3.0	2.8	Heintzenberg et al., 1998
Muncheberg	14.1	52.5	DF	3.0	2.8	Zimmerling et al., 2001
Ispra	8.5	45.8	CF	2.9	2.5	EMEP, 1997
Preila	21.1	55.4	CF	0.6	1.3	EMEP, 1997
Rucava	21.2	55.2	CF	1.3	1.0	EMEP, 1997
Zoseni	25.9	57.1	CF	1.1	0.9	EMEP, 1997
De Zilk	4.5	52.3	DF	2.2	2.7	RIVM, 1997
Wieringerwerf	5.0	52.8	DF	2.7	2.4	RIVM, 1997
Bilthoven	5.2	52.1	DF	2.7	3.5	RIVM, 1997
Kolummerwaard	5.3	53.3	DF	2.3	2.4	RIVM, 1997
Vreedepeel	5.9	51.5	DF	2.5	4.3	RIVM, 1997
Jarczew	22.0	51.3	CF	2.5	2.7	EMEP, 1997
Diabla Gora	17.5	54.8	CF	1.7	1.6	EMEP, 1997
Wallisellen*	8.6	47.4	DF	3.1	2.5	Thöni et al., 2000
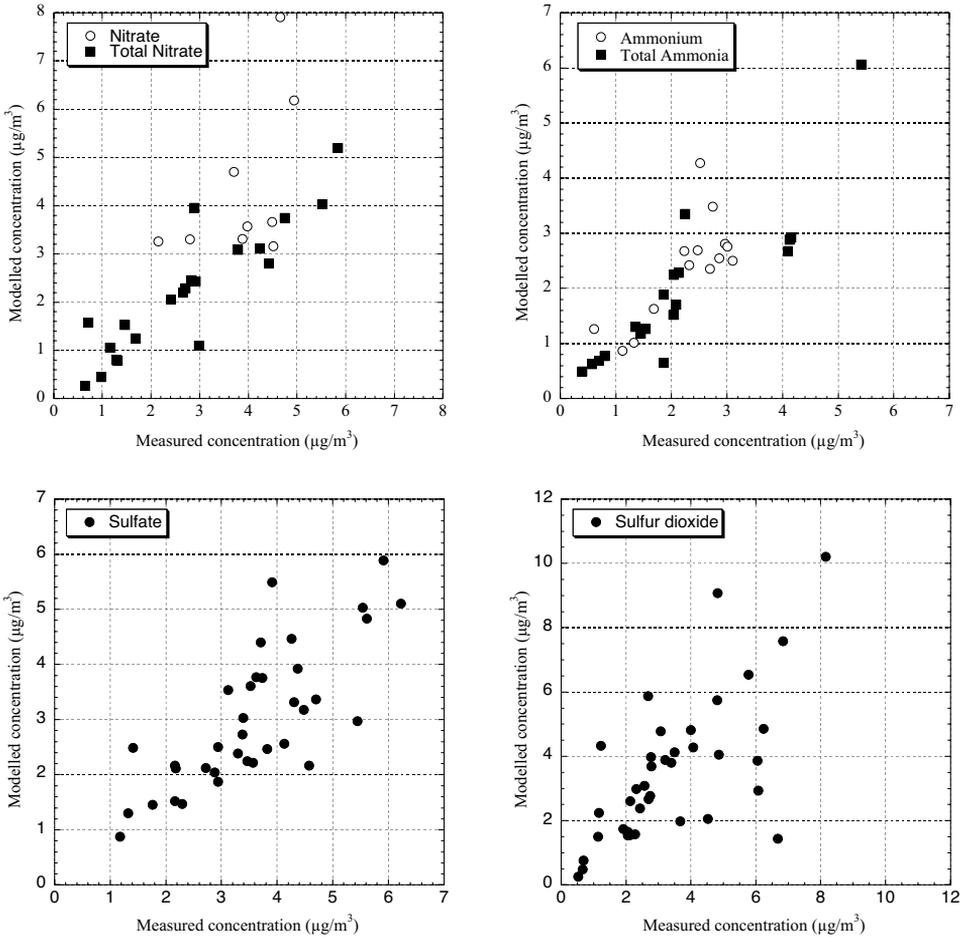
Figure 4.6 Comparison of simulated and measured annual averaged concentrations of the inorganic aerosol components and sulphur dioxide

Table 4.4 Statistics on model to observation comparison

	SO_4	SO_2	NO_3	TNO_3	NH_4	TNH_4
aver(mo)/aver(me)	0.92	1.10	1.10	0.81	1.08	0.88
residual	1.77	2.57	2.47	1.45	1.08	1.01
RMSE	2.60	4.15	3.57	2.31	1.54	1.50
sigma (model/meas)	0.99	0.69	0.91	0.85	0.86	0.66
Correlation coeff	0.60	0.48	0.58	0.52	0.62	0.58
% within factor 2	65.4	50.3	56.9	57.6	68.8	68.3
Number of Sites	42	39	9	21	13	18

Sulphate

On average simulated and measured sulphate concentrations agree fairly well (ratio = 0.92). Also, the time series show that the model is able to simulate the general behaviour of the sulphate in the atmosphere surprisingly well (r = 0.6). The overall variability of the modelled concentrations compares favourably, albeit that the model does not always reproduce the amplitude of single events. However, for the German EMEP stations we find the measured data to be consistently lower than the modelled data. This behaviour has also been observed in a larger model intercomparison (Hass et al., 2003). They showed that the measurement data are systematically underestimating the actual concentrations and could exclude the influence of emissions being too low.

Ammonium

Aerosol nitrate and sulphate are associated with ammonium. In reality, this is only the case in air masses with a continental signature. Aerosol ammonium is mainly measured at continental stations and the computed ammonium data compare well with measured data. Moreover, on average the comparison for ammonium is better than for nitrate and sulphate, as indicated by the lower average residual (1.08), RMSE (1.54) and higher correlation coefficient (0.62). Underestimation and overestimation of (ammonium) sulphate appear to be somewhat balanced by (ammonium) nitrate. Overestimation and underestimation of ammonium are found at the same sites as for nitrate, compare Tables 4.3 and 4.4.

Total nitrate and total ammonia

Indirect information to verify simulated aerosol nitrate and ammonium concentrations is provided by measurements of total nitrate (NO_3+HNO_3) and total ammonia (NH_4+NH_3). The statistical parameters indicate that the simulated total nitrate and total ammonia levels are on average somewhat underestimated (19% and 12 %, respectively). As for sulphate, the model captures the daily variability in the measurements, although peak values are not allways represented well. Moreover, under or overestimation of these measures are correlated. At High Muffles (GB14) total nitrate peaks are overestimated, which are correlated with an overestimation of total ammonia. On the other hand, at Birkeness (NO01) events with high nitrate and ammonium levels are accurately reproduced, but peak values are underestimated. The relative amplitude of modelled TNH_3 is only 66 % of that measured, which may be explained by the influence of primary emitted ammonia on spatial scales not represented by our model (see next paragraph).
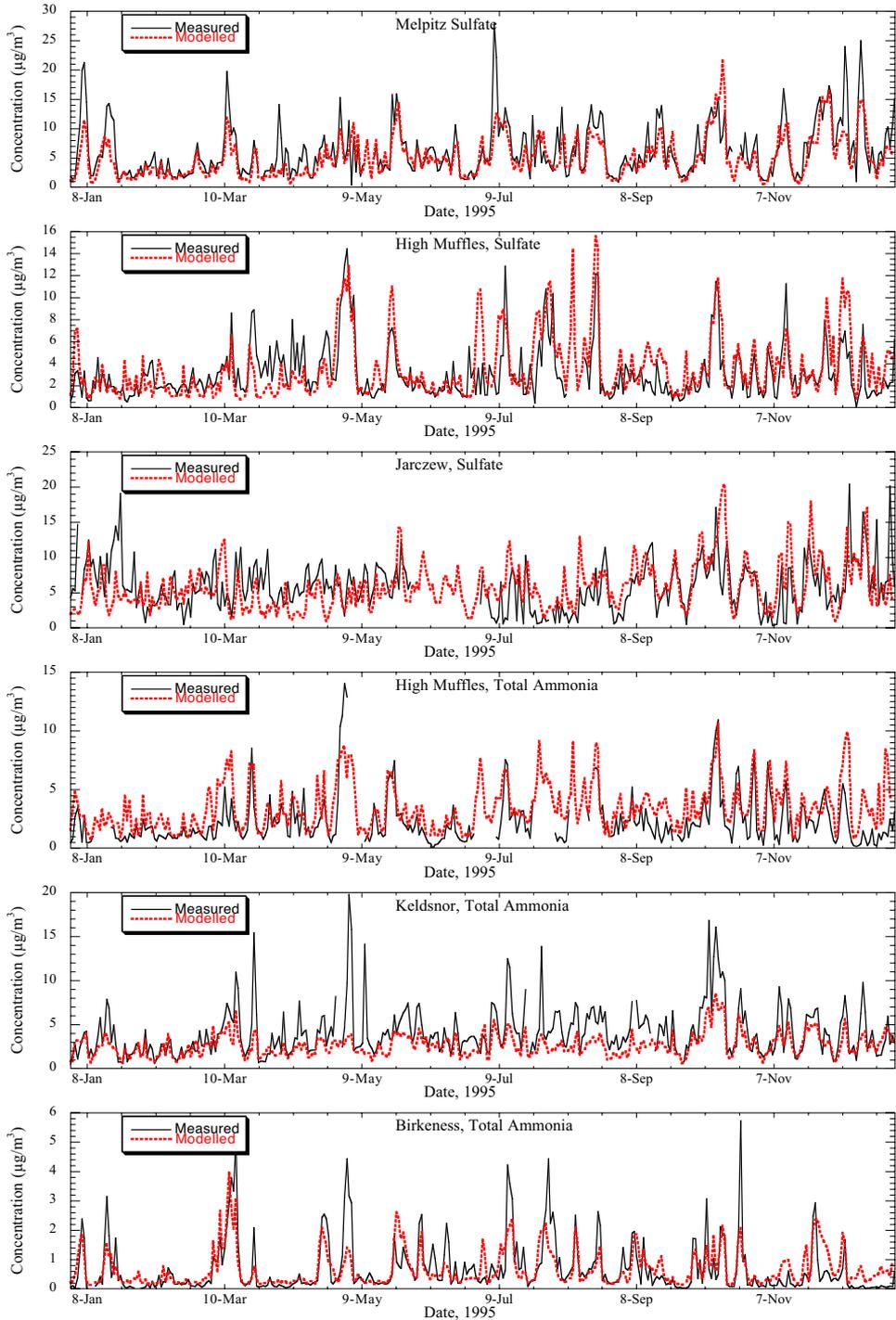
Figure 4.7 Modelled and measured time series of sulphate and total ammonia over 1995

Ammonia

It is difficult to compare our model results for ammonia concentrations with measurements, since ammonia concentrations may strongly vary over horizontal distances of hundreds of meters and may have strong vertical gradients. An additional complication arises due to the model structure. Secondary components like nitric acid are removed at the ground and, therefore, their vertical distribution near the ground can be calculated form the layer averaged concentration using information on their deposition velocity. In contrast, due to surface emissions ammonia concentrations decline with height in their source areas (Erisman et al., 1988). As calculation of the concentrations at a reference height of two meter takes deposition processes into account but not emission, the calculated ammonia concentrations at 2m in or nearby sources may be substantially underestimated. This feature is illustrated in Figure 4.10 where the ammonia concentration at the site with the highest emission density in Europe, Vredepeel, is shown. There the computed mixing layer concentration is on average twice the concentration at 2m. The deviation between measurement and model is highest for the summer months when the mixing layer is thick. Similar behaviour is observed for total ammonia measurements in ammonia rich areas, see DK05 (Fig 7e). For remote areas where there is a (large) net deposition the modelled concentration at 2 m are expected to be directly comparable to measured data. The data available in these areas are total ammonium data only, which show lower modelled concentrations as compared to observations as discussed above.

Nitric acid

Only two stations, i.e. Müncheberg and Rome, had gaseous nitric acid measurements covering the whole year of 1995. The model to measurement comparison for Müncheberg (D) is shown in Figure 4.9. Although the daily values are not always represented in detail, the correlation and variability on a daily basis as well as the seasonal variation compare reasonably well (r=0.72), which also applies for Rome (I) (r=0.71). Additional nitric acid data were compiled by Schaap et al. (2001), who estimated the nitric acid component of total nitrate concentrations north of the Alps. The estimates for the average nitric acid concentration during winter are shown in Table 4.5. These estimates show that average nitric acid concentrations are remarkably similar and below 0.5 $\mu g/m^3$ throughout northern Europe. At inland locations the modelled and estimated concentrations agree generally within a factor of 2. The simulated nitric acid concentrations for two stations located on small islands, Anholt (Dk) and Uto (F), show the largest deviations, more than a factor of 2, and are higher than the observed range of nitric acid levels evaluated by Schaap et al. (2001). It is much more difficult to evaluate the nitric acid concentrations in summer, since the measured data on nitric acid show higher variability than in winter. Nitric acid concentrations for campaigns at the same site during the same month in different years may vary a factor of 5 (Schaap et al., 2001). However, the maximum concentrations averaged over the duration of a campaign in summer is lower than 2 $\mu g/m^3$, indicating that nitric acid concentrations averaged over a whole summer are not expected to exceed 2 $\mu g/m^3$. This indicates that in coastal and marine areas in northern Europe the modelled nitric acid concentrations are overestimated (see section 4.4).
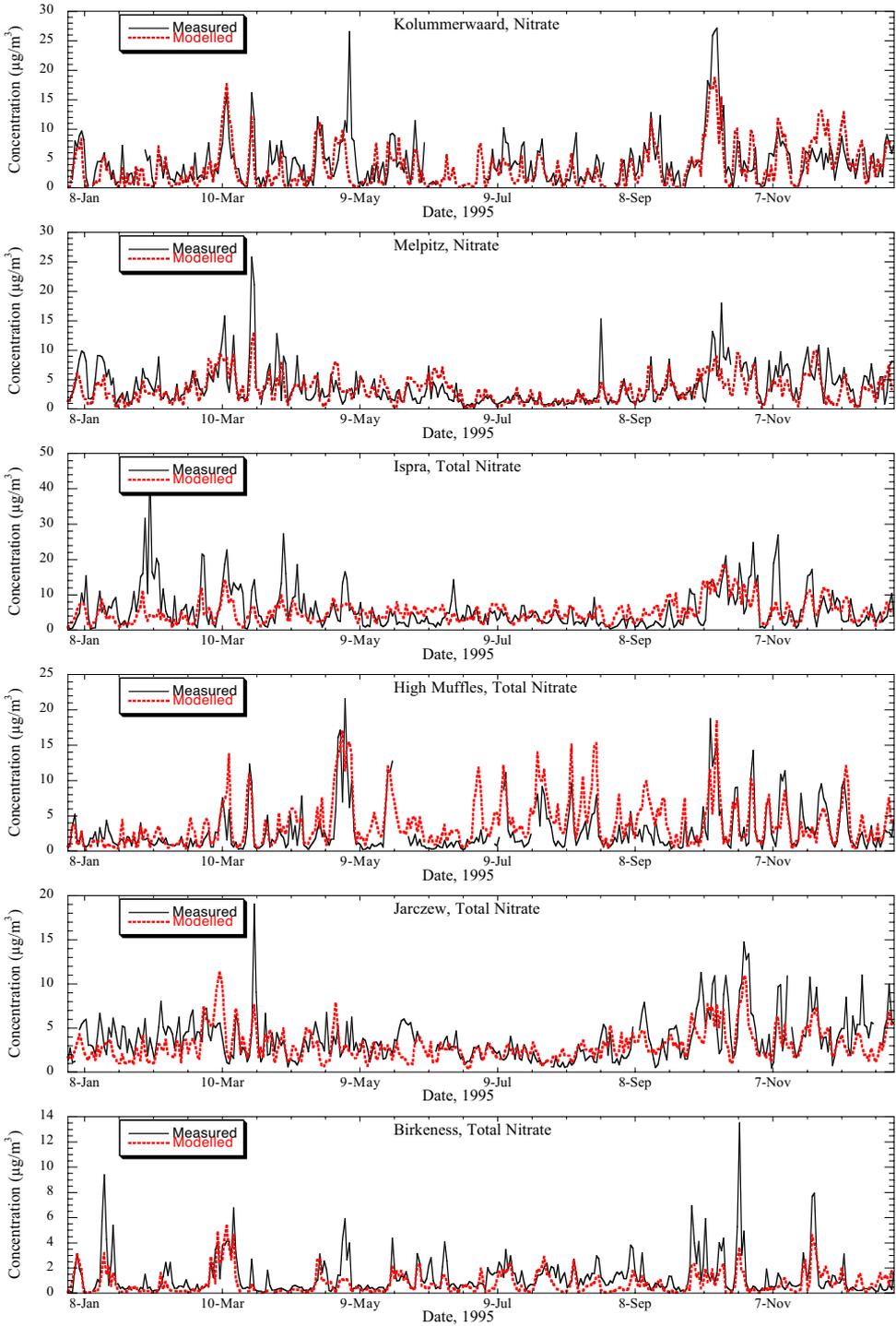
Figure 4.8 Modelled and measured time series of nitrate and total nitrate over 1995

Rainwater composition

An important data set giving information on atmospheric concentrations of aerosols and its precursors is that of rainwater composition. In Table 4.6 the statistics from the model to measurement comparison are shown. On average the rain intensities derived from the meteorological input fields compare well with observations. However, the daily correlation is low (0.40) and the mean root mean square of the difference is large (7.29 mm), which indicates large variability. On average the modelled wet deposition underestimates the actual wet deposition by a factor of 2 or more for all components. Inspection of the measurements shows that the largest part of the deposition flux is due to a few rain events, which are not represented in the model. Part of the discrepancy may also be explained by the input data on rain, however, the total amount of rain is not very different from the measurements which leads to the conclusion that in our model the wet deposition is strongly underestimated. Additional causes will be discussed in section 4.5.

Table 4.5 Comparison between modelled HNO_3 concentrations and those estimated by Schaap et al. (2001; 2002a) ($\mu g/m^3$)

Station	Country	Estimated	Modelled
Keldsnor	DK	0.4	0.8
Anholt	DK	0.4	0.9
Tange	DK	0.4	0.1
Ulborg	DK	0.4	0.2
Fredriksborg	DK	0.4	0.5
Payerne	CH	0.3	0.05
Eskdalemuir	GB	0.4	0.2
High Muffles	GB	0.4	0.2
Leba	PL	0.4	0.4
Diabla Gora	PL	0.4	0.2
Jarczew	PL	0.6	0.8
Rucava	LV	0.4	0.4
Birkenes	NO	0.2	0.4
Skreadalen	NO	0.2	0.2
Osen	NO	0.2	0.1
Vavihill	SE	0.4	0.2
Roervik	SE	0.4	0.8
Aspvreten	SE	0.4	0.4
Uto	FI	0.4	0.9
Virolahti	FI	0.4	0.2
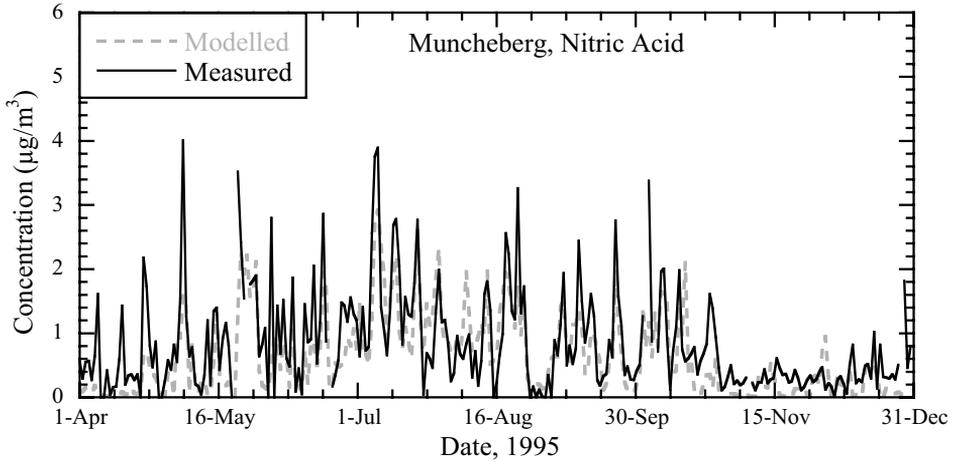
Figure 4.9 Modelled and measured time series of nitric acid at Muncheberg, Germany (Measured data from Zimmerling et al., 2000)
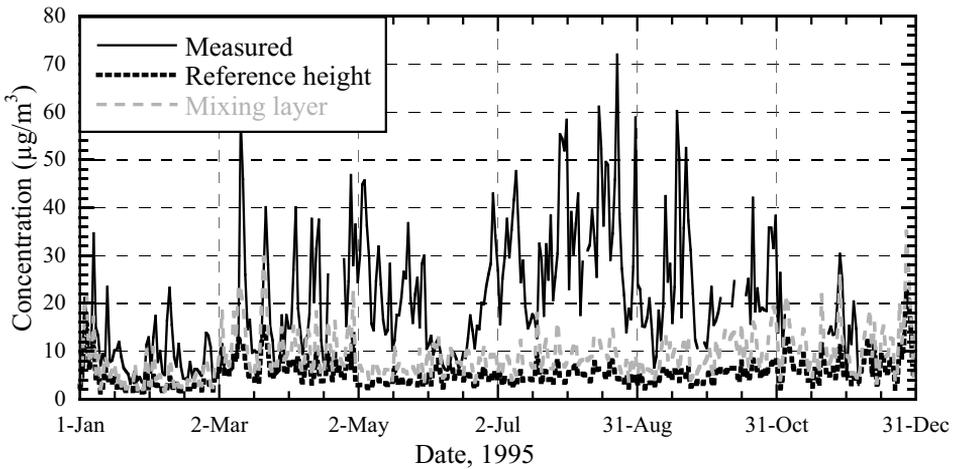
Figure 4.10 Measured and modelled time series of ammonia at Vredepeel, the Netherlands, for measuring height and the mixing layer.

Table 4.6 Comparison between observed and modeled rain water concentrations

	mm	Swet	NHwet	NOwet
aver(model)/aver(meas)	0.94	0.37	0.16	0.67
residual	4.56	0.73	0.91	0.69
RMSE	7.29	1.19	1.64	1.12
sigma (model/meas)*	0.78	0.51	1.32	1.46
Correlation coeff	0.40	0.20	0.04	0.03
% within factor 2	37.15	33.36	7.09	36.85

4.4 Implications for aerosol optical depth and radiative forcing

The calculated aerosol nitrate burden over Europe contributes to the aerosol optical depth (AOD) and aerosol radiative forcing over Europe. AOD is the extinction of light due to particles in the atmosphere and thus provides a measure of the column integrated aerosol burden. AOD can be measured from satellites as well as from the surface. From de modelled aerosol columns the AOD can also be derived, provided that correct assumptions on the physical and optical properties of aerosols are made. Below we present the modelled AOD for 1995. We compare the calculated AOD for August 1995 to that measured by the ATSR-II satellite in August 1997 (see section 4.5). Using the AOD the radiative forcing of nitrate and sulphate can be estimated.

4.4.1 Aerosol optical depth

Assuming that nitrate and sulphate have the same optical properties the AOD at 550 nm was computed from the modelled dry aerosol mass concentrations as described by Robles-Gonzales et al. (2003). To account for the variation of the aerosol scattering coefficient with relative humidity a growth factor obtained from humidity controlled nephelometry (Veefkind et al., 1996) was used in the AOD calculations. Effects due to hysteresis are not accounted for. In Figure 4.11a we show the modelled annual average AOD due to secondary inorganic aerosols. We present values for 12:00 GMT, the time of overpass of the ATSR-II satellite, to compare with satellite observations (Robles-Gonzales et al., 2000; 2003) in section 4.5. Annually averaged, modelled AOD at noon exceeds 0.25 in Rumania, Poland, the Czech Republic and the eastern part of Germany. Over the northwest and eastern Europe the AOD ranges between 0.15 and 0.25. The AOD decreases towards the north and south west and becomes lower than 0.1 in Scandinavia, Ireland and the Iberian Peninsula.

The calculated ratio of the aerosol optical depth by nitrate to that by sulphate is given as function of latitude and time of year in Figure 4.11b. Since nitrate concentrations are lowest around noon, the nitrate to sulphate ratio represents lower limits. The seasonal variation of nitrate is strongly visible in the calculated ratios. In July and August the ratio maximises at about 51°N but seldom exceeds 40 %, averaged for 10°W-30°E. Inspection of the fields show that during these months only over the Netherlands and the Po Valley comparable concentrations and AOD's for nitrate and sulphate are computed. During the winter half year, October to March, the AOD by nitrate exceeds that of sulphate over a large part of Europe, indicating its large importance in that season.
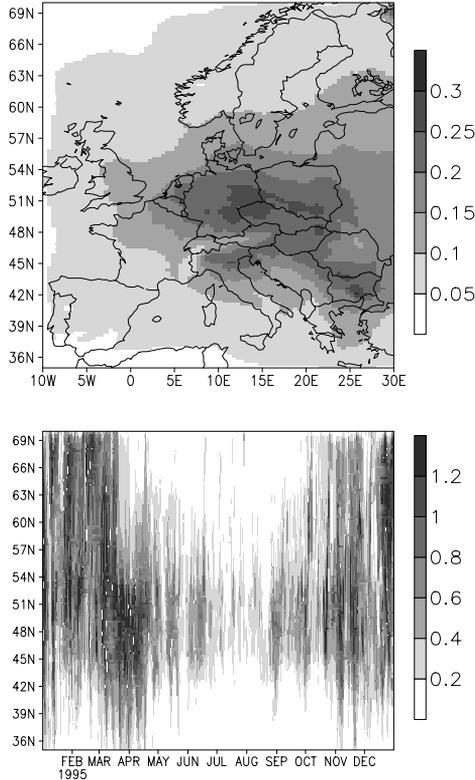
Figure 4.11 Annually averaged total AOD over Europe (upper panel) and the nitrate to sulphate AOD ratio as function of latitude (averaged over 10W to 30 E) and season (lower panel). Values represent noon values.

4.4.2   Radiative forcing

The radiative forcing by sulphate and nitrate is a function of the solar zenith angle and shows a maximum at a solar zenith angle of about 70-80° (Haywood and Shine, 1997; Haywood and Boucher, 2000). To assess the relative importance of nitrate the forcing calculations were performed on an hour by hour basis with a simple and easily reproducible method. We used an analytical fit for Koepke et. (1997) water soluble aerosol as described by van Dorland et al. (1997). Note that their formulation includes some absorption, which implies that the calculated values for the forcing will be lower limits. The AOD was calculated form the computed aerosol burden using a dry scattering coefficient of 4 m^2/g in the procedure as described by Robles-Gonzalez et al. (2003). Seasonal values for the surface albedo were taken from Matthews (1984). The calculations were scaled with the cloud free area.

The calculated direct aerosol forcing due to sulphate and nitrate is given in Figure 4.12. The calculated forcing averaged over different regions in Europe is shown in Table 4.7. The annual average sulphate forcing maximises where its concentration is highest, e.g. in a band over north western Europe, central Europe to south eastern Europe. In this
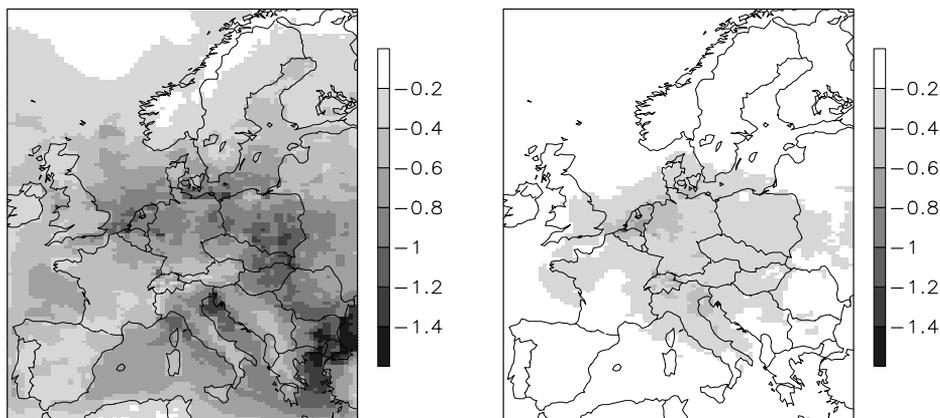
Figure 4.12 Modelled annual average forcing of sulphate (left panel) and nitrate (right panel)

band the forcing ranges between -0.8 to -2.0 W/m^2. Similar values are obtained over Northern Italy. The sulphate forcing is in the order of -0.5 W/m^2 in southern France and the Iberian Peninsula. Even lower values are obtained over northern Scandinavia. Over Europe as a whole the averaged forcing is -0.57 W/m^2. The sulphate forcing in 1995 maximises in the summer months in which the forcing is about twice the annual average forcing over large areas of Europe.

The annual average nitrate forcing over Europe between 45°N and 57°N is about -0.3 W/m^2 as compared to -0.8 W/m^2 for sulphate. In areas with a high ammonia emission density such as north western Europe and northern Italy the nitrate forcing is higher with a maximum over the Netherlands where it exceeds -0.7 W/m^2. In remote locations the forcing is low and the computed average over the modelled area in Europe is -0.14 W/m^2, about 25 % that of sulphate. In contrast to sulphate the nitrate forcing maximises during spring. The seasonal importance of nitrate is further explored in Figure 4.13. The upper left panel shows that over most of continental Europe in spring the ratio of the nitrate to sulphate forcing is 50 % or more. Lower contributions are found in Scandinavia and marine locations. During spring nitrate is as important as sulphate in the Benelux, southern UK, north western France, northern Italy and the Alpine region. During summer the thermal instability of ammonium nitrate causes the ratio to become lower, with the maxima in the same regions as mentioned above. During fall the importance of nitrate becomes larger again. The nitrate burden in autumn is lower than in spring, probably due to lower emissions of ammonia as compared to spring. During winter the distribution of the ratio shows a different picture. Maximum values are found over Scandinavia. However these values should be interpreted with care since the absolute concentrations are small. Over continental Europe, the nitrate forcing in winter is about 50% of that of sulphate. The gradients are smaller than in the other seasons due to a longer atmospheric lifetime. Consequently, the distribution of the ammonia emissions is less visible in both the burden and the nitrate forcing during winter than in summer.
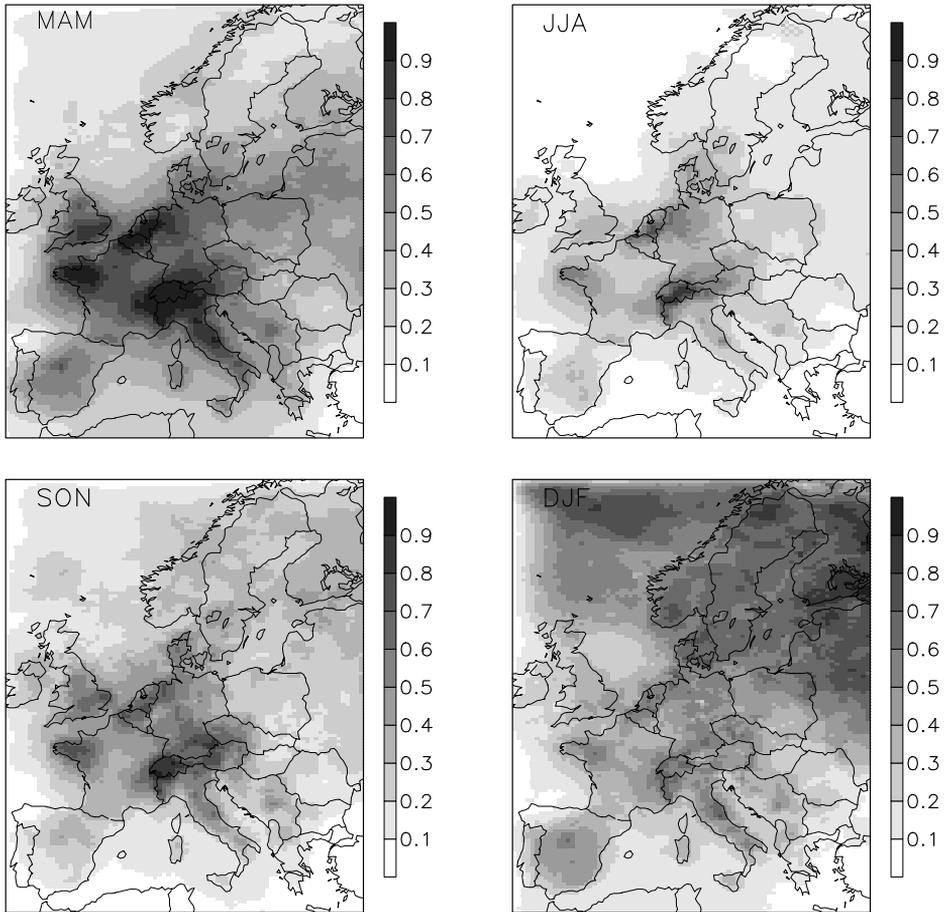
Figure 4.13 Distribution of the nitrate to sulphate forcing ratio as function of season.

4.5   Discussion and conclusions

In this paper aerosol calculations for the year 1995 are presented. The regional CTM used simulates the secondary inorganic aerosol, its precursors, as well as the oxidant concentrations over Europe. The model is able to simulate the general features of the secondary aerosol fields over Europe. Moreover, the model is able to simulate the daily variability reasonably well. Agreement between model and measurement is best for sulphate and ammonium. The performance of the model for nitrate and its precursors is not as good as indicated by higher residuals and RMSE. The comparison between the model and measurements shows higher deviations for nitrate than for sulphate and ammonium.

During the whole year nitrate concentrations are slightly overestimated by 10 % on average, when compared to 9 stations. However, at single stations the difference may be much higher. The emissions, dispersion and reaction of ammonia are likely to be the most

Table 4.7 Radiative forcing (W/m^2) by sulphate and nitrate for several regions in Europe

Region	Boundaries		Annual		Oct-March		March-May	
	Lon	Lat	SO$_4$	NO$_3$	SO$_4$	NO$_3$	SO$_4$	NO$_3$
Europe	-10 to 30	35 to 70	-0.57	-0.14	-0.44	-0.14	-0.54	-0.19
Northern E	-10 to 30	47 to 62	-0.61	-0.19	-0.4	-0.17	-0.57	-0.23
Northwest E	-5 to 15	47 to 57	-0.67	-0.28	-0.43	-0.23	-0.64	-0.36
Central E	0 to 25	45 to 54	-0.78	-0.29	-0.57	-0.26	-0.70	-0.37

important cause of deviations between modelled and measured concentrations. The LOTOS model is not able to represent strong vertical gradients in the source regions. Therefore, too much ammonia may be "effectively" emitted to the atmosphere as explained in section 4.2, which may result in an overestimation of ammonium nitrate as is observed for Bilthoven and Vredepeel, the Netherlands. The uncertainties in the representation of the ammonia sources and removal processes on the results are discussed in a separate paper (Schaap et al., 2003a; see also Appendix B). That work concludes that the computed nitrate concentrations in the source areas are very sensitive to the total amount of ammonia emissions, the temporal distribution as well as the horizontal distribution of these emissions. Thus the details of the description of the ammonia sources and sinks are the largest source of uncertainty in the calculation of secondary nitrate aerosol (see also Schaap et al, 2002b). A higher vertical resolution in the mixing layer is needed to describe the vertical gradient of ammonia more accurately as well as a better understanding of (the temporal variability) ammonia emissions in Europe. On the other hand, the vertical resolution required in this context demands a very large computational burden as discussed by Asman (2001).

In addition to the representation of ammonia, uncertainties are present in the formation processes of nitric acid. In comparison to other photo-oxidant models LOTOS has relatively high OH concentrations (Roemer et al., 2003) which may cause a slightly too fast nitric acid formation in summer. Similarly, the heterogeneous formation rate of nitric acid may be inaccurate because we used reaction probability $\gamma = 0.05$ for N_2O_5 hydrolysis, which is still under debate (Jacob, 2000; Mentel et al., 1999). Finally, other heterogeneous (NO3-radical) and homogeneous reactions (organic nitrates) of NO$_y$ may occur, which are not or very simplified included in our model.

Over the coastal and marine areas LOTOS predicts too high nitric acid concentrations. In the model, ammonia concentrations are decreasing from the continent towards the open sea, causing ammonium nitrate transported onto the ocean to evaporate. In addition, NO$_x$ is efficiently converted to nitric acid due to the high oxidant concentrations present over the sea. These phenomena were also found in observational data (Tamm and Schulz, 2003, Schulz et al., 1999). However, since LOTOS does not incorporate sea salt at the moment, it overestimates nitric acid which in reality resides in the coarse sea salt aerosol fraction (Tamm and Schulz, 2003). Inclusion of sea salt (and mineral dust) as a sink for nitric acid is therefore needed to describe the nitrate distribution in marine (and arid) areas more accurately.

In general, models have difficulties representing wet deposition correctly. For example, the wet deposition efficiency in de models participating in the COSAM study ranged over a factor of 4 (Roelofs et al., 2001). In LOTOS clouds are treated in a very simplified manner since the meteorological input only contains cloud cover. Underestimation of the concentrations of nitrate and other components in rainwater is most probably related to this issue. In-cloud scavenging, which is not represented in the model, accounts for a large part (~60 %) of the total wet deposition (Guttorp, 1986). We hypothesise that in our model a substantial part of the tracer mass, that would otherwise be removed by wet deposition, is transported through the model upper boundary in frontal activity. Unfortunately, we did not quantify the magnitude of this process. A better parameterisation for clouds and cloud processes should be included in the future. Experiments with faster scavenging rates show that the low correlation between the input and observed rain data causes the comparison between the modelled and measured concentrations in air to become much less favourably.

Comparison with other studies

Recent global modelling studies have provided more insight into the large scale ammonium nitrate formation. Adams et al. (1999; 2001) used off line calculated fields of nitric acid in combination with a sulphur chemistry model to calculate the partitioning of nitrate between the aerosol and gas phase. Their calculated nitrate concentrations were found to be too high on average in polluted continental areas. Improvements on the treatment of ammonia and the coupling with a full photo chemistry scheme were advised (Adams et al., 1999). The latter was taken up by Metzger et al. (2002a,b), who used the TM3 model to assess the global ammonium nitrate and sulphate distribution. In that study nitrate and total nitrate concentrations were highly overestimated by on average a factor of 2-3, with the highest overestimations during winter. The authors attributed these discrepancies to 1) the underestimation of sulphate concentrations during winter, 2) the uncertainties in the representation of the ammonia cycle and 3) a too stable planetary boundary layer. Interestingly, they also showed that the modelled nitrate burdens increased with increasing model resolution.

Compared to Metzger et al. (2002b), our results are not only closer to the observations for nitrate but also for sulphate during winter. As noted before, our simple SO_2 cloud oxidation scheme gives better results as compared to more detailed schemes. However, also the much higher resolution of the model specifically in respect to the ammonia emissions may explain a considerable part of the differences. Given the short lifetime of the species involved and the gradients in the ammonia emissions the equilibrium calculations are performed on a more appropriate spatial scale than in a global model with a horizontal resolution of several degrees. As a result, in contrast to Metzger et al. (2002b) our model does not show a large nitrate overestimation.

In Europe, the EMEP model (Tsyro, 2002) simulates nitrate on spatial and temporal scales similar to our model. Other regional model studies of nitrate formation are confined to episodes (Riemer et al., 2003) or the growing season, April – September (Hass et al., 2003). In the framework of a larger model intercomparison, results from an earlier version

of our model were compared to those of several other models with different complexity. Differences between the models were large with a tendency to overestimate nitrate levels. Inspection of the results obtained by EMEP (Tsyro, 2002) shows that these fall within the range of the models participating in the comparison. The differences illustrate the complex nature of nitrate modelling and the associated uncertainties. A large effort is required to better describe the processes involving nitrate formation in the atmosphere.

The results shown in this study are obtained with a new model tool to describe the inorganic aerosol distribution over Europe. Unfortunately, it is inherently difficult to measure the semi volatile ammonium nitrate. Hence, we could verify our results only with a small set of measurements. More reliable data sets on NO_3/HNO_3 and NH_3/NH_4 are urgently needed to test model results. Moreover, high resolution data are needed to test the diurnal variation of nitrate and its precursors, equilibrium calculations and nitric acid formation. Regions of interest would be England, the Netherlands, south western France, the Po valley, central Poland, south eastern Europe and southern Sweden. Given the strong gradients in ammonia levels, both vertical and horizontal, measurements on towers may be very useful to arrive at more spatial representative and mixed layer averaged properties.

AOD

Verification of modelled AOD is hampered by data availability, especially over land. An extensive comparison between modelled AOD from sulphate and nitrate for August 1997 and satellite observations is presented in Robles-Gonzales et al. (2003) and Jeuken et al. (2001), who used LOTOS and TM3, respectively. Our results for August 1995 are compared to these studies in Table 4.8.

The average calculated AOD with LOTOS for August 1995 is remarkably close to that for august 1997 by Roblez-Gonzalez et al. (2003). Only in north western Europe our previous calculations show a somewhat higher AOD, which can be fully attributed to differences in the calculated nitrate levels there (see Table 4.8). The LOTOS calculations for august 1997 show a more pronounced overestimation of nitrate levels over the Netherlands than the calculations for 1995. For TM3, our study is most comparable with the results of Jeuken et al. (2001), who used similar emissions (for Europe) and a 2.5x2.5 degrees resolution. For central Europe they calculated an average AOD of 0.08, which can be compared to LOTOS (0.20) and measurements (0.35), indicating large differences between LOTOS and TM3 calculations. A plausible explanation of the underestimation of total measured AOD in LOTOS and TM3 is the absence of carbonaceous, sea salt and mineral dust aerosols in the models.

*Table 4.8 Comparison between total AOD observed with ATSR-II and modeled by LOTOS and TM3 for the regions defined in Table 4.7. For ATSR-II a lower and upper estimate of the AOD is given (depending on treatment of missing values). For each model the AOD by nitrate is given between brackets. * RG2002 = Robles Gonzalez et al., 2000; RG2003 = Robles Gonzalez et al., 2003; J2001 = Jeuken et al., 2001*

| | ATSR-II | LOTOS | | LOTOS | | TM3 | |
	1997	1995		1997		1997	
Europe	0.21-0.28	0.11	[0.02]	0.11	[0.02]	0.05	[0.01]
Northern EU	0.25-0.31	0.13	[0.02]	0.14	[0.04]	0.06	[0.01]
NW EU	0.32-0.36	0.16	[0.03]	0.19	[0.06]	0.09	[0.02]
Central EU	0.34-0.36	0.20	[0.05]	0.21	[0.07]	0.08	[0.02]
Reference*	RG2000	This study		RG2003		J2001	

All studies show low AOD due to nitrate compared to that of sulphate for most of Europe in August. Only in north western Europe modelled nitrate contributed significantly to AOD. Moreover, regionally over the Netherlands comparable contributions of nitrate and sulphate to AOD were calculated, which are in line with the local observational evidence for the importance of nitrate there (ten Brink et al., 1997). However, our results for 1995 indicate that these conclusions for August can not be extrapolated to other seasons, when the contribution of nitrate to AOD is significantly higher over continental Europe. A longer time series of AOD over Europe is needed to assess the contribution of nitrate and sulphate to AOD in these seasons.

Radiative forcing

IPCC (2001) did not give a best estimate for the radiative forcing of nitrate because of contradictory forcing results presented by different authors. The differences in the estimates are largely determined by the assumptions on the size distribution of nitrate. Jacobson (2001) assumed 90 % of the global nitrate burden to be in the coarse aerosol fraction and arrives at a very small forcing. However, in Europe nitrate is found to be mainly in the fine aerosol fraction (Putaud et al., 2003; Schaap et al., 2002a; Heintzenberg et al., 1998; ten Brink et al., 1997). Studies including ammonium nitrate (Adams et al., 2001; Metzger et al., 2002b) are indicative for the importance of nitrate over Europe. As discussed above, we feel that our model results provide more reliable data than these coarse grid global models, especially for nitrate. For the whole year we find a forcing of -0.57 W/m^2 for SO_4 and -0.14 W/m^2 for nitrate. Over the model domain annual average forcing of nitrate peaks at -0.75 W/m^2 over the Netherlands, equal to the forcing of sulphate. During spring the forcing of nitrate equals that of sulphate in north western Europe and the Alpine region. Our forcing estimates are difficult to compare to other studies, since we only account for the aerosol up to 3.5 km. In addition, various authors have assumed different optical properties and used different ways to account for water uptake. As a consequence, the forcing efficiencies for sulphate for instance vary more than a factor of 3 (Adams et al., 2001). Therefore, the nitrate to sulphate forcing ratio is most probably the most robust indicator to assess the importance of nitrate.

Based on measured data the aerosol nitrate burden in winter was estimated to be 60 % that of sulphate (Schaap et al., 2002a). Nitrate was found to be mainly present in the fine mode. Assuming that nitrate and sulphate exhibit a similar diurnal cycle and that they are distributed homogeneously throughout the mixing layer, leads to the conclusion that the forcing by nitrate has a similar relative magnitude (Ten Brink and Schaap, 2002; Schaap et al., 2002a). In this study we find a nitrate forcing amounting to 43 % that of sulphate in winter. Taking into account the uncertainties in both estimates we do not feel that these estimates are significantly different.

All together, the forcing of nitrate is highly significant over Europe and should be taken into account to assess the impact of aerosol on regional climate change. Moreover, the impact of nitrate may gain importance in the future (Adams et al., 2001).

Concluding remarks
- We developed a model tool that is able to simulate the ammonium nitrate and sulphate concentrations over Europe on a daily basis.
- 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.
- Heterogeneous chemistry plays an important role in the formation of nitric acid and aerosol nitrate.
- The description of the ammonia sources and sinks is the largest source of uncertainty in the calculation of secondary nitrate aerosol.
- Sea salt should be included in the model to simulate nitrate partitioning in marine areas correctly.
- The forcing of nitrate is highly significant over Europe as compared to sulphate and should be taken into account to estimate the impact of regional climate change.

Appendix A: Statistical parameters

For the definition of the statistical parameters used for the comparison between modelled (M) and observed (O) data we follow the definition by Hass et al. (2003). The comparison is based on pairs of modelled and measured data for a number of stations (S) with available data for 1995. The number of days is given by D, whereas d and s represent the day and station number, respectively.

The ratio of model results $M_{s,d}$ and results from observations $O_{s,d}$ is defined as:

$$Ratio = \frac{\sum_{s=1}^{S} \sum_{d=1}^{D} M_{s,d}}{\sum_{s=1}^{S} \sum_{d=1}^{D} O_{s,d}} = \frac{\overline{M}}{\overline{O}}$$

The residual is the sum of the absolute deviations of model results and results from observations:

$$\mathrm{Re}\,sidual = \frac{1}{S} \sum_{s=1}^{S} \frac{1}{D} \sum_{d=1}^{D} \left| M_{s,d} - O_{s,d} \right|$$

The root mean square error is defined as:

$$RMSE = \frac{1}{S} \sum_{s=1}^{S} \sqrt{\frac{1}{D} \sum_{d=1}^{D} \left(M_{s,d} - O_{s,d} \right)^2}$$

The normalized ratio of standard deviation (given in the tables as sigma (mo/me)) is

$$\sigma^* = \frac{1}{S} \sum_{1}^{S} \frac{\overline{O_s}}{\overline{M_s}} * \frac{\sigma_{s,M}}{\sigma_{s,O}}$$

with the standard deviation

$$\sigma_{s,O} = \sqrt{\frac{1}{D} \sum_{1}^{D} (O_{s,d} - \overline{O_s})}$$

and the observed mean at a station s

$$\overline{O_s} = \frac{1}{D} \sum_{1}^{D} O_{s,d} \quad \text{and a similar definition for the modelled mean.}$$

The average correlation coefficient rho is defined as

$$rho = \frac{1}{S} \sum_{s=1}^{S} rho_s$$

using the correlation in time at the individual stations

$$rho_s = \frac{\sum_{d=1}^{D} (O_{s,d} - \overline{O_s})(M_{s,d} - \overline{M_s})}{\sigma_{s,O} * \sigma_{s,M}}$$

The percentage within a factor of 2 is given as the percentage of days where

$$0.5 \leq \frac{M_{s,d}}{O_{s,d}} \leq 2$$

.

Appendix B: Sensitivity studies

Nitrate is an important component of the total aerosol mass over Europe (Schaap et al., 2002). Models and measurements 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 (Ten Brink et al., 1997; Schaap et al., 2002; Putaud et al., 2003). Consequently, nitrate may at present exert a significant climate forcing over Europe in winter (Ten Brink and Schaap, 2002) and in some regions, e.g. the Netherlands, even during summer (Ten Brink et al., 1997). These observational indications were also recognized in regional (Chapter 4; Roblez-Gonzales et al., 2003) and global modelling studies (Adams et al., 1999; Jeuken et al., 2001, Metzger et al., 2002). Moreover, a model study by Adams et al. (2001) indicates that globally the forcing by nitrate and the relative importance of this forcing will probably increase in the future.

Due to the semi-volatile character of ammonium nitrate and the reactivity of nitric acid only few reliable data sets are available at this moment. Therefore, we strongly rely on modelling studies to assess the aerosol nitrate field over Europe. However, modelling nitrate aerosol is still associated with large uncertainties as evidenced by the large differences (up to 100%) in computed nitrate levels in a comparison of regional models for the summer half year (Hass et al., 2003). Hass et al. (2003) identified the most uncertain processes or factors controlling the model performance for nitrate to be:

- N_2O_5 hydrolysis reaction rate
- Ammonia availability, e.g. source description

LOTOS is very well suited to perform a large number of sensitivity runs. Therefore, we extend our study on ammonium nitrate formation over Europe and present four sensitivity studies to the indicated parameters. We have varied the reaction rate for the hydrolysis of N_2O_5 (B1) and used several emission inventories for ammonia (B2). The seasonal variation of ammonia emissions was also identified to be a key parameter describing the effective ammonia emissions and the influence of three seasonal variations on the model performance was investigated (B3). For this purpose we recalculated 1995 on a smaller grid, which also enabled us to investigate the influence of the domain size (B4).

Appendix B1. Sensitivity to the reaction probability for N_2O_5 hydrolysis

Introduction

The hydrolysis of N_2O_5 on wet aerosol surfaces is a very important pathway to convert NO_x to HNO_3 (Dentener and Crutzen, 1993; Riemer et al., 2003, Schaap et al., 2003). Moreover, this reaction is the dominant source of nitric acid during winter (Section 4.3.2). The reaction rate for this conversion is uncertain, since a range of reaction probabilities has been measured on different aerosol surfaces (Jacob, 2001). Studies on the influence of N_2O_5 hydrolysis on ozone levels in polluted areas indicated only small effects, i.e. less than 10 % (Riemer et al., 2003, Tie et al., 2001). However, the sensitivity of aerosol nitrate fields to various γ values remains to be explored.

Description of simulations

We performed four sensitivity runs with LOTOS version 5.2 (Section 4.2) to address the influence of the reaction probability on the calculated nitrate fields. Normally, the calculation of the reaction rate follows Dentener and Crutzen (1993), applying a reaction probability γ = 0.05. The sensitivity runs were performed with a γ = 0.1, as recommended by Jacob (2001), and γ = 0.01, to address the influence of a more and less effective conversion of N_2O_5 to nitric acid for July and December, 1995. All runs were spun up a month before the first output was generated.

Results

The results of the sensitivity runs are shown in Figure 4.14. In the figure the ratio of the average aerosol nitrate concentration of the sensitivity run (γ = 0.01/0.1) to that of the base run (γ = 0.05) is plotted. Below the effects of the more and less effective heterogeneous formation rates are discussed for July and December.

γ = 0.1

In December nitrate and nitric acid concentrations over central Europe are very similar to those in the base run. In these areas, the lifetime of N_2O_5 is very short, also due to the large reaction surface available. Therefore, the effects of higher reaction probability are small (<5%). In south western Europe, the ship tracks and southern Scandinavia both the nitrate and nitric acid levels are slightly enhanced, ~15%. In July the differences between the nitrate and nitric acid levels are even less than in winter, because the majority of the nitric acid is formed though the NO_2+OH reaction (Section 4.3.2). As a consequence of the somewhat higher aerosol nitrate levels, total nitrate concentrations increase slightly in both seasons.

The higher nitric acid formation rate also causes very small changes in the levels of ammonium and ammonia in both seasons. Increasing the reaction probability has negligible effects on ozone in central Europe.
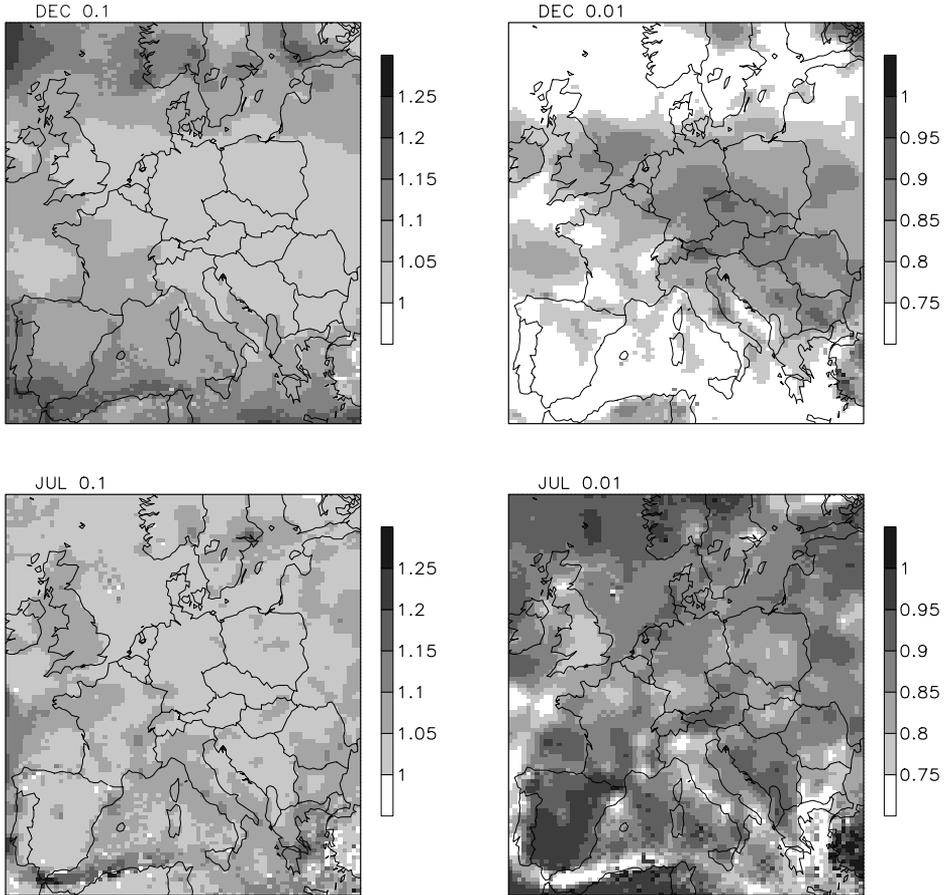
Figure 4.14 Relative difference of modelled nitrate levels for γ=0.01 and γ=0.1 for December and July as compared to the base case shown in Figure 4.17

γ = 0.01

Lowering the reaction probability leads to less nitric acid formation and lower nitrate levels. In December nitrate levels decrease significantly with 10-20% over continental Europe up to –40% in remote areas, such as the Atlantic. Nitric acid concentrations generally decrease 10-30%. The sensitivity appears to be a function of aerosol loading with lowest sensitivity in areas with the highest availability of aerosol surface.

In July, the reductions in nitric acid are smaller due to the competing reaction of NO_2 +OH. Nitric acid levels decrease with typically 5%. Nitrate levels decrease with 10-20 percent over the largest part of Europe. The decrease in nitrate is not in line with that of nitric acid, and can be explained by the higher stability of ammonium nitrate during the night, causing a night time maximum in the concentrations which is more sensitive to a lower night time conversion rate then the nitric acid levels that peak during the day. As

for nitric acid, the ammonia changes are less pronounced in July then in December. Total ammonia levels decrease slightly in both seasons due to the shift of ammonium to the shorter-lived gas phase ammonia. In both January and December less NO_x is converted to nitric acid causing small changes in ozone levels, less then +4%, in central Europe.

Conclusions
- Increasing the reaction probability from $\gamma = 0.05$ to $\gamma = 0.1$ causes small enhancements (<5%) of the aerosol nitrate levels over continental Europe in winter and summer
- Decreasing the reaction probability from $\gamma = 0.05$ to $\gamma = 0.01$ causes a significant reduction of aerosol nitrate levels of 10-20%.
- The sensitivity of nitric acid towards changing the reaction probability are less in summer than in winter due to the effective formation of nitric acid by the $NO_2 + OH$ reaction in summer.
- The hydrolysis of N_2O_5 has negligible effects on simulated ozone levels in central Europe, which is in accordance with previous studies.

Appendix B2. Sensitivity to ammonia emission inventory

Introduction

Ammonia emissions in Europe are for the largest part (80-95 %) associated with agricultural activities (van der Hoek, 1998). Ammonia emissions are a function of farming procedures, crop type, soil type and climatic conditions (Bouwman et al., 1997) and therefore show large spatial gradients. Below we assess the influence of the spatial distribution on the calculated nitrate fields. For this purpose the nitrate fields were recalculated with three different inventories. First, the TNO inventory for 1995 (Builtjes et al., 2003) was used and served as a reference. Second, the 1995 EMEP inventory was used (EMEP, 2002). The third inventory (further denoted HIRES) was composed using high-resolution ammonia emission inventories for the Netherlands (VROM, 1996), Germany (Gauger et al., 2002) and Denmark (Hutchings et al., 2001) by substituting the emissions of these countries in the TNO inventory. The emission totals are given in Table 4.9 and distributions are shown in Figure 4.15 and 4.16.

The total European emission derived by TNO is 4.6 Tg N/yr, which compares well with that by EMEP, 4.7 Tg N/yr. The agreement is caused by the comparable emission factors used to derive the emissions. However, this may also be coincidental since several other studies indicate similar emission estimates. Dentener and Crutzen (1994) derived an emission of 5.2 Tg N/yr using emission factors from Asman (1992), who derived 4.5 Tg N for Europe. The slightly higher emissions by Dentener and Crutzen (1994) may be explained by the small, and highly uncertain, contributions of wild animals, oceans and vegetation, not included in the other estimates.

Table 4.9 European ammonia emission totals for 1995 (KTonnes N/yr)

Area	Code	TNO	EMEP	HIRES
Denmark	DK	99.1	112.2	92.7
Germany	DE	622.5	635.0	627.3
The Netherlands	NL	146.6	186.2	167.4
Europe, excl. FSU#	EU	4,620.8	4,737.4	4,640.0*

* TNO emission data used for countries besides DK, DE and NL
 # FSU, Former Soviet Union

The national emission totals reveal the variability between the different estimates for a single country. The ammonia emission of the HIRES inventory for Denmark is lower than those by TNO and EMEP, whereas it lies between those of EMEP and TNO for the Netherlands and Germany. The estimates for Germany agree within 2 %, where the estimates for the Netherlands differ by as much as 25 %.

In Figure 4.15 we show the geographic distributed emissions from EMEP and TNO for Europe. The emissions have been spatially distributed according population for EMEP (EMEP, 2002); and a combination of animal statistics and land use data for TNO (Builtjes et al., 2003). The spatial variability of EMEP is less than in the TNO database. Compared to EMEP, the TNO data show higher maxima in e.g. Brittany, the Netherlands and England, but also areas with no or very small emissions, such as north eastern Spain, Ruhr area and north western Poland. At present, scientific debate is ongoing whether urban emissions of ammonia, e.g. (Perrino et al., 2002), are significant. These emissions are not incorporated in the inventories, since emission factors are not available. Hence, large emissions in urban areas, such as the Ruhr area and north eastern Spain may be inconsistent with the actual emission data.

In Figure 4.16 the distribution in north western Europe is displayed in more detail. The distributed emissions show large deviations. The EMEP emissions are more comparable to the HIRES data than those from TNO. For the Netherlands the HIRES data show a much lower gradient over the country than the TNO emissions. In Germany, the EMEP and HIRES emission databases show enhanced emissions in the north west and south east of the country, where the HIRES inventory gives higher peak values. The TNO emission database only represents the maximum in north west Germany, where emissions are higher than in the other estimates. For Denmark the geographical distribution in all three databases is very similar.

Run description

The inventories described above were used to simulate the nitrate field in July and December, 1995, with LOTOS version 5.2 (Section 4.2). These months were chosen because the sensitivities of the model are a function of the stability of ammonium nitrate, which minimize and peak in summer and winter, respectively. The model output is generated for a measurement height of 2 m. All runs were spun up a month before the first output was generated.
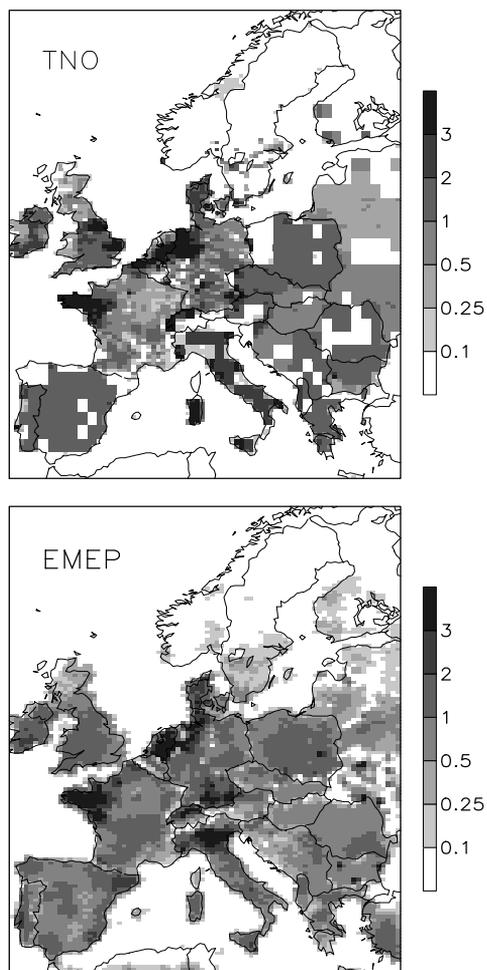
Figure 4.15 European distributions of ammonia emissions (Tonnes/yr)

Results

In this section we present the obtained results using different ammonia emission data-bases as input for the LOTOS model. In the top panels of Figure 4.17 the monthly averaged nitrate fields for December and July are shown. Below the absolute changes with respect to the base run are given for both the EMEP and HIRES inventory. For the HIRES inventory we focus on north western Europe since only the Dutch, German and Danish emissions are based on high resolution inventories.
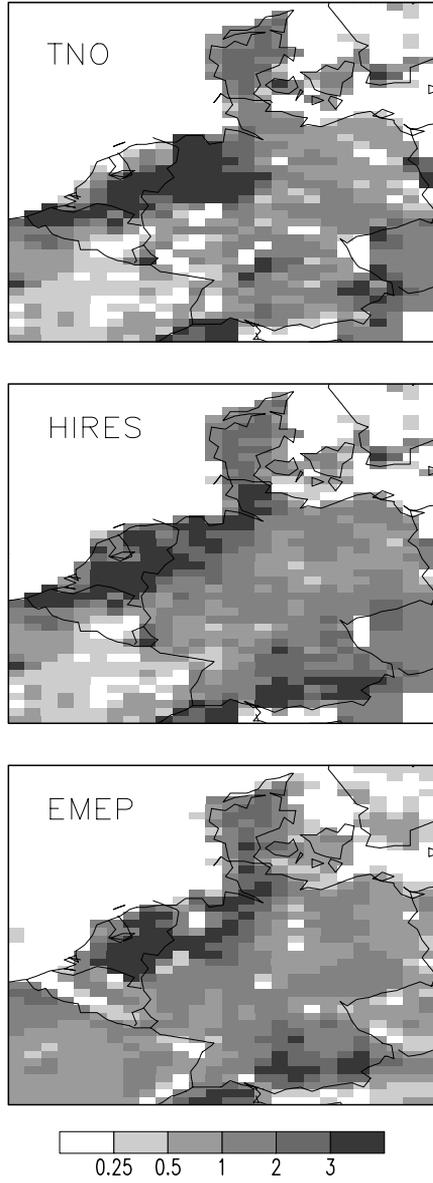
Figure 4.16 Ammonia emission distribution in north west Europe for several inventories (Tonnes/yr)

December

Aerosol nitrate concentrations above 3 µg/m3 are calculated in northern Italy and over most of north western and central Europe with all inventories. Highest levels (5 µg/m3 or more) are found in the Netherlands and the Po-valley. The EMEP inventory shows lower gradients in emissions and resulting nitrate concentrations than the TNO inventory, which is evidenced by the higher nitrate levels in the areas such as north eastern Spain, central France and western Poland, where TNO emissions are low. The EMEP inventory causes more pronounced maximum in the Po Valley and southern Germany, whereas the concentrations in southern Italy, Poland, England and Brittany are higher with the TNO inventory. In addition, the EMEP inventory results in lower concentrations in the Czech Republic.

In Germany, both the HIRES and the EMEP inventory result in a more pronounced maximum in southern Germany, caused by the higher emissions there. In addition, around Hamburg higher levels compared to TNO are observed. Both inventories cause lower concentrations in western Germany. Also, the HIRES inventory causes higher levels in the coastal areas of Germany and the Netherlands, which is not observed with the EMEP database. The differences in Danish nitrate levels are within 10%. Overall, the sensitivity of modelled nitrate concentrations to ammonia emission density shows an inverse relationship with the nitrate concentration, i.e. the sensitivity is highest in low nitrate areas.

Unfortunately, neither aerosol nitrate nor ammonia data are available in those areas with the highest discrepancies between the estimated ammonia emissions. Therefore, we compare the calculated concentrations of nitrate to observations from the Netherlands and Melpitz, Germany, in Table 4.10. Nitrate levels in December are slightly overestimated in the Netherlands, which is general feature of the model performance in this area, especially in summer (see Section 4.3.3). Although the differences between the modelled concentrations range up to 20 %, non of the inventories cause the modelled nitrate levels to be inconsistent with the measurements.

July

In contrast to the winter, high nitrate levels in summer are more local and confined to The Netherlands, England, Germany and the Alpine region. The high ambient temperatures and low relative humidity causes nitrate formation to be limited over large parts of Europe. Although the concentrations in December and July differ considerably, the relative sensitivity to the different inventories in July is only slightly larger than in December. The absolute differences on the other hand are (much) smaller in large parts of Europe due to the lower concentrations. The latter is illustrated for Melpitz in Table 4.10.
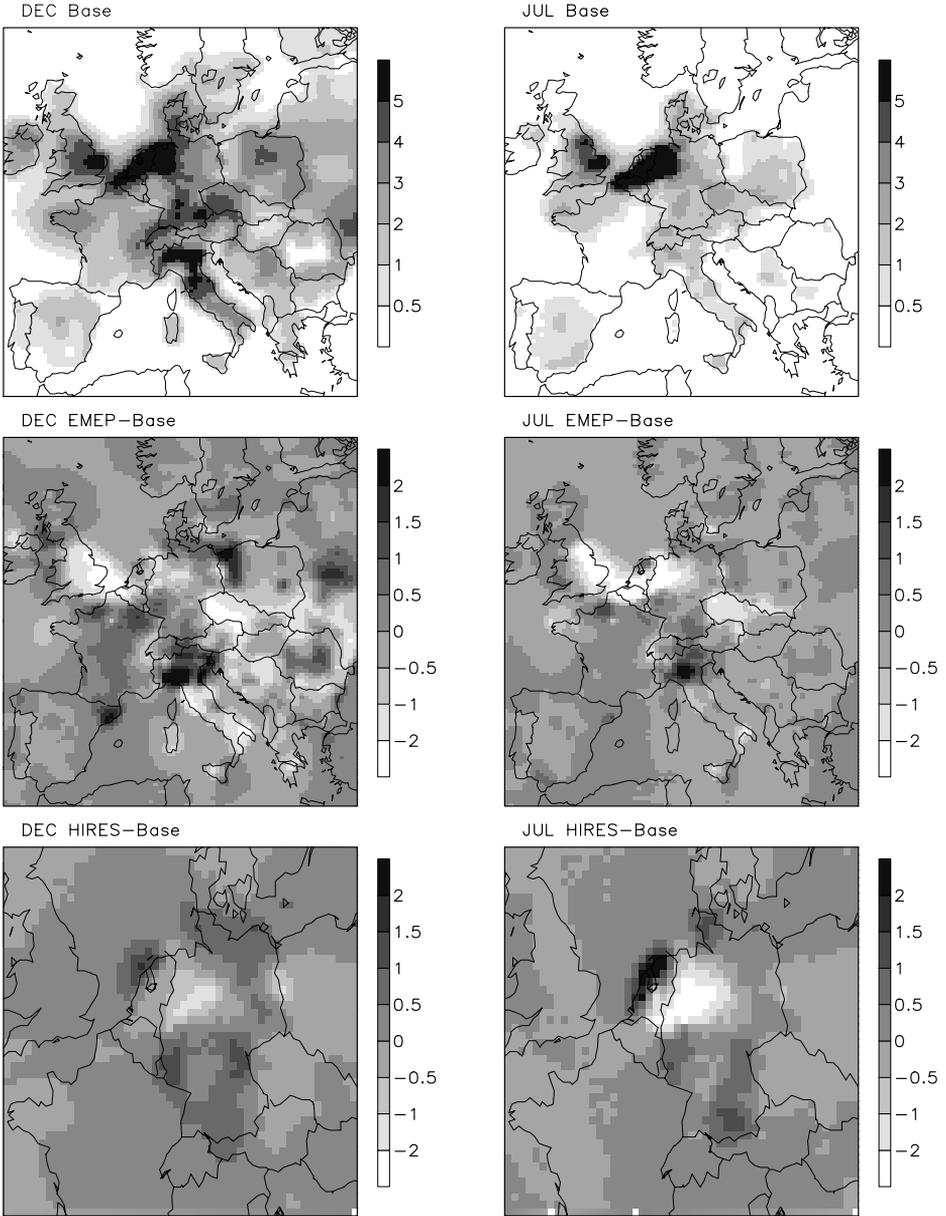
Figure 4.17 Aerosol nitrate distributions (µg/m³) (upper panel) and the absolute concentration change between the results with the TNO and the EMEP or HIRES ammonia inventories

Table 4.10 Comparison between modelled and measured nitrate concentrations for December and July, 1995.
Kolummmerwaard, De Zilk and Wieringerwerf are located along the Dutch coast.

December	Melpitz	Vredepeel	Kolummerwaard	De Zilk	Wieringerwerf
TNO	3.2	5.4	5.7	5.0	5.4
EMEP	3.6	4.9	5.6	4.3	5.6
HIRES	3.6	5.2	6.4	5.5	6.4
Measured	4.6	4.2	4.8	4.8	4.1
July	Melpitz	Vredepeel	Kolummerwaard	De Zilk	Wieringerwerf
TNO	1.9	12.5	3.1	3.7	2.9
EMEP	1.7	9.3	4.0	1.8	3.4
HIRES	2.0	10.9	5.5	5.3	5.3
Measured	1.5	7.1	4.3	-	5.3

Comparison with the measured data for the Netherlands shows that the differences between the modelled nitrate levels in July is much higher than in December. Using EMEP ammonia emissions generates the lowest concentrations at all stations, whereas the HIRES inventory causes highest levels at the coastal sites. Again, it is not possible to define the best model results based on one inventory due to the mixed performance at single stations.

Discussion

The model results show differences of 10-30% or more in areas with pronounced differences in ammonia emissions between the different databases. An inverse relationship between the nitrate levels and sensitivity towards ammonia emission/concentration is observed. The sensitivity is higher in summer than in winter due to the higher equilibrium constant at higher temperatures. Lowest sensitivity in the regions with high ammonia emissions is caused by a nitric acid limited nitrate production. Where ammonia is limiting the formation, ammonium nitrate is very sensitive to emission changes, but absolute differences are low. In marine areas the latter is the case. However, in these regions nitric acid is transferred from gaseous phase to sea salt aerosols, driving HCl out. Hence, nitrate is also present as sodium nitrate, complicating the analysis presented above.

Our previous simulations indicated that the nitric acid levels were too high in coastal areas. In the simulation with the HIRES database, ammonia emissions are higher in the coastal areas of the Netherlands and Germany. As a result, significantly more nitrate is in the aerosol phase, which lowers the overestimate of the nitric acid levels.
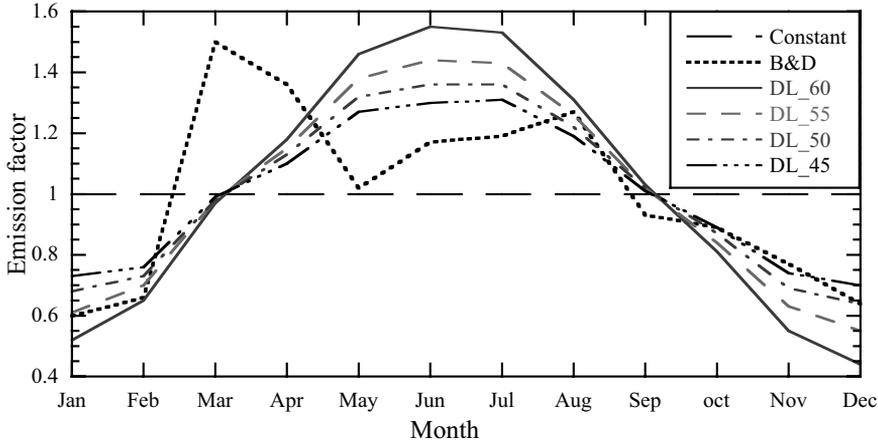
Figure 4.18 Monthly emission factors for ammonia: B&D (BD97) and as function of daylight hours(DL) at several latitudes(DC94)

Conclusions
- The different emission distributions cause modelled nitrate levels to vary up to 10-30%.
- The sensitivity to ammonia availability is inversely related to its absolute concentration
- It was not possible to define the best emission database by comparing model results with observations

Appendix B3. Sensitivity to seasonal variation of ammonia emissions

Introduction

The seasonal variation of ammonia emissions depends on timing of fertilizer application, livestock housing, agricultural practice as well as the dependence of ammonia volatilisation on temperature (Bouwman et al., 1997; Asman, 2001; Adams et al., 1999). Agricultural practice shows spatial variation and little is known about its effects on the temporal distribution of the European ammonia emissions, which caused several authors to neglect the seasonal emission variation (Asman, 2001; Hass et al., 2003).

Dentener and Crutzen (1994, further denoted as DC94), followed by Adams et al. (1999), weighted the ammonia emission by sunlight hours. Consequently, the seasonal cycle is a function of latitude. In Figure 4.18 we show the emission factor for 45°N to 60°N. In southern Europe the monthly emissions differ up to 30 % from the annual mean, which is much less than in northern Europe (~60%), where the number of daylight hours depends strongly on season. Adams et al. (2001) adjusted the seasonal cycle to find better agreement between modelled and measured concentrations at sites mainly located in the US. They derived a seasonal cycle proportional to the daylight hours to the fourth power, which would impose an even stronger seasonal cycle over emissions in Europe due to its higher location (not shown).

In our previous study (Chapter 4) we used a seasonal cycle for ammonia emissions representative for the Netherlands (Bogaard and Duijzer, 1997, further denoted as BD97), which corresponds well with that for Germany (Genemis project). The seasonal variation shows a distinct maximum in March and a slight maximum in August due to the application of manure on top of a function that roughly scales with daylight hours.

Comparison of the assumed seasonal variations reveals a large impact on the modelled ammonia emissions. Applying a seasonal cycle causes the emission in winter and summer to be lower and higher by 30-60 %, respectively, than by neglecting a seasonal cycle. The variations by DC94 and by BD97 compare well for fall and winter, but show differences up to 50 % for spring and summer since the increased emission after application of manure is not represented in DC94. The seasonal variations may impose larger differences in ammonia emissions than using different ammonia emission inventories and, hence, may have a larger influence on modelling results. Therefore, we addressed the influence of the seasonal emission variations for ammonia in three sensitivity simulations.

Description of the runs

We have recalculated the full year of 1995 using LOTOS version 5.2 with the three different seasonal variations described above. The base run includes the seasonal variation from BD97 in combination with the TNO emission inventory for ammonia (Builtjes et al., 2003). For these simulations we have reduced the model domain slightly to 40-62.5 N and 10W-30E. The reason is that there are no or very few monitoring stations in the excluded areas. Also, the computer time is significantly reduced (~40%). As a consequence, we could also address the influence of the domain size (see Appendix B4). The model output was generated for a measurement height of 2 m. Differences are studied in more detail by comparison with the measured nitrate data presented in Schaap et al. (2002), which were also used to evaluate our previous simulations (Chapter 4.3.3). Additional data for sulphate, ammonium and total ammonium were obtained from EMEP (EMEP, 1997). For comparison with observations 24-hour average concentrations were calculated from 06:00 to 06:00 GMT. The statistical parameters presented in Appendix A were used to address the model performance for the simulations over a full year.

Results

The statistical analysis of the annual model performance of all simulations is given in Table 4.11. Surprisingly, the annual averaged modelled concentrations do not differ much with the seasonal emission variation. Both the model to measured concentration ratios of nitrate and ammonium vary only 2%. For total nitrate and ammonium the differences are only 5%, with the highest model to measured concentration ratio and relative amplitude of the run without a seasonal variation. However, the correlation is on average somewhat higher in the other simulations. For single stations the differences between the runs range up to 14%, but are mostly about 5%.

Table 4.11 Annual model performance with different ammonia emission functions

	NO3			TNO3		
	Base	no cycle	daylight	Base	no cycle	daylight
av(mo)/av(me)	1.06	1.07	1.08	0.78	0.83	0.78
residual	2.67	2.59	2.58	1.47	1.44	1.48
RMSE	3.57	3.59	3.67	2.32	2.28	2.33
sigma (mo/me)	0.93	0.96	0.91	0.87	0.91	0.82
rho	0.58	0.58	0.55	0.52	0.55	0.52
% within factor 2	56.34	57.49	55.94	56.57	57.86	56.48
	NH4			TNH4		
	Base	no cycle	daylight	Base	no cycle	daylight
av(mo)/av(me)	1.04	1.06	1.05	0.87	0.91	0.86
residual	1.09	1.10	1.10	1.04	1.12	1.03
RMSE	1.55	1.56	1.57	1.53	1.62	1.50
sigma (mo/me)	0.89	0.91	0.88	0.76	0.80	0.74
rho	0.61	0.62	0.60	0.56	0.51	0.58
% within factor 2	66.97	67.44	66.59	65.80	63.42	65.96

In Figure 4.19 we show the weekly average nitrate concentration for the BD97 run divided by those computed without a seasonal cycle for several stations in Europe. At all these stations the concentration ratio follows the BD97 seasonal cycle. However, the ratio at the sites is very variable. The lowest ratios are observed for NL08 and GB14, which are located in high ammonia emission areas. There the sensitivity to the ammonia emission is higher during August than in spring, which can be attributed to the higher instability of ammonium nitrate at higher temperatures. The same tendency is observed for the other locations, except for PL02. Furthermore, at the other stations the sensitivity to the annual cycle is high, mostly in the range of 40-60%. For Birkeness, NO01, the sensitivity is large when polluted air masses are advected to the site. For clean air the sensitivity is negligible. Furthermore, the ratios vary considerable within a month as indicated by the high weekly variability. Thus, as the annual averaged differences are small the seasonal variation imposed by the ammonia emission cycle is large.

At most stations in Europe total nitrate is measured. Therefore, we compare the sensitivity for nitrate levels to that for total nitrate in Figure 4.20. In winter, the sensitivity of both parameters is most comparable. For example, at GB14 the response of total nitrate is only slightly lower then aerosol nitrate. At the more sensitive sites the difference is about 20% or less. In summer, however, the sensitivity of total nitrate is decoupled from that by nitrate at all the stations presented. Where the sensitivity of total nitrate is mostly 10-20 %, the sensitivity of nitrate is 40 -100%.
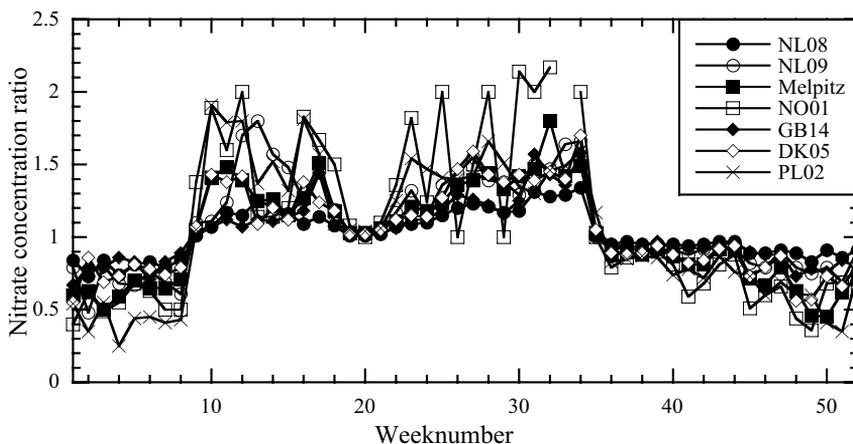
Figure 4.19 Ratio between the nitrate concentrations from the base case (BD97) and those obtained without seasonal emission function at several sites in Europe
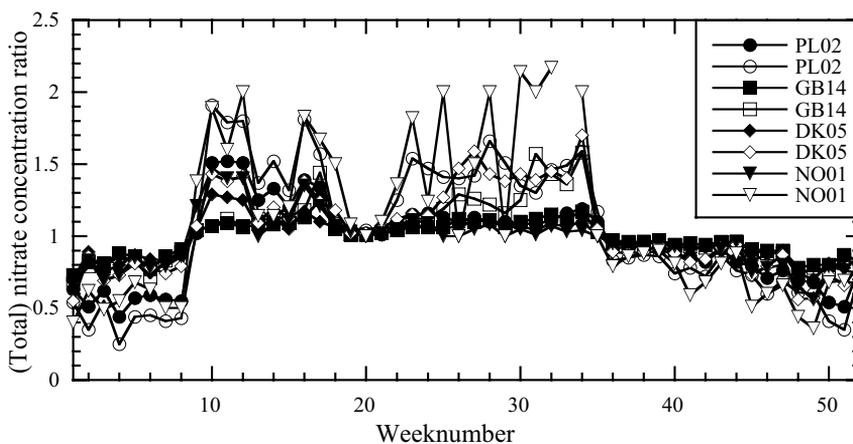
Figure 4.20 Ratio between the nitrate (open) ant total nitrate(closed) concentrations from the base case (BD97) and those obtained without seasonal emission function at several sites in Europe.

In Figure 4.21 we summarize the average model to measured concentration ratio for the four seasons. The ammonia emission functions show comparable factors in fall. Hence, the nitrate differences between the models are small, i.e. 17 % or less. The differences in ammonium levels correlate with those of nitrate. However, the relative changes are smaller than for nitrate since a large part of ammonium is associated with sulphate. As discussed in Section 4.2 ammonia concentrations are underestimated due to surface emissions, which are directly mixed over the boundary layer. As a consequence, underestimation of measured TNH4 is highest in summer, when the mixing layer is deep. In winter the boundary layer is shallow and the effect of the direct mixing is less pronounced and the underestimation of TNH4 is smallest. Moreover, without a seasonal cycle the TNH4 data are overestimated by 20-25%, which indicates that the ammonia emissions are too high,
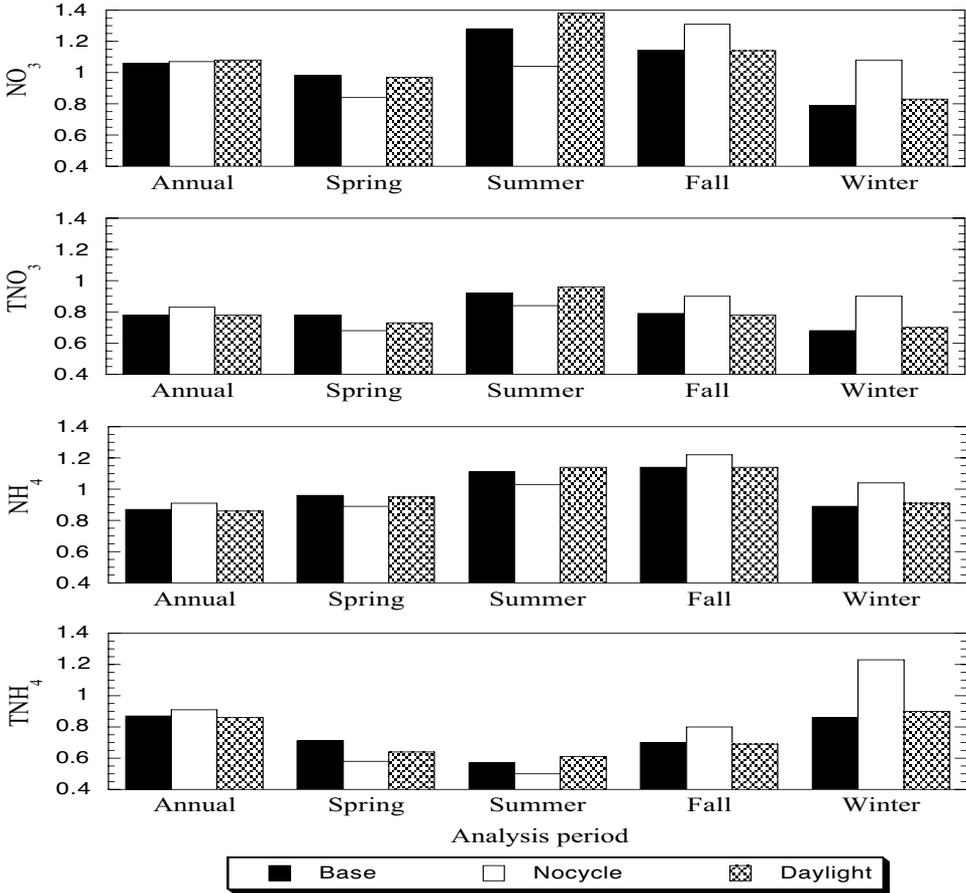
Figure 4.21 Comparison of the modelled to observed concentration ratio for the three scenarios as function of season

as we do not expect the modelled concentrations to exceed those measured. The runs with a seasonal variation give about 10-15 % lower TNH4 concentrations than those measured. However, the (total) nitrate concentrations on average compare much better with the measured values using no cycle. For spring, the comparison is least sensitive to the emission function. The average difference between the BD97 and DC94 functions is very small, whereas both are 20% higher than without a cycle.

Discussion

Considering only the average ratios of modelled to measured concentrations, the model performance of the run without a seasonal ammonia emission function seems to perform best. Without the seasonal emission function both the average (total) nitrate and total ammonia levels compare slightly better with observations than with a seasonal emission function. However, the differences are not significant. Moreover, the statistical analysis may be confusing since our model approach should underestimate the ammonia levels due

to the relatively coarse vertical resolution in summer. The overestimation of total ammonia throughout (northern) Europe indicates that the emissions in winter may be to high in the run without a seasonal variation. Therefore, the application of a seasonal cycle in northern Europe is advised.

The nitrate levels calculated with the different seasonal variations may differ by 50-100 percent. Seasonal averages show differences up to 40 % in summer. On the other hand, annually the average concentrations are mainly within 10 %. The comparison for regional models presented by Hass et al. (2003) has been performed for the summer half year. Therefore the emission function could be an important source for the (large) deviations found between the participating models. However, the total nitrate concentrations, which are less sensitive to the exact partitioning, also showed large differences between the different models. Hence, besides the chemical regimes effected by the ammonia emissions other sources for discrepancies exist.

The observed decoupling of the responses of total nitrate and aerosol nitrate in summer may be explained by the increased sensitivity of the nitrate partitioning at high temperatures. Total nitrate levels are only influenced by the net lifetime differences caused by a shift in the partitioning. When nitric acid concentrations are similar to those of aerosol nitrate, which occurs over large parts of Europe in summer, the latter is expected to be small. 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 from 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.

Conclusions
- Applying different seasonal variations of the ammonia emissions causes emission variations all over Europe of up to a factor of two for single months.
- The annual average model performances for (T)NO$_3$ and (T)NH$_4$ were only slightly influenced by the emission variation (< 10%), whereas on a monthly basis large differences ranging up to a 100% are found.
- Neglecting a seasonal variation results in an overestimation of ammonia emissions in winter.
- In summer the total nitrate response to changing ammonia emissions is much smaller than that of aerosol nitrate. This decoupling hampers the verification of model for aerosol nitrate.

Table 4.12 Comparison of model performance using the reduced domain (RD) to that with the full domain (FD). The statistical parameters are described in Appendix A.

	SO4		NO3		TNO3		NH4		TNH4	
	FD	RD	FD	RD	FD	RD	FD	RD	FD	RD
av(mo)/av(me)	0.92	0.81	1.10	1.06	0.81	0.78	1.08	1.04	0.88	0.87
residual	1.77	1.80	2.47	2.67	1.45	1.47	1.08	1.09	1.01	1.04
RMSE	2.60	2.61	3.57	3.57	2.31	2.32	1.54	1.55	1.50	1.53
sigma (mo/me)	0.99	1.00	0.91	0.93	0.85	0.87	0.86	0.89	0.66	0.76
rho	0.60	0.58	0.58	0.58	0.52	0.52	0.62	0.61	0.58	0.56
% within factor 2	65.4	64.4	56.9	56.3	57.6	56.6	68.8	67.0	68.3	65.8

Appendix B4. Sensitivity of the model performance to a reduced grid

Introduction

LOTOS is very well suited to perform a large number of sensitivity or scenario runs. However, also with LOTOS considerable reductions of CPU time can be achieved by a reduction of the domain, which is flexible. Here we show the sensitivity of the model performance using a run with a reduced grid as compared to our base study. The smaller domain focuses on north western Europe, which is studied most intensive with LOTOS.

Description of the run

For 1995 LOTOS version 5.2 (Section 4.2) was run with a smaller domain bounded between 40-62.5N and 10W-30E. The same boundary conditions were prescribed as for the full domain. The CPU time required for this run is about 40 % less than the original domain. The measurement stations used here are all located (just) within the reduced grid. The results for these stations were analysed following the procedures for the base case (Section 4.3.3).

Results

The model performance using the reduced grid is compared to our previous study (Section 4.3) in Table 4.12. The annual model performance of the runs, which only differ in domain size, is on average very similar. The differences in the model to measured concentration ratios differ up to 4%, with exception of sulphate. The ratio of the latter component is on average 10% lower than with the full grid. The larger sensitivity as compared to the other components is most likely due to the longer lifetime of sulphate in the atmosphere. In addition, the boundaries of the smaller domain were located in areas with low ammonia and nitrate concentrations. Therefore, the difference between the concentrations using the full domain and the boundary conditions are expected to be small, especially in case of clean air advected towards central Europe.

Conclusion
- The smaller domain which focuses on north western Europe does not significantly affect the model performance there, except for sulphate.

References

Adams, P.J., Seinfeld, J.H., Koch, D.M. (1999), Global concentrations of tropospheric sulphate, nitrate, and ammonium aerosol simulated in a general circulation model, J. Geophys. Res., 104 (D11), 13791-13823

Adams, P.J., Seinfeld, J.H., Koch, D.M., Mickley, L., Jacob, D. (2001), General circulation model assessment of direct radiative forcing by the sulphate-nitrate-ammonium-water inorganic aerosol system, J. Geophys. Res., 102 (D1), 1097-1111

Ansari, A.S., Pandis, S.N. (1998), Responce of Inorganic PM to Precursor Concentrations, Environ. Sci. Technol., 32, 2706-2714

Asman, W.A.H. (1992), Ammonia emissions in Europe: Updated emission and emission variations, RIVM-Report 228471008, RIVM, Bilthoven, the Netherlands

Asman W.A.H. (1998), Factors influencing local dry deposition of gases with special reference to ammonia, Atmos. Environ., 32, 415-421

Asman, W.A.H. (2001), Modelling the atmospheric transport and deposition of ammonia and ammonium: an overview with special reference to Denmark, Atmos. Environ., 35, 1969-1983

Asman, W.A.H., and Janssen, A.J. (1987), A long-range transport model for ammonia and ammonium for Europe, Atmos. Environ., 21, 2099-2119

Basset, M., and Seinfeld, J.H. (1983), Atmospheric equilibrium model of sulphate and nitrate aerosols, Atmos. Environ., 17, 2237-2252

Bogaard, A., and Duyzer, J. (1997), Een vergelijking tussen resultaten van metingen en berekeningen van de concentratie van ammoniak in de buienlucht op een schaal kleiner dan5 kilometer, TNO-report, TNO-MEP-R97/423, Apeldoorn, the Netherlands

Bouwman, A.F., Lee, D.S., Asman, W.A.H., Dentener, F.J., VanderHoek, K.W., Olivier, J.G.J. (1997), A global high-resolution emission inventory for ammonia, Global Biogeochemical Cycles, 11, 561-587

Builtjes P. J. H. (1992), The LOTOS - Long Term Ozone Simulation - project. Summary report. TNO-report, TNO-MW-R92/240

Builtjes, P.J.H., van Loon, M., Schaap, M., Teeuwisse, S., Visschedijnk, A.J.H., Bloos, J.P. (2003), Project on the modelling and verification of ozone reduction strategies: contribution of TNO-MEP, TNO-report, MEP-R2003/166, Apeldoorn, the Netherlands

Charlson, R.J., Schwartz, S.E., Hales, J.M., Cess, R.D., Coakley, J.A., Hansen , J.E., Hofmann, D.J. (1992), Climate forcing by anthropogenic aerosols, Science, 255, 423-430

De Leeuw, F.A.A.M., van Rheineck Leyssius, H.J., van den Hout, K.D., Diederen, H.S.M.A., Berens, M., Asman, W.A.H. (1988), RIVM Report 228471004, National Institute of Public Health and the Environment, Bilthoven, the Netherlands

Dentener, F.J, and Crutzen, P.J. (1993), Reaction of N2O5 on tropospheric aerosols: Impact on the global distributions of NO_x, O_3, and OH, J. Geophys. Res., 7149-7163

Dentener, F.J, and Crutzen, P.J. (1994), A three-dimensional model of the global ammonia cycle, J. Atmos. Chem., 19, 331-369

Eatough, N.L., McGregor, S., Lewis, E.A., Eatough, D.J., Huang, A.A. and Ellis, E.C. (1988), Comparison of sic denuder methods and a filter pack for the collection of ambient HNO_3 (g), HNO_2 (g) and SO_2 (g) in the 1985 NSMC study, Atmos. Environ., 22, 1601-1618

EMEP (1997), Data report 1995. Part 1: Annual summaries, EMEP/CCC-Report 4/97, NILU, Oslo, Norway

EMEP (1999), Data quality 1997, quality assurance, and field comparisons, EMEP/CCC-Report 6/99, NILU, Oslo, Norway

EMEP (2002), the WEBDAB database, www.emep.int

Erisman, J.W., Vermetten, A.W.M., Asman, W.A.H., Waijers-Ijpelaan, A., Slanina, J. (1988), Vertical distribution of gases and aerosols, the behavior of ammonia and related compounds in the lower atmosphere, Atmos. Environ., 22, 1153-1160

Erisman, J.W., van Pul, A., Wyers, P. (1994), Parametrization of surface-resistance for the quantification of atmospheric deposition of acidifying pollutants and ozone, Atmos. Environ., 28, 2595-2607

Gauger, Th., Anshelm, F., Schuster, H., Erisman, J.W., Vermeulen, A.T., Draaijers, G.P.J., Bleeker, A., Nagel, H. (2002), Mapping of ecosystem specific long-term trends in deposition loads and concentrations of air pollutants in Germany and their comparison with Critical Loads and Critical Levels, Part 1: Deposition Loads 1990-1999, UBA Report 299 42 210, Umweltbundesamt, Berlin, Germany

Guttorp, P. (1986), Models for transportation and deposition of atmospheric pollutants, http://www.stat.washington.edu/peter/498/transport/section3_5.html, University of Washington, Seattle

Hass, H., Builtjes, P.J.H., Simpson, D., Stern, R. (1997), Comparison of model results obtained with several European air quality models, Atmos. Environ., 31, 3259-3297

Hass, H., van Loon, M., Kessler, C., Stern, R., Matthijsen, J., Sauter, F., Zlatev, Z., Langner, J., Foltescu, V., Schaap, M. (2003), Aerosol Modelling: Results and Intercomparison from European Regional-scale Modelling Systems, Eurotrac publication in press, Eurotrac-ISS, Garmisch Partenkirchen, Germany

Haywood, J.M., and Boucher, O. (2000), Estimates of the direct and indirect radiative forcing due to troposheric aerosols: A review, Review of Geophysics, 38, 513-543

Haywood, J.M., and Shine, K.P. (1997), Multi-spectral calculations of the direct radiative forcing of tropospheric sulphate and soot aerosols using a column model, Q. J. R. Meteorol.Soc., 123, 1907-1930

Hering, S., and Cass, G. (1999), The magnitude of bias in the measurement of $PM_{2.5}$ arising from volatilisation of particulate nitrate from Teflon filters, J. Air & Waste Manage. Assoc., 49, 725-733

Heintzenberg, J., Müller, K., Birmili, W., Spindler, G., Wiedensohler, A. (1998), Mass related aerosol properties over the Leipzig Basin, J. Geophys. Res, 103, 13125-13135

Hutchings, N.J., Sommer, S.G., Andersen, J.M., Asman, W.A.H. (2001), A detailed ammonia inventory for denmark, Atmos. Environ., 35, 1959-1968

IPCC, Climate Change 2001: The Scientific Basis, Contribution of Working Group I to

the Third Assessment Report of the Intergovernmental Panel on Climate Change (IPCC), IPCC 2001

Jacob, D.J. (2000), Heterogeneous chemistry and tropospheric ozone, Atmospheric Environment, 34, 2131-2159

Jacobson, M.Z. (2001), Global direct radiative forcing due to multicomponent anthropogenic and natural aerosols, J. Geophys. Res., 196, 1551–1568

Janssen, A.J., and Asman, W.A.H. (1988), Effective removal parameters in long-range air pollution transport models, Atmospheric Environment, 22, 359-367

Jeuken A., Veefkind, J.P., Dentener, F., Metzger, S., Robles Gonzalez, C. (2001), Simulation of the aerosol optical depth over Europe for August 1997 and a comparison with observations, J. Geophys. Res., 106, 28295-28311

Kasibhatla, P., Chameides, W.L., John, J.S. (1997), A three-dimensional global model investigation of seasonal variations in the atmopheric burden of anthropogenic sulphate aerosols, J. Geophys. Res., 102, 3737-3759

Kerminen V.M., Hillamo, R., Teinila, K., Pakkanen, T., Allegrini, I., Sparapani, R. (2001), Ion balances of size-resolved tropospheric aerosol samples: implications for the acidity and atmospheric processing of aerosols, Atmos. Environ., 35 (31), 5255-5265

Kiehl, J.T., and Briegleb, B.P. (1993), The relative roles of sulphate and greenhouse gases in climate forcing, Science, 260, 311-314

Koepke, P., Hess, M., Schult, I., Shettle, E.P. (1997), Global aerosol data set, Max-Planck Institut für Meteorologie, Report No 243, Hamburg, Germany

Kouvarakis, G., Doukelis, Y., Mihalopoulos, N., Rapsomanikis, S., Sciare, J., Blumthaler, M. (2002), Chemical, physical, and optical characterization of aerosols during PAUR II experiment, J Geophys Res., 107(D18), 8141, doi:10.1029/2000JD000291

Matthews, E. (1984), Vegetation, land-use and seasonal albedo data sets: Documentation and archived data tape, NASA Tech. Memo, 86107

Meng, Z., and Seinfeld, J.H. (1996), Timescales to achieve atmospheric gas-aerosol equilibrium for volatile species, Atmos. Environ., 30, 2889-2900

Mentel, T.F., Sohn, M., Wahner, A. (1999), Nitrate effect in the heterogeneous hydrolysis of dinitrogen pentoxide on aqueous aerosols, Phys. Chem. Chem. Phys., 1, 5451-5457.

Metzger, S., Dentener, F.J., Pandis S.N., Lelieveld, J. (2002a), Gas/aerosol partitioning: 1. A computationally efficient model, J. Geophys. Res., 107, 0.1029/2001JD001102

Metzger, S.M., Dentener, F.J., Jeuken, A., Krol, M., Lelieveld, J. (2002b), Gas/aerosol partitioning II: Global modelling results, J Geophys. Res., 107, doi: 0.1029/2001JD001103

Mozurkewich, M. (1993), The dissociation constant of ammonium nitrate and its dependence on temperature, relative humidity and particle size, Atmos. Environ., 27A, 261-270

Nenes A., Pilinis, C., Pandis, S.N. (1998), Isorropia: A new thermodynamic model for multiphase multicomponent inorganic aerosols, Aquatic Geochemistry, 4, 123-152

Nijenhuis,W.A.S. and Groten, S.M.E (1999), Surface cover related input data for 3-D atmospheric-chemistry models, NRSP-2, Proj.4.1/DE-01

Perrino, C., M. Catrambone, A. Di Menno Di Bucchianico, I. Allegrini (2002), Gaseous ammonia in the urban area of Rome, Italy and its relationship with traffic emissions, Atmos. Environ., 36, 5385-5394

Poppe, D., Andersson-Skold, Y., Baart, A., Builtjes, P.J.H., Das, M., Diedler, F., Hov, O., Kirchner, F., Kuhn, M., Makar, P.A., Milford, J.B., Roemer, M.G.M., Ruhnke, R., Simpson, D., Stockwell, W.R., Strand, A., Vogel, B., Vogel, H. (1996), Gas-Phase Reactions in Atmospheric Chemistry and Transport Models: a Model Intercomparison, Eurotrac special publication, ISS, Garmisch-Partenkirchen, Germany

Putaud, J-P., Baltensperger, U., Erika Brüggemann, E., Facchini, M.C., Fuzzi, S., Gehrig, R., Hansson, H-C., Harrison, R.M., Jones, A.M., Laj, P., Maenhaut, W., Mihalopoulos, N., Müller, K., Palmgren, F., Querol, X., Rodriguez, S., Spindler, S., ten Brink, H.M., Tunved, P., Van Dingenen, R., Wehner, B., Weingartner, E., Wiedensohler, A., Wåhlin, P., Raes, F. (2003), A European Aerosol Phenomenology: physical and chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe, JRC-IES report, Http://ies.jrc.cec.eu.int/Download/cc

Riemer, N., Vogel, H., Schell, B., Ackermann, I., Kessler, C., Hass, H. (2003), Impact of the heterogeneous hydrolysis of N2O5 on chemistry and nitrate aerosol formation in the lower troposphere under photosmog conditions, J. Geophys. Res., 108(D4), 4144, doi:10.1029/2002JD002436.

RIVM (1997), Luchtkwaliteit. Jaaroverzicht 1995 (in English: Airquality. 1995 Results, RIVM Report 722101028, National Institute of Public Health and the Environment, Bilthoven, the Netherlands

Robles Gonzalez C., Veefkind, J.P., de Leeuw, G. (2000), Aerosol optical depth over Europe in August 1997 derived from ATSR-2 data, GRL, 27, 955-958

Robles-Gonzalez, C., Schaap, M., de Leeuw, G., Builtjes, P.J.H., van Loon, M. (2003), Spatial variation of aerosol properties derived from satellite observations, Atmos. Chem. Phys., 3, 1-13

Roelofs, G.J., Kasibhatla, P., Barrie, L., Bergmann, D., Bridgeman, C., Chin, M., Christensen, j., Easter, R., Feichter, J., Jeuken, A., Kjellstrom, E., Kock, D., Land, C., Lohmann, U., Rasch, P. (2001), Analysis of regional budgets of sulphur species modeled for the COSAM exercise, Tellus, 53B, 673-694

Roemer, M. (1995), The tropospheric budgets and trends of methane, carbon monoxide and ozone on a global scale. TNO-publication P95/035, Delft, The Netherlands

Roemer, M., Beekmann, M., Bergström, R., Boersen, G., Feldmann, H., Flatøy, F., Honore, C., Langner, J., Jonson, J.E., Matthijsen, J., Memmesheimer, M., Simpson, D., Smeets, P., Solberg, S., Stern, R., Stevenson, D., Zandveld, P., Zlatev, Z. (2003). Ozone trends according to ten dispersion models, Eurotrac publication in press, Eurotrac-ISS, Garmisch Partenkirchen, Germany

Schaap, M., Muller, K., ten Brink, H.M. (2001), Constructing the European aerosol nitrate concentration field from experimental data, ECN-report RX--01-033, ECN, Petten, the Netherlands

Schaap, M., Muller, K., ten Brink, H.M. (2002a), Constructing the European aerosol nitrate concentration field from quality analysed data, Atmos. Environ, 36, 1323-1335

Schaap, M., van Loon, M., Visschedijk, A., Dentener, F.J., Builtjes, P.J.H. (2002b), Modelling PM2.5 concentrations over Europe: the role of agriculture, Landbauforschung Völkenrode, Special Issue 235, 49-55

Schaap, M., van Loon, M., ten Brink, H.M., Dentener, F.J., Builtjes, P.J.H. (2003a), The nitrate aerosol field over Europe: a model sensitivity study, MS in preperation

Schaap, M., Spindler, G., Schulz, M., Acker, K., Maenhaut, W., Berner, A., Wieprecht, W., Streit, N., Müller, K., Brüggemann, E., Putaud, J-P., Puxbaum, H., Baltensperger, U., ten Brink, H.M. (2003b), Artefacts in the sampling of nitrate studied in the "INTERCOMP" campaigns of EUROTRAC-AEROSOL, Submited to Atmospheric Environment

Schulz, M., Van Beusekom, J., Bigalke, K., et al (1999), The atmospheric impact on fluxes of nitrogen, POPs and energy in the German Bight, Deutsche Hydrographische Zeitschrift, 51, 133-154

Tamm, S, and Schulz, M. (2002), open ocean aerosol composition obtained during 15 months on a North Sea ferry, submitted for publication to Atmospheric Environment

Tarrason, L., and Iversen, T. (1998), Modelling intercontinental transport of atmospheric sulphur in the northern hemisphere, Tellus B 50 (4), 331-352

Ten Brink, H.M, Kruisz, C., Kos, G.P.A., Berner, A. (1997), Composition/size of the light-scattering aerosol in the Netherlands, Atmospheric Environment, **31**, 3955-3962

Ten Brink H. M., Hensen, A., Khystov, A., van Dorland, R., Jeuken, A., van Velthoven, P., Lelieveld, J., van den Berg, A., Swart, D.P.J., Bergwerff, J.B., Apituley, A. (2001), Aerosol; cycle and influence on the radiation balance, Cluster-project in the National Research Program on Global Air Pollution and Climate Change, npr2, report no. 410200064

Ten Brink, H.M., and Schaap, M. (2002), Aerosol Nitrate, a Dominant Atmospheric Trace Component in Europe?!, Proceedings of the workshop: Air Pollution as a Climate Forcing, April 29-May 3, 2002, Honolulu, Hawaii, http://www.giss.nasa.gov/meetings/pollution02/d2/tenbrink.html, 2002.

Tie, X., Brasseur, G., Emmons, L., Horowitz, L., Kinnison, D. (2001), Effects of aerosols on tropospheric oxidants: A global model study, J. Geophys. Res., 106, 22931-22964

Thöni, L. Seitler, E., Schnyder, N., Künzli, B., Marti, S. (2000), Depositionsuntersuchungen im Kanton Zürich - Wallisellen: Resultate 1999, Wallisellen und Bachtel: Entwicklung über die Jahre. FUB-report, FUB, Rapperswill, Switzerland

TNO (2001), The CEPMEIP emission database, http://www.air.sk/tno/cepmeip

Tsyro, S. (2002), First estimates of the effect of aerosol dynamics in the calculation of PM10 and PM$_{2.5}$, EMEP report MSC-W Note 4/02, Norwegian Meteorological Institute, Oslo, Norway

Van der Hoek (1998), K.W., Estimating ammonia emission factors in Europe: Summary of the work of the UNECE ammonia expert panel, Atmos. Environ., 32, 315-316

Van Dorland, R., Dentener, F.J., Lelieveld, J. (1997), Radiative forcing due to tropospheric ozone and sulphate aerosols, J. Geophys. Res., 102 (D23), 28079-28100

Veefkind J. P., van der Hage, J.C.H., and ten Brink, H.M. (1996), Nephelometer derived

and directly measured aerosol optical depth of the atmospheric boundary layer, Atmos. Res., 41, 217-228

Verwer, J.G. (1994), Gauss-Seidel iteration for stiff ODEs from chemical kinetics. SIAM J. Sci. Comput., 15, 1243-1250

VROM (1996), Emissions in the Netherlands (In Dutch: Emissies in Nederland, Bedrijfsgroepen en regio's 1994 en ramingen 1995), Publikatiereeks Emissieregistratie, nr. 33, Ministerie VROM, The Hague, the Netherlands

West, J.J, Pilinis, C., Nenes, A., Pandis, S.N. (1998), Marginal direct climate forcing by atmospheric aerosols, Atmos, Environ., 32, 2531-2542

West, J.J, Ansari, A.S., Pandis, S.N. (1999), Marginal $PM_{2.5}$: Nonlinear Aerosol Mass Response to Sulphate Reductions in the Eastern United States, J. Air & Waste Manage. Assoc, 49, 1415-1424

Whitten G., Hogo, H., Killus, J. (1980), The Carbon Bond Mechanism for photochemical smog, Env. Sci. Techn. 14, 14690-700

Zhang Y., Seigneur, C., Seinfeld, J.H., Jacobson, M., Clegg, S.L., Binkowski, F.S. (2000), A comparative review of inorganic aerosol thermodynamic equilibrium modules: differences, and their likely causes, Atmospheric Environment, 34, 117

Zimmerling, R., Daemmgen, U., Behrens, U., 2000: Konzentrationen versauernd und eutrophierend wirkender Spurengase und Aerosol-Bestandteile in Nordost-Brandenburg. Landbauforschung Volkenrode, special issue 213, 43-93

5 Anthropogenic Fine Aerosol Distribution over Europe with special emphasis on primary PM2.5 and Black Carbon

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Abstract

Primary particles are an important component of fine aerosol mass over Europe. 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 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 µg/m^3 and lower in remote regions to more than 0.5 µg/m^3 in central Europe. Peak levels above 1 µg/m^3 are calculated over large urban areas. The BC concentration is about 25% of the total primary aerosol concentration. The primary aerosol fields were combined with previously calculated secondary aerosol concentrations to obtain an estimate of the anthropogenic fine aerosol distribution. Modelled BC levels contribute only 4-10% to the total fine aerosol mass, where sulphate and nitrate contribute 25-50% and 5-35%, respectively. Comparison with experimental data revealed that the model underestimates PM2.5 levels, caused by the underprediction of BC and additional primary material by about a factor of 2. The underestimate could be explained by (a combination) of local emissions, measurement uncertainties, representation of wet deposition. In addition, the uncertainties associated with the emission inventory play a role.

The black carbon emission inventories have evolved over the years leading to much lower emission estimates. However, using the most recent inventories the observed BC concentrations are severely underestimated. Unaccounted sources contribute at most 15 % to the total BC emission. Emission factors, most notably those for traffic, were identified as the cause of the largest uncertainty in the emission estimates.

5.1   Introduction

Atmospheric particulate matter (PM) is a complex mixture of anthropogenic and natural airborne particles. Particulate matter in ambient air has been associated consistently with excess mortality and morbidity in human populations (e.g., Dockery et al., 1993; Pope et al., 1995; Brunekreef, 1997; Hoek et al., 2002). Inhalation is the only route of exposure that is of concern in relation to the effects of PM on human health. Therefore, the European air quality standards currently focus on all particles smaller than 10 µm (PM10), which covers the inhalable size fraction of PM. Mass and composition of PM10 tend to divide into two principal groups: coarse particles, mostly larger than 2.5 µm in aerodynamic diameter, and fine particles, mostly smaller than 2.5 µm in aerodynamic diameter (PM2.5). The fine particles contain secondary aerosols, combustion particles and condensed organic and metal vapours. The larger particles usually contain sea salt, earth crust materials and fugitive dust from roads and industries (WHO, 2000). Although adverse health effects are associated with elevated levels of both PM10 and PM2.5, these health effects were most strongly and consistently associated with particles derived from fossil fuel combustion (e.g. Hoek et al. 2002), which mostly occur in the PM2.5 size range. Another reason to study PM2.5 rather than PM10 is that long range transport of aerosols also depends strongly on aerosol size.

Moreover, various components of fine particulate matter (PM2.5) in the atmosphere also have climate-forcing impacts, either contributing to or offsetting the warming effects of greenhouse gases (Kiehl and Briegleb, 1993; Hansen and Sato, 2001, Menon et al. 2002). In particular, black carbon (BC) has recently been identified as an important contributor to radiative heating of the atmosphere (Haywood et al., 1997; Myhre et al., 1998; Jacobson, 2001; 2002). Organic carbon (OC), which is often emitted along with BC, may act to offset some of the global warming impact of BC emissions (Hansen and Sato, 2001). In case of biomass burning aerosol, OC is thought to completely offset the warming potential of BC (Penner et al., 1998; Grant et al., 1999). However, for fossil fuel derived emissions this is not the case and a net positive forcing remains (Penner et al., 1998; Cooke et al., 1999). Control of fossil fuel black carbon may be a cost effective way to reduce global warming emissions (Jacobson, 2002) in conjunction with abatement of GHG emissions. So measures to abate climate-forcing by reducing BC emissions often would have collateral benefits by reducing emissions of health-related pollutants.

The main sources for carbonaceous aerosols are incomplete combustion of fossil fuel and biomass, and the oxidation of biogenic volatile organic compounds (VOC) (Seinfeld and Pandis, 1998). Carbonaceous aerosol is predominantly present in the sub-micron size fraction (Echalar et al., 1998; Cooke, et al., 1999). The global emissions of black carbon and organic carbon from fossil fuel burning has been estimated at 6 to 8 Tg/yr and 10 to 30 Tg/yr, respectively (Penner et al., 1993; Cooke and Wilson, 1996; Liousse, et al., 1996; Cooke, et al., 1999; Scholes and Andreae, 2000). However, recent studies by Bond et al. (1998, 2002), in which a different technique for the determination of black carbon emissions was used, suggest significantly lower emissions. The differences indicate that there is still a large uncertainty associated with emission estimates of carbonaceous

aerosols.

Most of the studies on primary aerosols have been performed with global models. However, satellite retrieved aerosol optical depth (AOD), a measure for the aerosol burden, over Europe shows a large spatial variation and strong gradients around industrialized areas, indicating the influence on AOD of local emissions of primary aerosols and/or precursor gases (Robles Gonzalez et al., 2000). Therefore, we expect that a model with a higher horizontal resolution is more suitable to assess aerosol fields and especially those of primary particles than global models.

In this paper we present a regional model study of the composition of anthropogenic-induced PM2.5 in Europe with special emphasis on the mass concentration of primary particles and more specifically BC. For this purpose we use a recent emission inventory of anthropogenic primary particulate matter in Europe (TNO, 2001), which is based on the fuels used in different anthropogenic activities. As BC is formed by the incomplete combustion from e.g. diesel engines, cooking fires and coal burning, a BC emission inventory can be derived from the PM inventory based on the fractions of BC in the respective (ultra) fine PM emissions (e.g. Cooke et al., 1999, Streets et al., 2001). The burdens of primary emitted particles over Europe are calculated with the LOTOS model (Builtjes, 1992; Schaap et al., 2003a). By combining these results with earlier calculations for the secondary aerosol components sulphate, nitrate and ammonium (Schaap et al., 2003a), estimates of PM2.5 levels over Europe are obtained. The consistency of the model calculations is checked with the observations at a number of European locations.

5.2   Emission data

Black Carbon (BC) is mostly released from incomplete combustion of carbonaceous fuels. We made an estimate of BC sources and their distributions over the Europe using the results of CEPMEIP (TNO, 2001), which is a spatially distributed pan-European inventory of anthropogenic PM emissions for the year 1995. Currently CEPMEIP covers nearly all of the relevant sources of primary anthropogenic TSP, PM10, PM4, PM2.5 and PM0.95 emissions, however, without chemical speciation. To derive an European BC emission inventory from CEPMEIP, the fraction of BC in PM2.5 for each of the source categories has to be attributed.

Streets et al. (2001) describe such an effort for China. These authors present a review study for BC emission factors from anthropogenic sources, in which also earlier work by Penner et al. (1993), Cooke and Wilson (1996) en Cooke et al. (1999) is discussed. We use the BC fractions from Streets et al. (2001) to estimate the BC emission from the sub-micron particle emissions in CEPMEIP. The BC fractions of the sub micron particles for different fuels, listed in Table 5.1, are almost exclusively based on western technology. Combining these data on SNAP level 2 results in a BC fraction of the PM2.5 emission. In this study, we followed the procedure for each country separately. The European BC emissions and averaged BC fractions of PM2.5 are given per major source category (SNAP level 1) in Table 5.2. The European total emission, excluding the Former Soviet Union (FSU), is 473 Gg/yr, excluding sea ships. The largest contributions are from transport followed by wood burning in house holds. Other important sources are industrial

Table 5.1 Black carbon fractions of PM0.95 emissions by fuel type used

SNAP[a]	Description	Solid fuels	Light liquid fuels	Medium/ heavy liquid fuels	Gaseous fuels	Waste/ biomass
1	Energy transformation	0.005	0.32	0.52	0.9	0.25
2	Small combustion sources	0.5	0.32	0.55	0.9	0.25
3	Industrial combustion	0.1	0.32		0.9	0.25
5	Extraction of fossil fuels				0.9	
7	Road transport	0.1	0.32	0.55	0.9	
8	Non road transport	0.1	0.32	0.55	0.9	
9	Waste handling and disposal					0.005
10	Agriculture					0.25

[a] *Selected Nomenclature Air Pollution*

combustion, energy transformation (especially with liquid fuels), gas flaring at oil platforms, agricultural waste burning and emissions from sea ships in international waters. The particle emissions have been gridded to the LOTOS grid. Area and point sources have been distinguished. For area sources, which the spatial patterns follow population density (majority of area sources), we used the CIESIN-NOAA high resolution gridded population data (NGCIA, 2000). Agricultural emissions are distributed according to animal populations by NUTS 3 regions (Eurostat,1998) and the distribution of arable land and pastures. International shipping emissions were distributed using the EMEP SO_2 ship emissions (EMEP, 2003). Large point sources (LPS) are distributed according to their exact location and characteristics (fuel types, capacities etc.). Point sources include large combustion plants, large industrial processes (steel, non-ferrous, cement etc.), waste combustors, refineries and off shore oil production platforms. Point source data has been updated to the reference year 1995 by means of a questionnaire. About 70% of all countries responded and for the remaining countries various literature sources have been used to update point source lists. The gridded emissions as input for the LOTOS model are shown in Figure 5.1.

The temporal variation of the emissions is broken down for each source category using a monthly factor. This value is divided by a factor for the day of the week (i.e. Monday, Tuesday etc.) and finally by a factor for the hour of the day (local time). The procedure was developed for ozone precursor emissions and is described by Builtjes et al. (2003).

Table 5.2 Particulate matter smaller than 2.5 μm from the CEPMEIP database, the source specific black carbon fractions and estimated black carbon emissions for anthropogenic activities in Europe excluding the former USSR.

SNAP[a]	Description	PM2.5 (Ktonnes)	Black Carbon emission (Ktonnes)	Derived Fraction Black Carbon of PM2.5[b]
1	Energy transformation	256	28	0.11
2	Small combustion sources	460	96	0.21
3	Industrial combustion	258	64	0.25
4	Industrial process emissions	197	0	0.00
5	Extraction of fossil fuels	36	30	0.85
6	Solvent and product use	81	0	0.00
7	Road transport	332	158	0.48
	• Gasoline	44	14	0.32
	• Diesel	262	144	0.55
	• Volatilisation losses	27	0	0.00
8	Non road transport	160	83	0.52
9	Waste handling and disposal	25	0.1	0.004
10	Agriculture	83	15	0.17
11	Nature[c]	n.e.	n.e.	n.e.
	Total	1889	473	
	International Shipping[d]		23	0.12

[a] *Selected Nomenclature Air Pollution* [b] *These fractions are the net result of a mix of activities and fuels within each category. The original calculations are based on the fractions presented in Table 5.1* [c] *n.e. = not estimated. The CEPMEIP database only considers anthropogenic sources* [d] *International sea going ships are not included in the inventory*

5.3   Model description

A chemistry transport model was applied to calculate the distribution of fine primary aerosol over Europe. For this purpose the LOTOS model (LOng Term Ozone Simulation) has been used. LOTOS has been applied for oxidant modelling (Builtjes, 1992; Hass et al., 1997) and for the calculation of secondary aerosol fields over Europe (Schaap et al., 2003a; Robles-Gonzalez et al., 2003). The geographical domain of LOTOS ranges from 10°W to 40°E and from 35°N to 70°N with a spatial resolution of 0.5x0.25 degrees lon-lat. The vertical domain is divided in three layers and extends to 3.5 km. The lowest layer represents the variable mixing layer on top of which two layers with equal, but variable, depth are located. Hence, due to the continuously changing mixing height, the grid volumes vary in space and time. The mixing height is part of the meteorological input for 1995, which is diagnostic and derived from ECMWF using procedures developed by the Free University of Berlin (Kerschbaumer and Reimer, 2003). Every hour, the mixing layer height is updated and the mass in the three layers is redistributed by mass conserving linear interpolation. The vertical coverage of the model is considered sufficient, since it has been shown that 80 to 90 % of the aerosol burden is located below 3 Km (Banic et al., 1996; ten Brink et al., 2001).

We assumed all BC and additional primary material (APPM) to be hydrophyllic direct after emission, thus wet and dry deposition are represented as for the highly soluble sulphate. All boundary conditions for BC were assumed to be zero. At the eastern boundary, however, the assumed boundary conditions and, hence, the model results are highly uncertain and we choose to present results only west of 30°E. For a full description of the model including the secondary inorganic aerosol formation we refer to Schaap et al. (2003a).

In this study we used LOTOS to calculate the distribution of primary emitted particles for the base year of 1995. The calculated distributions can be combined with previously calculated distributions of the inorganic species (Schaap et al., 2003a) to obtain an estimate for the total PM2.5 concentration field due to anthropogenic sources.
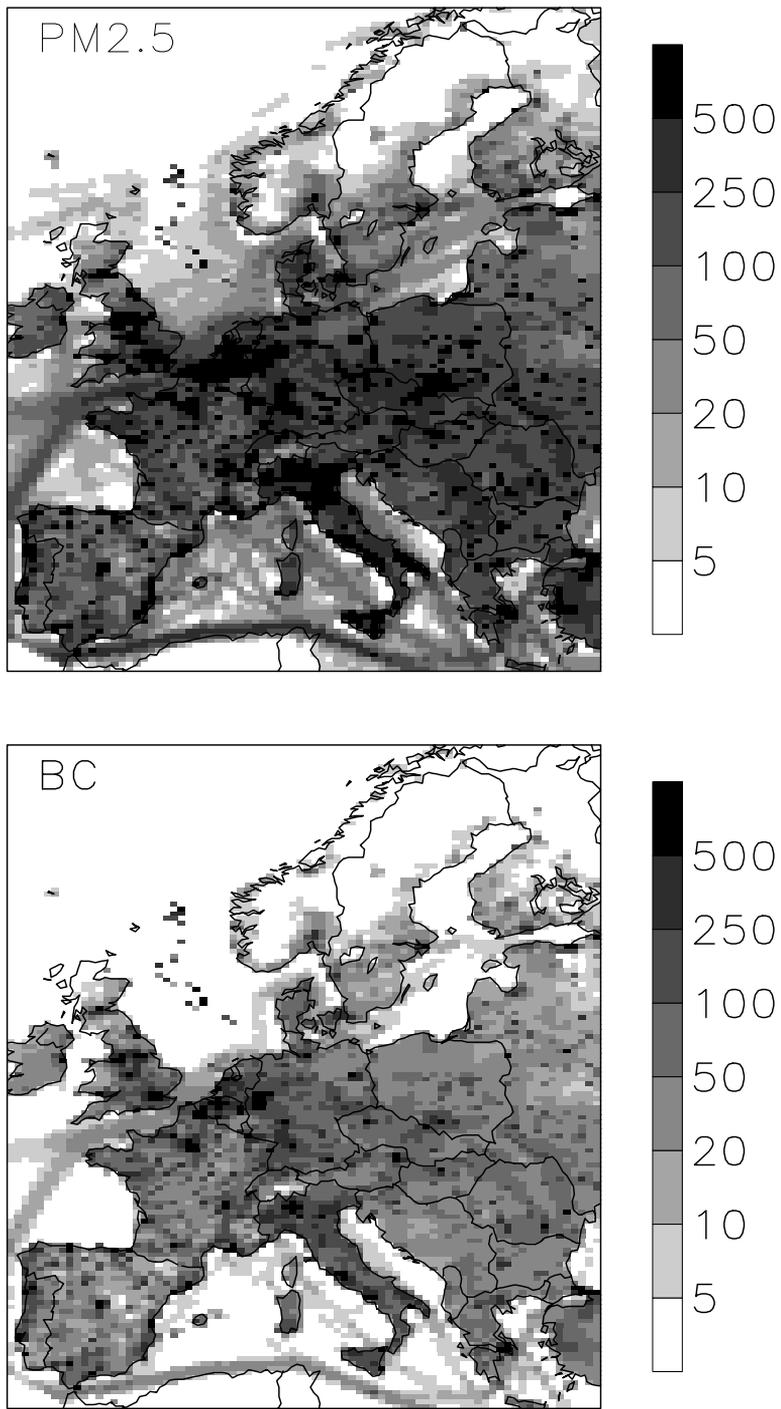
Figure 5.1 Emissions (Tonnes/yr) of PM$_{2.5}$ and black carbon for 1995

5.4   Results and preliminary discussion

5.4.1   Primary aerosol distribution

In Figure 5.2 the simulated annual averaged distribution of the total primary material and its black carbon content are presented for 1995. Annual averaged concentrations of primary material range up to 5 µg/m^3 over Europe. Areas with the highest concentrations are found in industrialised and/or densely populated regions, e.g. north western Europe, the Po valley and southern Poland. Secondary maxima can be identified over a number of large cities, such as London, Manchester, Athens, Madrid and Oslo. The local peaks over the North Sea can be explained by the emissions from oil platforms. Over more rural regions, which cover most of continental Europe, the levels of primary components are between 1 µg/m^3 and 2.5 µg/m^3. In Scandinavia concentrations trail off from about 1 µg/m^3 in the south to less then 0.25 µg/m3 over mid and northern Scandinavia. Important ship routes are mainly located near the European continent and, hence, the concentrations of primary particles trail of from the edges of the continent to the open sea due to dry and wet deposition.

The black carbon content of the primary aerosol shows a very similar distribution as the total primary components because the source categories with the highest PM emissions also have the highest BC fractions. In western Europe the black carbon levels are about one fifth of the total primary aerosol. Over eastern Europe the BC content is calculated to be slightly less. Modelled concentrations are lower than 50 ng/m^3 over remote regions such as the northern Scandinavia. In relatively clean areas over Spain and southern Scandinavia BC are about 250 ng/m^3 whereas the calculated BC concentrations exceed 500 ng/m^3 over central Europe and 1000 ng/m^3 in the densely populated areas.

5.4.2   Comparison with measured data

For 1995 monitoring data on BC (or EC) are not available. Therefore, we have compared our calculated BC concentrations with a number of studies as shown in Figure 5.3 and in Table 5.6. The data represent a period ranging from the end of the 1980s to 2001 and are often obtained in campaigns. The comparison shows that the simulated BC concentrations underestimated those measured by about a factor of 2. The relative underestimation is found to be rather constant for remote to rural sites (see Figure 5.3). This is an indication that the distribution of the concentrations and the main sources are well represented in the model, however, the absolute concentration is not. For urban sites the underestimation is larger, which can be explained by the high influence of local emissions.

Since we do not know the chemical speciation of the non-BC emissions (APPM) direct comparison with measurements is not possible. However, using the total PM2.5 concentrations and those of OC conclusions can be drawn on this part of PM, see below.
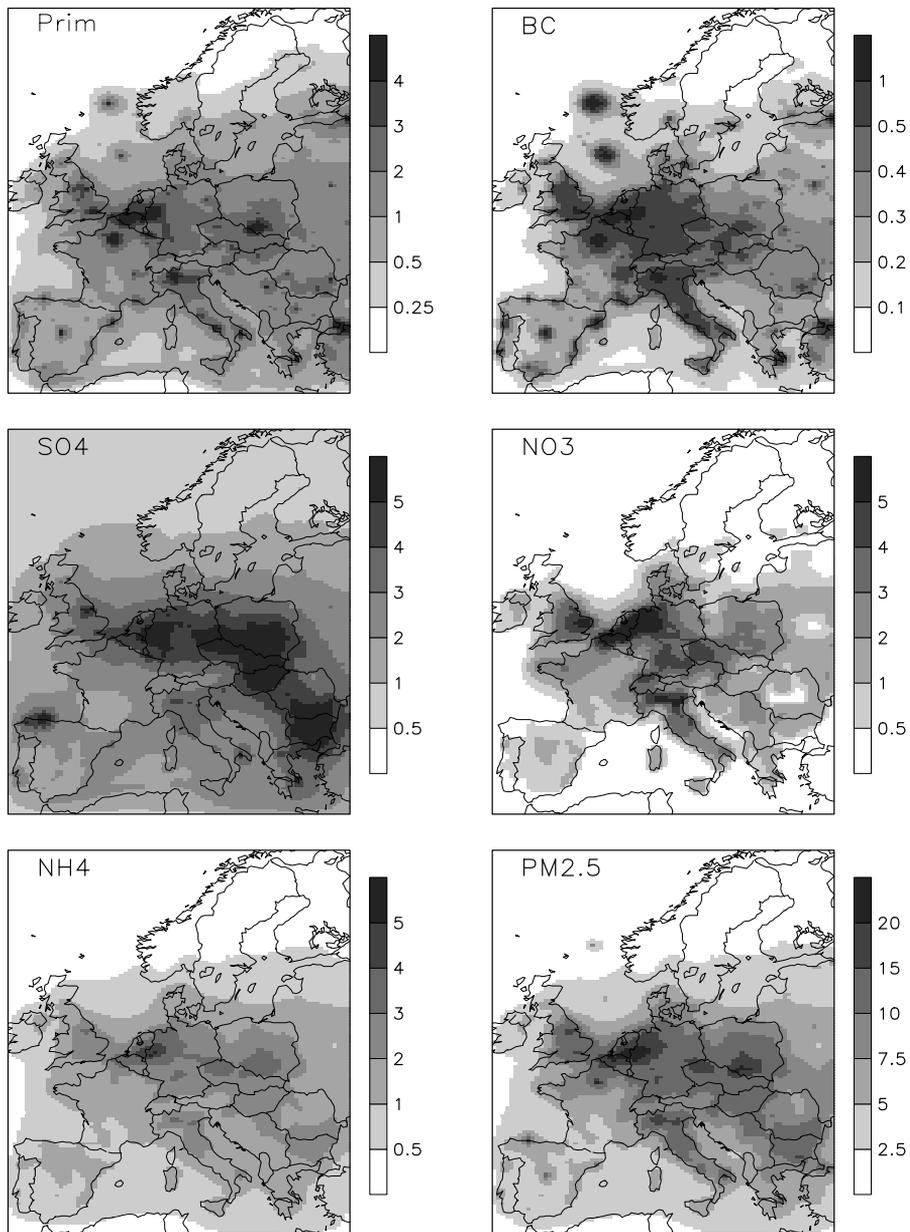
Figure 5.2 Annual average distribution of the indicated aerosol components (µg/m3)
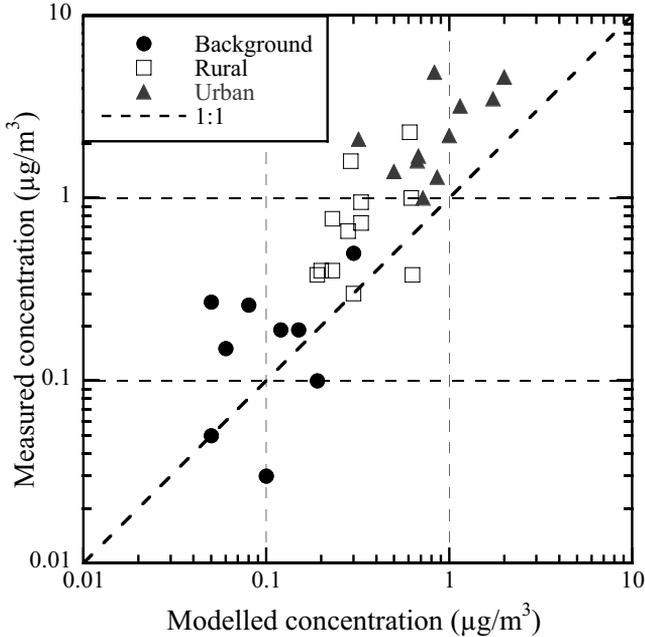
Figure 5.3 Comparison between modelled and measured BC concentrations at background, rural and urban locations

5.5   Fine aerosol distribution

5.5.1   PM2.5 distribution

To investigate the PM2.5 distribution over Europe we added to the primary particle simulations the fields of the inorganic components from Schaap et al. (2003a), shown in Figure 5.2 c, d and e. Sulphate contributes more than 3 µg/m^3 to PM2.5 over a region that spans from England, over north western Europe to south eastern Europe. Similar contributions are found in the Po valley and the north west of Spain. Maximum contributions are calculated in the Ruhr area, southern Poland, Hungary and Rumania and are markedly different from those of the primary aerosols. North of 57 N the annual averaged sulphate concentrations are lower than 2 µg/m^3, whereas those in more remote continental areas are between 2 and 3 µg/m^3.

High concentrations of nitrate are confined to continental areas, with maxima in north western Europe, the UK and the Po valley. Annual averaged nitrate concentrations are as high as those of sulphate in western Europe, whereas those of sulphate are higher in (south) eastern Europe and Scandinavia. In contrast to sulphate nitrate levels show a distinct seasonal variation. Maximum concentrations occur in winter, when ammonium nitrate is stabile. However, ammonium nitrate formation is limited during summer over the largest part of Europe due to high ambient temperatures. Sulphate and nitrate are neutralised by ammonium. Therefore, ammonium concentrations are significant and only

somewhat lower than those of its associated ions alone.

The sum of all modelled anthropogenic components of PM2.5 is shown in figure 5.2f. Highest concentrations of PM2.5 are found in the most industrialised and populated areas of Europe. Concentrations exceed 20 µg/m^3 over the south of the Netherlands, Belgium, the Ruhr area and southern Poland. Secondary maxima can be found in the Po valley, the Czech Republic and metropolitans of London, Manchester and Paris. Over central and south eastern Europe concentrations are calculated to range between 10 and 15 µg/m3. Towards the north the anthropogenic induced concentration of PM2.5 trails of from about 4 in southern Scandinavia to less than 2.5 µg/m^3 further north. Also, the rural areas in Spain and southern France are relatively clean with respect to anthropogenic PM2.5. As mentioned before, our simulation does not consider mineral dust, which is known to contribute strongly to PM in Spain (Rodriguez et al., 2002). Further, a number of cities can be recognised, e.g. Madrid, Barcelona and Athens.

5.5.2 Composition of PM$_{2.5}$

In figure 5.4 the relative contribution of the main components to the total fine aerosol mass is shown. Primary emitted particles (including BC) contribute 15 to 20 % of the total fine aerosol mass over continental Europe. This fraction is rather constant. Higher contributions (>30 %) are found in densely populated regions. For BC the contribution to PM2.5 ranges between 3 % and more than 10 %. Similar to the total primary contribution highest values occur over the most densely populated regions in Europe. The high values of BC over the North Sea are due to the presence of oil platforms there. The low relative contribution of BC over eastern Europe is striking; less than 4 %. The region where this applies coincides with the band of high sulphate concentrations. This minimum is only slightly visible in the contribution of total primary material and illustrates that the BC emissions are largely due to diffuse sources as traffic and off-road transport (e.g. river ships, trains) whereas the sulphur and, to a lesser extent, non-BC emissions have a large stationary point source component.

Sulphate contributes the largest calculated mass fraction to PM2.5 over Europe. Its contribution is about 30-35 % over most of continental Europe. The mass fraction increases towards more remote locations and is slightly lower in those areas where primary material and nitrate are important. The percentage of nitrate in PM2.5 over continental Europe is modelled to be 20 to 30 %. Contributions over 30 % are found in the regions with high ammonia emissions such as north western Europe and the Po valley. The nitrate contribution trails off from the coast towards the open sea, since in our model ammonia is rapidly deposited (Schaap et al., 2003a). In reality, the reaction of nitric acid with sea salt plays an important role by transferring nitrate from the fine to the coarse aerosol fraction (Vignati et al., 1999). Ammonium, which neutralises both sulphate and nitrate, contributes about 15 to 25 % to the fine aerosol mass; maxima in ammonium coincide with those of nitrate.
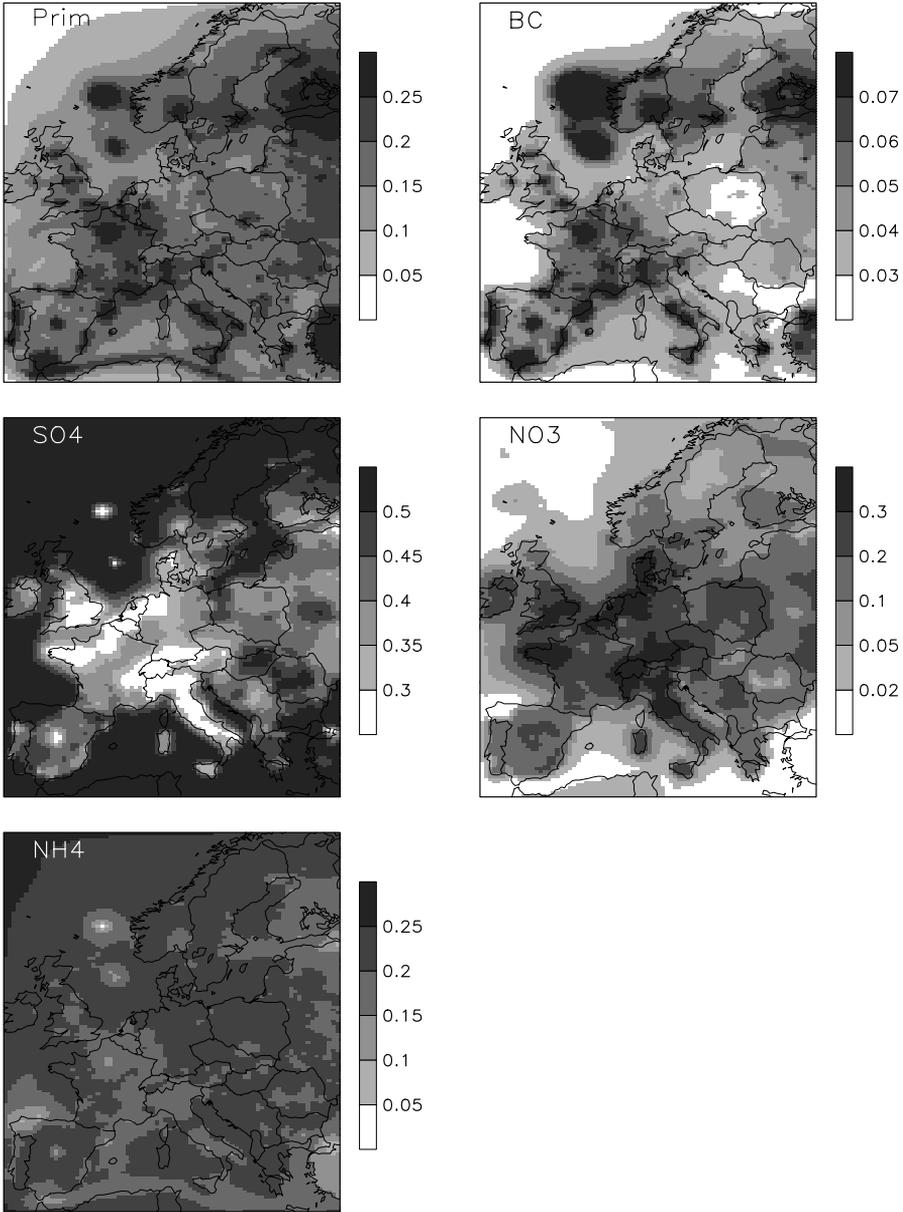
Figure 5.4 The relative contribution of different species to the modelled fine aerosol mass

5.5.3   *Comparison with measured data*

Before we compare our calculations to measured data we shortly discuss the uncertainties inherent to the sampling of PM and its composition. PM is mostly sampled using filters (Teflon, quartz, cellulose) or impactors. Several mechanisms may cause artefacts during sampling. Volatile compounds such as ammonium nitrate and a number of organic species may evaporate from inert filters (Chow, 1995). On the other hand, nitric acid or organic vapours may be adsorbed to the filter or previously collected material (Spicer and Schumacher, 1977; ten Brink et al., 2003). In case of nitrate artefacts are probably not significant during winter (Schaap et al., 2002; 2003b). However, evaporation from inert filters is thought to be significant at temperatures above 20 degrees Celsius (Hering and Cass, 1999; Schaap et al., 2003b). Such losses have not been observed for impactors (Hering and Cass, 1999). A field comparison for total carbon (the sum of OC and EC) at Melpitz showed differences between filter samplers of up to 20 % for a 10 day average (ten Brink et al., 2003). A similar range was found for the impactors although they recovered only 75 % of the TC measured on the filter samplers. The TC data agreed reasonably, however, its OC and EC content is difficult to determine. EC and BC are ideally both elemental carbon but are named according to their detection technique, thermal and optical respectively. Measured EC and BC concentrations showed differences up to a factor of three. As a consequence of these possible artefacts the determination of PM mass is associated with a rather large uncertainty.

In the analysis of the composition data part of the PM mass is unaccounted for. Putaud et al. (2003) suspect a large fraction of this gap to be water. This hypothesis is substantiated by data from Helsinki, where 5% of the ambient PM2.5 mass was found to be water (Pakkanen et al., 1999). Another part of the unaccounted mass may be due to the uncertainty in the conversion factor for the non-carbon atoms in organic carbon (Putaud et al., 2003).

Numerous studies have described measurements of aerosol composition in Europe. Very recently, a number of studies has been compiled by Putaud et al. (2003). The compilation contains data for sites at which the total particulate mass was available in combination with its chemical composition, including carbonaceous aerosols. In addition, we have compared our inorganic aerosol simulations to EMEP data (EMEP, 1997) and data compiled by Schaap et al. (2002) (Schaap et al., 2003a). We briefly summarize the main findings below. Since the EMEP data do not comprise carbonaceous aerosol and PM2.5 data, but contains a larger number of sites, the data sets should be used complementary.

The comparison of the modelled annual mean data against the compilation by Putaud et al. (2003) is shown in Table 5.6. Because sea salt and dust are not included in the model, this table also contains the measured PM2.5 concentration (PMcorr) corrected for their contributions. The model shows an increasing underestimation (listed as not modelled (NM)) with increasing PM levels. Hence, underestimation is largest at the kerbside stations. The chemical data allow us to address this increasing gap in more detail.

The secondary components compare rather well with observed data by Putaud et al. (2003). Comparison is best for sulphate showing a slight underestimation of the averaged sulphate levels by 12 %. Comparison with measured data from EMEP also revealed that the annual average modelled sulphate concentrations were slightly underestimated (6%). The correlation on a daily basis was on average reasonable (r = 0.58).

For nitrate the picture is more complicated. Except for Barcelona the modelled values are within a factor of 2 of the measured data (Putaud et al., 2003). The model overestimates the annual average concentrations at the Swiss sites (Zurich and Basel). However, independent data show annual average concentrations of 4.7 μg/m^3 for two sites in the Swiss valleys (Schaap et al., 2002). The difference may be explained by losses during sampling since inert filters were used in Zurich and Basel. The large underestimation in Barcelona, however, can not be explained by sampling artefacts. A plausible explanation is the formation of sodium or dust nitrate, which are the main nitrate compounds in this region in summer (Rodriguez et al., 2002). Comparison of the modelled nitrate concentrations to EMEP data showed that the modelled concentrations are on average 10 % too high. At single stations deviations of a factor of 2 were observed. Largest overestimation was found in the south of the Netherlands, where ammonia emissions are highest. For a detailed discussion on the comparison with measured data for nitrate, sulphate and ammonium we refer to Schaap et al. (2003a; Chapter 4).

The compilation by Putaud et al. (2003) also contains data on EC (=BC). The calculated BC concentrations are lower than those measured. Best agreement is found for the Belgian site Waasmunster, where the calculated value is within 10 % of the measured one. However, at the rural and near city stations the underestimation lies mostly about a factor of 2-3, consistent with the data presented in section 5.2. Underestimation is highest at the kerbside stations of Vienna and Bern, a factor of 9.

To address the non-BC emissions or additional primary PM (APPM) we compare the modelled APPM levels to those measured of OC. Biogenic secondary organic aerosols (BSOA, neglected in this study) cause the measured OC levels to be an upper estimate for primary OC. However, in polluted areas such as continental Europe the contribution of BSOA is probably negligible, as is anthropogenic SOA (Schell et al., 2001). In addition, although a majority of APPM is organic carbon it is not fully OC. Therefore we assume APPM to be an upper estimate for OC. The OC concentrations measured at the sites (Putaud et al., 2003) are underestimated in much the same way as BC. Hence, the same applies to the total primary particulate concentration as compared to the measured total carbon content.

The measured ratio of OC to BC ranges from 0.95 to 4.0. Surprisingly, at the three urban sites the ratio is very similar, 2.7 or 2.8. However, due to the large uncertainty in the BC levels this ratio is highly uncertain. Assuming APPM to be OC, the OC to BC emission ratio for the European countries as a whole is on average 3. This ratio for transport emissions is about 1, which indicates that in areas with large traffic emissions, e.g. cities, the ratio could be significantly lower than 3. Moreover, based on the emission estimates ratios down to 1 could be expected at sites where traffic emissions are dominant. Disregarding Barcelona, such a tendency is observed in the observations. Modelled and

measured ratios are between 2.5 and 2.8 at the urban sites. As expected for a regional model, at the kerbside stations similar ratios are simulated as for the urban background sites. In reality, APPM is not fully OC. However, we feel that the uncertainty present in the measured OC to BC ratios is much larger than that induced by the APPM=OC assumption.

Not all components of PM2.5 were determined for all sites. For instance for the Belgian sites, Waasmunster and Ghent, the nitrate, ammonium and OC contents of PM2.5 were not measured. The unaccounted fraction is therefore large at these stations. The modelled concentrations of these unaccounted species can largely fill the gap. For Ghent, the sum of the modelled fraction even exceeds the unaccounted fraction, which can be explained by an overestimation of the nitrate levels in this region (Schaap et al., 2003a). Modelling may provide a tool to assess the aerosol composition in regions without (complete) measurements as shown for this case.

5.6   Discussion

The comparison between modelled and measured BC concentrations strongly suggests that the model underestimates BC concentrations. Since the inorganic ions are simulated reasonably well (see also Schaap et al. (2003a) and discussion therein), it could be deduced that the underestimation of PM2.5 levels is mainly caused by primary carbonaceous particles. Therefore, the discussion here focuses on the gap between modelled and measured concentrations of primary carbonaceous components.

5.6.1   Comparison of modelled and measured concentrations

The BC data compiled in this study cover a large time span (1980s – 2001). Data from campaigns of only a few months may be influenced by the specific meteorological conditions prevailing during the campaign. In addition, inter annual variability and an expected decreasing trend in BC emissions (see below) may introduce variability and uncertainty in the model to measurement comparison. In addition, recent intercomparison tests show that BC measurements with different techniques are associated with an uncertainty of about a factor of 3 (ten Brink et al., 2003). However, the model results show often an underestimation of a factor of two or more for both older and more recent data than 1995, obtained with different techniques. EC/BC data may be systematically too high, e.g. due the charring (Schmid et al., 2001). However, total carbon concentrations, which are to be measured with a much higher accuracy (ten Brink et al., 2003), are also underestimated in much the same way. Since the measured and modelled BC to TC ratios are very similar, we conclude that the observation that the modelled BC values are too low appears to be robust and not obscured by the measurement uncertainties.

The modelled concentrations represent grid box average concentrations. The tendency for increasing deviation between the modelled and measured data going from rural to urban sites can be explained by the influence of local sources. It is therefore difficult to draw strong conclusions about the performance of the model, which predicts background concentrations, based on the measurements of PM2.5 and primary components (BC) in an

Table 5.3 Overview of black carbon emissions estimates for Europe and the former USSR

Year	Black Carbon (Tg yr^{-1})		Aerosol	Remark	Author
	Europe	Former USSR			
1980	3.80	5.60	Bulk	Based on BC/SO$_2$ ratio's	Penner et al. 1993
1980	2.14	1.93	Bulk	Based on emission factors and fuel use	Penner et al. 1993
1984	2.65	1.55	Bulk		Cooke and Wilson, 1996
1984	1.74	1.07	Bulk	Fossil fuel BC emission only	Cooke et al., 1999
1984	1.26	0.69	sub-micron	Fossil fuel BC emission only	Cooke et al., 1999
1996	0.44 (0.33-1.20)	0.36 (0.22-1.24)	sub-micron		Bond, 2002
1995	0.47 (0.23-0.70)	0.26 (0.12-0.40)	sub-micron	Only anthropogenic sources	This work

urban environment. Unfortunately, PM2.5 and BC measurements are mostly done in the urban environment. However, the modelled BC concentrations for the available back-ground sites and rural sites are also associated with a systematic underestimation of a factor of 2. The influence of local emissions is assumed to be small in these locations suggesting that the representativity of the stations also does not explain our finding that the modelled values are too low.

Uncertainties in the removal of BC may also affect our results. We assume BC to be hydrophyllic at the same time scale as our emissions are mixed in the model grid, e.g. up to a few hours. The ageing time scale is under scientific debate and ranges from hours (Kohler et al., 2001; Riemer et al., 2003) to 1.5 day (Cooke and Wilson, 1996, Wilson et al., 2001). Although in our model wet deposition is not very effective (Schaap et al., 2003a) and a longer ageing time scale will probably not yield significant different results, a more detailed study using explicit aerosol dynamics seems necessary to assess this ageing time scale under ambient conditions prevailing in Europe.

5.6.2   Emission data
Comparison with previous emission inventories

The black carbon emission data used here (Table 5.2) will be compared with emission estimates presented in previous studies (Table 5.3). The year for which the emissions have been estimated is an important variable in such a comparison because PM2.5 and associ-ated black carbon emission are expected to change considerably over time due to

Table 5.4 European BC emission (Ktonnes) based on a re-evaluation of the data from Cooke et a1(1999) for 1984 and an extension of the activity data to the year 1995.

Year	1984	1995	This study
C sector = combined traffic	299	401	241
D sector = domestic	637	295	96
I sector = industrial	510	347	137
Total	1446	1043	474

economical and technological changes. Furthermore, it is important to consider the aerosol size - bulk versus sub-micron aerosol -, which is covered by each emission inventory. This can be illustrated with the data from Cooke et al. (1999) for 1984 that indicate that about 70% of the bulk aerosol black carbon is in the sub-micron range. The contribution of the sub-micron range to the bulk aerosol has probably increased over time in Europe due to a further increase in air pollution control measures, which tend to capture coarse particles more efficiently.

The emission estimates in Table 5.3 suggest a strong decline of black carbon emissions between 1980 and 1995 for both Europe and the former Soviet Union (FSU). Emission estimates for Europe range from 2.1-3.8 Tg in 1980 (Penner et al., 1993) to 0.47 Tg in 1995 (This study). This decline is partly real due to technological improvements, air quality control measures and economical and political changes, most notably those in Eastern Europe and the USSR after 1989. For example, there is a strong trend in the FSU to the use of natural gas for power generation, which has reduced emissions, particularly in European Russia (Hill, 1997). However, the decrease of emissions over time has not been as dramatic as suggested in Table 5.3. The lower emission estimates are also caused by a more accurate assessment of the PM emitting activities in relation to their technological level, the resulting PM emissions and their fractional black carbon content. In the past such improvements resulted in revisions of inventories. For 1984 Cooke et al. (1999) revised the inventory of Cooke and Wilson (1996) resulting in a 30 % lower emission estimate.

Recently, Bond et al. (2002) presented a new bottom up BC emission inventory using the latest available emission factors. Their European emission estimate is very similar to our estimate. The range reported here is narrower than reported by Bond (2002) most likely because 1) the CEPMEIP database provides a relatively good insight in the technological level , which has a large impact on the resulting emissions, of different countries and facilities within a country and 2) Bond (2002) uses a different procedure for quantifying the uncertainty range (adding up the standard deviations for each source instead of the variances). The uncertainty range in our estimates of total BC emissions from Europe and FSU has been estimated from two components: the uncertainty in sub-micron particle emissions which has been assessed at ± 20% (Visschedijk, 2002) and the uncertainties in the BC fractions for the different fuel categories as reported in Table 5.1.

The more recent estimates (Bond et al. (2002) and this study) compare very well, but are more than a factor of 2 lower than the previous estimates. These estimates are not

necessarily in contradiction with each other since the uncertainty of the previously reported data is at least a factor of 2 (e.g., Liousse et al., 1996, Cooke et al., 1999). However, our model results and those obtained with the Bond et al. (2002) inventory both underpredict the observed BC concentrations (see also Table 5.7) whereas the results from studies using the older emission estimates as model input agreed better with observations (Cooke et al., 1999; Jacobson, 2001; Chung and Seinfeld, 2003). Are the older inventories better than the present ones and if not, why do these older emission estimates than result in more realistic simulation results?

   The current emission inventories (this study and Bond (2002)) are bottom-up inventories using the relatively good insight in PM2.5 emissions to derive BC emissions. The BC emissions can be derived using the available data on the BC fraction of combustion-derived PM because we have knowledge on fuel types used in different sectors and activities. It is important to realize that this is the proper way to derive the BC emissions because the fuel type and the way it is consumed are causal factors in the process of BC production and subsequent emission. Hence, we are confident that the approach taken in the current emission inventories is an improvement. Then, why do older inventories produce a better match with observational data? A part of the discrepancy may be explained by the year of study. We revisited the data of Cooke et al. (1999) for 1984 and extended the emission inventory to 1995 by using activity data for 1995 in combination with the original emission factors by Cooke et al. (Table 5.4). The revisited emission inventory for 1984 (1.44 Tg yr^{-1}) is somewhat higher than the original figure (1.26 Tg yr^{-1}) by Cooke et al. (1999). These differences can be attributed to corrections of small errors and improvements of the activity data. More important, by changing the activity data only the estimated BC emission decreases about 30% in ~10 years. The emissions from domestic sources and industrial sources decrease significantly but this is partly compensated by the increase of especially the transport and traffic sections (Table 5.4). Since, the emission changes between 1984 and 1995 are due to changing activities only, the improved knowledge on emission factors is crucial to explain the difference between the extrapolated (1.04 Tg) and our estimate (0.47 Tg), which is still a factor of two.

Traffic emissions

   Bond et al. (2002) suggested two major reasons for underprediction of BC emissions: fuel use and emission factors. Underreporting of fuel use may occur when a portion of the fuel supply (e.g. wood or coal) does not pass through official channels, or when some "fuels" are not considered at all (e.g. house fires, waste paper). Emission factors may be underestimated if measurements come from better technology or more careful practice than the average. Increased emission factors might be associated with transient operation, poor-quality or adulterated fuels, or badly maintained units. These factors are of particular interest for the traffic emissions. It should be realised that the emission factors for traffic used in earlier studies (Kohler et al., 2001; Cooke et al., 1999) are very crude. In fact, two emission factors are used: 2 en 10 gC / kg for diesel for OECD and non OECD countries respectively. In reality a range of emission factors are present without sharp differences related to technology, age of the motors used as well as maintenance. Such a crude

separation causes large uncertainties in the emissions from traffic on a regional perspective.

There are presently various sets of PM emission factors for mobile sources e.g., for the Netherlands (VROM, 2002), Germany (INFRAS, 1999) or Europe (Ntziachristos and Samaras, 1999). The proposed emission factors are influenced by e.g. sampling strategies, definitions of standard driving cycles, assumed effect of motor aging and may differ substantially for some source categories such as diesel-fuelled vehicles. In the CEPMEIP inventory (TNO, 2001) emission factors for diesel-fuelled vehicles were taken from the German inventory (INFRAS, 1999), whereas the Dutch emission factors (VROM, 2002) were taken for all other vehicles. The results were found to be in line with the COPERT estimates for country totals (Ntziachristos and Samaras, 1999) and IIASA model results (T. Pulles, 2003, personal communication). The selected emission factors are not necessarily the most representative. By applying the different emission factors the uncertainty surrounding the estimate for total traffic-related PM emissions was found to amount to a factor of ~2. Furthermore, the contribution of gasoline vehicles to daily PM levels may be substantial especially due to cold starts (Watson et al., 1998), suggesting that PM emissions due to gasoline vehicles may be underestimated. In general, it can be concluded that the emission factor methodologies need to be harmonized and further validated to come to an accurate and consistent European set of emission factors for traffic, which is however outside the scope of the present paper.

Unaccounted sources

A possible underestimation of the traffic BC emissions is caused by the PM2.5 particle emissions and not their BC fraction. Although traffic is a major source of primary particles, there are more uncertainties in the PM2.5 emissions. In Table 5.5 we present emission estimates for the US (Battye et al., 2002) from sources that are not present in the CEPMEIP database. The most important source missing in CEPMEIP is fugitive dust accounting 43 % of the total emissions in the US. Although these emissions are difficult to extrapolate to Europe due to different road and climatic conditions, it indicates that the European PM2.5 emission may be underestimated significantly, especially in southern Europe where climatic conditions compare best with the US. The most important missing industrial source is metal processing which contributes only 2 % of the total fine particle emissions in the US. For BC, these missing sources contribute only 7-11 % of the total US emission and are, therefore, not likely to explain a large underestimation of the European BC emissions.

In addition, the emissions from (controlled) vegetation fires are unaccounted for. Prescribed and/or intentional burning of grasslands and forest does not or hardly occur in Europe and is not considered in our black carbon emission inventory. Burning of agricultural residue has been considered although its importance has rapidly decreased in recent years due to policies to ban residue burning. On the other hand, accidental or lightning-ignited fires may cause an underestimation of the BC emissions in Europe. In the US these emissions are thought to be about 8 % of the total emission (Battey et al., 2002). Lavoue et al. (2000) estimated the European emissions from wildfires to be 0.01 Tg in

Table 5.5 Relative contribution of sources not included in Table 5.2 to reported US PM$_{2.5}$ emissions, BC to PM$_{2.5}$ ratio for these sources and derived relative contribution to total estimated US Black carbon emissions (recalculated from Battye et al., 2002).

Category	Percentage of reported US PM$_{2.5}$ emissions[a]	BC to PM$_{2.5}$ ratio		Percentage of total estimated BC emissions	
		Best estimate	High estimate	Best estimate[b]	High estimate[b]
Industrial - metals processing	1.6%	0.1	0.3	2.1%	3.9%
Industrial - asphalt manufacture	0.1%			0.0%	0.6%
Rubber and plastics products	0.0%			0.0%	0.3%
Fugitive dust - unpaved roads	21.8%	0.01	0.019	2.8%	3.3%
Fugitive dust - paved roads	10.5%	0.017	0.028	2.5%	2.3%
Fugitive dust - construction	6.0%		0.005	0.0%	0.3%
Fugitive dust - other	2.3%	0.006	0.013	0.2%	0.3%
Total relative contribution of the above sources to reported US emissions	42.3%			7.6%	10.9%
Wildfires	3.6%	0.072	0.12	3.5%	3.4%
Prescribed forest burning	8.1%	0.072	0.12	7.9%	7.7%

a) Total reported US PM2.5 emissions is 5894 Ktonnes/yr (Battye et al., 2002) b) Best estimate BC emissions 433 Ktonnes/yr, high estimate BC emissions 727 Ktonnes/yr (Battye et al.,2002)

1995. The annual and seasonal variation in wild fire emissions is large (Schultz, 2003, Lavoue et al., 2000) and the contribution may be 2 to 3 times higher in other years. The majority of the emissions occur in southern Europe, where the influence may be significant during specific episodes with forest fires. However, for Europe as a whole the contribution of wild fires to the BC emissions is small (2 - 5 %).

The unaccounted sources may contribute largely to PM2.5 emissions but probably less than 15 % to the European BC emissions. We therefore conclude that the traffic emission factors are associated with the highest uncertainty and need to be further addressed in the future.

5.7 Conclusions and recommendations

We presented a model study dedicated to European PM2.5 levels with special attention to primary emitted particles including BC. We used the PM emissions from CEPEIP (TNO, 2001) and combined those with estimated BC fractions to derive a European BC emission inventory on 0.5-0.25° 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.

Calculated distributions of primary particles were combined with those previously calculated for secondary inorganic components. Sulphate was found to contribute most to the total PM2.5 mass, followed by nitrate and total primary material. The BC content of PM2.5 was estimated to range between 4-10%. The modelled PM2.5 concentrations underestimate measured concentrations, especially as compared with urban stations. The gap between modelled and measured PM2.5 concentrations appears to be strongly correlated with the primary carbonaceous particles. BC concentrations on background and rural locations are often underestimated by a factor of 2.

The underestimation may be explained by several factors. Local emissions cause an underestimation of primary pollutants in the source regions but not in remote locations. The representation of the ageing process may cause an unknown underestimation at remote locations, although it is unlikely to be a factor of 2. Unaccounted sources are estimated to cause a maximum underestimation of the BC emissions of 15 %. The most important uncertainty is still associated with the emission factors. The black carbon emission inventories have evolved over the years leading to much lower emission estimates. However, using the most more recent inventories the observed BC concentrations are severely underestimated.

At this moment we cannot conclude with certainty that we underestimate the emissions of BC in Europe, because the underestimation may be explained by a number of other factors. However, since the most important and uncertain source of BC is traffic, better emissions estimates for traffic are urgently needed.

Appendix

Table 5.6 Comparison of simulated and measured PM2.5 concentrations and its composition. PM2.5cor gives the comparison of PM2.5 correct for mineral dust and sea salt. Modelled non-BC primary material is assumed to be fully OC. The observed unaccounted mass (UA) is compared to those model components that were not determined in the measurements. NM is the difference between the PM2.5cor and modelled PM2.5. Observational data from Putaud et al. (2003). B = Background, R =Rural, U = Urban, K = Kerbside, MD = Mineral dust, SS = Sea Salt, UA = Unaccounted

Cat.	Site (Country)		$PM_{2.5}$	MD	SS	SO4	NH4	NO3	OC	BC	UA	PM2.5cor	NM
B	Sevettijarvi (F)	Obs	3.41	0.15	0.46	1.29	0.15	0.02	-	0.23	1.12	2.80	
		Sim		-	-	0.54	0.22	0.09	0.09	0.03	0.09	0.97	1.83
B	Skreadalen (N)	Obs	5.05	0.18	0.29	1.28	-	-	-	0.48	2.33	4.58	
		Sim		-	-	1.32	0.56	0.26	0.29	0.15	1.11	2.58	2.0
B	Birkenes (N)	Obs	4.66	0.25	0.34	1.61	-	-	-	0.52	1.59	4.07	
		Sim		-	-	1.42	0.61	0.34	0.38	0.18	1.33	2.93	1.14
R	Illmitz (A)	Obs	19.94	0.26	0.11	3.97	2.04	2.28	5.49	1.66	4.12	19.56	
		Sim		-	-	3.98	2.6	3.81	2.65	0.83	-	13.87	5.69
R	Waasmunster (B)	Obs	25.58	0.98	1.13	5.04	-	-	-	1.42	15.12	23.48	
		Sim		-	-	4.84	3.84	6.96	3.92	1.38	14.72	20.94	2.54
R	Melpitz (D)	Obs	16.85	1.80	-	2.69	1.99	3.43	-	-	10.83	15.04	
		Sim		-	-	5.34	2.99	3.64	1.59	0.58	2.15	14.14	0.90
U	Zuerich (CH)	Obs	18.98	1.18	0.17	3.27	1.84	2.68	4.44	1.66	3.60	17.63	
		Sim		-	-	2.72	2.27	4.28	1.77	0.65	-	11.69	5.98
U	Basel (CH)	Obs	17.85	1.40	0.25	3.80	1.83	2.47	4.21	1.54	2.57	16.21	
		Sim		-	-	2.84	2.41	4.58	1.87	0.7	-	12.40	3.81
U	Gent (B)	Obs	26.39	1.05	1.31	6.17	-	-	-	1.83	13.70	24.02	
		Sim		-	-	4.87	3.85	6.94	4.52	1.24	15.31	21.42	2.60
U	Bologna (I)	Obs	35.82	2.89	0.84	4.62	4.12	8.54	8.24	2.91	7.55	32.10	
		Sim		-	-	3.55	2.74	4.89	1.98	0.80	-	13.96	18.1
K	Barcelona (E)	Obs	34.61	3.79	0.81	5.60	3.31	4.27	11.89	2.98	1.96	30.01	
		Sim		-	-	3.61	1.19	0.27	3.44	1.76	-	10.27	19.7
K	Bern (CH)	Obs	22.65	1.35	0.21	2.67	1.40	2.32	6.68	3.95	4.07	21.09	
		Sim		-	-	2.43	1.94	3.52	1.36	0.49	-	9.74	11.3
K	Wien (A)	Obs	38.51	2.37	0.41	4.44	2.18	3.57	8.62	9.10	7.84	35.74	
		Sim		-	-	4.2	2.53	3.34	1.72	0.53	-	12.32	23.4

Table 5.7 Comparison of simulated and observed BC concentrations (μg/m³). For Mace head and South Uist the range of measured data is tabulated

Site	Lon	Lat	Period	Sim.	Obs.	Reference
Background						
Mace Head	-9.5	53.2	Jul-Aug	0.10	0.03	Krivacsy et al., 2001
Mace Head	-9.5	53.2	Year	0.09	0.05-1.0	Derwent et al., 2001
Hyytiala	24.3	61,9	Jun	0.15	0.19	Alves et al., 2002
South Uist	-7	57	Winter	0.06	0.02-0.33	Loew et al. 1996
South Uist	-7	57	Summer	0.05	0.03-0.08	Loew et al. 1996
Finokalia	25.6	35.2	May	0.09	0.26	Kouvarakis et al., 2002
Prasses	25.1	35.2	May	0.13	0.19	Kouvarakis et al., 2002
Aspvreten	17.4	58.8	Jun-Jul	0.15	0.10	Zappoli et al., 1999
NE Atlantic	-5.0	61.0	Oct-Nov	0.05	0.27	O'Dowd et al., 1993
Rural						
Kap Arkona	13.2	57.4	Year	0.21	0.4	Zier, 1991
Melpitz	12	51	Year	0.61	2.3	Heintzenberg et al., 1998
Corsica	9	42	Spring	0.23	0.38	Cachier et al., 1989
Landes Forest	-1	44	Autumn	0.30	0.3	Cachier et al., 1989
Edgbaston	-1	51	Year	0.65	0.38	Smith et al., 1996
K-Puszta	19.5	46.9	Jul-Aug	0.28	0.60	Molnar et al., 1999
K-Puszta	19.5	46.9	Jul-Aug	0.28	0.75	Krivacsy et al. 2001
Po-Valley	11.4	44.4	Sep	0.63	1.0	Zappoli et al., 1999
Anadia	-8.4	40.3	Aug	0.29	1.59	Castro et al., 1999
Areao	-8.8	40.5	Year	0.34	0.95	Castro et al., 1999
Aveiro	-8.4	40.4	Jul	0.23	0.77	Alves et al., 2002
Ebro	-0.2	40.5	Year	0.24	0.4	Rodriguez et al., 2002
Roervik	12.1	57.2	Jan-May	0.21	0.73	Brostrom-Lunden et al., 1994
Urban						
Vienna	16.2	48.1	Year	0.83	4.9	Hitzenberger and Tohno, 2001
Gent	3.4	51	Summer	0.77	1.7	Kubatova et al., 2002
Gent	3.4	51	Winter	1.24	3.2	Kubatova et al., 2002
Gorlitz	14.6	41.1	Year	0.87	1.3	Zier, 1991
Halle	12	51.3	Year	0.68	1.6	Zier, 1991
Potsdam	13.4	52.3	Year	0.73	1.0	Zier, 1991
Radebeul	13.6	51.6	Year	0.51	1.4	Zier, 1991
Gif sur Yvette	2.8	48.4	Year	1.03	1.6 / 2.7	Cachier et al., 1989; Bremond et al., 1989
Paris	2.2	48.5	Year	2.04	4.6	Ruellan and Cahier, 2001
Aveiro	-8.4	40.4	Year	0.32	11.8	Nunes and Pio, 1993
Lisbon	-9.2	38.4	Jun	0.36	2.1	Alves et al., 2002
Barcelona	2.0	41.2	Year	1.76	3.0	Rodriguez et al., 2002

References

Alves, C., A. Carvalho, and C. Pio (2002), Mass balance of organic carbon fractions in atmospheric aerosols, J. Geophys. Res., 107(D21), 8345, doi:10.1029/2001JD000616

Banic, C.M., Leaitch, W.R., Isaac, G.A., Couture, M.D., Kleinman, L.I., Springston, S.R., MacPherson, J.I. (1996), Transport of ozone and sulfur to the North Atlantic atmosphere during the North Atlantic Regional Experiment, J. Geophys. Res., 101 (D22), 29,091-29,104

Battye W., K. Boyer and T. G. Pace (2002), Methods for Improving Global Inventories of Black Carbon and Organic Carbon Particulates, paper presented at 11th International Emission Inventory Conference, "Emission Inventories - Partnering for the Future," Atlanta, GA, April 15-18, 2002

Bond, T.C., R.J. Charlson and J. Heintzenberg (1998), Quantifying the emission of light-absorbing particles: Measurements tailored to climate studies, Geophys. Res. Lett., **25**, 337-340

Bond, T. (2002), Black carbon inventories, in Hansen, J.E (ed.) proceedings of Air pollution as a Climate Forcing: A Workshop, IPRC, Hawaii, April 29 – May 3, 2002, pp 89-90, 2002, available at http://www.giss.nasa.gov/meetings/pollution02/

Bremond, M. P., H. Cachier, and P. Buat-Menard (1989), Particulate carbon in the Paris region atmosphere, Environ. Technol. Lett., 10, 339– 346

Brostrom-Lunden, E., A. Lindskog, and J. Mowrer (1994), Concentrations and fluxes of organic compounds in the atmosphere of the Swedish west coast, Atmos. Environ., 28, 3605– 3615

Builtjes, P. J. H. (1992), The LOTOS - Long Term Ozone Simulation - project. Summary report. TNO-report, TNO-MW-R92/240

Builtjes, P.J.H., van Loon, M., Schaap, M., Teeuwisse, S., Visschedijnk, A.J.H., Bloos, J.P. (2003), Project on the modelling and verification of ozone reduction strategies: contribution of TNO-MEP, TNO-report, TNO-MEP-R2003/166, Apeldoorn, the Netherlands

Brunekreef, B., (1997), Air pollution and life expectancy: Is there a relation?, Occup Environ. Med., 54, 781–784

Cachier, H., M-P. Bremond, and P. Buat-Menard (1989), Determination of atmospheric soot carbon with a simple thermal method, Tellus, 41B, 379– 390

Castro, L. M., C. A. Pio, R. M. Harrison, and D. J. T. Smith (1999), Carbonaceous aerosol in urban and rural European atmospheres: Estimation of secondary organic carbon concentrations, Atmos. Environ., 33, 2771–2781

Chow, J.C. (1995), Measurement Methods to Determine Compliance with Ambient Air Quality Standards for Suspended Particles, J.A.W.M.A., 45, 320-382

Chung, S.H., Seinfeld, J.H. (2002), Global Distribution and Climate Forcing of Carbonaceous Aerosols, J. Geophys. Res., 107 (D19), 4407, doi:10.1029/2001JD001397

Cooke W.F. and J.J.N. Wilson (1996) A global black carbon aerosol model. J. Geophys. Res., 101, 14, 19395-19409.

Cooke, W.F.; C. Liousse; H. Cachier; J. Feichter (1999), Construction of a I' x I' fossil

fuel emission data set for carbonaceous aerosol and implementation and radiative impact in the ECHAM4 model, Journal of geophysical research 104, 22137-22162

Cooke W.F., B. Koffi and J.-M. Gregoire (1996) Seasonality of vegetation fires in Africa from remote sensing data and application to a global chemistry model. J. Geophys. Res., 101, 15, 21051-21065.

Derwent, R. G., D. B. Ryall, S. G. Jennings, T. G. Spain, and P. G. Simmonds (2001), Black carbon aerosol and carbon monoxide in European regionally polluted air masses at Mace Head, Ireland during 1995 – 1998, Atmos. Environ., 35, 6371– 6378

Dockery DW, Pope CA III, Xu X, Spengler JD, Ware JH, Fay ME, Ferris BG Jr, Speizer FE. (1993), An association between air pollution and mortality in six US cities, N Engl J Med 329, 1753–1759.

Echalar, F., Artaxo, P., Martins, J.V., Yamasoe, M., Gerab, F., Maenhaut, W., Holben, B. (1998), Long-term monitoring of atmospheric aerosols in the Amazon Basin: Source identification and apportionment, J. Geophys. Res, 103, 31849-31864

EMEP (1997), Data report 1995. Part 1: Annual summaries, EMEP/CCC-Report 4/97, NILU, Oslo, Norway

EMEP (2003), The WEBDAB database, www.emep.int

Eurostat (1998), New Cronos database, Eurostat, Luxembourg

Grant, K.E., C.C. Chuang, A.S. Grossman, and J.E. Penner (1999), Modeling the spectral optical properties of ammonium sulfate and biomass aerosols: Parametrization of relative humidity effects and model results, Atmos. Environ., 33, 2603-2620

Hansen, J.E., Sato, M. (2001), Trends of measured climate forcing agents, Proceedings of the National Academy of Sciences of the United States of America, 98, 26, 14778-14783

Hass, H., Builtjes, P.J.H., Simpson, D., Stern, R. (1997), Comparison of model results obtained with several European air quality models, Atmospheric Environment, 31, 3259-3297

Haywood, J. M., D. L. Roberts, A. Slingo, J. M. Edwards, and K. P. Shine (1997), General circulation model calculations of the direct radiative forcing by anthropogenic sulfate and fossil-fuel soot aerosol, J. Clim., 10, 1562–1577

Heintzenberg, J., K. Muller, W. Birmili, G. Spindler, and A. Wiedensohler (1998), Mass-related aerosol properties over the Leipzig basin, J. Geophys. Res., 103, 13,125 – 13,135

Hering, S., and Cass, G. (1999), The magnitude of bias in the measurement of PM2.5 arising from volatilisation of particulate nitrate from Teflon filters, J. Air & Waste Manage. Assoc., 49, 725-733

Hill, M.R. (1997), Environment and Technology in the Former USSR : The Case of Acid Rain and Power Generation, Edward Elgar: Cheltenham, 1997, p261 (New Horizons in Environmental Economics)

Hitzenberger, R., and S. Tohno (2001), Comparison of black carbon (BC) aerosols in two urban areas: Concentrations and size distributions, Atmos. Environ.,35, 2153– 2167

Hoek, G., B. Brunekreef, S. Goldbohm, P. Fischer and P.A. van den Brandt (2002), Association between mortality and indicators of traffic-related air pollution in the

Netherlands: a cohort study, The lancet, 360, 1203-1209

INFRAS (1999), Handbuch Emissionsfaktoren des Straßenverkehrs, Version 1.2 (CD-ROM); im Auftrag des Bundesamtes für Umwelt, Wald und Land-schaft Bern und des Umweltbundesamtes, Bern/Berlin

Jacobson, M. Z. (2001), Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols, *Nature*, 409, 6821, 695-697

Jacobson, M. Z. (2002), Control of fossil-fuel particulate black carbon and organic matter, possibly the most effective method of slowing global warming, J. Geophys. Res., 107(D19), 4410, DOI:10.1029/2001JD001376

Kerschbaumer, A., and Reimer, E. (2003), Meteorological Data Preparation for the REM/CALGRID-model (in German), UBA-project 29943246, Freie Universität Berlin, Berlin, Germany

Kiehl, J. T., and B. P. Briegleb (1993), The relative roles of sulfate aerosols and greenhouse gases in climate forcing, Science, 260, 311 – 314

Köhler, I., Dameris, M., Ackermann, I., Hass, H. (2001), Contribution of road traffic emissions to the atmospheric black carbon burden in the mid-1990s, J. Geophys. Res., 106, 17997-18014

Kouvarakis, G., Y. Doukelis, N. Mihalopoulos, S. Rapsomanikis, J. Sciare, and M. Blumthaler (2002), Chemical, physical, and optical characterization of aerosols during PAUR II experiment, J Geophys Res, 107(D18), 8141, doi:10.1029/2000JD000291

Krivacsy, Z., A. Hoffer, Zs. Sarvari, D. Temesi, U. Baltensperger, S. Nyeki, E. Weingartner, S. Kleefeld, and S. G. Jennings (2001), Role of organic and black carbon in the chemical composition of atmospheric aerosol at European background sites, Atmos. Environ., 35, 6231– 6244

Kubatova, A., R. Vermeylen, M. Claes, J. Cafmeyer, and W. Maenhaut (2002), Organic compounds in urban aerosols from Gent, Belgium: Characterization, sources, and seasonal differences. J. Geophys. Res., 107(D21), 8343, doi:10.1029/2001JD000556

Lavoue, D., Liousse, C., Cachier, H., Stocks, B.J., Goldammer, J.G. (2000), Modeling of carbonaceous particles emitted by boreal and temperate wildfires at northern latitudes, J. Geophys. Res., 105, 26871-26890

Loew, J. A., M. H. Smith, B. M. Davison, S. E. Benson, M. K. Hill, C. D. O'Dowd, R. M. Harrison, and C. N. Hewitt (1996), Physicochemical properties of atmospheric aerosol at South Uist, Atmos. Environ., 30, 3765– 3776

Liousse, C., J.E. Penner; C. Chuang, J.J. Walton, H. Eddleman, H. Cachier (1996), A global three-dimensional model study of carbonaceous aerosols, Journal of geophysical research 101, 19411-19432

Menon,S, J. Hansen, L. Nazarenko and Y. Luo (2002), Climate Effects of Black Carbon Aerosols in China and India, Science, 297, 2250-2253

Molnar, A., E. Meszaros, H. C. Hansson, H. Karlsson, A. Gelencser, G. Y., Kiss, and Z. Krivacsy (1999), The importance of organic and elemental carbon in the fine atmospheric aerosol particles, Atmos. Environ., 33, 2745–2750

Myhre, G., F. Stordal, K. Restad, and I. S. A. Isaksen (1998), Estimation of the direct radiative forcing due to sulfate and soot aerosols, Tellus, 50B, 463–477

Ntziachristos and Samaras (1999), COPERT III Computer Programme to Calculate Emissions from Road Transport - Methodology and Emission Factors, Final Draft Report, European Environment Agency, European Topic Centre on Air Emissions

NGCIA (2000), Gridded Polulation of the World (GWP) data set, Version 2, available at: http://sedac.ciesin.org/plue/gpw, Center for International Earth Science Information Network (CIESIN), Columbia University, USA

Nunes, T. V., and C. A. Pio (1993), Carbonaceous aerosols in industrial and coastal atmospheres, Atmos. Environ., 27A, 1339– 1346

O'Dowd, C. D., M. H. Smith, and S. G. Jennings (1993), Submicron particle, radon, and soot carbon characteristics over the northeast Atlantic, J. Geophys. Res., 98, 1123–1135

Pakkanen, T.A., Hillamo, R.E., Aurela, M., Andersen, H.V., Grundahl, L., Ferm, M., Persson, K., Karlsson, V., Reissell, A., Royset, O., Floisand, I., Oyola, P., and Ganko, T. (1999), Nordic intercomparison for measurement of major atmospheric nitrogen species, J. Aerosol Sci, 30, 247-263

Penner, J.E., Eddleman, H., Novakov, T. (1993), Towards the development of a global inventory for black carbon emissions Atmospheric environment, 27 1277-1296.

Penner, J.E., Chuang, C.C., Grant, K. (1998), Climate forcing by carbonaceous and sulfate aerosols, Clim. Dyn., 14, 839– 851

Pope, C.A. III, Thun, M.J., Namboodiri, M.M., Dockery, D.W., Evans, J.S., Speizer, F.E., Heath, C.W. (1995), Particulate air pollution as a predictor of mortality in a prospective study of US adults, Am. J. Respir. Crit. Care Med., 151, 669–674.

Putaud, J-P., Baltensperger, U., Erika Brüggemann, E., Facchini, M.C., Fuzzi, S., Gehrig, R., Hansson, H-C., Harrison, R.M., Jones, A.M., Laj, P., Maenhaut, W., Mihalopoulos, N., Müller, K., Palmgren, F., Querol, X., Rodriguez, S., Spindler, S., ten Brink, H.M., Tunved, P., Van Dingenen, R., Wehner, B., Weingartner, E., Wiedensohler, A., Wåhlin, P., Raes, F. (2003), A European Aerosol Phenomenology: physical and chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe, JRC-IES report, Http://ies.jrc.cec.eu.int/Download/cc

Riemer, N., Vogel, H., Vogel, N. (2003), Modelling the ageing process of soot, J. Aerosol. Sci., 34, Supplement 1, S131-S132

Robles Gonzalez C., Veefkind, J.P., de Leeuw, G. (2000), Aerosol optical depth over Europe in August 1997 derived from ATSR-2 data, Geophysical Research Letters, 27, 955-958

Robles-Gonzalez, C., Schaap, M., de Leeuw, G., Builtjes, P.J.H., van Loon, M. (2003), Spatial variation of aerosol properties derived from satellite observations, Atmos. Chem. Phys., 3, 1-13

Rodriguez, S., Querol, X., Alastuey, A., Plana, F. (2002), Sources and processes affecting levels and composition of atmospheric aerosol in the western Mediterranean, J. Geophys. Res-A, 107 (D24), art no: 4777

Ruellan, S., and H. Cachier, Characterization of fresh particulate vehicular exhausts near a Paris high flow road, Atmos. Environ., 35, 453– 468, 2001

Schaap, M., Muller, K., ten Brink, H.M. (2002), Constructing the European aerosol

nitrate concentration field from quality analysed data, Atmos. Environ, 36 (8), 1323-1335

Schaap, M., van Loon, M., ten Brink, H.M., Dentener, F.J., Builtjes, P.J.H. (2003a), The nitrate aerosol field over Europe: simulations with an atmospheric chemistry-transport model of intermediate complexity, submitted to ACP

Schaap, M., Spindler, G., Schulz, M., Acker, K., Maenhaut, W., Berner, A., Wieprecht, W., Streit, N., Müller, K., Brüggemann, E., Putaud, J-P., Puxbaum, H., Baltensperger, U., ten Brink, H.M. (2003b), Artefacts in the sampling of nitrate studied in the "INTERCOMP" campaigns of EUROTRAC-AEROSOL, Submited to Atmospheric Environment

Schell, B., Ackermann, I.J., Hass, H., Binkowski, F.S., Ebel, A. (2001), Modelling the formation of secondary organic aerosol within a comprehensive air quality system, J. Geophys. Res., 106, 28275-28293

Schmid, H., Laskus, L., Abraham, H.J., Lavansky, V., Bizjak, M., Burba, P., Cahier, H., Crow, D., Chow, J., Gnauk, T., Even, A., ten Brink, H.M., Giesen, K.P., Hitzenberger, R., Hueglin, C., Maenhaut, W., Pio, C., Putaud, J.P., Toom-Sauntry, D., Puxbaum, H. (2001), Results of the "carbon conference" international aerosol carbon round robin test stage 1, Atmos. Env., 35, 2111-2121

Scholes, M., Andreae, M.O. (2000), Biogenic and pyrogenic emissions from Africa and their impact on the global atmosphere, Ambio, 29 , 23-29

Schultz, M.G. (2002), On the use of ATSR fire count data to estimate the seasonal and interannual variability of vegetation fire emissions, Atmos. Chem. Phys., 2, 387-395

Seinfeld, J.H. and Pandis, S.N. (1998), Atmospheric chemistry and physics: From air pollution to climate change, John Wiley & Sons, Inc., New York, USA

Smith, D. J. T., R. M. Harrison, L. Luhana, C. A. Pio, L. M. Castro, M. N., Tariq, S. Hayat, and T. Quraishi (1996), Concentrations of particulate airborne polycyclic aromatic hydrocarbons and metals collected in Lahore, Paki-stan, Atmos. Environ., 30, 4031–4040

Spicer, C.W, and Schumacher, P.M. (1979), Particulate nitrate: Laboratory and field studies of major sampling interferences, Atmos. Environ., 13, 543-552

Streets, D.G., Gupta, S., Waldhoff, S.T., Wang, M.Q., Bond, T.C., Yiyun B., Black carbon emissions in China, Atmospheric environment, vol. 35, 4281-4296. (2001)

Ten Brink H. M., Hensen, A., Khystov, A., van Dorland, R., Jeuken, A., van Velthoven, P., Lelieveld, J., van den Berg, A., Swart, D.P.J., Bergwerff, J.B., Apituley, A. (2001), Aerosol; cycle and influence on the radiation balance. Cluster-project in the National Research Program on Global Air Pollution and Climate Change, npr2, report no. 410200064

ten Brink, H.M., Maenhaut, W., Hitzenberger, R., Gnauk, T., Spindler, G., Even, A., Chi, X., Bauer, H., Puxbaum, H., Putaud, J.-P., Tursic, J., Berner, A., (2003), Comparability of methods in use in Europe for measuring the carbon content of aerosol, Submitted to Atmospheric Environment

TNO (2001), The CEPMEIP database, http://www.air.sk/tno/cepmeip/

Vignati, E., de Leeuw, G., Schulz, M., Plate, E. (1999), Characterization of aerosols at a

coastal site near Vindeby (Denmark), J. Geophys. Res.,104, 3277-3287

Visschedijk, A.J.H., Onzekerheid en deeltjesgrootte-specificatie van de CEPMEIP emissie-bestanden, TNO-MEP Rapportnummer R 2002/162, 2002 (in Dutch)

VROM (2002), Methoden voor de berekening van de emissies door mobiele bronnen in Nederland (Methods to calculate the emissions of mobile sources in the Netherlands), Rapportagereeks MilieuMonitor Nr 4, Taakgroep Verkeer en Vervoer, Nederland

Watson, J.G., E. Fujita, J.C. Chow, B. Zielinska, L.W. Richards, W. Neff, and D. Dietrich (1998), Northern Front Range Air Quality Study (NFRAQS) Final Report, DRI Document No. 6580-685-8750.2F2, Desert Research Institute, Reno, USA

Wilson, J., Cuvelier, C., Raes, F. (2001), A modelling study of global mixed aerosol fields, J. Geophys. Res., 106, 34081-34108

WHO (2000), Air Quality Guidelines - Second Edition, Chapter 7.3 Particulate matter, WHO Regional Office for Europe, Copenhagen, Denmark

Zappoli, S. et al. (1999), Inorganic, organic and macromolecular components of fine aerosol in different areas of Europe in relation to their water solubility, Atmos. Environ., 33, 2733–2743

Zier, M. (1991), Mass concentrations of total dust and soot in the near surface air in east Germany, J. Aerosol Sci., 22, S597– S600

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.

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 $\mu g/m^3$. 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 extend of the evaporation artefact in a general way as a function of temperature. Complete evaporation occurs at temperatures exceeding 25 ºC and full retention at temperatures less than 20 ºC. At temperatures between 20 and 25 ºC 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 ºC. 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 µg 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 (PM2.5). 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, 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 con-centrations 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 μg/m^3 and lower in remote regions to more than 0.5 μg/m^3 in central Europe. Peak levels above 1 μg/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 PM2.5 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.

Nederlandse Samenvatting

Het centrale thema van dit proefschrift is het nitraat gehalte in aërosolen (of fijn stof (PM)). Aërosolen spelen een belangrijke rol in het klimaatsysteem. De aarde absorbeert de kortgolvige straling van de zon, het meeste aan het oppervlak, maar ook een klein deel in de atmosfeer. Gemiddeld over het jaar en over de aarde wordt de ontvangen energie gecompenseerd door het uitstralen van langgolvige straling. Elk proces dat de hoeveelheid inkomende of uitgaande stralingsenergie dan wel de herverdeling van de energie over aarde verandert, kan het klimaat beïnvloeden. Een dergelijk proces wordt klimaatforcering genoemd welke is uitgedrukt in Watts per vierkante meter (W/m^2). Aërosolen verstrooien of, in mindere mate, absorberen zonlicht en beïnvloeden zo direct de stralingsbalans van de aarde. Indirect forceren aërosolen het klimaat door hun invloed op de levensduur en optische eigenschappen van wolken. Naast klimaatverandering spelen aërosolen een belangrijke rol in de verzurings- en vermestingsproblematiek en worden ze geassocieerd met nadelige effecten op de gezondheid.

Aërosolen hebben een levensduur in de atmosfeer van ongeveer een week. Broeikasgassen daarintegen verblijven vele (tientallen) jaren in de atmosfeer. De effecten van aërosolen hebben dan ook een sterk regionaal karakter in vergelijking met die van broeikasgassen welke homogeen over de aarde worden verdeeld. Sinds de tachtiger jaren wordt er veel onderzoek verricht om de forcering van verschillende aërosolen te kwantificeren. Traditioneel werd de meeste aandacht gericht op het in de atmosfeer gevormde sulfaat. Deze component kan in de verontreinigde gebieden eenzelfde forcering uitoefenen als broeikasgassen maar met een omgekeerd teken. Sulfaat draagt echter niet meer dan 30-40 % bij aan de aërosolconcentraties in verontreinigde gebieden. Recentelijk wordt er dan ook meer en meer onderzoek verricht naar de effecten van de andere aërosolbestanddelen. De belangrijkste zijn roet en organisch koolstof, welke worden uitgestoten bij verbrandingsprocessen, (bodem) stof en nitraat. Het IPCC (International Panel on Climate Change) vat elke vijf jaar de resultaten van het wetenschappelijk klimaatonderzoek samen. Met uitzondering van nitraat geeft het IPCC een schatting van de forcering van de bovenstaande componenten.

In het Third Assessment Report (TAR) uit 2001 geeft het IPCC aan dat een schatting van het effect van nitraat niet mogelijk is vanwege het geringe aantal gegevens en de notoire onbetrouwbaarheid van deze data. Data verkregen m.b.v. filters zijn moeilijk te interpreteren doordat de concentratie door verdamping van ammoniumnitraat en/of adsorptie van gasvormig salpeterzuur mogelijk onder- of overschat wordt. Daarnaast geven de spaarzame modelstudies naar de invloed van nitraat tegenstrijdige resultaten, hetgeen terug te voeren is op de aannames over de grootteverdeling van nitraat alsmede de complexe processen die een rol spelen bij de vorming van nitraat.

Voor Nederland is experimenteel aangetoond dat de klimaatforcering van nitraat vergelijkbaar is t.o.v die van sulfaat. Echter, dergelijke experimentele bewijzen zijn niet beschikbaar voor andere delen van Europa en de rest van de wereld. Daarom wordt een hoge forcering door nitraat wel eens betiteld als een Nederlands verschijnsel. In dit proefschrift wordt een vierjarig onderzoek gepresenteerd naar het belang van nitraat over Europa.

De volgende activiteiten werden verricht om het belang van nitraat vast te stellen:

- Evaluatie van de artefacten die optreden bij het verzamelen van aerosol-nitraat op verschillende filters.
- Constructie van het nitraatveld over Europa met beschikbare gegevens gebruik-makend van de kennis over artefacten.
- Het ontwikkelen van een chemisch transportmodel (CTM) om de formatie, ver-spreiding en verwijdering van nitraat en andere aërosolcomponenten in de atmosfeer te beschrijven.

Hoofdstuk 2 beschrijft de analyse van een serie experimenten waarbij onder verschillende condities meetmethodes voor aerosol-nitraat met elkaar zijn vergeleken. Het grootste experiment was een twee weken durende campagne op het meetstation Melpitz in het oosten van Duitsland. Hier werden samplers met de meest gebruikelijke filters vergeleken. De concentratie nitraat, voornamelijk geassocieerd met ammonium, was gemiddeld 4 $\mu g/m^3$. De concentraties gemeten met de verschillende apparaten kwamen goed met elkaar overeen met een spreiding van 10 % op het gemiddelde niveau en een lagere spreiding voor hogere concentraties. De lage spreiding bewijst dat de invloed van artefacten verwaar-loosbaar was. De afwezigheid van artefacten kan verklaard worden door de extrapolatie van een aantal laboratoriumexperimenten. Daar werd gevonden dat verliezen van ammonium-nitraat van Teflon en kwarts filters alleen significant zijn wanneer de temperatuur veel hoger is dan gedurende de campagne het geval was. In het labaratorium verzamelden de cellulose en cellulose-acetaat filters kwantitatief zowel aerosol-nitraat als salpeterzuur. In Melpitz echter waren de concentraties van salpeterzuur te laag om adsorptie aan te kunnen tonen. De laboratoriumdata zijn ook gebruikt in de evaluatie van een campagne in de Po-vallei, welke werd gehouden onder veel warmere omstandigheden. Daar vonden we bewijs voor adsorptie van salpeterzuur aan cellulose filters en van verdampingsverliezen van nitraat van kwarts filters. We konden de verliezen op de volgende manier generaliseren. Complete verdamping treedt op bij temperatuur boven 25 graden Celsius en volledige retentie treedt op onder 20 graden Celsius. Bij temperaturen tussen 20 en 25 graden is de verdamping gemiddeld 50 %, maar deze toont een grote spreiding. De hoofdconclusies van dit onderzoek zijn dat kwarts een geschikt materiaal is voor het verzamelen van nitraat, zolang de temperatuur niet boven de 20 graden stijgt en dat cellulose filters kwantitatief salpeterzuur verzamelen.

In hoofdstuk 3 wordt de constructie van het concentratieveld van aerosol-nitraat over Europa door interpolatie van gemeten data beschreven. De eerste stap in deze studie was het verzamelen van lange termijn data, waarna een beoordeling van de kwaliteit werd uitgevoerd. Daarom wordt in dit hoofdstuk eerst een uitgebreid overzicht van filter materialen en geassocieerde artefacten gepresenteerd. Artefacten bij gebruik van denuder filter combinaties zijn klein en data van deze instrumenten zijn dan ook als uitgangspunt gebruikt. Aangezien er maar een klein aantal tijdreeksen beschikbaar is met deze tech-nieken, werden ook data afkomstig van filtermethoden gebruikt na een kritische analyse van mogelijke artefacten. Data van inerte filters (teflon en kwarts) zijn door de mogelijke verdamping van ammoniumnitraat geïnterpreteerd als minimum waarden. Vervolgens werden data van totaal nitraat filters, welke naast aërosol nitraat ook salpeterzuur verzame-len, gecorrigeerd voor de bijdrage van salpeterzuur. De afstanden over welke nitraat concentraties correleren is vervolgens onderzocht. Hieruit bleek dat deze afstand in het

winterhalfjaar voldoende was om tussen de data punten te interpoleren.

Het geïnterpoleerde concentratie veld voor de (winter) periode van 1994 tot 1997 is succesvol getest met onafhankelijke data van campagnes. Concentraties hoger dan 5 µg/m³ komen voor in een groot gebied dat zich uitstrekt van Zuid-Engeland over West-Europa tot in Polen. De experimentele data wijzen erop dat het nitraat in dit gebied voornamelijk in fijn aërosol (PM2.5) voorkomt. Naar het noorden toe tonen de concentraties een sterke gradiënt van 2,5 µg/m³ in Zuid-Zweden tot minder dan 0,5 µg/m³ in Midden-Scandinavië. Ten oosten en westen van het maximum in centraal Europa lopen de concentraties minder snel af. De aerosol-last van nitraat ten noorden van de Alpen, met uitzondering van Frankrijk waarvoor geen data zijn gevonden, is ongeveer 60 % dat van sulfaat. Opmerkelijk is dat de nitraatconcentraties in de Po-vallei net zo hoog zijn als in West-Europa.

In hoofdstuk 4 worden de resultaten van een modelstudie naar het (ammonium-) nitraat-veld over Europa gepresenteerd. Het LOTOS model, oorspronkelijk ontwikkeld voor ozonsimulaties, is verder uitgebreid om aërosol velden te kunnen berekenen. Daartoe werd een evenwichtsmodule voor de vorming van ammoniumnitraat en andere relevante processen met betrekking tot de formatie en verwijdering van aërosolen ingebouwd. De metingen, zoals hierboven beschreven, zijn gebruikt om de berekende velden voor 1995 te valideren.

Tijdens de herfst, winter en het voorjaar worden hoge concentraties van nitraat berekend over Noordwest-, Centraal- en Oost-Europa. In de winter zijn de nitraatconcentraties het hoogste in de Po-vallei, Noord-Italië. Deze resultaten komen overeen met het uit gemeten data geconstrueerde veld. In de winter wordt salpeterzuur, de voorloper van aërosol nitraat, gevormd door reacties op aërosol oppervlak. Significante nitraat niveaus in de zomer worden berekend in gebieden met hoge ammoniak emissies, zoals Nederland, aangezien hoge ammoniakniveaus nodig zijn om nitraat in aërosol te stabiliseren. Over een groot deel van Zuid- en Oost-Europa worden dan ook lage ammoniumnitraatconcentraties berekend. Gemiddeld over alle stations is het model in staat de concentraties van nitraat, sulfaat, ammonium, totaal nitraat, totaal ammonium en zwavel dioxide binnen 20 % te berekenen. De dagelijkse variatie wordt redelijk goed gemodelleerd. Echter, het model is niet altijd in staat de amplitude van episodes te representeren. Voorts worden salpeterzuur-concentraties overschat in kustgebieden. Het model onderschat de concentraties in regenwater en daarmee de natte verwijdering, hetgeen terug te voeren is op de beschrijving van de rol van wolken. Het modelleren van zeezout aerosolen is noodzakelijk om in kustgebieden de verdeling van nitraat tussen de aërosol en gasfase goed te beschrijven

Er wordt extra aandacht gegeven aan de gevoeligheid van de modelresultaten met betrek-king tot de beschrijving van ammoniakemissies. Grote verschillen in de gemodelleerde nitraatconcentraties werden gevonden door verschillende seizoensvariaties aan te brengen in de emissies van ammoniak. De gevoeligheid van de nitraatconcentraties voor de beschik-baarheid van ammoniak is omgekeerd evenredig met de nitraatconcentratie, aangezien bij hoge nitraatconcentraties salpeterzuur en niet ammoniak de limiterende stof is voor nitraatformatie. We konden afleiden dat het negeren van een seizoensvariatie resulteert in een te hoge ammoniakemissie in de winter. De gevoeligheid van nitraat en totaal nitraat-concentraties voor de ammoniakbeschikbaarheid is ontkoppeld in de zomer, wanneer salpeterzuurconcentraties gelijk of hoger zijn dan die van aërosol-nitraat. Data over de aërosol/gasfaseverdeling van nitraat zijn noodzakelijk voor verdere model ontwikkeling en

verificatie van de resultaten.

In hoofdstuk 5 wordt het ontwikkelde modelsysteem toegepast op roet en andere geëmitteerde deeltjes. Gebaseerd op een emissie database voor (totaal) fijn stof zijn Europese emissies van roet afgeleid door deze per broncategorie te combineren met roetfracties van fijn stof. De totale Europese emissie in 1995 wordt geschat op 0.47 Tg per jaar. Met name de transportsector, huishoudens en industriële verbrandingsprocessen dragen sterk bij aan de totale emissie.

De gemodelleerde roetconcentraties variëren jaargemiddeld van 0.05 µg/m^3 en lager over afgelegen gebieden, tot meer dan 0.5 µg/m^3 in centraal Europa. Maxima boven 1.0 µg/m^3 worden berekend boven sterk verstedelijkte gebieden. Echter, de gesimuleerde roetconcentraties worden onderschat met ongeveer een factor twee. Deze onderschatting kan mogelijk verklaard worden door verschillende factoren zoals lokale emissies, onzekerheden in de meetgegevens en de gemodelleerde natte verwijdering. Daarnaast spelen ook de onzekerheden in de geschatte emissies een rol. Niet meegenomen bronnen bedragen echter hooguit 15 % van de totale emissie en kunnen het verschil dus niet verklaren. De emissie factoren zijn waarschijnlijk de belangrijkste bron van onzekerheden in het schatten van de BC emissies. Met name die van verkeer staan ter discussie.

De berekende velden van roet en additioneel primair fijn stof, waarvan het meeste organisch koolstof is, zijn gecombineerd met die van nitraat, sulfaat en ammonium. Deze componenten zijn de belangrijkste antropogene bestanddelen van PM2.5. De berekende roetconcentraties beslaan maar 4-10% van de totale berekende aërosolmassa. Toch, speelt deze component een belangrijke rol in het klimaat systeem omdat het effectief licht absorbeert. Sulfaat (25-50%) draagt het meest bij aan de fijne aërosolconcentraties over Europa, gevolgd door nitraat (5-35%) en primair (10-25%) materiaal (incl. roet). In vergelijking met de gemeten fijne aërosolmassa over Europa wordt PM2.5 onderschat door het model. De onderschatting kon worden gerelateerd aan de onderschatting van de primaire aërosolniveaus.

De nitraatvelden, zoals deze gedurende het onderzoek zijn afgeleid, bieden de mogelijkheid om de forcering van nitraat over Europa te schatten. Op basis van de model-simulaties werd de jaarlijks gemiddelde forcering door nitraat berekend op 25% van dat door sulfaat. In de zomer is nitraat regionaal belangrijk, bijv. in Nederland, waar de forcering van nitraat gelijk is aan die van sulfaat. Gedurende de herfst, winter en het voorjaar is de forcering van nitraat ruwweg de helft van sulfaat. Over Noordwest-Europa en de Alpen wordt een gelijke forcering van nitraat aan die van sulfaat berekend. De berekening voor de winter komt overeen met de verhouding van de respectievelijke aerosol-lasten. In het algemeen is de forcering door nitraat significant en behoort meegenomen te worden in studies om de impact te berekenen van regionale klimaatverandering.

Dankwoord

De laatste loodjes wegen het zwaarst. Een bekend gezegde dat zeker opgaat voor het schrijven van een proefschrift. Ik ben dan ook heel blij dat mijn proefschrift af is. Let mij mijn laatste (onmogelijke) taak: het bedanken van alle mensen die tot de vorming van dit proefschrift hebben bijgedragen.

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Vele anderen hebben bijgedragen aan het tot stand komen van dit boekje. Hiertoe behoren mijn paranimfen, collega's, vrienden en familie. Tot slot wil ik mijn vader, moeder, zusje en Michelle uitdrukkelijk bedanken voor alle steun die jullie mij gegeven hebben.

List of Publications

Based on this thesis:

Schaap, M., Muller, K., ten Brink, H.M. (2002a), Constructing the European aerosol nitrate concentration field from quality analysed data, Atmos. Environ, 36 (8), 1323-1335

Schaap, M., Spindler, G., Schulz, M., Acker, K., Maenhaut, W., Berner, A., Wieprecht, W., Streit, N., Müller, K., Brüggemann, E., Chi, X., Putaud, J-P., Hitzenberger, R., Puxbaum, H., Baltensperger, U., ten Brink, H.M. (2003b), Artefacts in the sampling of nitrate studied in the "INTERCOMP" campaigns of EUROTRAC-AEROSOL, Accepted for publication in Atmospheric Environment (with minor revisions).

Schaap, M., van Loon, M., ten Brink, H.M., Dentener, F.J., Builtjes, P.J.H. (2003), The nitrate aerosol field over Europe: simulations with an atmospheric chemistry-transport model of intermediate complexity, published in Atmos. Chem. Phys. Disc.

Schaap, M., Denier Van Der Gon, H.A.C., Visschedijk, A.J.H., Van Loon, M., ten Brink, H.M., Dentener, F.J., Putaud, J-P., Guillaume, B., Liousse, C., and Builtjes, P.J.H., Anthropogenic Fine Aerosol Distribution over Europe with special emphasis on primary $PM_{2.5}$ and Black Carbon, Submitted to J. Geophys. Res.

Other publications:

Schaap, M., van Loon, M., Visschedijk, A., Dentener, F.J., Builtjes, P.J.H. (2002), Modelling $PM_{2.5}$ concentrations over Europe: the role of agriculture, Landbauforschung Völkenrode, Special Issue 235, 49-55

Robles-Gonzalez, C., Schaap, M., de Leeuw, G., Builtjes, P.J.H., van Loon, M. (2003), Spatial variation of aerosol properties derived from satellite observations, Atmos. Chem. Phys., 3, 1-13

Erisman, J.W., Schaap, M. (2003), The need for ammonia abatement with respect to secondary PM reductions in Europe, accepted for publication in Environ. Pollut.

Curriculum Vitae

Martijn Schaap is geboren op 24 juli 1977 in Apeldoorn. Hij behaalde in 1995 zijn VWO diploma aan het Christelijk Lyceum (CLA) in Apeldoorn, waarna hij begon aan zijn zwerftocht aan de universiteit van Utrecht. Op 1 september 1995 begon hij daar aan de studie Scheikunde. Na twee jaar, met zijn propedeuse op zak, stapte hij over naar de kopstudie Milieukunde aan de faculteit Ruimtelijke Wetenschappen. Gedurende zijn afstudeerstage op TNO werd hij gevraagd om aio te worden op een gezamenlijk project van ECN en TNO. Op 15 oktober 1999 begon hij aan zijn promotie onderzoek op het Instituut voor Marien en Atmosferisch onderzoek (IMAU) aan de faculteit Natuurkunde. Op 8 december 2003 hoopt hij zijn doctorstitel te hebben verkregen. Martijn houdt na zijn promotie zijn reislustige reputatie hoog door twee maanden te gaan fietsen in Nieuw Zeeland.