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
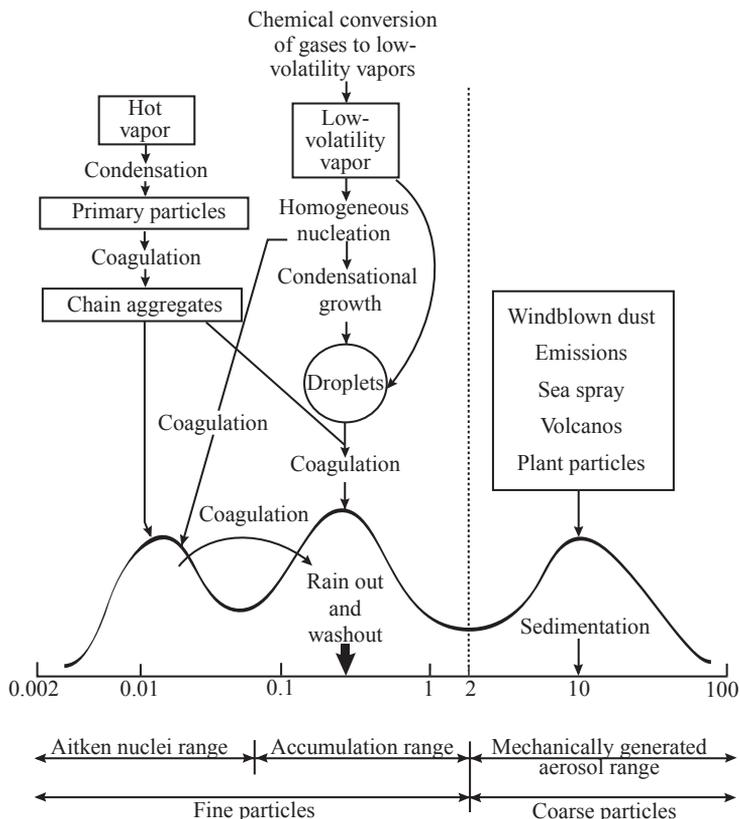
Figure 1.1 Schematic of the aerosol size distribution and the most important processes governing the size distribution

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.
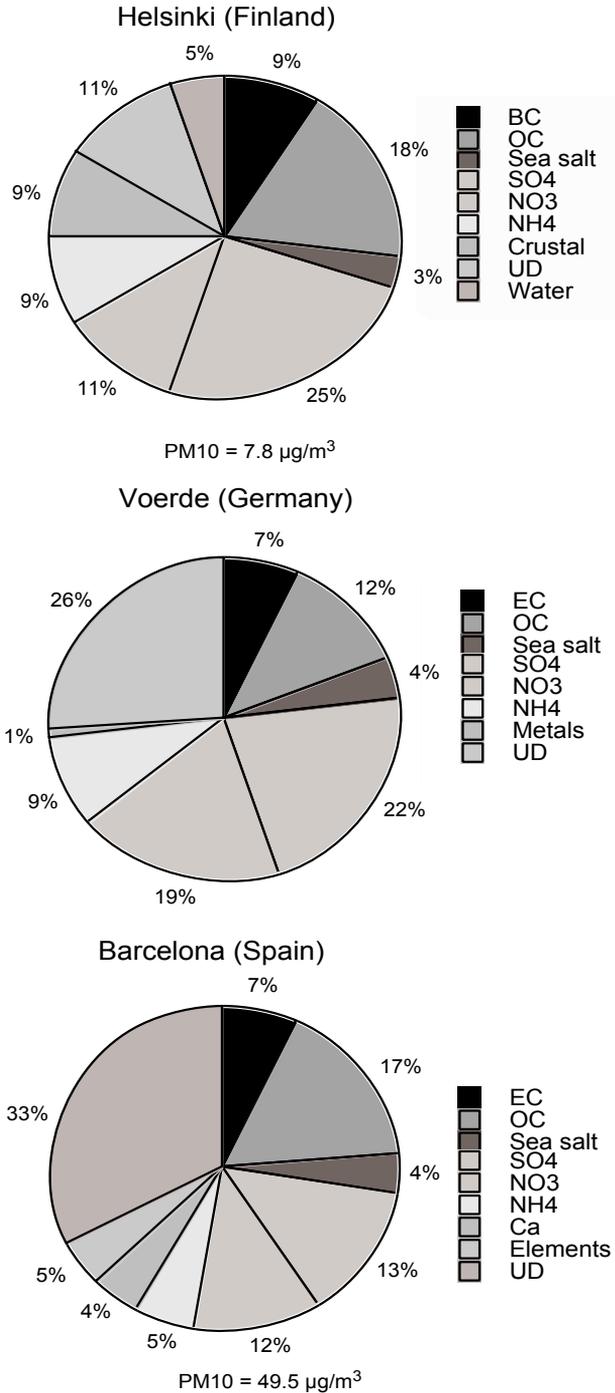
Helsinki (Finland)

Legend:
- BC
- OC
- Sea salt
- SO4
- NO3
- NH4
- Crustal
- UD
- Water

Segments: 5%, 9%, 18%, 3%, 25%, 11%, 9%, 9%, 11%

PM10 = 7.8 µg/m^3

Voerde (Germany)

Legend:
- EC
- OC
- Sea salt
- SO4
- NO3
- NH4
- Metals
- UD

Segments: 7%, 12%, 4%, 22%, 19%, 9%, 1%, 26%

Barcelona (Spain)

Legend:
- EC
- OC
- Sea salt
- SO4
- NO3
- NH4
- Ca
- Elements
- UD

Segments: 7%, 17%, 4%, 13%, 12%, 5%, 4%, 5%, 33%

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)
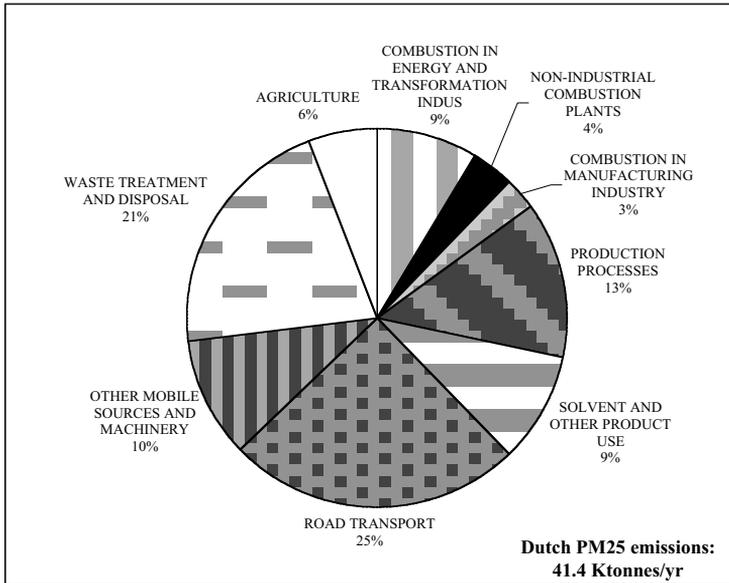
Figure 1.3 Dutch particulate matter emissions for 1995 (TNO,2001)

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.
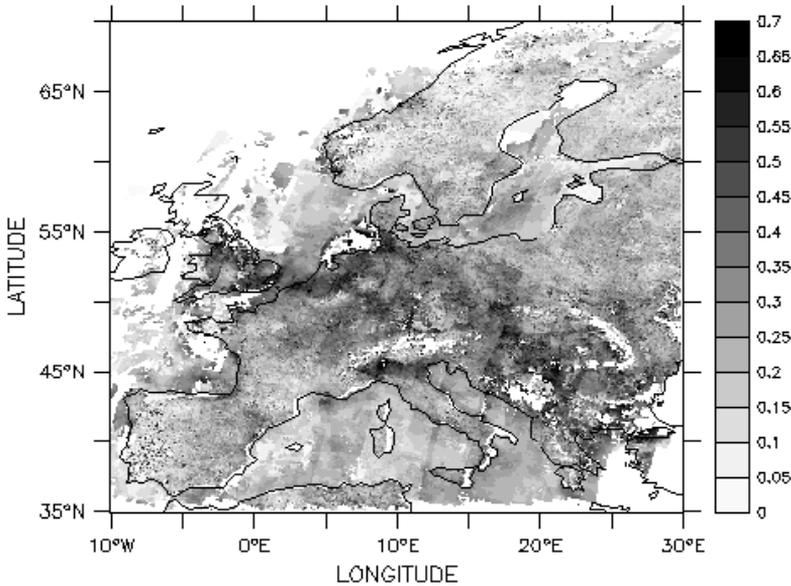
Figure 1.4 Aerosol optical depth over Europe for August, 1997 (Robles-Gonzalez et al., 2000)

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
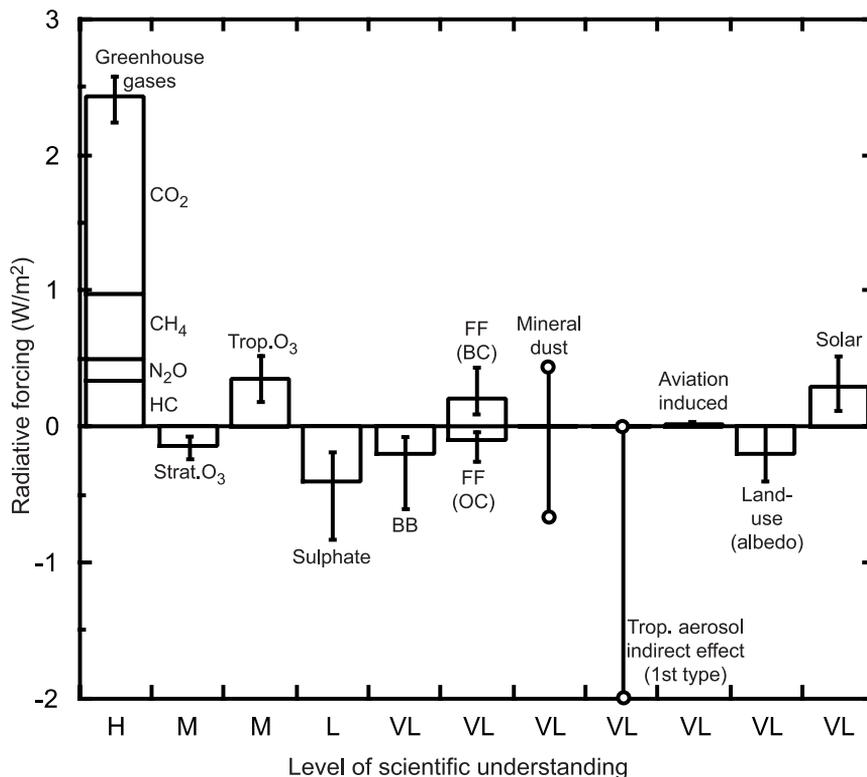
Figure 1.5 Overview of radiative forcing estimates by IPCC(2001). Confidence levels are indicated as: H=High, M=Medium, L=Low and Vl=Very Low. Further: HC = Halocarbons, BB = Biomass burning, FF = Fossil Fuel

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 photo-chemical 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
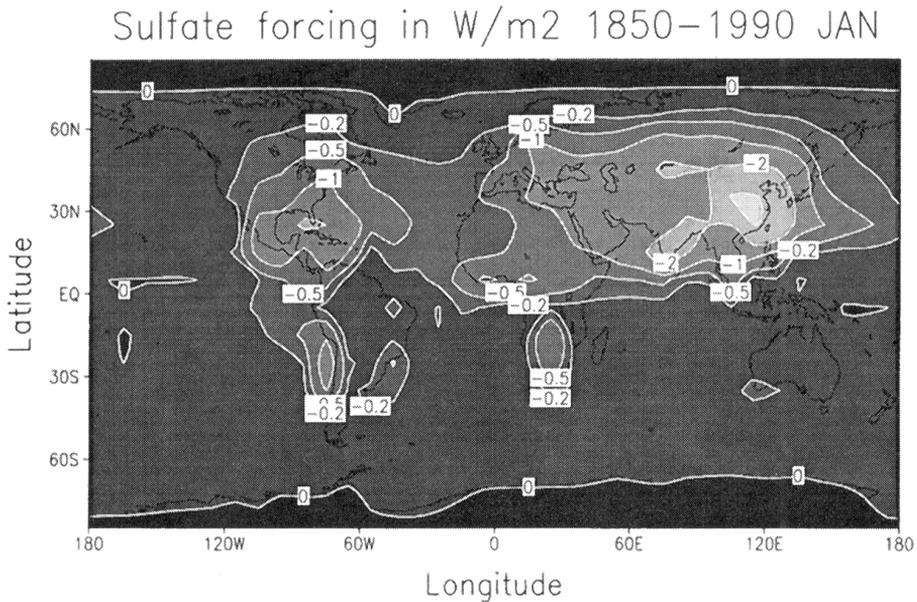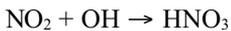
Figure 1.6 Sulphate radiative forcing (W/m^2) for January (Source: Van Dorland et al., 1997)

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:

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

$$NO_3 + NO_2 \leftrightarrow N_2O_5$$

$$N_2O_5 + H_2O \rightarrow 2\ HNO_3$$
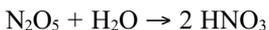
Hydrolysis of N_2O_5 takes place on the surface of aerosols yields two equivalents of nitric acid. This process is not important during the day, since the NO_3 radical is readily photodissociated:
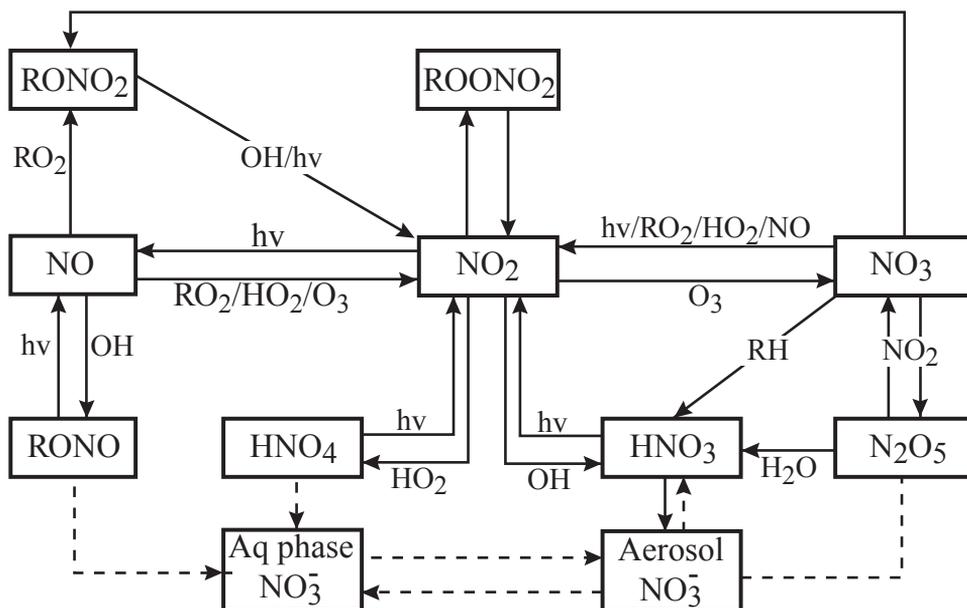
$$NO_3 + h\nu \rightarrow NO + O_2$$
$$NO_3 + h\nu \rightarrow NO_2 + O$$
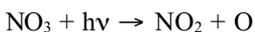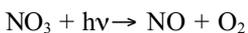
Figure 1.7 Overview of tropospheric chemistry of oxidized nitrogen. Hydrocarbon branches are denoted as R.

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:

$$HNO_3 + NH_3 \leftrightarrow NH_4NO_3$$
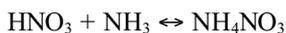
Particulate ammonium nitrate is a semi-volatile compound, which will maintain an equilibrium with its gaseous counterparts. Due to its low vapour pressure ammonium nitrate will condense on pre-existing aerosol, where the largest surface is available. Ammonium nitrate is therefore predominantly found 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
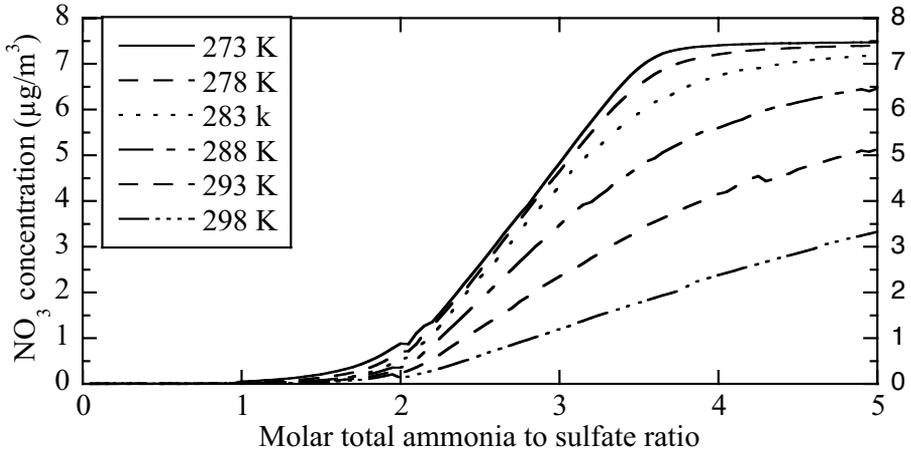
Figure 1.8 The nitrate concentration as function of ammonia availability for different temperatures at 80 % relative humidity. The available amount of both nitrate and sulphate was 7.5 μg/m³.

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.

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