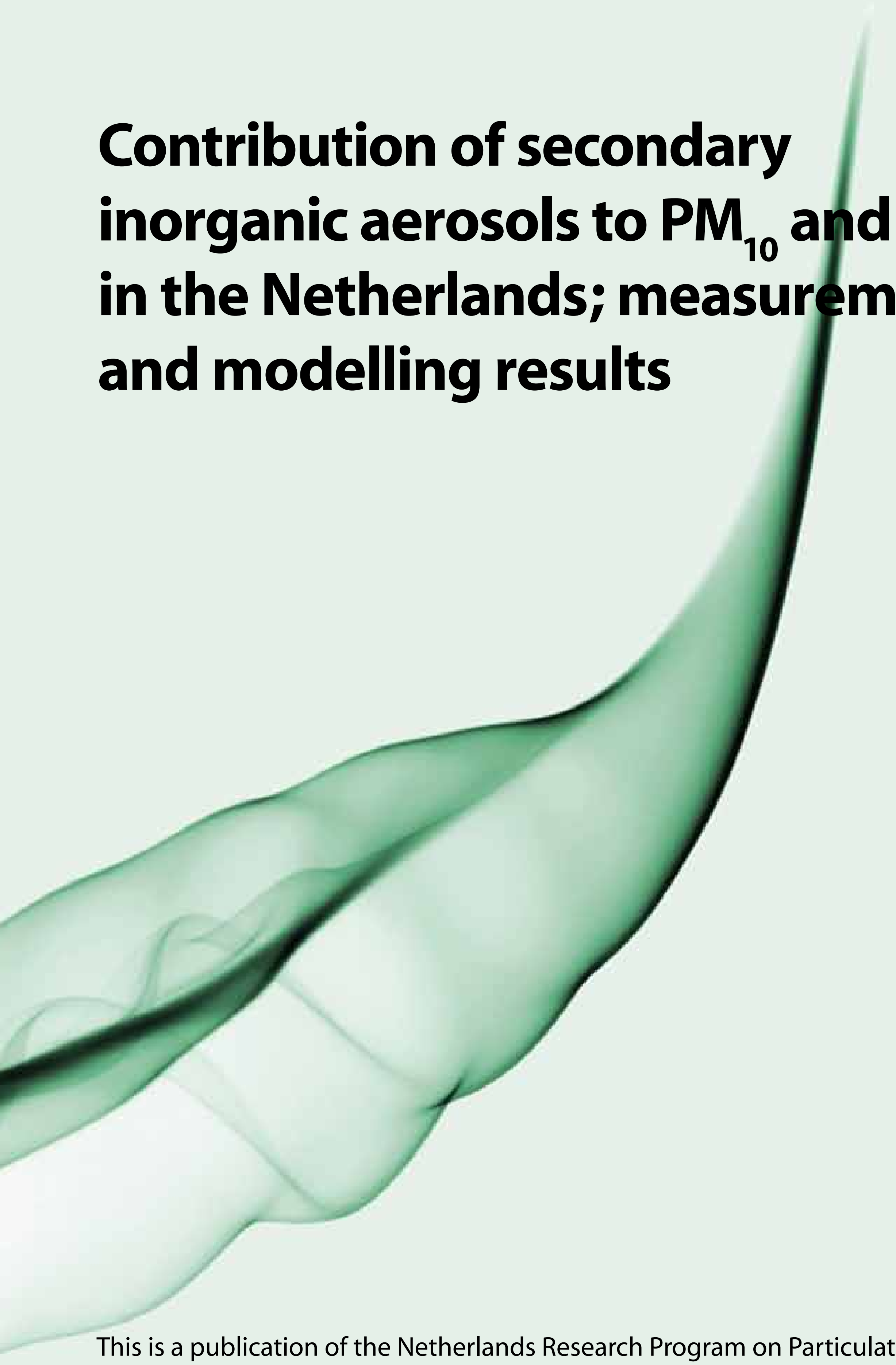
# Contribution of secondary inorganic aerosols to $PM_{10}$ and $PM_{2.5}$ in the Netherlands; measurement and modelling results



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Netherlands Environmental Assessment Agency ECN rivm TNO

# Contribution of secondary inorganic aerosols to $PM_{10}$ and $PM_{2.5}$ in the Netherlands; measurement and modelling results

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Netherlands Environmental Assessment Agency

ECN Energy research Centre of the Netherlands

TNO

rivm
National Institute
for Public Health
and the Environment

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PBL Netherlands Environmental Assessment Agency
TNO Built Environment and Geosciences
RIVM National Institute for Public Health and the Environment

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# Rapport in het kort

Secundair anorganisch aërosol (SIA) vormt het grootste bestanddeel in fijn stof (PM). SIA, ammoniumnitraat en ammoniumsulfaat, is vrijwel geheel van antropogene oorsprong, en kan daarom beïnvloed worden door beleidsmaatregelen. Precursor gassen ($NO_x$, $SO_2$, $NH_3$) worden geëmitteerd door verkeer, energieproductie en landbouw. Dit rapport draagt bij aan de kennis over SIA, en geeft een verbeterde schatting van de bijdrage aan PM10 en PM2.5. De nadruk ligt op de interpretatie van metingen (LML filter data, BOP meetcampagnes). De studie geeft inzicht in de variabiliteit in tijd en ruimte en de bijdrage aan de stedelijke achtergrondniveaus.

De gemiddelde concentraties van secundair inorganisch aërosol in Nederland zijn hoger dan voorheen werd aangenomen. De in deze studie gemeten bijdrage aan PM10 lag tussen 30 en 40%. Dit stijgt naar meer dan 50% tijdens periodes met hoge PM concentraties (zoals 'overschrijdingsdagen'). De voornaamste redenen zijn lange-afstandstransport en ongunstige meteorologie. Over de hele periode 1994-2007 zijn de SIA concentraties afgenomen. Echter vanaf 2001, verliep de afname minder snel wat overeen komt met veranderingen in de Europese emissies. De verschillende data sets in het BOP programma waren een goede test voor het LOTOS-EUROS model. Een van de conclusies is dat de huidige beleidsinstrumenten (monitoring, modellering), verdere verbetering behoeven.

Trefwoorden
secundair anorganisch aërosol, ammonium nitraat, ammonium sulfaat, fijn stof, $PM_{10}$, $PM_{2.5}$, precursor gassen, metingen, modellering, trend, temporele variabiliteit, ruimtelijke variabiliteit, Nederland

# Contents

- Rapport in het kort 5
- 1 Summary 9
- 1 Introduction 11
  - 1.1 Background 11
  - 1.2 Literature review 12
- 2 Experimental methods 15
  - 2.1 Measurements 15
  - 2.2 Modelling 17
- 3 Descriptive statistics 19
  - 3.1 LML data set 19
  - 3.2 BOP filter data set 21
  - 3.3 MARGA system data set 21
- 4 Results 25
  - 4.1 Spatial variability 25
  - 4.2 Temporal variability 28
- 5 Discussion 35
  - 5.1 Trends for $NH_4$, $NO_3$ and $SO_4$ during 1994 to 2007 in the LML data set 35
  - 5.2 Representativeness of the LML data set 38
  - 5.3 Levels of secondary inorganic aerosol at regional, city background and traffic locations 42
  - 5.4 Modelling of SIA by LOTOS-EUROS compared to the filter and MARGA measurements 49
- References 57
- Acknowledgements 59

# Summary

Secondary inorganic and organic aerosols form a major fraction of particulate matter (PM). In the Netherlands, secondary inorganic aerosol (SIA) comprises on average up to 50% of the total PM concentrations. SIA, containing ammonium nitrate and ammonium sulphate, is produced in air, in droplets and on particles from sulphur dioxide, nitrogen oxides and ammonia, following complex chemical reactions. SIA is almost completely of anthropogenic origin, as its precursor gases are largely emitted by traffic, energy production and agricultural sources. Emission densities of ammonia and nitrogen oxides in the Netherlands are among the highest in Europe. SIA not only plays an important role in air quality but also in environmental issues, such as climate change, acidification and eutrophication. To efficiently reduce SIA concentrations, emissions of precursor gases are regulated on a European scale, by means of, for instance, national emission ceilings. Important uncertainties regarding SIA still exist, even though considerable progress has been made over the last decades. Filter measurements have at least 25% uncertainty. In addition, ammonium nitrate is semi-volatile, which hampers a precise measurement. Consequently, uncertainties when dealing with SIA in the Netherlands are:

- absolute concentration and relative distribution
- spatial and temporal behaviour, especially during episodes of high PM concentrations
- contribution to urban levels of PM
- chemical formation
- agreement between modelling and measurement

The SIA climatology and variability in time and space is treated in this report, in relation to PM standards. Special attention was given to the urban increment and modelling performance. The basis for this study consisted of dedicated and routine measurements, and LOTOS-EUROS simulations. Three different data sets were used:

- daily BOP filter series (2007-2008)
- hourly MARGA system series (2007-2008)
- daily LML filter series (1994-2008)

In addition, SIA filter data sets from abroad (Belgium, Germany) were used for comparison (2006-2008).

The most important results from this study are summarised here.

- The contribution of SIA to PM$_{10}$ and PM$_{2.5}$ in the Netherlands is larger than previously thought. This notion should be taken into account in air pollution policy as emission reductions regarding SIA(-precursors) could then become more effective in the attainment of PM standards. It is envisaged that tools for monitoring and modelling, that are vital in air quality management in the Netherlands, need improvement and that more research is necessary.
- SIA dominates the PM composition, especially when increased PM levels occur. The average contribution of SIA to PM$_{10}$ in the Netherlands was estimated to be 30 to 40%. This increased to between 45 and 55% on days when PM$_{10}$ was above 40 ug/m$^3$ (and became 25 to 35% when PM$_{10}$ was less than 40 µg/m$^3$). Long-range transport and meteorology are the main factors influencing these higher levels.
- The trends in SIA concentrations have been determined for the period between 1994 and 2007. Up to 2000, a considerable decrease was estimated for all SIA components (especially for sulphate). From 2001 onwards, the downward trends become weaker. These trends are in line with changes in precursor emissions. Because the amount of SIA in PM appears to be higher than previously thought (see above), such trends estimations have become less certain.
- The various data sets acquired in the BOP programme provided a good test for the LOTOS-EUROS model. The model underestimated the SIA levels and did not reproduce the observed gradients in SIA. This affected the estimates of the presence of SIA in PM. The temporal variability (seasonal, daily, hourly) was captured rather well. Further research is necessary to improve the model's performance.

## Contribution of SIA to PM larger than previously thought

Substantial differences were observed between the SIA concentrations in the Netherlands Air Quality Monitoring Network (LML) (PM$_{3\text{-}4}$) and those measured simultaneously in the BOP campaign for PM$_{2.5}$. The LML concentration for total SIA, on average, was 36% lower. This was particularly the case for nitrate and sulphate. Deviations with simultaneously measured PM$_{10}$ levels in the Belgian data set Chemkar were of the same magnitude as those in the BOP data. It was concluded that the LML data appeared to underestimate the (assumed) PM$_{3\text{-}4}$ fraction. As a consequence, the contribution of SIA to PM$_{10}$ and PM$_{2.5}$ is in fact larger than was assumed until now. The reason for the discrepancy is unknown and further research is necessary.

### Spatial and temporal variability

The various data sets suggested that SIA concentrations in PM are larger in the southern and western part of the Netherlands. In particular, higher levels were observed in the urbanised regions, such as in Breda and Rotterdam, and in a rural region like Vredepeel. The regional contribution dominated the presence of SIA at the urban locations. Urban increments of SIA in $PM_{10}$ of up to 3.8 µg/m³ were estimated (depending on the compared locations). Similar results were calculated in German and Belgian data sets. The largest contribution to the urban $PM_{10}$ increment came from nitrate (2 µg/m³), followed by anthropogenic sulphate (1.2 µg/m³). Parts of these increments are in the coarse mass fraction . The data suggest that coarse sea salt particles act as reactive sinks for nitric and sulphuric acid resulting in Cl depletion and HCl gas release. Street increments due to SIA appeared negligible in both $PM_{10}$ and $PM_{2.5}$.

### Exceedance days

On exceedance days, or more general, on days with high PM concentrations, the increase in SIA was larger than the average increase in PM (or any other component therein). The SIA contribution on such days rose to 55%, making SIA (and nitrate, in particular) primarily responsible for these high PM levels. A relationship with wind direction was established: the high levels occurred when the wind direction was within 50° to 220°, where the major source areas are localised. Such wind directions often coincided with the occurrence of high pressure systems (mainly in winter). Under such circumstances, the supply of cold air from the European continent leads to stagnant (non-dispersive) conditions and lower mixing heights. However, next to the long-range contribution, an additional local production is suggested, which needs further clarification.

### Trends

Linear trends were calculated from the LML data set (1994-2007). A decrease in the SIA contribution of 5.1 µg/m³ was estimated over these 14 years. Presumably, this is a lower limit for a corresponding decrease of SIA in $PM_{10}$ (the cut-off diameter in the LML data set is assumed to be between 3 and 4 µm). The change was largest for sulphate: -2.3 µg/m³ and lowest for ammonium (-1.2 µg/m³). The change for nitrate was -1.7 µg/m³. The trends for the components at the various LML locations did not differ greatly. Only at Vredepeel trends were weaker or absent. Downward trends between 1994 and 2000 were stronger than those starting in 2001.

The trends between 1994 and 2007 were qualitatively in line with decreasing emissions of the precursors derived from the European emissions data set, as reported by the European Monitoring and Evaluation Programme (EMEP). The slowing down after the year 2000 can be explained by the decreasing pace in precursor emission reductions. Decreases in the precursor emissions do not cause an equal decrease in SIA concentrations. Non-linear processes determining the conversion from precursor gas to SIA constituent, depend on prevailing chemical composition of the atmosphere and meteorological conditions (temperature, humidity).

During the course of this study, it became apparent that the representativeness of the LML data, for PM10 and PM2.5, is less clear (see above). Trends given here will only be valid for the mass fraction captured. It is this mass fraction that needs to be determined more precisely.

### Modelling with LOTOS-EUROS

The various data sets acquired in the BOP programme, provided a good test for the LOTOS-EUROS (LE) model. The comparison showed that the model underestimates the SIA levels and does not reproduce the observed spatial gradients. It was noted that the underestimation compared to the LML data (used for validation in the past decade) was lower or absent. Further inspection revealed that baseline values appeared well estimated for ammonium and sulphate, and that the underestimation predominantly took place at the peak concentrations. For nitrate, the variability towards high concentrations was much better captured, and a systematic relative underestimation was found. The model is able to reproduce the seasonal and average diurnal variation of the SIA components. The performance of the LE model could improve further by verification of the equilibrium module, inclusion of coarse mode nitrate, and through a better understanding of the processes concerning SIA formation with a detailed analysis of the hourly data set, which is currently available.

# 1

# Introduction

## 1.1 Background

This report describes research on the presence and properties of secondary inorganic aerosol (SIA) in the Netherlands, as executed within the BOP programme. SIA (ammonium, nitrate and sulphate) is important as it contains the major constituents of the particulate matter fractions $PM_{10}$ and $PM_{2.5}$. In reference to the new EU Air Quality Directive , the dominating presence of SIA is essential to the attainability of the concentration limit values of $PM_{10}$ and $PM_{2.5}$, as prescribed by thise directive. In particular, their role in the occurrence of the so-called exceedance days is important.

The majority of SIA precursors ($SO_2$, $NH_3$ and $NO_x$) is of anthropogenic origin. It has long been known that their reaction products play a role in the acidification of soil and water and eutrophication of ecosystems. The main cause of acidification is the airborne deposition of sulphur. The deposition of nitrogen compounds (nitrogen oxides and ammonia) is the cause of eutrophication of many ecosystems both on land and in the sea, but also contributes increasingly to acidification.

Air pollution may travel over long distances and cross national borders. In order to limit air pollution (including ground-level ozone) and its consequences, the European Community has policies in place, limiting individual sources and national totals of atmospheric emissions of pollutants. In 2001, the European Directive 2001/81/EC - or NEC Directive - came into force. The NEC directive sets National Emission Ceilings for sulphur dioxide ($SO_2$), nitrogen oxides ($NO_x$), volatile organic compounds (VOCs) and ammonia ($NH_3$), and is binding for every EU Member State (ceilings to be adhered to by 2010). Parallel to the development of the EU NEC Directive, the EU Member States – together with central and eastern European countries, the United States and Canada – have negotiated the 'multi-pollutant' protocol under the Convention on Long-Range Transboundary Air Pollution (the so-called Gothenburg protocol, agreed on in November 1999). These two agreements are the most important instruments to bring about emission reductions within Europe.

Although the emissions of the different pollutants drastically decreased over the last 20 years, there still is a need for additional reduction measures to meet the NEC requirements in the Netherlands. This is particularly the case for the $NO_x$ ceiling (industry en transport) and the $SO_2$ ceiling (industry). The determination of levels and trends of the SIA components is important in the assessment of the effects of these abatement strategies.

### *Netherlands Research Program on Particulate Matter (BOP)*

*This study is conducted under the auspices of the Netherlands Research Program on Particulate Matter (BOP), a national program on $PM_{10}$ and $PM_{2.5}$, funded by the Netherlands Ministry of Housing, Spatial planning and the Environment (VROM). The program is a framework of cooperation, involving four Dutch institutes: the Energy research Centre of the Netherlands (ECN), the Netherlands Environmental Assessment Agency (PBL), the Environment and Safety Division of the National Institute for Public Health and the Environment (RIVM) and TNO Built Environment and Geosciences.*

*The goal of BOP is to reduce uncertainties about particulate matter (PM) and the number of policy dilemmas, which complicate development and implementation of adequate policy measures. Uncertainties concerning health aspects of PM are not explicitly addressed.*

*The approach for dealing with these objectives is through the integration of mass and composition measurements of $PM_{10}$ and $PM_{2.5}$, emission studies and model development. In addition, dedicated measurement campaigns have been conducted to research specific PM topics.*

*The results of the BOP research program are published in a special series of reports. The subjects in this series, in general terms, are: sea salt, mineral dust, secondary inorganic aerosol (this report), elemental and organic carbon (EC/OC), and mass closure and source apportionment. Some BOP reports concern specific PM topics: urban background, PM trend, shipping emissions, EC/OC emissions from traffic, and attainability of $PM_{2.5}$ standards. Technical details of the research program are condensed in two background documents; one on measurements and one on model developments. In addition, all results are combined in a special summary for policy makers*

Although vast scientific knowledge on SIA exists (as described in the next section), uncertainties remain regarding spatial and temporal variability, chemical mechanisms and modelling issues. Some of these items were selected within the BOP programme for further research. In particular, the following has been addressed in this report:

- background levels, increments of city and street levels due to SIA
  - One of the research goals formulated in the BOP programme regarding secondary inorganic aerosol is the assessment of its presence in regional background air, as well as in urban air. In the design of reduction policy this issue is of interest because the (summated) SIA constitutes the largest contribution to airborne PM in the Netherlands, and can, to a certain degree, be manipulated by the implementation of political and technical measures aimed at the limitation of the emissions of the respective precursors. In particular, with (daily) exceedances for $PM_{10}$ occurring mainly in city areas, it is important to know to which extent the SIA components are 'responsible' for the increments in particulate matter in the urban background environment and in city streets. Also of interest are the conditions during which these days occur, in particular, the meteorological circumstances.
- long-term trends in $NH_4$, $NO_3$ and $SO_4$.
  - Because of its timespan (1994-2007), the LML data set provides an exquisite base for estimating the changes in SIA concentrations over the past years. Obviously, from a political point of view, it is important to assess whether the reduction strategies have been successful. The questions here are (1) if the trends observed correspond to expectations one may have considering the reduction measures limiting the emissions of SIA precursors, over the past years (in the EU), and (2) what are the reasons behind the trends and are these trends in line with current understanding? For this report, these questions have been addressed in qualitative terms, including a comparison with emission data from outside the Netherlands.
- representativeness of the LML data set
  - A precise estimate of the measured mass fraction in the LML data set is not known. As these results are used for modelling purposes (OPS/LOTOS-EUROS) there is an increasing need for a more precise determination. The BOP measurement campaigns allow the comparison between LML data (Vredepeel; $PM_{3-4}$) and simultaneously measured filter data, at the same location, for $PM_{2.5}$ (and $PM_{10}$).
- agreement between modelling results and measurements (LOTOS-EUROS)
  - The complex formation pathways for SIA are represented in chemistry transport models in a simplified manner. In the Netherlands, the LOTOS-EUROS model (LE) is used to assess SIA levels in Europe, and for the Netherlands in particular. Although the BOP programme was not aimed to improve the modelling approaches for SIA, the data from the BOP campaign did provide a good test case for the LE model. This is especially true considering the fact that, for the first time, an hourly data set was available for a full-year period (at Cabauw). Hence, for this report, LE results were compared to the MARGA data to study the performance in the simulation of time series and to estimate the average levels of nitrate, sulphate and ammonium. Furthermore, the report presents possible explanations of the differences that were noted, and gives directions for model improvement.

This research could be carried out, because of the availability of three different data sets, containing the results from analyses of the chemical content of particulate matter over various time scales:

- daily filters ($\approx PM_{3-4}$) collected in the 1994-2007 period from 6 regional sites within the National Air Quality Monitoring Network (LML)
- daily filters ($PM_{10}$ and $PM_{2.5}$) collected between August 2007 and September 2008 from 5 different types of sites (regional, urban background, traffic) (within the BOP programme)
- 'on-line' hourly measurements of SIA ($PM_{10}$) concentrations, at Cabauw, Schiedam and Hoek van Holland (partly within the BOP programme)

First, a concise review of recent literature on SIA is given.

## 1.2 Literature review

### 1.2.1 Chemical composition

Secondary Inorganic Aerosol (SIA) is composed of acids (sulphuric acid, nitric acid) and ammonium sulphate ($NH_4HSO_4$, $(NH_4)2SO_4$) and ammonium nitrate ($NH_4NO_3$) salts. Other (less abundant) constituents are sodium sulphate ($Na_2SO_4$), calcium sulphate ($CaSO_4$), sodium nitrate ($NaNO_3$) and calcium nitrate ($CaNO_3$). They are denoted 'secondary' since they are the products of physical and chemical processes after emission into the atmosphere. The majority of the secondary sulphates in $PM_{10}$ are a combination of sulphuric acid and ammonium sulphate. The dominant secondary nitrate is ammonium nitrate, while a small portion may be associated with sodium.

'Primary' aerosols are emitted directly into the atmosphere, either by industry or natural phenomena (sea spray, wind blown dust). The SIA levels are dominant in particulate matter (PM). In urban areas they compromise up to 50% of the measured PM mass (e.g., Tsyro *et al.*, 2003; Erisman and Schaap, 2004; Putaud *et al.*, 2003) and are of great importance during periods with high PM concentrations (in particular, on exceedance days of $PM_{10}$). SIA and the precursors have a serious environmental impact when deposited on the earth's surface (acidification and eutrophication). Due to their lifetimes (days to weeks) these effects are observed in ecosystems that are far away from the source areas. In addition, the SIA components play an important role in climate: directly, through the reflection and absorption of incoming solar radiation, and indirectly through the formation of condensation nuclei for cloud and fog droplets (IPCC, 2007).

### 1.2.2 Emission sources

Gaseous precursors of SIA are sulphur dioxide ($SO_2$), nitrogen oxides (NO sand $NO_2$; generic term is $NO_x$) and ammonia ($NH_3$). $SO_2$ is released by coal-burning power plants, cement industry and other industrial sources, such as smelters, industrial boilers, and oil refineries. Nitrogen mono-oxides and di-oxides are mostly emitted during fossil-fuel combustion, especially in cars, trucks, off-road vehicles (e.g., construction equipment and ships), power plants, and other industrial sources. Other sources of NO are bacterial processes, wildfires and lightning. Agricultural activity is the major emission source of ammonia. Additional (much smaller) contributions come from non-agricultural sources, such as oil refineries and fuel combustion. The presence of precursor gases is generally related to the strength of the corresponding emissions. However, ambient concentrations of sulphate and nitrate are not necessarily proportional to the concentrations of the precursor gases, because the rate at which they form depends on factors, such as temperature, relative humidity, and availability of $NH_3$/$NH_4$ (Seinfeld and Pandis,1998; Bergin *et al.,* 2005).

Measurements and modelling studies indicate that sulphur compounds may travel regional and even intercontinental distances, although emission takes place at point (industry) or line sources (e.g., Andrea *et al.,* 1988; Park *et al.,* 2004; Bergin *et al.,* 2005). Since the oxidation of sulphate from sulphur oxide is slow, complete oxidation takes several days. During this long residence time in the air, sufficient atmospheric mixing occurs, such that pollutants generally are well distributed, regionally. Both local and regional sources contribute to the particle pollution. In practice, local and regional contributions to PM mass can be estimated by subtracting the rural concentration from the measured urban concentration after pairing a monitoring site in urban areas with a nearby rural site (e.g., EPA, 1997). The same practice was used in this study. As a result of such measurements in the highly urbanised region around (and including) New York, the percentage of transported sulphate was estimated at above 93%, while for nitrate this was between 54 and 65% (Allen and Turner, 2008). Since 1980 there has been an increased awareness of the effects of regional transport of air pollution. $SO_2$ emission and sulphate particles in 20 European countries have been reduced by 80 and 65%, respectively, since the LRTAP Convention in 1979 (EMEP report, 2004).

In an increasing number of studies, nitrate has been found to be an important component in fine particulate matter (Magliano *et al*., 1999; Putaud *et al*. 2003; Schaap *et al*., 2008; Ten Brink *et al*., 2007). Observations and model results showed that in regions of elevated $NO_x$ and $NH_3$ emissions, such as in Europe and parts of North America, ammonium nitrate concentrations may be quite high and actually exceed those of sulphate (Schaap *et al*., 2003; Christoforou *et al*., 2000; Wieprecht *et al.,* 2004). Similar to sulphate, the contribution of nitrate to particulate matter has also been found on a regional scale, but there is still not enough experimental data available on Europe (Ten Brink *et al.,* 1997; Schaap 2003; EMEP report, 2004).

### 1.2.3 Formation pathways

#### Sulphate particles

$SO_2$ changes into particulate sulphate on a gas-phase or aqueous-phase transformation path. In the first case, $SO_2$ is converted into sulphuric acid gas ($H_2SO_4$) by reacting with hydroxyl radicals (OH·), oxygen ($O_2$) and small amounts of water vapour, as shown in the reactions 1 to 3, below. Sulphuric acid gas has a low vapour pressure, indicating a slow evaporation rate (Bauer *et al*., 2007). It condenses on existing particles and nucleates at high relative humidity, to form a $H_2SO_4$ droplet or, in the presence of $NH_3$ gas, becomes neutralised as (bi-)ammonium sulphate (reactions 4 to 5). In the marine or remote continental troposphere and in the stratosphere, where the major aerosol component is $H_2SO_4$ near the sources of gaseous $NH_3$, ammonium sulphate dominates, depending on the supply of $NH_3$ relative to the rate of $H_2SO_4$ formation. Since the conversion of hydrogen sulfite ($HSO_3$) to sulphuric acid ($H_2SO_4$) is fast, the oxidation of sulphur dioxide ($SO_2$) critically depends on the presence of OH· radical. Since these radicals are formed by photochemistry, the gas-to-particle-conversion of $SO_2$ knows a diurnal, seasonal and latitudinal cycle in relation to the varying solar intensities.

$$OH\cdot + SO_2 \rightarrow HSO_3 \qquad (1)$$

$$HSO_3 + O_2 \rightarrow HO_2 + SO_3 \qquad (2)$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad (3)$$

$$H_2SO_4 + NH_3 \rightarrow NH_4HSO_4 \qquad (4)$$

$$NH_4HSO_4 + NH_3 \rightarrow (NH_4)_2SO_4 \qquad (5)$$

The aqueous pathway takes place when $SO_2$ is dissolved in a droplet produced by fog or clouds. If ozone ($O_3$) and hydrogen peroxide ($H_2O_2$) are also dissolved in this droplet, $SO_2$ is quickly oxidised to $H_2SO_4$. If, in addition, $NH_3$ is present, the $H_2SO_4$ is neutralised to $NH_4HSO_4$ (Claes, 1998). Compared to the gas-phase oxidation of $SO_2$, the aqueous pathway is much faster and depends on cloudiness. Therefore, it dominates in the winter period, in the lower and middle troposphere when clouds are abundantly present.

#### Nitrate particles

Generally, atmospheric nitrate arises from the oxidation of nitrogen dioxide ($NO_2$) to nitric acid ($HNO_3$), producing particles as the result of reactions with ammonia or sodium chloride. NO rapidly oxidises to $NO_2$ giving an extra contribution. During the daytime, the main pathway of nitric acid formation is the reaction of $NO_2$ with the OH radical (reaction 6), which has a larger reaction rate than the $SO_2$ oxidation by OH (reaction 1). During the night-time, due to low OH concentrations, the reaction of $NO_2$ with $O_3$ becomes important (reactions 7 to 9). Ammonia gas reacts reversibly with $HNO_3$ to form the ammonium salt $NH_4NO_3$ (reaction 10), which is semi-volatile and may release its gas-phase precursors under conditions of low atmospheric $NH_3$, or at high temperatures (e.g., Claes *et al.,* 1998; Worobiec *et al.,* 2003). The concentrations of $NH_4NO_3$, therefore, are often seen to be higher during the night-time or colder periods of the year (e.g., Pun and Seigneur, 2001; Ten Brink *et al.*, 2007).

$$OH\cdot + NO_2 \rightarrow HNO_3 \quad (6)$$

$$O_3 + NO_2 \rightarrow NO_3 + O_2 \quad (7)$$

$$NO_2 + NO_3 \rightarrow N_2O_5 \quad (8)$$

$$N_2O_5 + H_2O \rightarrow 2\ HNO_3 \quad (9)$$

$$NH_3 + HNO_3 \leftrightarrows NH_4NO_3 \quad (10)$$

In marine and coastal atmospheres, $HNO_3$ is also converted into sodium nitrate ($NaNO_3$) through the reaction with sea salt particles, resulting in the release of HCl (reaction 11). In contrast to $NH_4NO_3$, $NaNO_3$ is non-volatile (Schaap, 2003), meaning that the partitioning of $HNO_3$ into sea salt is irreversible. Similarly, in the presence of soil dust, $HNO_3$ is adsorbed easily onto these particles, forming stable products, such as $Ca(NO_3)_2$ and $Mg(NO_3)_2$ (reactions 12 to 13).

$$NaCl + HNO_3 \rightarrow NaNO_3 + HCl \quad (11)$$

$$CaCO_3 + 2\ HNO_3 \rightarrow Ca(NO_3)_2 + CO_2 + H_2O \quad (12)$$

$$MgCl_2 + 2\ HNO_3 \rightarrow Mg(NO_3)_2 + 2\ HCl \quad (13)$$

Generally, the chemical transformations of $SO_2$ to particulate sulphate and $NO_2$ to particulate nitrate reactions compete with each other for the available OH· radicals and $NH_3$. Ammonia is preferentially trapped by sulphate to form ammonium sulphate. The amount of ammonium nitrate becomes significant when the total $NH_3$ exceeds the sulphate by a factor of two or more on a mole basis (Schaap, 2003). Therefore, in an $NH_3$-limited environment, reducing $(NH_4)_2SO_4$ concentrations by one molecule would increase $NH_4NO_3$ concentrations by two molecules. This implies that reducing $SO_2$ emissions might actually result in an $NH_4NO_3$ increase that exceed the reductions in $(NH_4)_2SO_4$ where the availability of $NH_3$ is limited.

### 1.2.4 Contribution of SIA components to $PM_{10}$ and $PM_{2.5}$

Compiled experimental data between 1994 and 1997 have shown that nitrate concentrations in the wintertime range between 4 and 6 µg/m³ over large areas of Europe. An apparent maximum of 7 µg/m³ exists in Switzerland and northern Italy. In the north of Europe, nitrate levels are below 2.5 µg/m³. Sulphate concentrations were measured between 3 and 7 µg/m³ in large parts of Europe. Only in the more remote regions, the concentrations were of the order of 2 to 3 µg/m³. Modelled concentration values suggest that sulphate and nitrate contribute 25 to 50% and 5 to 35% to $PM_{2.5}$, respectively, in Europe (Schaap, 2003).

In an extensive seven-week long field campaign to determine the chemical composition of $PM_{2.5}$ at six different urban background sites (Duisburg, Prague, Amsterdam, Helsinki, Barcelona and Athens; 2002-2003), the secondary inorganic aerosols, on average, accounted for about 40% of the $PM_{2.5}$ mass. The contribution of sulphate to $PM_{2.5}$ ranged between 14 and 31%. Sulphate was the dominant secondary anion in all cities, except for Amsterdam, where nitrate concentration was higher than sulphate. The contribution of $NH_4$ to $PM_{2.5}$, was between 7 and 10%. The ammonium nitrate concentration typically peaked in wintertime when the ambient temperatures were low (Sillanpaa *et al.*, 2006).

At different measuring locations in the Flemish region of Belgium (between 2001 and 2003), sulphate was the SIA component contributing most with an average concentration of 3.2 µg/m³ (contribution to $PM_{2.5}$ was 18%). Nitrate and ammonium showed an average of 2.6 µg/m³ and 2.1 ug/m³, respectively (being contributions to $PM_{2.5}$ of around 10 and 8%). On a seasonal basis, nitrate was of comparable level to sulphate in winter, but in summer sulphate was obviously more important, having a larger thermal stability (Torfs *et al.*, 2007).

In another field campaign (in three different urban background locations in Germany; 2002-2003) the secondary ions comprised 40% of total $PM_{10}$ (more specifically: 17% (nitrate), 16% (sulphate) and 7% (ammonium)). The presence of SIA in the $PM_{2.5}$ fraction was only slightly higher: 17, 18 and 9%, confirming that most of these compounds are found in the fine particulate mass fraction (Quass *et al.*, 2004).

Measured and modelled SIA concentrations at different sites in the Netherlands fall within the range observed for the rest of Europe. In a comparison study of two sites (Vredepeel and De Zilk; 1998 to 1999), the nitrate and sulphate concentrations were 2.2 to 4.2 and 2.7 to 6 µg/m³, respectively (Visser *et al.*, 2001). A campaign in November 2001 at rural Cabauw resulted in concentration values for nitrate and sulphate of 3.3 and 2.1 µg/m³, respectively (with a maximum of 12 µg/m³ for both components) (Weijers *et al.*, 2002).

# Experimental methods

# 2

## 2.1 Measurements

### 2.1.1 Location and measurement period

The locations of the monitoring sites are shown in Figure 2.1. With respect to the SIA measurements, eight locations of the Dutch National Air Quality Monitoring Network (LML) are included:

- Central region: De Zilk and Bilthoven
- Region North: Kollumerwaard, Valthermond, Witteveen and Wieringerwerf
- Region South: Vredepeel and Huijbergen

All locations are defined as 'regional'. Bilthoven, however, is part of the Utrecht agglomeration. Daily filter collection took place from 1 January 1994 to 31 December 2007. In the remainder the data set is denoted by 'LML data set'. In the year 2000, the filter collection at Witteveen was ceased and moved to Valthermond (some 22 kilometres to the north-east).

The BOP filter measurements took place every second day, at the following six locations (between 15 August 2007 and 04 September 2008):

- rural: Hellendoorn, Cabauw (roughly 50 km northeast of Rotterdam) and Vredepeel
- urban background: Schiedam
- traffic: Rotterdam-Overschie and Breda A full chemical analysis (including SIA) was performed every fourth day.

The MARGA systems were situated at Schiedam (urban; DCMR), Hoek van Holland (marine; maintenance by DCMR) and Cabauw (regional). These instruments were deployed for seven months (1 August 2007 to 21 February 2008) at Schiedam, for 12 months at Cabauw (1 August 2007 to 31 July 2008) and for two months (1 September 2007 to 10 October 2007) at Hoek van Holland. In this way, the MARGA data set of hourly measurements was fully overlapped by the BOP filter data set, and for four months by the LML data set. A number of daily filters was selected to provide a data set of interesting episodes (e.g., days with high concentrations). These data were not included when calculating average concentrations or periodical behaviour. A description of the measurement strategies and experimental techniques will be included in the BOP report 'Measurements in the BOP national program on $PM_{10}$ and $PM_{2.5}$: a technical background document' (Matthijsen *et al.*, 2010 to be published).

### 2.1.2 LML data set

$NO_3$, $SO_4$ and $NH_4$ (as well as Cl) are measured by the LML, on a daily basis, using Low Volume Samplers (LVS). A constant flow (2500 l per 24 hours) passes a PM filter. Concentrations of SIA are then determined with the aid of ion-chromatography. For a diagram of the instrument see Visser *et al.* (2001). Data quality of this set is guaranteed by the Dutch National Institute for Public Health and the Environment (RIVM).

In the LML data set, concentration values for nitrate and sulphate are sometimes labelled as 'below detection limit (DL)'. For the ammonium data, no DL is given. For the period between 1994 and 2001, the detection limits were 0.744 µg/m³ ($NO_3$) and 0.769 µg/m³ ($SO_4$). After 2001, the DLs were changed to 0.992 µ/m³ and 1.153 µg/m³. The number of nitrate concentration values below DL varied between 8 and 21%; for sulphate, this was between 4 and 14% (Table 2.1). In terms of percentage, the number of data points below DL was largest for Valthermond and Witteveen. The amount of missing data relates to the absolute concentration at a location. Concentrations at Witteveen and Valthermond were among the lowest in the LML data set.

Concentration values denoted 'below DL' were replaced by 0.5*DL. In case of the sulphate time series, values lower than the DL were also listed. These were left unaltered, as were the (small) negative concentrations observed in the ammonium series.

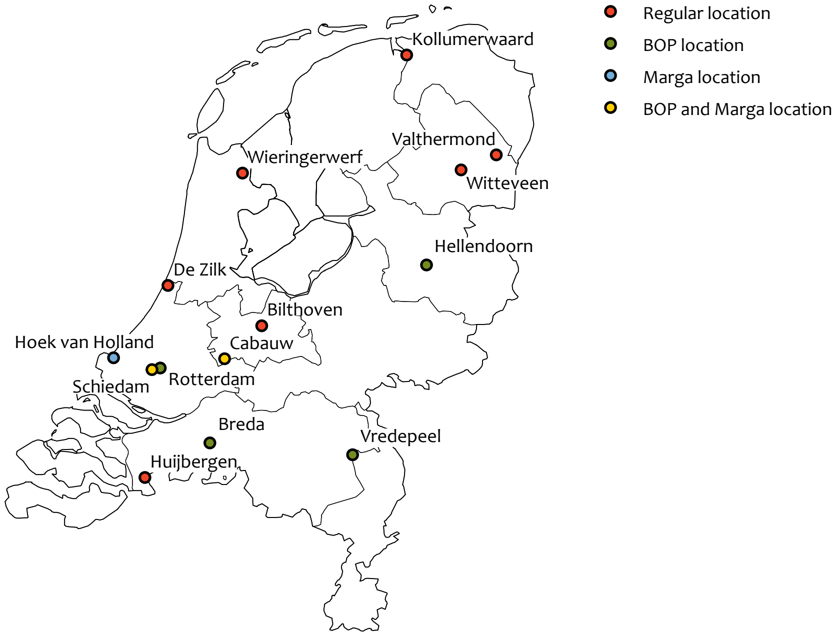
### 2.1.3 BOP filter data set

The filters were collected according to the reference method described in the European Standard (EN12341). The measurement instrument was SEQ47/50 (Leckel GmbH, Germany). The chemical analyses for SIA were performed at the ECN. The number of days on which one of the SIA concentrations was lower than the DL was 17 (out of 1041). These were replaced by zero.

### 2.1.4 MARGA system data set

During the BOP campaign, hourly concentrations of inorganic components of aerosol (sulphate, nitrate, ammonium, sodium, chloride, potassium, calcium and magnesium) and the related gas-phase components in ambient air (nitric acid, nitrous acid, $SO_2$, ammonia and hydrochloric acid) were measured by the MARGA system (Monitoring instrument for AeRosols and GAses). The MARGA consists of two boxes: a sampling unit and an analytical unit. A mass flow

**Overview of regular and BOP measurement locations** **Figure 2.1**



*Locations of the measurement sites. Green for LML sites; blue for BOP sites and MARGA sites.*

**Number of samples with concentration values below the detection limit** **Table 2.1**

| | | **# <DL** | **# all data** | **%** |
|---|---|---|---|---|
| *$NO_3$* | Bilthoven | 387 | 4844 | 8 |
| | De Zilk | 820 | 4680 | 18 |
| | Huijbergen | 738 | 4652 | 16 |
| | Kollumerwaard | 691 | 4818 | 14 |
| | Valthermond | 541 | 2615 | 21 |
| | Vredepeel | 434 | 4797 | 9 |
| | Wieringerwerf | 595 | 4669 | 13 |
| | Witteveen | 301 | 2055 | 15 |
| *$SO_4$* | Bilthoven | 177 | 4845 | 4 |
| | De Zilk | 333 | 4680 | 7 |
| | Huijbergen | 472 | 4652 | 10 |
| | Kollumerwaard | 361 | 4815 | 7 |
| | Valthermond | 350 | 2615 | 13 |
| | Vredepeel | 332 | 4797 | 7 |
| | Wieringerwerf | 335 | 4669 | 7 |
| | Witteveen | 287 | 2055 | 14 |

controlled air pump draws 1 m$^3$ ambient air per hour through the sampling box. During the campaign, an URG PM$_{10}$ head impactor was positioned as inlet on a height of four metres. The sampler unit has a Wet Rotating Denuder (WRD) for gas sampling and a Steam Jet Aerosol Collector (SJAC). Gasses are dissolved in water in the WRD, which is present as a thin film on its wall. Aerosol components have a slow diffusion speed and therefore do not dissolve in the WRD. Aerosol is collected in the SJAC (Khlystov *et al.*, 1995). The air, stripped from water-soluble gases, is drawn through a glass mixing chamber and a 2-micron cut-off glass cyclone. In the mixing chamber, a water supersaturated condition is created by means of steam injection, forcing a water vapour condensation process. Through condensational growth, aerosol components are quantitatively separated in the cyclone.

The detection system was continuously controlled by internal calibration with components not found in ambient air. Sample flows from the MARGA were tested once a month. The systems were compared twice (before and after the campaign) by means of external standard solutions containing all relevant components. All data were processed with the purpose to increase the quality and quantity of the data set. The data coverage ranged between 58 and 66% at Schiedam and between 68 and 82% at Cabauw. Software crashes were the main reason for the absence of data. Other data were lost due to servicing events and the validation process. Results from 31 December 2007 and 01 January 2008 were excluded from the data set, as New Year's Eve fireworks lead to unusually high SIA concentrations, that is, above 100 µg/m³.

The MARGA data were compared with BOP filter data for the overlapping period (August 2007 - February 2008). For Cabauw, the absolute levels were in good agreement. However, the MARGA measurements in Schiedam appeared to deviate from the filter results. Assuming the routine filter measurements were executed without errors, the deviation was ascribed to the MARGA system in Schiedam. Both MARGA instruments were regularly tested during experimental campaigns with standard solutions. No significant differences were observed during these control tests. It was therefore concluded that the inlet flow entering the MARGA did not correspond to the measured flow. With this in mind, was decided to recalculate the MARGA concentrations at Schiedam. The correlation coefficients between the MARGA data and the filter data, for SIA, were high at this location: 0.91 ($NH_4$), 0.93 ($NO_3$), 0.98 ($SO_4$) and 0.93 (Cl). For the correction factor, the average of the 4 regression coefficients was used: 0.67, 0.65, 0.69 and 0.58 (average is 0.65). In view of the regression coefficients for Cabauw (0.87 ($NH_4$), 1.01 ($SO_4$), 1.00 ($NO_3$) and 1.18 (Cl); average is 1.01), no change was made for the MARGA time series at Cabauw and Hoek van Holland.

## 2.2 Modelling

LOTOS-EUROS is a three-dimensional chemistry transport model (CTM) of intermediate complexity, covering Europe, developed by the Netherlands Organisation for Applied Scientific Research (TNO) and the National Institute for Public Health and the Environment (RIVM). The idea behind the model is that it should contain all relevant processes (explicitly or in a parameterised form) in such a way that hourly calculations over periods of years are feasible. The European domain ranges between 10° W to 60° E, and 35° to 70° N, with a regular 0.5 x 0.25 longitude/latitude grid. The model includes nesting and zoom options. In the vertical, the model covers the lower 3.5 kilometres of the atmosphere, divided into three dynamical vertical layers and a boundary layer of 25 metres. ECMWF analysis fields are used as the meteorology that is driving the transport. The model is used for several gases and aerosol compositions, and photochemistry with the CBM-IV scheme is included. The model yields output of hourly concentrations. The full model is described in Schaap *et al.* (2008).

Secondary inorganic aerosol formation in the model is represented along different pathways. The oxidation of $SO_2$ to sulphate and $NO_x$ to nitric acid are described in the CBM-IV gas-phase chemistry routine. The routine incorporates the gas-phase reactions presented in Section 1.2.3. Besides the oxidation of sulphur dioxide by the OH radical, another important oxidation pathway, particularly in winter, is the formation of sulphate in clouds. Due to insufficient data on clouds, this process is difficult to explicitly represent in a model. Therefore, it is represented with a first order reaction constant that varies with cloud cover and relative humidity, similar to the approach followed by Matthijsen *et al.* (2002). The sulphuric acid formed is assumed to condense directly and is neutralised by ammonia. When sulphuric acid is completely neutralised, excess ammonia (further denoted as free ammonia) can react with nitric acid under formation of (volatile) ammonium nitrate. This equilibrium is very sensitive to ambient conditions, and is calculated in LOTOS-EUROS using ISORROPIA (Nenes *et al.*, 1999). Note that the model does not include the formation of coarse mode nitrate.

Within the framework of this study, LOTOS-EUROS v1.3 was used to simulate the year of the BOP measurement programme, to compare its results to the detailed data on both the SIA components and their gaseous counterparts. The model validation against LML data was laid down in the technical background report by Schaap *et al.* (2009). Here, the model was run from 1 August 2007 to 31 July 2008. Two sets of runs were made: one on the 0.5° lon x 0.25° lat grid of the full model domain, and one nested run over the Netherlands, from 3° to 9° E and from 49° to 55° N, on a 0.125° lon x 0.0625° lat grid. We have used the results of the nested simulation to compare against observations.

# 3

# Descriptive statistics

This chapter summarises the basic features of the different data sets. The statistics provide insight in central tendency and dispersion. In order to obtain a first impression of the behaviour in time, validated series and correlation coefficients are presented.

## 3.1 LML data set

Table 3.1 provides the averages, as well as other statistics for the LML locations, with respect to SIA.

Figure 3.1 shows the validated time series as calculated for the LML data set (average monthly concentrations). The corresponding correlation coefficients (based on daily values) are given in Table 3.2.

Generally, correlation between time series was moderate (0.50-0.75) to high (>0.75) which was (obviously) reflected in the rather similar behaviour in time, in Fig 3.1. The largest coefficients (0.55-0.86) were calculated for sulphate and the lowest (0.49-0.80) for nitrate. For every SIA component, the strongest relationship was observed between the sites at Bilthoven and De Zilk. The weakest similarity existed between

**Descriptive statistics of the LML data set** **Table 3.1**

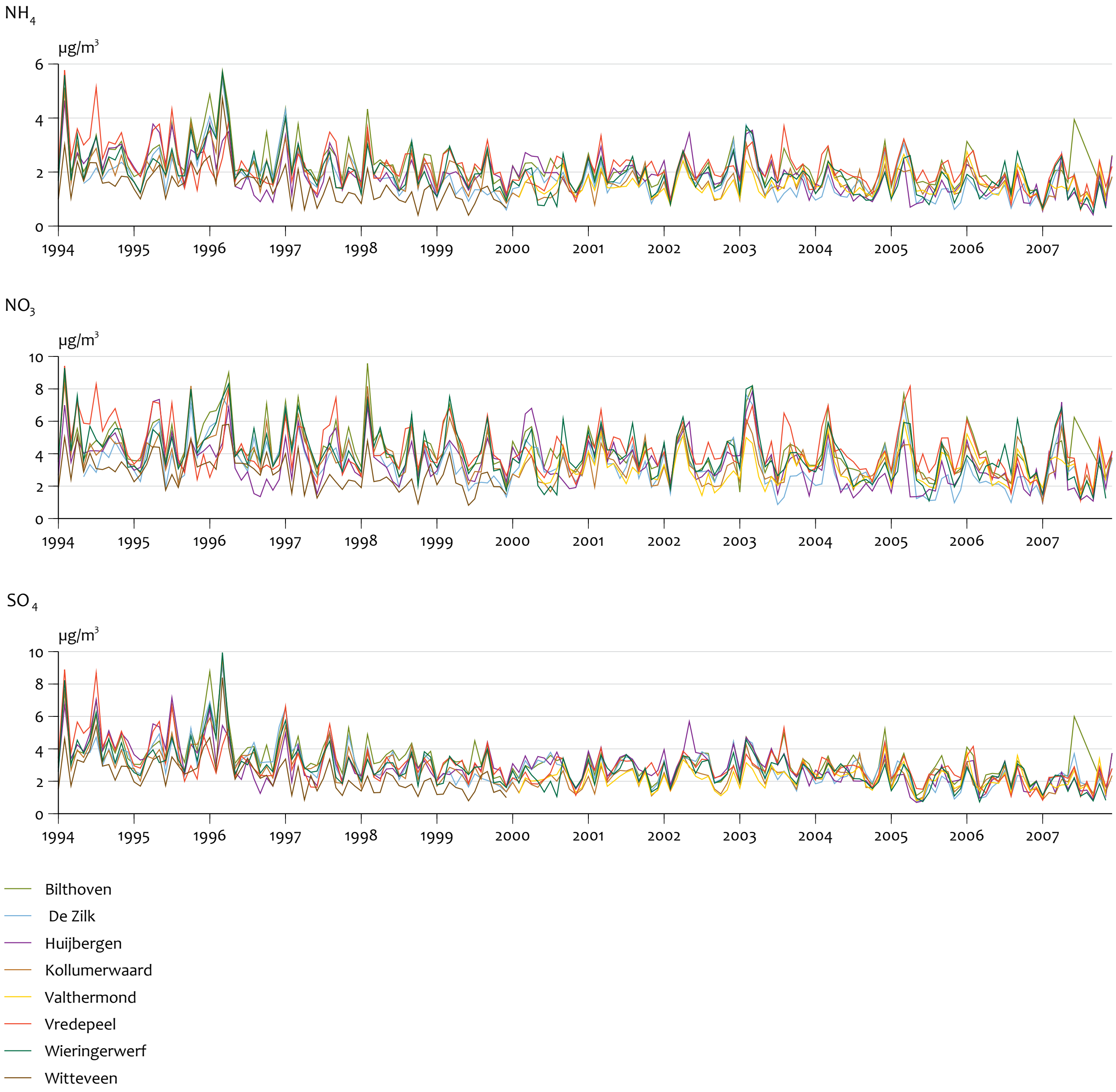
| **$NH_4$** | **Bilthoven** | **De Zilk** | **Huijbergen** | **Kollumerwaard** | **Valthermond** | **Vredepeel** | **Wieringerwerf** | **Witteveen** |
|---|---|---|---|---|---|---|---|---|
| *Valid cases* | 4844 | 4680 | 4652 | 4818 | 2614 | 4797 | 4669 | 2054 |
| *Average* | 2,3 | 1,8 | 1,9 | 1,8 | 1,5 | 2,2 | 2,0 | 1,5 |
| *Variance* | 3,1 | 2,6 | 2,9 | 2,7 | 1,2 | 3,2 | 3,1 | 2,6 |
| *Std. deviation* | 1,8 | 1,6 | 1,7 | 1,6 | 1,1 | 1,8 | 1,8 | 1,6 |
| *Maximum* | 16,2 | 18,3 | 18,3 | 19,1 | 8,6 | 22,9 | 17,4 | 13,6 |
| *25th percentile* | 1,0 | 0,7 | 0,8 | 0,7 | 0,7 | 1,0 | 0,8 | 0,4 |
| *Median* | 1,8 | 1,3 | 1,5 | 1,4 | 1,2 | 1,7 | 1,4 | 1,0 |
| *75th percentile* | 2,9 | 2,3 | 2,6 | 2,4 | 2,0 | 2,9 | 2,6 | 2,2 |

| *$NO_3$* | Bilthoven | De Zilk | Huijbergen | Kollumerwaard | Valthermond | Vredepeel | Wieringerwerf | Witteveen |
|---|---|---|---|---|---|---|---|---|
| *Valid cases* | 4844 | 4680 | 4652 | 4818 | 2615 | 4797 | 4669 | 2055 |
| *Average* | 4,3 | 3,4 | 3,5 | 3,7 | 3,1 | 4,3 | 4,1 | 2,9 |
| *Variance* | 11,7 | 10,2 | 10,1 | 11,0 | 6,2 | 12,3 | 13,2 | 8,1 |
| *Std. deviation* | 3,4 | 3,2 | 3,2 | 3,3 | 2,5 | 3,5 | 3,6 | 2,9 |
| *Maximum* | 34,2 | 34,0 | 34,5 | 28,5 | 15,9 | 35,1 | 35,4 | 26,0 |
| *25th percentile* | 2,0 | 1,1 | 1,2 | 1,4 | 1,5 | 1,9 | 1,5 | 0,8 |
| *Median* | 3,5 | 2,5 | 2,6 | 2,9 | 2,5 | 3,5 | 3,1 | 2,1 |
| *75th percentile* | 5,7 | 4,6 | 4,7 | 5,2 | 4,2 | 5,7 | 5,5 | 4,2 |

| *$SO_4$* | Bilthoven | De Zilk | Huijbergen | Kollumerwaard | Valthermond | Vredepeel | Wieringerwerf | Witteveen |
|---|---|---|---|---|---|---|---|---|
| *Valid cases* | 4845 | 4680 | 4652 | 4815 | 2615 | 4797 | 4669 | 2055 |
| *Average* | 3,3 | 2,9 | 3,0 | 2,7 | 2,1 | 3,0 | 2,9 | 2,5 |
| *Variance* | 6,9 | 5,8 | 6,6 | 5,7 | 2,5 | 6,7 | 6,3 | 6,6 |
| *Std. deviation* | 2,6 | 2,4 | 2,6 | 2,4 | 1,6 | 2,6 | 2,5 | 2,6 |
| *Maximum* | 25,0 | 25,2 | 29,8 | 27,8 | 14,2 | 36,4 | 24,3 | 23,9 |
| *25th percentile* | 1,5 | 1,3 | 1,2 | 1,2 | 1,1 | 1,2 | 1,2 | 0,6 |
| *Median* | 2,7 | 2,3 | 2,3 | 2,0 | 1,8 | 2,3 | 2,2 | 1,7 |
| *75th percentile* | 4,2 | 3,6 | 3,8 | 3,5 | 2,7 | 3,9 | 3,7 | 3,5 |

*Descriptive statistics of the LML data set. The Witteveen data series covers the period between 1994 and 1999. From 2000 onwards, they are replaced by data from nearby Valthermond.*

**Time series of average monthly concentrations of LML data over 14 years** **Figure 3.1**



*Time series of average monthly concentrations of LML data over 14 years.*

Vredepeel and Witteveen. After averaging the entire data set, correlations between ammonium and sulphate and between ammonium and nitrate appeared highest (0.93 and 0.92); nitrate and sulphate correlated considerably less (0.73).

**Correlation coefficients between the LML sites calculated for the daily concentrations (1994-2007)** **Table 3.2**

| $NH_4$ | Bilthoven | De Zilk | Huijbergen | Kollumerwaard | Valthermond | Vredepeel | Wieringerwerf |
|---|---|---|---|---|---|---|---|
| *Bilthoven* | | | | | | | |
| *De Zilk* | 0,85 | | | | | | |
| *Huijbergen* | 0,74 | 0,67 | | | | | |
| *Kollumerwaard* | 0,77 | 0,74 | 0,55 | | | | |
| *Valthermond* | 0,80 | 0,67 | 0,57 | 0,80 | | | |
| *Vredepeel* | 0,73 | 0,58 | 0,68 | 0,54 | 0,62 | | |
| *Wieringerwerf* | 0,77 | 0,77 | 0,60 | 0,76 | 0,63 | 0,58 | |
| *Witteveen* | 0,68 | 0,66 | 0,56 | 0,71 | | 0,52 | 0,69 |

| *$NO_3$* | Bilthoven | De Zilk | Huijbergen | Kollumerwaard | Valthermond | Vredepeel | Wieringerwerf |
|---|---|---|---|---|---|---|---|
| *Bilthoven* | | | | | | | |
| *De Zilk* | 0,80 | | | | | | |
| *Huijbergen* | 0,73 | 0,66 | | | | | |
| *Kollumerwaard* | 0,73 | 0,68 | 0,50 | | | | |
| *Valthermond* | 0,78 | 0,63 | 0,55 | 0,79 | | | |
| *Vredepeel* | 0,73 | 0,56 | 0,68 | 0,51 | 0,61 | | |
| *Wieringerwerf* | 0,73 | 0,73 | 0,58 | 0,72 | 0,62 | 0,57 | |
| *Witteveen* | 0,63 | 0,60 | 0,51 | 0,65 | | 0,49 | 0,63 |

| *$SO_4$* | Bilthoven | De Zilk | Huijbergen | Kollumerwaard | Valthermond | Vredepeel | Wieringerwerf |
|---|---|---|---|---|---|---|---|
| *Bilthoven* | | | | | | | |
| *De Zilk* | 0,86 | | | | | | |
| *Huijbergen* | 0,74 | 0,67 | | | | | |
| *Kollumerwaard* | 0,77 | 0,75 | 0,56 | | | | |
| *Valthermond* | 0,78 | 0,67 | 0,55 | 0,80 | | | |
| *Vredepeel* | 0,73 | 0,61 | 0,69 | 0,56 | 0,60 | | |
| *Wieringerwerf* | 0,78 | 0,77 | 0,60 | 0,78 | 0,63 | 0,59 | |
| *Witteveen* | 0,70 | 0,67 | 0,57 | 0,74 | | 0,55 | 0,72 |

## 3.2 BOP filter data set

The statistics concerning the BOP filter data is presented in Table 3.3.

The correlation coefficients differed more than those calculated for the LML dataset. For both mass fractions, the strongest correlations existed between the urban locations (Schiedam – Rotterdam: ≥ 0.86; Schiedam and Breda: ≥0.81). The weakest correspondences were mostly observed for the Cabauw series. $PM_{2.5}$ showed similar results to $PM_{10}$: a strong(er) correspondence between the Rotterdam and Schiedam locations was calculated, but correlation with Cabauw remained relatively low. When averaging over all sites, the strongest correlation in both $PM_{10}$ and $PM_{2.5}$ was between ammonium and nitrate (0.90 and 0.86, respectively), indicating the formation of ammonium nitrate. As in the LML data set, the lowest correlation was observed between nitrate and sulphate (0.63 and 0.67).

## 3.3 MARGA system data set

The statistics concerning the MARGA data (hourly concentrations) are presented in Table 3.4.

The time series at the three sites showed a high similarity with respect to SIA (Table 3.5). The largest correlation coefficients were calculated between Schiedam and Hoek van Holland.

Figure 3.2 shows the time series of the hourly SIA concentrations at the three MARGA sites, between August 2007 and February 2008. Note the high similarity in time variation (hourly) between measurements at locations some 50 km apart.

## Descriptive statistics of BOP filter data

Table 3.3

| | | | PM$_{10}$ | | | |
|---|---|---|---|---|---|---|
| **$NH_4$** | **Hellendoorn** | **Breda** | **Vredepeel** | **Rotterdam** | **Schiedam** | **Cabauw** |
| *Valid cases* | 98 | 79 | 99 | 86 | 88 | 105 |
| *Average* | 1,4 | 2,3 | 2,2 | 1,9 | 1,8 | 1,8 |
| *Variance* | 1,6 | 5,5 | 4,6 | 6,2 | 5,0 | 4,1 |
| *Std. deviation* | 1,3 | 2,3 | 2,1 | 2,5 | 2,2 | 2,0 |
| *Maximum* | 7 | 11 | 11 | 15 | 10 | 10 |
| *25th percentile* | 0,5 | 0,6 | 0,7 | 0,4 | 0,4 | 0,5 |
| *Median* | 1,1 | 1,6 | 1,7 | 1,1 | 0,9 | 1,2 |
| *75th percentile* | 1,8 | 3,3 | 2,7 | 2,1 | 2,1 | 2,3 |
| | | | | | | |
| *$NO_3$* | Hellendoorn | Breda | Vredepeel | Rotterdam | Schiedam | Cabauw |
| *Valid cases* | 98 | 79 | 100 | 86 | 88 | 105 |
| *Average* | 4,1 | 5,4 | 5,3 | 5,0 | 4,9 | 4,8 |
| *Variance* | 8,5 | 16,1 | 17,0 | 18,4 | 18,3 | 14,2 |
| *Std. deviation* | 2,9 | 4,0 | 4,1 | 4,3 | 4,3 | 3,8 |
| *Maximum* | 16 | 20 | 26 | 22 | 24 | 17 |
| *25th percentile* | 2,0 | 2,6 | 2,4 | 2,5 | 2,2 | 2,1 |
| *Median* | 3,3 | 4,5 | 4,3 | 3,5 | 3,2 | 3,5 |
| *75th percentile* | 5,5 | 7,5 | 7,3 | 6,9 | 7,3 | 6,5 |
| | | | | | | |
| *$SO_4$* | Hellendoorn | Breda | Vredepeel | Rotterdam | Schiedam | Cabauw |
| *Valid cases* | 98 | 79 | 100 | 86 | 88 | 105 |
| *Average* | 2,5 | 3,9 | 3,2 | 3,3 | 3,5 | 2,7 |
| *Variance* | 2,6 | 11,6 | 7,5 | 7,8 | 8,0 | 5,1 |
| *Std. deviation* | 1,6 | 3,4 | 2,7 | 2,8 | 2,8 | 2,3 |
| *Maximum* | 11 | 23 | 16 | 21 | 23 | 17 |
| *25th percentile* | 1,4 | 2,1 | 1,6 | 1,9 | 2,0 | 1,3 |
| *Median* | 2,1 | 3,1 | 2,4 | 2,7 | 2,9 | 2,2 |
| *75th percentile* | 3,3 | 4,6 | 3,7 | 3,4 | 3,6 | 3,2 |
| | | | | | | |
| | | | PM$_{2.5}$ | | | |
| *$NH_4$* | Hellendoorn | | Vredepeel | Rotterdam | Schiedam | Cabauw |
| *Valid cases* | 103 | | 105 | 99 | 94 | 85 |
| *Average* | 1,5 | | 2,0 | 1,6 | 1,7 | 1,6 |
| *Variance* | 2,3 | | 3,6 | 3,7 | 4,1 | 2,3 |
| *Std. deviation* | 1,5 | | 1,9 | 1,9 | 2,0 | 1,5 |
| *Maximum* | 9 | | 10 | 9 | 9 | 7 |
| *25th percentile* | 0,5 | | 0,7 | 0,4 | 0,4 | 0,6 |
| *Median* | 1,2 | | 1,5 | 0,9 | 0,9 | 1,1 |
| *75th percentile* | 2,1 | | 2,8 | 2,2 | 2,0 | 2,1 |
| | | | | | | |
| *$NO_3$* | Hellendoorn | | Vredepeel | Rotterdam | Schiedam | Cabauw |
| *Valid cases* | 103 | | 105 | 99 | 94 | 84 |
| *Average* | 3,6 | | 4,4 | 3,6 | 3,9 | 4,1 |
| *Variance* | 11,5 | | 12,6 | 13,9 | 16,6 | 12,1 |
| *Std. deviation* | 3,4 | | 3,6 | 3,7 | 4,1 | 3,5 |
| *Maximum* | 21 | | 20 | 21 | 20 | 16 |
| *25th percentile* | 1,4 | | 1,8 | 1,0 | 1,1 | 1,7 |
| *Median* | 2,6 | | 3,1 | 2,1 | 2,1 | 3,1 |
| *75th percentile* | 4,9 | | 6,1 | 4,7 | 5,6 | 5,8 |
| | | | | | | |
| *$SO_4$* | Hellendoorn | | Vredepeel | Rotterdam | Schiedam | Cabauw |
| *Valid cases* | 103 | | 105 | 99 | 94 | 84 |
| *Average* | 2,5 | | 2,9 | 2,5 | 2,9 | 2,6 |
| *Variance* | 3,6 | | 4,8 | 4,1 | 5,5 | 4,5 |
| *Std. deviation* | 1,9 | | 2,2 | 2,0 | 2,3 | 2,1 |
| *Maximum* | 10 | | 14 | 16 | 18 | 16 |
| *25th percentile* | 1,2 | | 1,5 | 1,5 | 1,6 | 1,3 |
| *Median* | 2,3 | | 2,3 | 2,1 | 2,5 | 2,2 |
| *75th percentile* | 3,3 | | 3,5 | 2,9 | 3,4 | 3,3 |

### The statistics concerning the MARGA data

**Table 3.4**

| **$PM_{10}$** | | **$NH_4$** | | | **$NO_3$** | | | **$SO_4$** | |
|---|---|---|---|---|---|---|---|---|---|
| | **Schiedam** | **Cabauw** | **HvH** | **Schiedam** | **Cabauw** | **HvH** | **Schiedam** | **Cabauw** | **HvH** |
| *Valid cases* | 3332 | 3807 | 1112 | 3297 | 4064 | 1081 | 3142 | 4028 | 1030 |
| *Average* | 2,4 | 2,2 | 1,6 | 6,0 | 5,7 | 4,5 | 4,1 | 2,9 | 3,1 |
| *Std. deviation* | 2,9 | 2,3 | 2,3 | 5,6 | 5,1 | 4,8 | 3,7 | 2,6 | 2,6 |
| *Maximum* | 24 | 18 | 11 | 37 | 34 | 28 | 39 | 27 | 18 |
| *25th percentile* | 0,5 | 0,6 | 0,1 | 2,0 | 2,1 | 1,1 | 1,9 | 1,3 | 1,5 |
| *Median* | 1,2 | 1,3 | 0,6 | 4,0 | 4,1 | 2,8 | 3,1 | 2,1 | 2,3 |
| *75th percentile* | 3,3 | 3,1 | 2,3 | 8,1 | 8,0 | 6,5 | 4,9 | 3,6 | 3,7 |

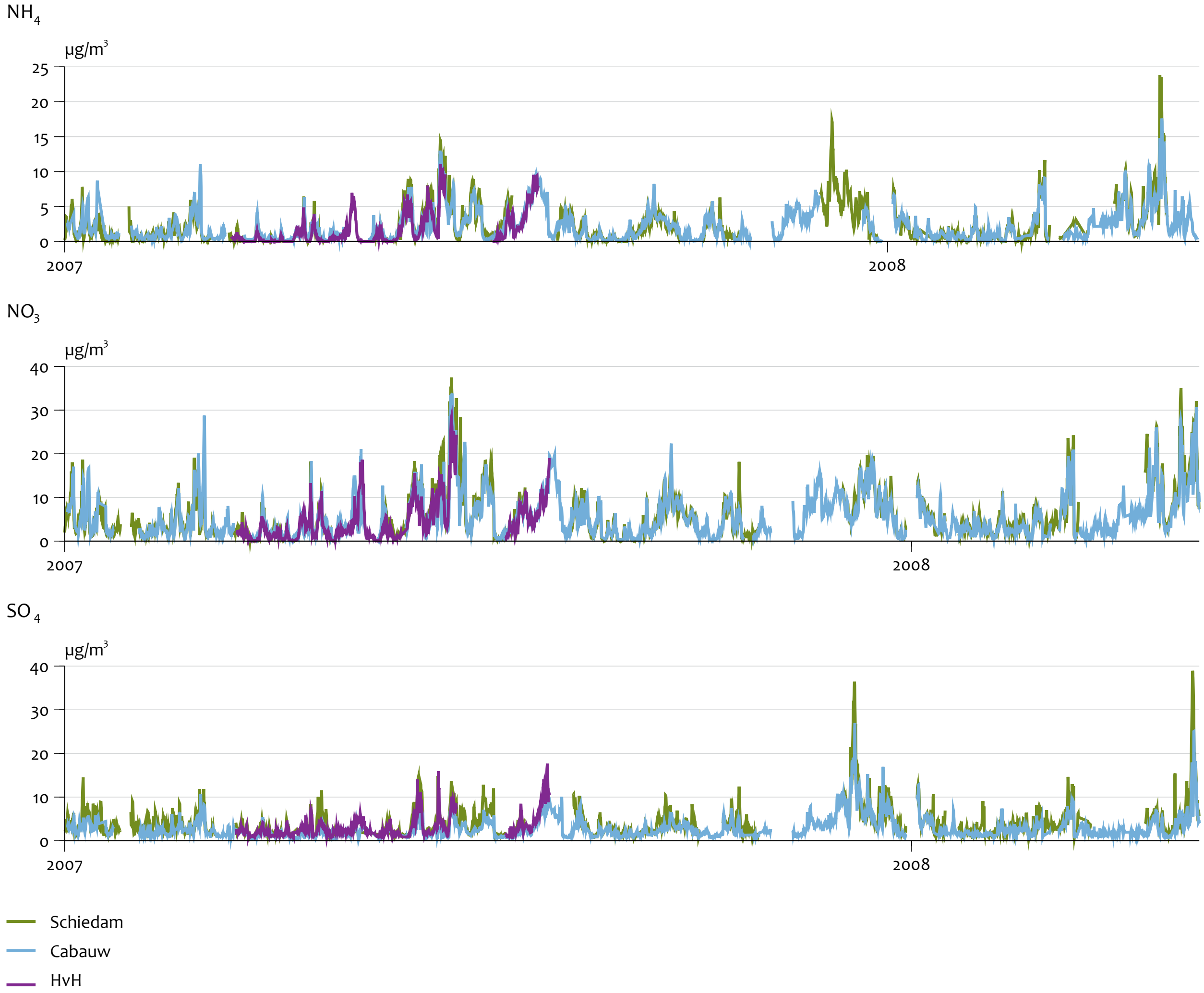
### Correlation coefficients between the MARGA sites calculated for the hourly concentrations

**Table 3.5**

| **$NH_4$** | Schiedam | Cabauw | **$NO_3$** | Schiedam | Cabauw | **$SO_4$** | Schiedam | Cabauw |
|---|---|---|---|---|---|---|---|---|
| *Cabauw* | 0.90 | | Cabauw | 0.90 | | Cabauw | 0.81 | |
| *HvH* | 0.96 | 0.93 | HvH | 0.97 | 0.86 | HvH | 0.90 | 0.84 |

### Time series of hourly $NH_4$, $NO_3$ and $SO_4$ concentrations (MARGA) at the three locations

**Figure 3.2**



*Time series of hourly $NH_4$, $NO_3$ and $SO_4$ concentrations at the three MARGA sites, between August 2007 and February 2008.*

# 4

# Results

## 4.1 Spatial variability

### 4.1.1 LML data

Averages per LML location (with standard deviation) are shown in Figure 4.1 and summarised in Table 4.1. Irrespective of the component, the highest concentrations were observed at Bilthoven (Utrecht agglomeration), Vredepeel (rural, region south) and, to a lesser extent, Wieringerwerf. The lowest levels were measured at Witteveen and Valthermond (region north: Witteveen: 1994-1999; Valthermond: 2000-2007). No attempt was made to correct for the contribution of sea salt to sulphate (as data for sodium were not available).

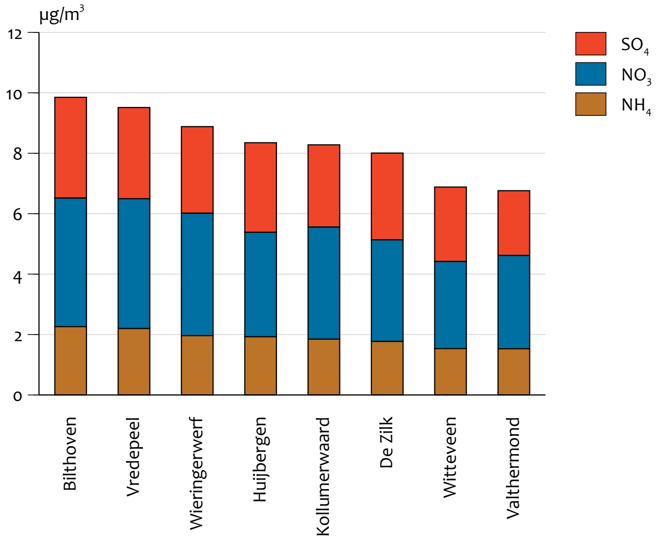
The high SIA concentrations at Bilthoven were comparable to those observed at Vredepeel, a location known to be affected by the nearby emissions from livestock activity. It is likely that the relatively high SIA presence at Wieringerwerf occurred for the same reason. It was noted that the distribution for the three components, in terms of percentage, was rather independent of location (Table 4.1).

### 4.1.2 BOP filter measurements

Averages per location (with standard deviation) are shown in Figure 4.2 and summarised in Table 4.2. The highest levels were measured for every component, at the urban traffic location Breda, which resulted in the largest contribution of SIA to $PM_{10}$ in the BOP filter data set (11.6 µg/m³). Especially sulphate was enhanced here ($SO_2$ emissions possibly coming from the Antwerp region).

Regarding the other BOP locations, higher levels of ammonium and nitrate, in both $PM_{10}$ and $PM_{2.5}$, were measured at Vredepeel (similar to the LML network), resulting in the second largest contribution to PM: 10.6 µg/m³ ($PM_{10}$) and 9.4 µg/m³ ($PM_{2.5}$). This was followed by the two sites in the Rotterdam region, where maximum concentrations of sulphate prevailed (probably caused by nearby industry). Furthermore was observed that the Rotterdam location showed rather low levels of $PM_{2.5}$ (as yet unexplained). The lowest concentrations were measured at Hellendoorn: here, the SIA contribution to $PM_{10}$ and $PM_{2.5}$ was 8.0 µg/m³ and 7.6 µg/m³, respectively.

**Average concentrations of $NH_4$, $NO_3$ and $SO_4$ over 14 years at all LML sites** **Figure 4.1**



*Average concentrations of $NH_4$, $NO_3$ and $SO_4$ over 14 years, at all LML sites (measurements at Witteveen performed up to 1999; after that replaced by the Valthermond location).*

### Average concentrations of NH4, NO3 and SO4 and their contribution to SIA

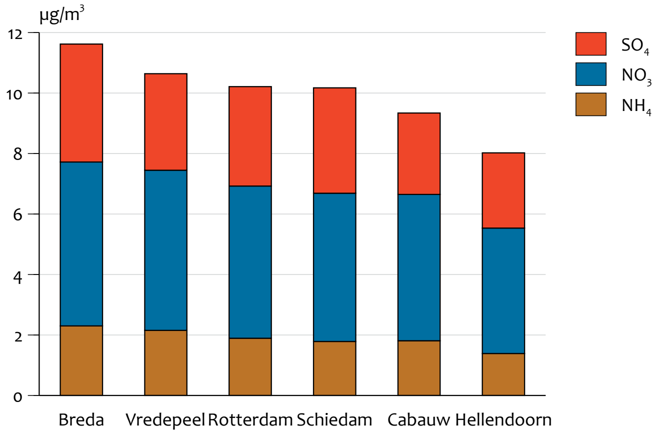
Table 4.1

| **LML** | **$NH_4$** | **$NO_3$** | **$SO_4$** | **SIA** | **$NH_4$** | **$NO_3$** | **$SO_4$** |
|---|---|---|---|---|---|---|---|
| **Jan 1994 - Dec 2007** | | **µg/m³** | | | | **% in SIA** | |
| *Bilthoven* | 2.3 | 4.3 | 3.3 | 9.9 | 23 | 43 | 34 |
| *De Zilk* | 1.8 | 3.4 | 2.9 | 8.0 | 22 | 42 | 36 |
| *Huijbergen* | 1.9 | 3.5 | 3.0 | 8.3 | 23 | 41 | 35 |
| *Kollumerwaard* | 1.8 | 3.7 | 2.7 | 8.3 | 22 | 45 | 33 |
| *Valthermond* | 1.5 | 3.1 | 2.1 | 6.8 | 23 | 46 | 32 |
| *Vredepeel* | 2.2 | 4.3 | 3.0 | 9.5 | 23 | 45 | 32 |
| *Wieringerwerf* | 2.0 | 4.1 | 2.9 | 8.9 | 22 | 46 | 32 |
| *Witteveen* | 1.5 | 2.9 | 2.5 | 6.9 | 22 | 42 | 36 |
| *Total average* | 1.9 | 3.6 | 2.8 | 8.3 | 23 | 44 | 34 |

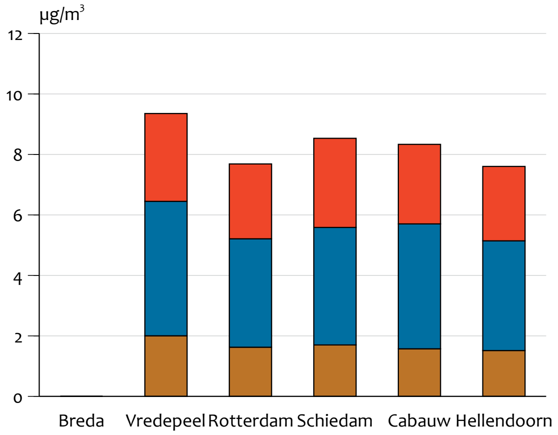
### Average concentrations of $NH_4$, $NO_3$ and $SO_4$ at six BOP locations

Figure 4.2

measured in $PM_{10}$



measured in $PM_{2.5}$



*Average concentrations of $NH_4$, $NO_3$ and $SO_4$ measured in $PM_{10}$ and $PM_{2.5}$, for the period from September 2007 until August 2008, at the six BOP locations.*

### 4.1.3 MARGA measurements

Averages for the two (three) locations (with standard deviation) are shown in Figure 4.3 and summarised in Table 4.3. In general, SIA levels at Schiedam were higher, compared to Cabauw. The largest increase was observed for sulphate: +1.2 µg/m³ (+41%). In the case of nitrate and ammonium, differences with Cabauw appeared moderate, that is, less than 0.3 µg/m³ (<8%). Sulphate at Hoek van Holland was comparable with that at Schiedam (3.4 to 3.5; averages over two months), but the nitrate concentration was considerably lower here.

In summary, we concluded that the three data sets led to similar observations. Always, nitrate contributed most to the PM fractions, followed by sulphate and ammonium. When averaged over all data sets, the total SIA concentrations were

## Average concentrations of $NH_4$, $NO_3$ and $SO_4$ and total SIA in $PM_{10}$ and $PM_{2.5}$ Table 4.2

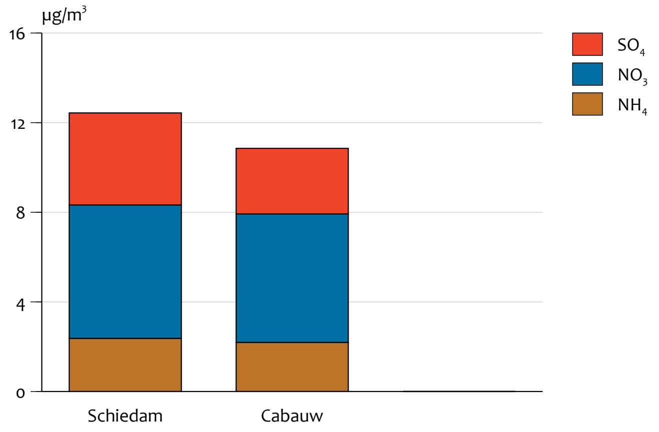
| **BOPfilter-$PM_{10}$**<br>**Aug 2007 - Aug 2008** | **$NH_4$** | **$NO_3$**<br>**µg/m³** | **$SO_4$** | **SIA** | **$NH_4$** | **$NO_3$**<br>**% in SIA** | **$SO_4$** |
|---|---|---|---|---|---|---|---|
| *Hellendoorn* | 1.4 | 4.1 | 2.5 | 8.0 | 17 | 52 | 31 |
| *Breda* | 2.3 | 5.4 | 3.9 | 11.6 | 20 | 47 | 34 |
| *Vreedenpeel* | 2.2 | 5.3 | 3.2 | 10.6 | 20 | 50 | 30 |
| *Rotterdam* | 1.9 | 5.0 | 3.3 | 10.2 | 19 | 49 | 32 |
| *Schiedam* | 1.8 | 4.9 | 3.5 | 10.2 | 18 | 48 | 34 |
| *Cabauw* | 1.8 | 4.8 | 2.7 | 9.3 | 19 | 52 | 29 |
| *Total average* | 1.9 | 4.9 | 3.2 | 10.0 | 19 | 49 | 32 |

| **BOPfilter-$PM_{25}$**<br>**Aug 2007 – Aug 2008** | **$NH_4$** | **$NO_3$**<br>**µg/m³** | **$SO_4$** | **SIA** | **$NH_4$** | **$NO_3$**<br>**% in SIA** | **$SO_4$** |
|---|---|---|---|---|---|---|---|
| *Hellendoorn* | 1.5 | 3.6 | 2.5 | 7.6 | 20 | 48 | 32 |
| *Breda* | | | | | | | |
| *Vreedenpeel* | 2.0 | 4.4 | 2.9 | 9.4 | 21 | 48 | 31 |
| *Rotterdam* | 1.6 | 3.6 | 2.5 | 7.7 | 21 | 47 | 32 |
| *Schiedam* | 1.7 | 3.9 | 2.9 | 8.5 | 20 | 46 | 35 |
| *Cabauw* | 1.6 | 4.1 | 2.6 | 8.3 | 19 | 50 | 32 |
| *Total average* | 1.7 | 3.9 | 2.7 | 8.3 | 20 | 47 | 32 |

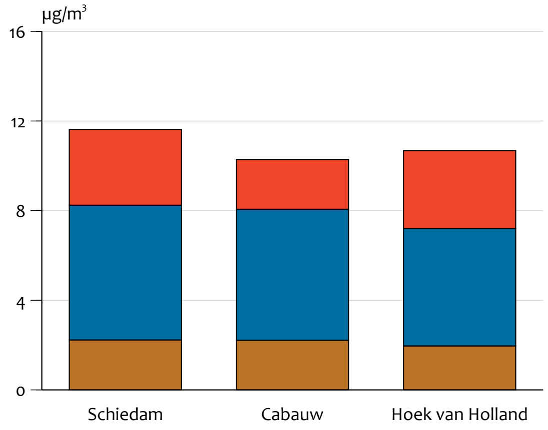
*Average concentrations of $NH_4$, $NO_3$ and $SO_4$ and total SIA in $PM_{10}$ and $PM_{2.5}$, as measured between September 2007 and August 2008, at the six BOP locations.*

## Average concentrations of $NH_4$, $NO_3$ and $SO_4$ in PM10 (MARGA) at the three locations Figure 4.3

August 2007 - February 2008



September 2006 - October 2007



*Averages of $NH_4$, $NO_3$ and $SO_4$ (in $PM_{10}$) over the period from August 2007 to February 2008, at Schiedam and Cabauw (above), and over a two-month period (September-October) in 2007 that included the MARGA operation at Hoek van Holland (HvH).*

**Total averages of $NH_4$, $NO_3$ and $SO_4$** **Table 4.3**

| **MARGA** | **$NH_4$** | **$NO_3$** | **$SO_4$** | **SIA** | **$NH_4$** | **$NO_3$** | **$SO_4$** |
|---|---|---|---|---|---|---|---|
| *Aug 2007 – Feb 2008* | | µg/m³ | | | | % in SIA | |
| *Schiedam* | 2.4 | 6.0 | 4.1 | 12.4 | 19 | 48 | 33 |
| *Cabauw* | 2.2 | 5.7 | 2.9 | 10.9 | 20 | 53 | 27 |
| *Total average* | 2.3 | 5.8 | 3.5 | 11.6 | 20 | 50 | 30 |

*Total averages of $NH_4$, $NO_3$ and $SO_4$ (in $PM_{10}$) and their contribution to SIA over the seven-month period at Schiedam and Cabauw.*

lowest in the LML data set and highest in the MARGA ($PM_{10}$) data set. It is supposed that – apart from different types of locations, collection cut-off diameters, instrumental design and measurement periods – volatilisation losses from the filters (absent in the MARGA system) also played a role here.

In spite of the concentration differences measured between locations, the above shows that the component distributions in PM appeared rather similar. In the MARGA data set, the distribution, on average, was 50% for nitrate, 30% for sulphate and 20% for ammonium, rather close to what was found in the BOP filter data (49%, 32% and 19%, respectively). In the LML set (restricted to regional locations) relatively more ammonium and less nitrate and sulphate was measured.

The comparability between the various data sets is discussed further in Section 5.2.

## 4.2 Temporal variability

### 4.2.1 Linear trend analysis LML filter data

The average annual SIA concentrations during the period from 1994 to 2007 are shown in Figure 4.4, for every LML location. On average, concentration levels decreased during these 14 years. Downward trends could be observed between 1994 and 2000, particularly in the case of sulphate. After the year 2000, however, the downward trend seemed to weaken or was even absent, with exceptions during shorter time intervals. For example, for sulphate, there was a rise up to 2003 and a decrease from 2004 onwards. The year 2003 was characterised by enduring dry episodes in the summer.

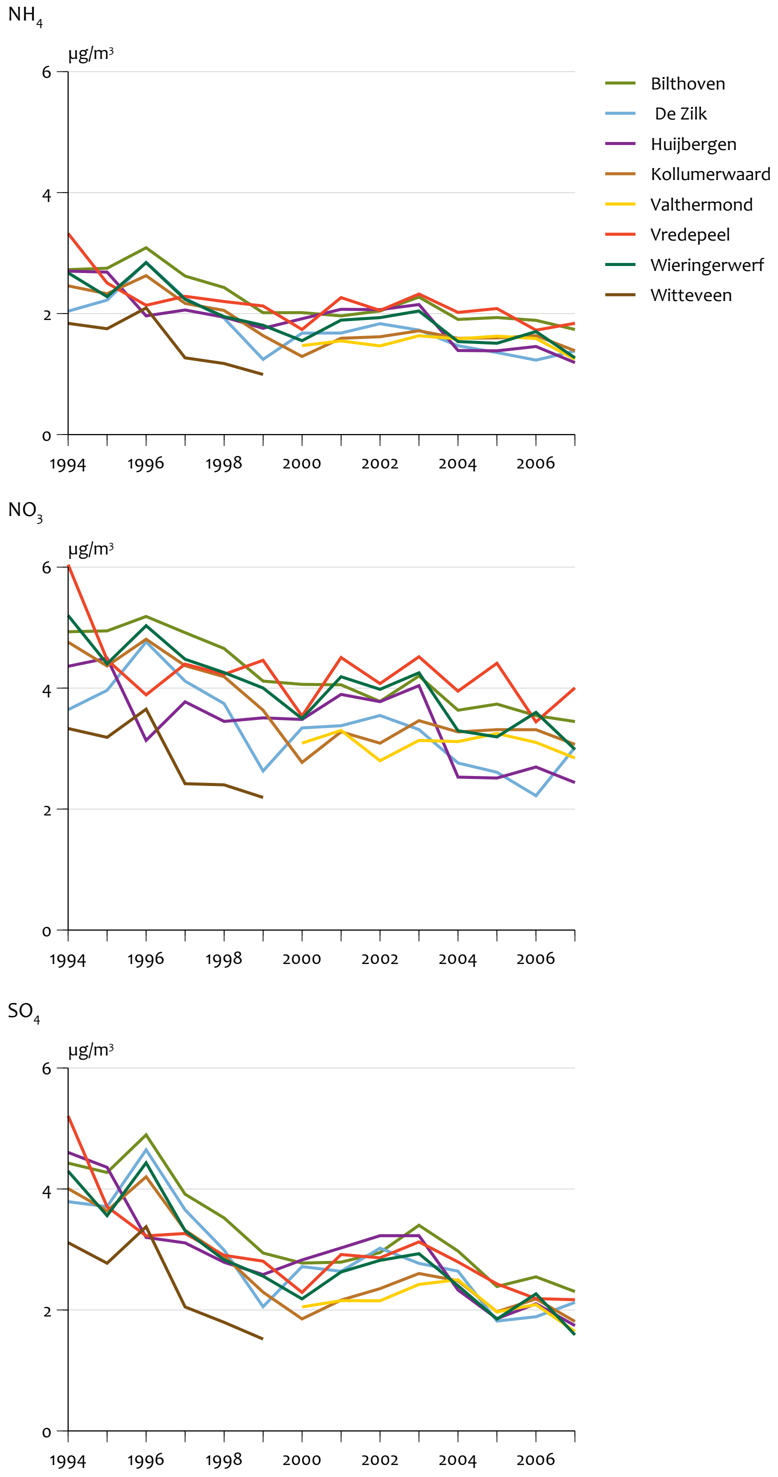
In the figure, the variation between the trends at the various locations appeared smallest for sulphate and largest for nitrate. This could already be anticipated from the correlation coefficients (Table 3.2). After the localised emissions (main source areas: Rotterdam and surroundings, southern part of the province Zeeland, Antwerpen area and IJmuiden) and fast chemical conversion, the meteorological variability determined the concentration levels in the (downwind) regions. The same kind of argument could be applied for $NH_3$ and $NH_4$. At first, the formation of $NH_4$ depended on the quantity of $SO_2$. With sufficient $NH_3$, the formation of ammonium nitrate started. Precursors of nitrate were emitted from traffic in the highly urbanised areas in the western (except Zeeland) and southern part of the country, and, hence, large gradients may have existed. These emissions may have easily influenced measurements at an LML location. Moreover, the chemical formation route was more complex and slower.

From Figure 4.1 it was concluded that the Valhermond and Witteveen levels were rather similar, in spite of the fact that these were calculated for different (consecutive) periods. Figure 4.4 shows that the trends for these two locations did not match very well for the year 2000: concentrations at Valthermond appeared higher than at Witteveen.

The long-term behaviour has been quantified in Table 4.4, which summarises the results from linear regression analyses. The dependent variable here was the concentration. The number of years since the start of the measurements was chosen as the independent variable. The resulting regression coefficient gave the change in concentration in µg/m³ per year. The so-called *p*-value has been estimated, giving the chance that the calculated result was based on coincidence. In general, when $p<0.05$, the linear relationship was considered to be 'statistically significant', meaning that, with a 95% certainty, the change in concentration could not be attributed to coincidental circumstances.

## Yearly averages of $NH_4$, $NO_3$ and $SO_4$ at the LML sites from 1994 to 2007

**Figure 4.4**



*Annual averages of $NH_4$, $NO_3$ and $SO_4$ at the LML sites, from 1994 to 2007 (Witteveen data were only available between 1994 and 1999, and for Valthermond between 2000 and 2007).*

**Linear regression equations for the $NH_4$, $NO_3$ and $SO_4$ LML time series for 1994 to 2007** **Table 4.4**

| | $NH_4$ | | | $NO_3$ | | | $SO_4$ | | |
|---|---|---|---|---|---|---|---|---|---|
| **1994 - 2007** | | $R^2$ | *p*-value | | $R^2$ | *p*-value | | $R^2$ | *p*-value |
| *Bilthoven* | y=-0.08x+2.88 | 0.74 | 8E-05 | y=-0.13x+5.22 | 0.87 | 9E-07 | y=-0.18x+4.55 | 0.75 | 6E-05 |
| *De Zilk* | y=-0.08x+2.40 | 0.58 | 0.002 | y=-0.12x+4.28 | 0.56 | 0.002 | y=-0.16x+4.09 | 0.66 | 4E-04 |
| *Huijbergen* | y=-0.09x+2.58 | 0.69 | 2E-04 | y=-0.12x+4.34 | 0.54 | 0.003 | y=-0.17x+4.16 | 0.70 | 2E-04 |
| *Kollumerwaard* | y=-0.08x+2.43 | 0.65 | 5E-04 | y=-0.13x+4.67 | 0.67 | 4E-04 | y=-0.16x+3.87 | 0.68 | 3E-04 |
| *Valthermond* | | | | | | | | | |
| *Vredepeel* | y=-0.06x+2.67 | 0.47 | 0.007 | y=-0.08x+4.86 | 0.27 | 0.06 | y=-0.14x+4.06 | 0.59 | 0.001 |
| *Wieringerwerf* | y=-0.09x+2.61 | 0.69 | 2E-04 | y=-0.14x+5.05 | 0.74 | 7E-05 | y=-0.17x+4.11 | 0.73 | 1E-04 |
| *Witteveen* | | | | | | | | | |

| | $NH_4$ | | | $NO_3$ | | | $SO_4$ | | |
|---|---|---|---|---|---|---|---|---|---|
| **1994 - 2000** | | $R^2$ | *p*-value | | $R^2$ | *p*-value | | $R^2$ | *p*-value |
| *Bilthoven* | y=-0.15x+3.13 | 0.69 | 0.02 | y=-0.17x+5.37 | 0.72 | 0.02 | Y=-0.32x+5.11 | 0.78 | 0.01 |
| *De Zilk* | y=-0.14x+2.59 | 0.37 | 0.15 | y=-0.16x+4.40 | 0.29 | 0.22 | Y=-0.29x+4.54 | 0.56 | 0.05 |
| *Huijbergen* | y=-0.15x+2.75 | 0.72 | 0.02 | y=-0.15x+4.36 | 0.43 | 0.11 | Y=-0.33x+4.68 | 0.80 | 0.01 |
| *Kollumerwaard* | y=-0.20x+2.86 | 0.80 | 0.01 | y=-0.29x+5.28 | 0.75 | 0.01 | Y=-0.37x+4.67 | 0.85 | 0.003 |
| *Valthermond* | | | | | | | | | |
| *Vredepeel* | y=-0.20x+3.11 | 0.73 | 0.02 | y=-0.26x+5.46 | 0.49 | 0.08 | Y=-0.39x+4.90 | 0.81 | 0.01 |
| *Wieringerwerf* | y=-0.19x+2.93 | 0.76 | 0.01 | y=-0.24x+5.37 | 0.78 | 0.01 | Y=-0.35x+4.73 | 0.81 | 0.01 |
| *Witteveen* | y=-0.19x+2.20 | 0.70 | 0.04 | y=-0.27x+3.79 | 0.68 | 0.04 | Y=-0.35x+3.66 | 0.75 | 0.03 |

| | $NH_4$ | | | $NO_3$ | | | $SO_4$ | | |
|---|---|---|---|---|---|---|---|---|---|
| **2001 - 2007** | | $R^2$ | *p*-value | | $R^2$ | *p*-value | | $R^2$ | *p*-value |
| *Bilthoven* | y=-0.05x+2.15 | 0.38 | 0.14 | y=-0.10x+4.16 | 0.61 | 0.04 | Y=-0.12x+3.23 | 0.43 | 0.11 |
| *De Zilk* | y=-0.09x+1.88 | 0.73 | 0.01 | y=-0.16x+3.61 | 0.52 | 0.07 | Y=-0.17x+3.09 | 0.62 | 0.04 |
| *Huijbergen* | y=-0.17x+2.33 | 0.78 | 0.01 | y=-0.29x+4.28 | 0.72 | 0.02 | Y=-0.27x+3.57 | 0.79 | 0.01 |
| *Kollumerwaard* | y=-0.03x+1.69 | 0.29 | 0.21 | y=-0.01x+3.30 | 0.03 | 0.69 | Y=-0.07x+2.51 | 0.33 | 0.19 |
| *Valthermond* | y=-0.02x+1.62 | 0.14 | 0.40 | y=-0.02x+3.17 | 0.07 | 0.57 | Y=-0.08x+2.43 | 0.33 | 0.18 |
| *Vredepeel* | y=-0.08x+2.35 | 0.62 | 0.04 | y=-0.10x+4.54 | 0.33 | 0.18 | y=-0.15x+3.25 | 0.77 | 0.01 |
| *Wieringerwerf* | y=-0.10x+2.11 | 0.64 | 0.03 | y=-0.19x+4.42 | 0.68 | 0.02 | y=-0.19x+3.11 | 0.68 | 0.02 |
| *Witteveen* | | | | | | | | | |

*Linear regression equations for the $NH_4$, $NO_3$ and $SO_4$ LML time series (annual averages) for 1994 to 2007, 1994 to 2000 and 2001 to 2007 (data from Witteveen and Valthermond were only available between 1994 and 1999 and 2000 and 2007, respectively). Non-significant results have been shaded.*

The calculated trends at the various LML locations did not differ much per component. At 5 locations (out of 6) the (negative) change per year was quite similar: 0.08 to 0.09 µg/m³ ($NH_4$), 0.12 to 0.14 µg/m³ ($NO_3$) and 0.16 to 0.18 µg/m³ ($SO_4$). The weakest trends over the entire (14-year) period were observed at Vredepeel. Here, no trend was estimated for $NO_3$.

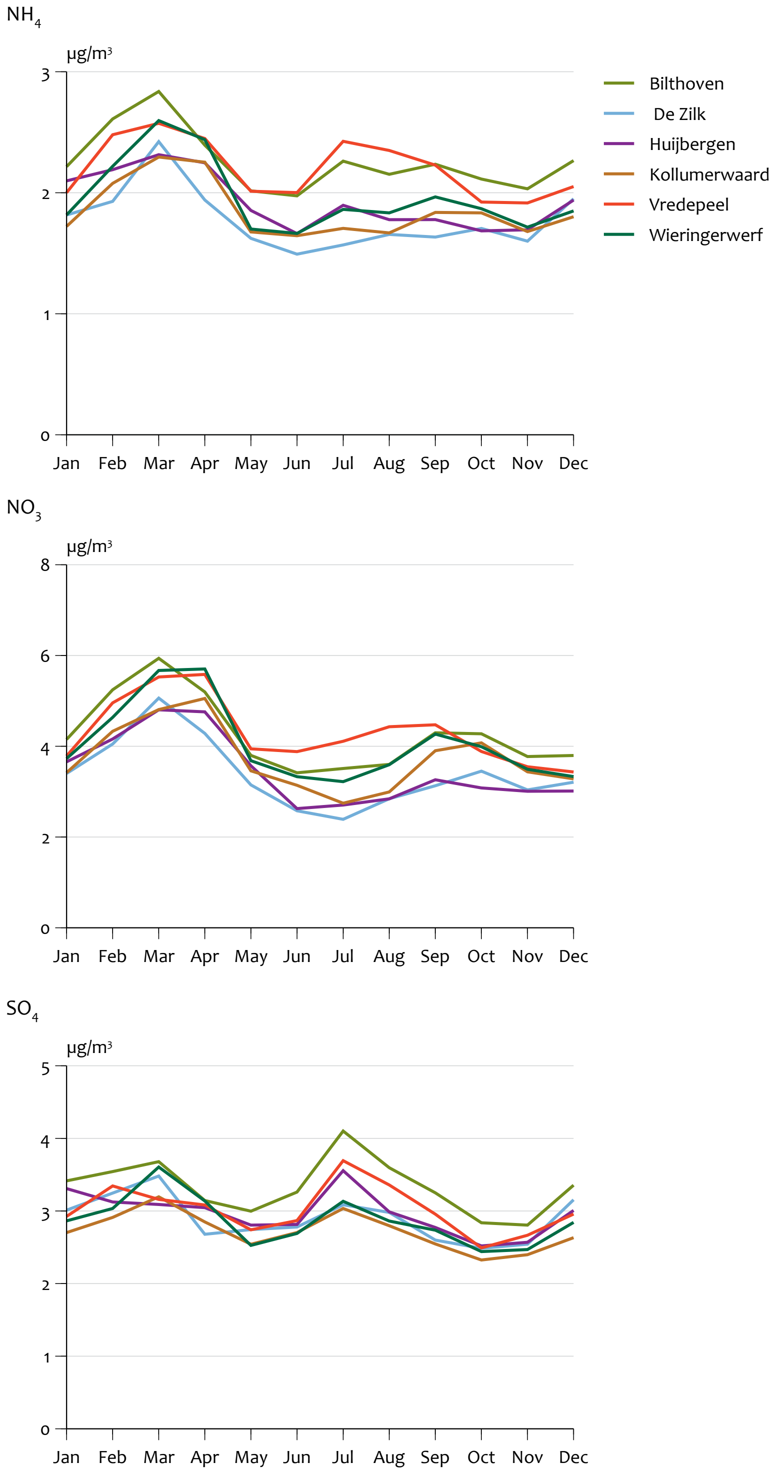
As already visually observed, downward trends for 1994 to 2000 were (somewhat) stronger than for 2001 to 2007. However, during the second period negative regression coefficients still existed for most locations, but with less significance. It was concluded that the decreasing trends observed over the period 1994 to 2000 slowed down after the year 2000, and in some cases became insignificant.

### 4.2.2 Annual cycle LML data set

The annual cycles estimated form the LML data set are shown in Figure 4.5 (averages per month over 14 years). The behaviour in time, during one year, appeared rather independent of the location (except for their respective absolute values) for each individual component. The formation of ammonium sulphate and ammonium nitrate was observed in the course of the year. For example, ammonium and nitrate both exhibited higher concentrations in late winter – early spring (formation of ammonium nitrate), while sulphate was only slightly higher (and with respect to timing, preceded the maximum for nitrate and ammonium). Apparently, the emissions of $NH_3$ that are known to occur in this period first led to (some) ammonium sulphate and, over a longer period, to relatively high levels of ammonium nitrate.

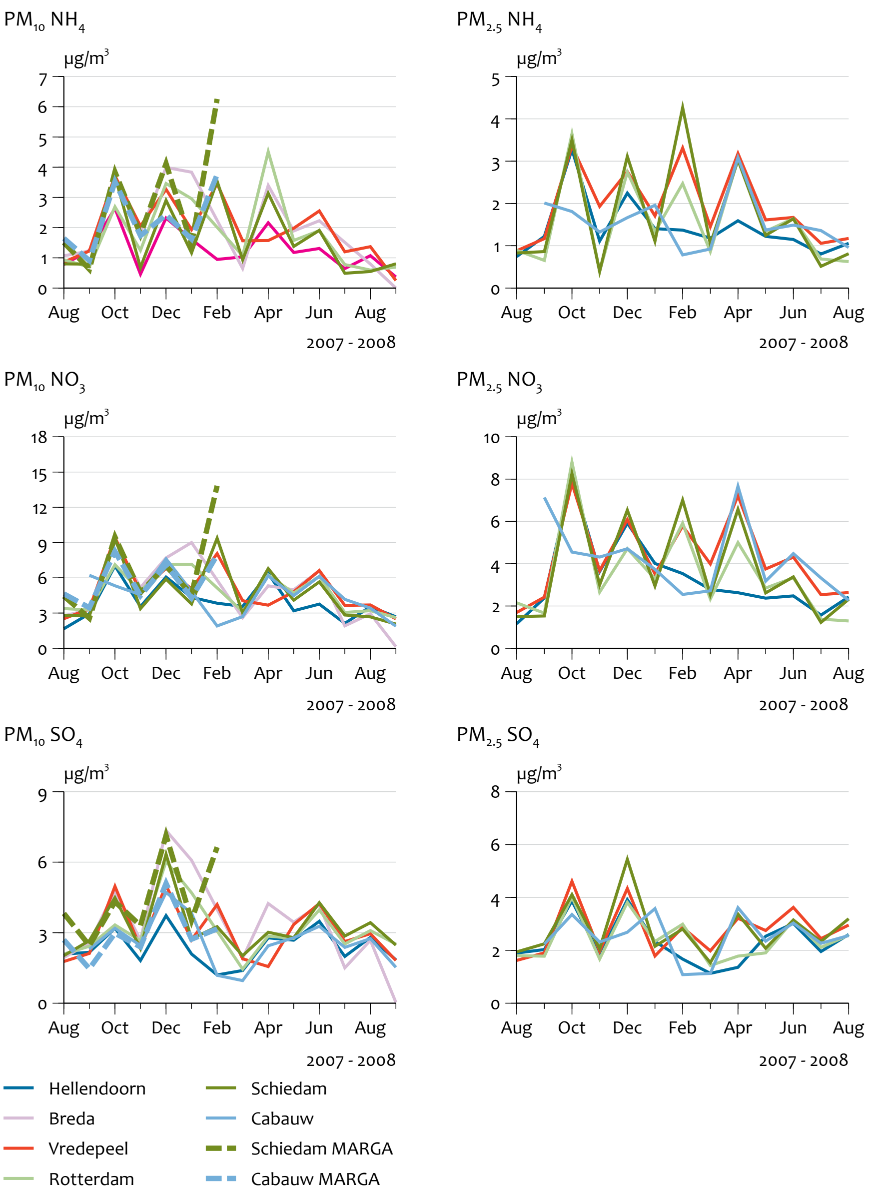
Rather low nitrate values were observed in summer (June to August) which was due to the temperature effect. In July, a peak value for sulphate was measured, coinciding with relatively higher ammonium levels (ammonium sulphate). This was followed by a slow decrease in ammonium and a slow increase in nitrate, with (relative) maxima in September and October. At the same time, sulphate decreased fairly rapidly.

**Monthly averages of $NH_4$, $NO_3$ and $SO_4$ over 14 years at all LML sites** **Figure 4.5**



*Monthly averages of $NH_4$, $NO_3$ and $SO_4$ over 14 years, at all LML sites (Witteveen and Valthermond measurements were excluded from these calculations*

**Monthly averages of $NH_4$, $NO_3$ and $SO_4$ in $PM_{10}$ and $PM_{2.5}$** **Figure 4.6**



*Monthly averages of $NH_4$, $NO_3$ and $SO_4$ in $PM_{10}$ and $PM_{2.5}$, over a one-year period, between 2007 and 2008, at all BOP sites.*

### 4.2.3 Monthly variation

The monthly variation during the BOP measurement campaigns (Figure 4.6) appeared quite comparable for the two campaigns, at the different locations, and for the different components: a (somewhat surprisingly) alternation of high and low monthly values occurred in consecutive months, starting low in September. Contrasting behaviour was seen during the winter period for Cabauw, which was probably related to a lack of data. Clearly, the correspondence observed between SIA components stress the dominance of meteorological driven behaviour.

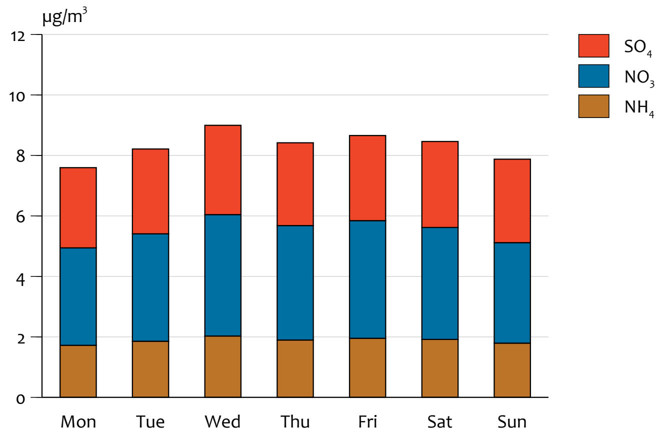
### 4.2.4 Weekly cycle

The LML dataset offered the possibility of looking at weekly average variability. (Figure 4.7). Although differences appeared only minor over the period of a week, an increase was observed on Wednesdays, for all three components. Concentrations appeared at a minimum on Sundays and Mondays, suggesting a delay between emission and measurement.

The weekly cycle in the BOP data set (Figure 4.8) appeared more outspoken than in the LML data set. Again, high SIA levels were observed on Wednesdays, but also on Fridays. The lowest values were measured during weekends.

## Averages of $NH_4$, $NO_3$ and $SO_4$ per day as calculated from the LML data set

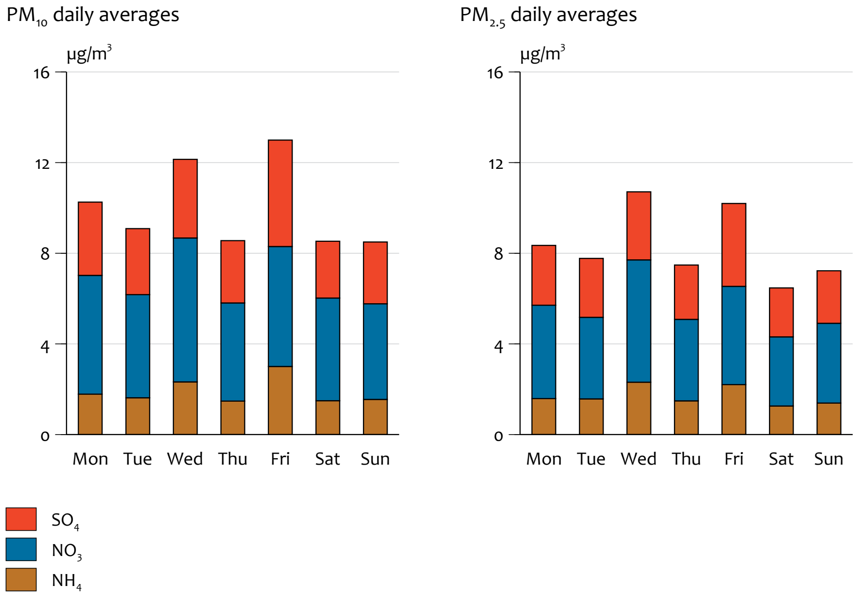
Figure 4.7



*Daily averages of* $NH_4$, $NO_3$ *and* $SO_4$, *as calculated from the LML data set.*

## Averages of $NH_4$, $NO_3$ and $SO_4$

Figure 4.8


$PM_{10}$ daily averages

$PM_{2.5}$ daily averages

*Daily averages of* $NH_4$, $NO_3$ *and* $SO_4$, *as calculated from the BOP filter data set.*

# 5

# Discussion

## 5.1 Trends for $NH_4$, $NO_3$ and $SO_4$ during 1994 to 2007 in the LML data set

### 5.1.1 Introduction

European Community policy is designed to limit atmospheric emissions of pollutants. In 2001 the NEC Directive came into force, giving emission ceilings for sulphur dioxide ($SO_2$), nitrogen oxides ($NO_x$), volatile organic compounds (VOCs) and ammonia ($NH_3$). These ceilings are binding for every EU Member State. Parallel to this development the Gothenburg protocol was agreed in November 1999. From a political point of view, it is very important to assess whether these costly reduction strategies are successful. Of particular interest is the period after 2000, when effects of both international agreements should have become apparent.

Due to its timespan (1994 to 2007), the LML data set provided an appropriate base for estimating changes in concentrations of SIA over the past years. Two questions were explored: (1) what are the possible trends and corresponding (statistical) significances, and (2) do trends correspond with known emission reductions in SIA precursors. The answers are elaborated in quantitative and qualitative terms.

### 5.1.2 Trends and significance

Various statistical methods for detecting trends in data exist. If environmental data sets are analysed over 10 years or more, alternating periods of increase and decrease are recognised, as well as periods when the variable is more or less constant. The statistical detection of such ‘flexible trends’ (Visser, 2004), though certainly present in the LML time series, was not part of this study. Here, trends were estimated by simple linear regression combined with visual inspection. The influence of periodical variation (changing meteorology) and non-periodical variation (varying local emissions) was reduced by calculating the annual average over six LML locations (Witteveen and Valthermond were not included). Trends calculated for the locations have been summarised in Table 4.4 (in Chapter 4).

Figure 5.1 shows the result from the linear regression calculation. Already obvious from Table 4.4, distinct downward trends existed for every SIA component. The trends are statistically significant. The change in concentrations over the entire period was -2.3 µg/m$^3$ (-54%; sulphate), -1.7 µg/m$^3$ (-36%; nitrate) and -1.2 µg/m$^3$ (-45%; ammonium), yielding a decrease in the SIA contribution to PM of 5.2 µg/m$^3$ since 1994. Taking the regression results for the individual locations as a measure of deviation, this varied between 3.9 and 5.8 µg/m$^3$. The lowest change was calculated for the Vredepeel location and this was very likely caused by ammonia emissions from nearby. The precise PM fraction captured with the LVS instruments of the LML SIA network data set was not known, but assumed to be $PM_{3\text{-}4}$. Values and percentages given acted as a lower limit for $PM_{10}$.

The figure further indicated that the rate of change in the first seven years was roughly twice as high as in the second period of 7 years. Loosely formulated, 1999 to 2000 was the starting point of a period during which levels decreased at a lower pace. This was especially true for sulphate and nitrate, and more or less observed at each location and appeared related to changing emissions in this period (see discussion below).

### 5.1.3 Emissions of precursors

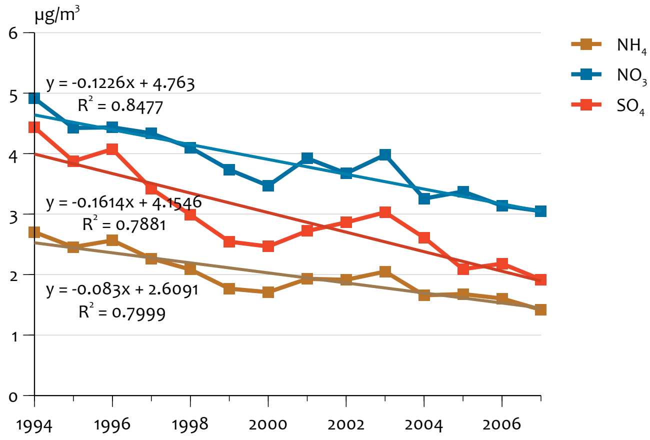
A literature study on the emissions of sulphur, nitrogen oxides and ammonia covers the patterns over the past years. The most up-to-date references were given by Vestreng (2007; 2008). His analyses were based on European emission data that had been compiled and reported under the Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) (part of the work under the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP).

In 2007 Vestreng showed that European anthropogenic sulphur emissions had been steadily decreasing over the last twenty-five years. The period from 1990 to 1999 was characterised by high annual emission reductions (up to 11% reduction per year and 54% for the whole period), most pronounced in central and eastern Europe. The annual emission reductions in the period from 2000 to 2004, however, were medium to low (below 6% reduction per year and 17% for the entire period), reflecting the unified Europe, with equally sized reductions in both east and west. The majority of European countries reduced their emissions by more than 60% between 1990 and 2004, and one quarter already achieved sulphur emission reductions of more than 80%.

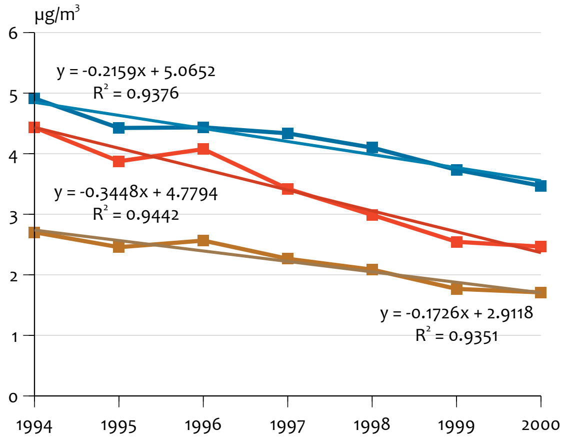
European nitrogen oxide emissions declined by more than 30% since 1990, but are since increasing in eastern recovering economies. Road transport has been the dominating source of $NO_x$ emissions since 1970. For $NO_x$, there is a general decrease in Europe from 1990 to 2000. For eastern Europe, the decrease in emissions has been linked to the decreasing

**Annual averages with corresponding linear regression equations** **Figure 5.1**

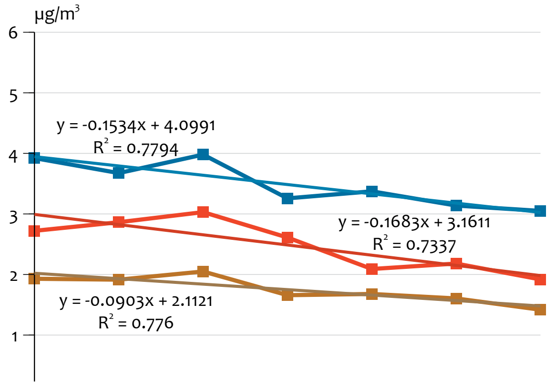
1994 - 2007



1994 - 2000



2001-2007



*Annual averages with corresponding linear regression equations from 1994 to 2007, 1994 to 2000 and 2001 to 2007.*

fuel consumption in the former Soviet republics, and to a reduced number of high $NO_x$ emitting vehicles in other eastern European countries. At the same time, the efficiency of technological abatement in western Europe has been instrumental in controlling road-traffic emissions in this region, despite the increase in fuel consumption. From 2000 to 2005, the economic recovery in eastern Europe implied new increases in road traffic emissions. However, emissions in western Europe have continued to decrease, despite the increase in fuel consumption, due to the implementation of strict measures for controlling $NO_x$ emissions. (Vestreng *et al.*, 2008).

In the 32 member countries of the European Environment Agency (EEA), ammonia emissions have declined by 20% between the years 1990 and 2005 (http://reports.eea.europe.ee). Agriculture was responsible for 93% of $NH_3$ emissions in 2005. The reduction in emissions within the agricultural sector was primarily due to a reduction in livestock numbers since 1990, changes in the handling and management of organic manures and the decreased use of nitrogenous fertilisers. The reductions achieved in the agricultural sector have been marginally offset by the increased emissions in sectors, such as transport and, to a lesser extent, the energy industry and other (non-energy) sectors. Emissions from road transport, although relatively small, have been rising as a result of increased use of three-way catalytic converters in vehicles (this is due to an unwanted reaction involving hydrogen, which reduces NO to $NH_3$).

### 5.1.4 Conclusions

The downward patterns in the LML SIA network between 1994 and 2007 are in line with decreasing emissions of the precursors reported in the European emission data base from EMEP. Also, the slowing down in the rate of change after the year 2000 could be explained by a decreasing pace of reductions starting in 1999 to 2000, caused by the recovering economies in eastern Europe. The penetration of control technologies all over Europe still leads to a small but continuous decrease in European emissions.

The highest decrease was found for sulphate, corresponding with the large reduction in $SO_2$ emissions. It should be noted, however, that decreases in the precursor emissions could not be translated into equal changes in SIA concentrations. Processes that determine the distribution between the different sulphur components and nitrogen components depended on the prevailing chemical composition in the atmosphere, as well as on meteorological conditions (temperature, humidity). For instance, the oxidation of sulphur dioxide to sulphate depends on the presence of oxidants, that is, the amount of oxidants is a limitation for the conversion from $SO_2$ to sulphate, especially in winter (Fagerli *et al.*, 2003). Today, larger proportions of $SO_2$ are converted to sulphate, leading to a smaller decrease in sulphate concentrations than in $SO_2$ emissions.

## 5.2 Representativeness of the LML data set

### 5.2.1 Introduction

The linear trends presented in Sections 4.2.1 and 5.1 were derived from the LML measurement time series (starting in the 1990s), using Low Volume Samplers (LVS). The advantage of this data set is that the experimental sampling technique has not changed over the years, which obviously strengthens the interpretative basis for trend studies. However, there is also a negative aspect; the LVS instruments have an undetermined cut-off point. The assumption was that the measured mass fraction would be $PM_{3\text{-}4}$, and, hence, rather close to $PM_{2.5}$. However, doubt exists on the representativeness of the absolute concentration values established by the LVS.

In 1998, RIVM (van Putten and Mennen) reported an underestimation (10 to 25%) of the SIA contribution, when compared with an Annular Denuder System. No attempt was made to establish correction factors. Another indication was given by Visser *et al.*, (2001) (in the ‘Bronstof’ experiment, on the origin of particulate matter), who compared LML results with Dichote measurements (cut-off point: 10 µm) at two LML locations (De Zilk and Vredepeel). On average, ammonium and nitrate concentrations were within 30%. It was concluded that because volatilisation in particular affects ammonium and nitrate, the instruments behaved similar. However, in case of sulphate, an underestimation of approximately 40 to 50% was measured while chloride was lower by a factor of two.

In order to determine whether doubt would be justified, the SIA data acquired in the BOP campaign were compared with data from co-located LML measurements. BOP filter measurements followed the reference method. To broaden the investigation, a comparison with data sets collected in neighbouring countries (Belgium and Germany) was performed.

An artefact in the LVS operation would have implications, not only from a scientific point of view, but also for future use of measurements in the framework of national reports on air quality and attainability of air quality standards. SIA measurements from LML are used to verify and calibrate model results in the assessment of PM background concentrations in the Netherlands. If SIA concetrations would be larger than the levels as they are measured in the national monitoring network (LML), this could cause current and proposed policies on SIA precursor gases to have more effect on SIA and PM than was recently assessed (e.g. Velders *et al.*, 2009).

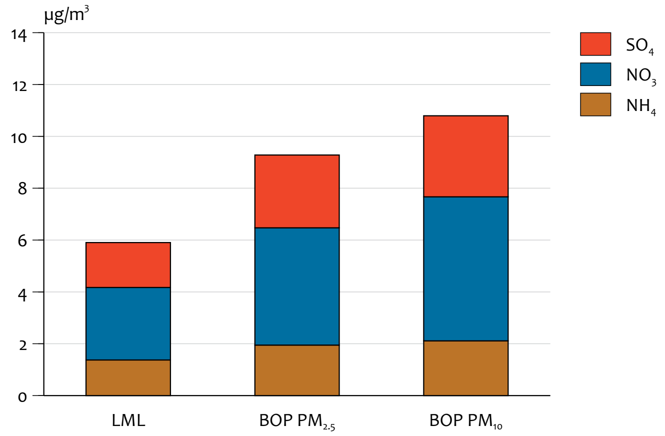
### 5.2.2 Comparison with the BOP filter data

The BOP filter data ($PM_{2.5}$/$PM_{10}$) collected at Vredepeel were compared with collocated LML data from August 2007 to September 2008. Only ‘complete’ days were incorporated, meaning that the subset studied contained days on which the concentrations for each SIA component (in all three mass fractions) were available. This yielded a subset of 80 days. The average results are given in Figure 5.2. Clearly, the SIA levels measured in LML at Vredepeel were lower than those obtained from the BOP $PM_{2.5}$ (and $PM_{10}$) filter data. The average (summated) SIA contributions were 5.9 µg/m³ (LML), 9.3 µg/m³ (BOP $PM_{2.5}$) and 10.8 µg/m³ (BOP $PM_{10}$). The SIA distributions in the different data sets were very similar (Figure 5.3). Roughly, this was 30% (sulphate), 50% (nitrate) and 20% ($NH_4$), originating from the dominant presence of ammonium nitrate and ammonium sulphate in the fine fraction.

The ratios between the individual components are summarised in Table 5.1. The LML concentration for total SIA was 36% lower than in the corresponding BOP data set for $PM_{2.5}$ (and 45% lower for $PM_{10}$). The largest differences were noted for nitrate and sulphate, which was attributed to their contribution to coarse PM (see Section 5.3.2).

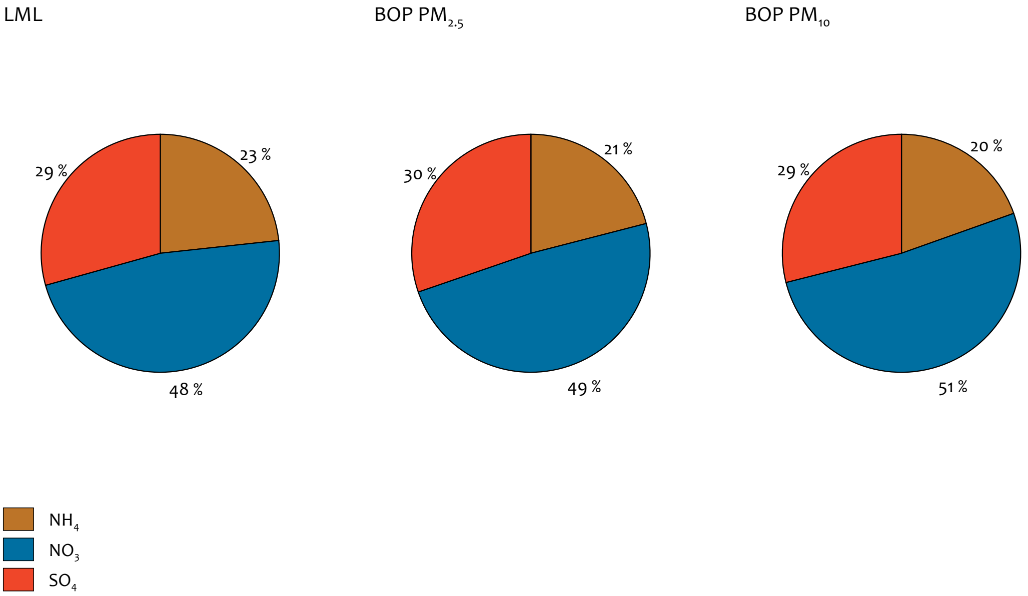
**Daily concentrations measured simultaneously in LML network and BOP campaign at Vredepeel station** **Figure 5.2**

August 2007 - September 2008



*Daily concentrations (ug/m³) measured simultaneously in LML network and BOP campaign at Vredepeel.*

**Percentual distributions of daily concentrations measured in LML network and BOP campaign at Vredepeel station** **Figure 5.3**



*As Figure 5.2, but now with percentual distributions.*

XY plots, showing the interrelationships between the different data sets, are presented in Figure 5.4. The SIA measurements in the BOP campaign for $PM_{2.5}$ and $PM_{10}$ appeared rather consistent with slopes slightly higher than one (indicating contributions to the coarse fraction). Due to considerable scatter, correlation coefficients with the LML data ($PM_{3-4}$) were much lower. It was anticipated that the uncertainty in the average annual (LML) concentrations would probably be much less. For example, the year-to-year variability agreed well with that for $PM_{10}$.

### 5.2.3 Comparison with foreign data

Another comparison was made with data sets collected in Belgium and Germany. These are referred to as 'Chemkar' (Vercauteren, VMM, Belgium) and 'IUTA' (Quass, IUTA, Germany). In the Chemkar campaign, $PM_{10}$ was measured once every six days, during the period September 2006 to September 2007 (preceding the BOP campaign). The IUTA campaign resulted in a set of 43 daily composition data during March to August 2008.

**Ratios between average LML and BOP filter concentrations** **Table 5.1**

| | $NH_4$ | $NO_3$ | $SO_4$ | total SIA |
|---|---|---|---|---|
| *LML/BOP $PM_{2.5}$* | 0.71 | 0.62 | 0.62 | 0.64 |
| *LML/BOP $PM_{10}$* | 0.65 | 0.50 | 0.55 | 0.55 |

**Ratios between LML and Chemkar concentrations** **Table 5.2**

| | SIA | $NO_3$ | $SO_4$ | $NH_4$ |
|---|---|---|---|---|
| *LML / Chemkar $PM_{10}$ Houthem total* | 0.62 | 0.52 | 0.69 | 0.87 |
| *LML / Chemkar $PM_{10}$ Aarschot* | 0.66 | 0.59 | 0.64 | 0.88 |

### Chemkar (Belgium)

The two rural background locations in Chemkar are Houthem and Aarschot. Time series of Houthem and Vredepeel are shown in Figure 5.5. A reasonable correspondence existed, but baseline level as well as peak values in the LML series were systematically lower (comparable with what was observed in the XY plots in Figure 5.4). Average levels over 51 daily filter samples are presented in Figure 5.6, which also includes Hasselt. Ratios were slightly higher than in the LML – BOP $PM_{10}$ comparison (Table 5.2), which was over a different period. Here, SIA at Vredepeel was 38 and 34% lower than the average $PM_{10}$ concentrations at Houthem and Aarschot. Again, the largest deviations were noted for nitrate and sulphate. It should be kept in mind that, in the LML data set, Vredepeel was the location with the second highest SIA levels.

### North Rhine-Westphalia (Germany)

The North Rhine-Westphalia State Agency for Nature, Environment and Cunsumer Protection (LANUV NRW) provided data for comparison with the results of BOB. The measurement were carried out by IUTA.
The two measurement locations in the data set are Styrum (urban background) and Eifel (rural background). $PM_{10}$ averages were calculated and compared with the $PM_{10}$ BOP averages for Vredepeel, for the the same days (resulting in a subset of only 16 matching days). Regarding sulphate and ammonium, the BOP filter data compared well with the IUTA data. In the case of nitrate, Vredepeel levels in the BOP campaign were clearly higher and probably related to local emissions at Vredepeel. However, the data (sub)sets were too small to draw firm conclusions.

### 5.2.4 Conclusions

Substantial differences were observed between the SIA concentrations in the LML network (PM undefined but assumed in the range 3 to 4 µm) and those measured in the BOP campaign for $PM_{2.5}$. On average, total SIA levels were some 36% lower in the LML data set. The comparison with simultaneously measured SIA in the Belgian data set Chemkar also indicated that the LML data are substantially lower than the PM10 reference instrument data. The BOP filter data ($PM_{10}$; rural Vredepeel) agreed with the IUTA data ($PM_{10}$; urban background Styrum and regional Eifel), except for nitrate. However, the data set considered here was rather small (16 days). The agreement between the $PM_{10}$ and $PM_{2.5}$ concentrations in the BOP filter data set suggested that BOP data were accurate.

The reason for the discrepancy is not completely known yet. The most likely cause is the obvious difference in sampling device, a tube funnel construction compared to modern well defined sampling heads. Also other sources of uncertainty, e.g. chemical analyses method, sample flow values, and filter handling may affect the result. Laboratory routines were considered but did not justify the observed findings (personal communication F. van Arkel, RIVM). Recently, LML replaced the old LVS method by a method based on the $PM_{10}$ reference method (equal to BOP). The comparability will be assessed by a relatively long parallel experiment at a number of LML stations. Results will be published in 2010. The development of a EU reference method for the analytical chemical analysis of SIA is currently under development. ECN (as convener) and RIVM will participate in the development/validation process.

## 5.3 Levels of secondary inorganic aerosol at regional, city background and traffic locations

### 5.3.1 Gradients

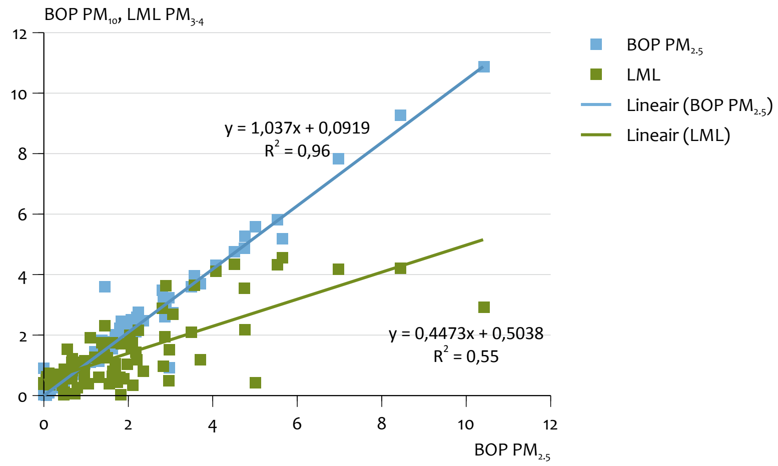
In order to distinguish and locate possible source regions, an analysis of the gradient over the Netherlands is of interest. The LML sites could be classified according to their (summated) location averages for SIA: maximum levels at (suburban) Bilthoven, Vredepeel and, to a lesser extent, Wieringerwerf (due to nitrate), lowest concentrations at Valthermond and Witteveen, and intermediate levels at De Zilk, Huijbergen and Kollumerwaard. The largest difference in concentration was some 3 µg/m³ (Bilthoven - Witteveen/ Valthermond). However, the differences between the LML locations were not statistically significant.

It would be fairly speculative to derive a gradient for SIA over the Netherlands from these average results, as no LML sites were located in the Rijnmond area. However, a ‘ridge’ of higher levels in LML following the line Vredepeel-Bilthoven(-Wieringerwerf) could be identified. It probably represented the influence of the industrial emissions in the Rijnmond area and Antwerp (with south-westerly winds). Near the sea, intermediate concentration levels occurred (Huijbergen, De Zilk, Wieringerwerf, Kollumerwaard) where the sea salt contribution increased the presences of sulphate during westerly winds.

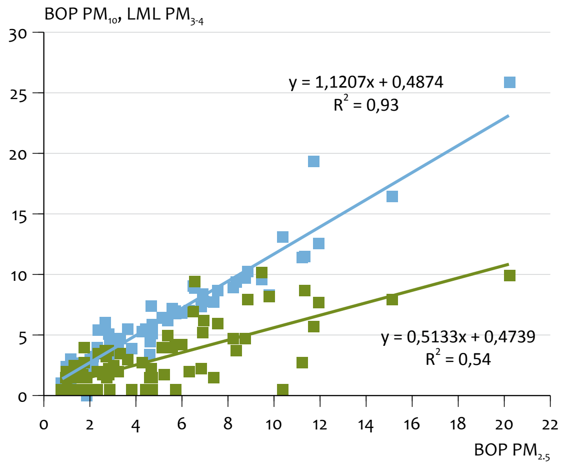
The average (spatial) variation in summated SIA levels within the BOP data set (duration one year) was also moderate (see Figure 4.2 in Section 4.1.2). For $PM_{10}$, the maximum difference was 2.6 µg/m³, and for $PM_{2.5}$ this was 1.8 µg/m³ (in both

**XY-plots for $NH_4$, $NO_3$ and $SO_4$ on different PM fractions** **Figure 5.4**

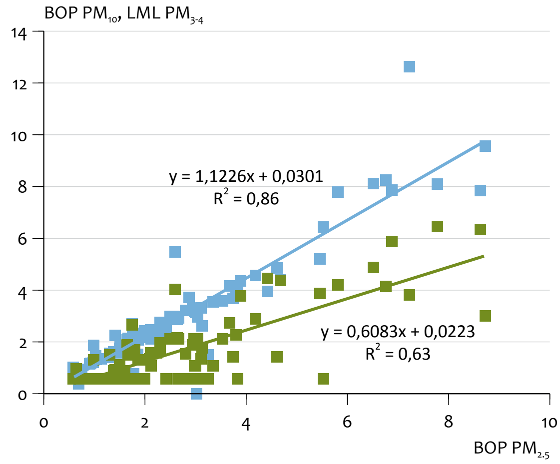
$NH_4$ Vredepeel



$NO_3$ Vredepeel



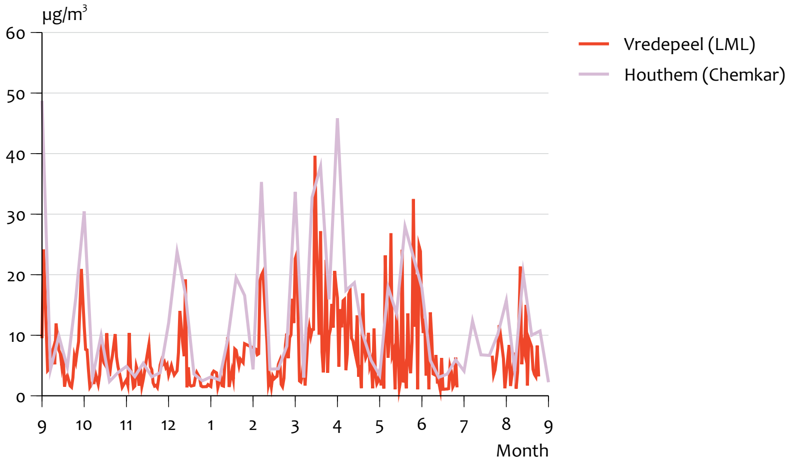
$SO_4$ Vredepeel



*XY plots for LML $PM_{3\text{-}4}$ and BOP $PM_{10}$ versus BOP $PM_{2.5}$.*

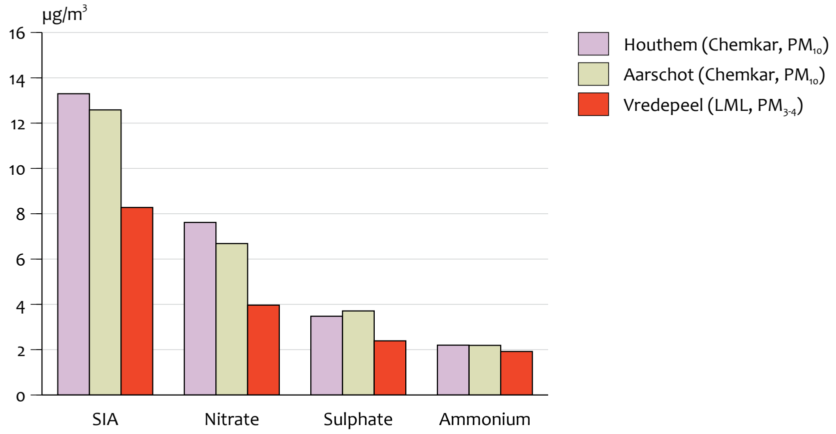
cases sites are Vredepeel and Hellendoorn). The BOP filter data set further suggested higher levels for the urbanised Rijnmond region and Breda, and lowest concentrations east of Hellendoorn (not far from Witteveen/Valthermond). The third regional BOP location was Cabauw (some 30 kilometres south-west of Bilthoven) showing intermediate and clearly higher levels, with respect to Hellendoorn. The Rijnmond region (Rotterdam, Schiedam) showed levels closer to those at Vredepeel (for $PM_{10}$). The Rotterdam average for SIA

**Time series of SIA for Vredepeel and Houthem from 16/9/2006 till 11/9/2007** **Figure 5.5**



*Time series of SIA for Vredepeel (LML) and Houthem (rural background location in Chemkar).*

**Average SIA concentrations for Houthem and Aarschot and Vredepeel** **Figure 5.6**



*Average daily concentrations at Houthem and Hasselt (PM10, rural background Chemkar data) and Vredepeel (PM3-4, LML), calculated over 51 days.*

in $PM_{2.5}$ was deviated for all three SIA components, being considerably larger, for reasons unknown.

Concluding, the various data sets suggested SIA concentrations (in $PM_{10}$ and $PM_{2.5}$) were higher in the south (Vredepeel, Breda) and in the west (Randstad area) of the Netherlands. Consequently, the lowest levels were measured in the eastern and northern parts of the country.

### 5.3.2 Increments

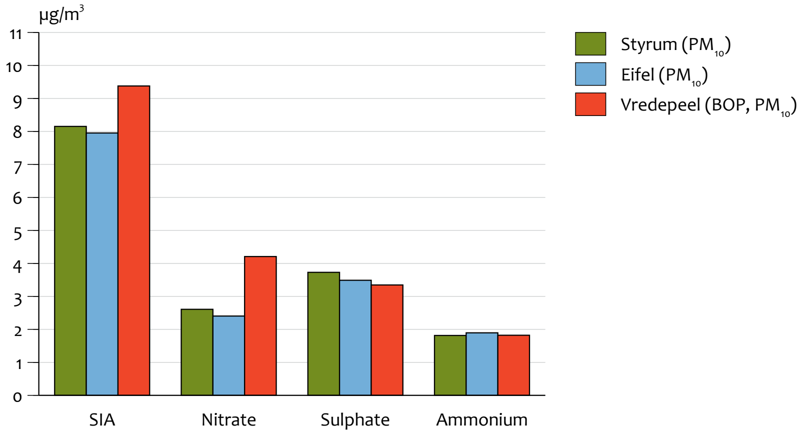
One of the goals of the BOP research programme is to make a more precise assessment of SIA in regional background air and in urban air, in the Netherlands. Such a precise assessment is of importance, because (summated) SIA constitutes the largest contribution to PM and can, to a certain extent, be influenced by implementation of political and technical measures regarding the various precursors. In particular, with (daily) exceedances for $PM_{10}$ occurring mainly in city areas, the relevant question would be to which extent the SIA components contribute to possible increments in the urban environment. A second question of interest would be which mechanisms and/or sources explain an additional SIA presence. The overall averages as calculated from the data sets treated here already provided a first indication. For a summary, see Table 5.3 and Figure 5.8.

The levels measured at the urban background locations were systematically higher than in the regional setting. The only exception was BOP $PM_{2.5}$ data. Based on Figure 5.8, the urban increment for SIA was between 1.5 and 2 µg/m³. However, this value largely depended on the particular pair of (regional and urban) locations compared.

The network average for SIA in LML data was 8.3 µg/m³, in which all locations were classified as regional. However, Bilthoven (9.9 µg/m³), located in the Utrecht agglomeration, was some 3 µg/m³ above Valthermond/Witteveen (6.8 to 6.9 µg/m³); associated increments for sulphate, nitrate and

## Average SIA concentrations at Styrum, Eifel and Vredepeel

Figure 5.7



*Average concentrations at Styrum (urban background) and Eifel (rural background) ($PM_{10}$, IUTA) and Vredepeel ($PM_{10}$, BOP filter), calculated over 16 days.*

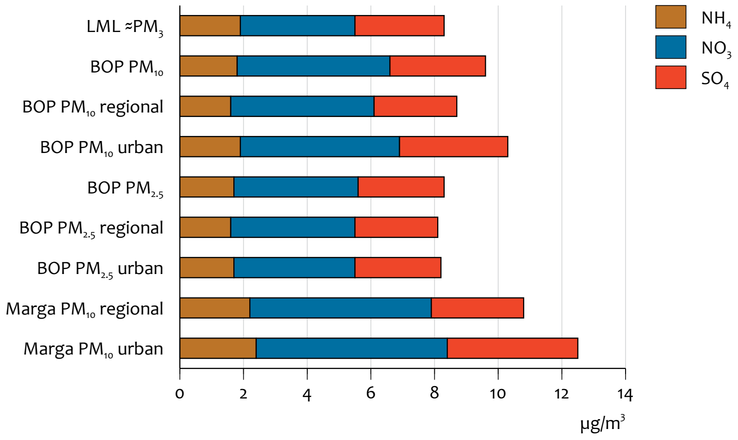
## Overall averages and specifics for the LML, BOP and MARGA data sets

Table 5.3

| | period | fraction | type | SIA | $NH_4$ | $NO_3$ | $SO_4$ | data used from |
|---|---|---|---|---|---|---|---|---|
| *LML filter* | 1994-2007 | $\approx PM_{3-4}$ | regional | 8.3 | 1.9 | 3.6 | 2.8 | 8 locations |
| *BOP filter* | Aug/07 - Aug/08 | $PM_{10}$ | regional/urban/traffic | 9.7 | 1.8 | 4.8 | 3.0 | 5 locations |
| | | $PM_{10}$ | regional | 8.7 | 1.6 | 4.5 | 2.6 | Cabauw and Hellendoorn |
| | | $PM_{10}$ | urban | 10.2 | 1.9 | 5.0 | 3.4 | Rotterdam and Schiedam |
| | | $PM_{2.5}$ | regional/urban/traffic | 8.3 | 1.7 | 3.9 | 2.7 | 5 locations |
| | | $PM_{2.5}$ | regional | 8.0 | 1.6 | 3.9 | 2.6 | Cabauw and Hellendoorn |
| | | $PM_{2.5}$ | urban | 8.1 | 1.7 | 3.8 | 2.7 | Rotterdam and Schiedam |
| *MARGA* | Aug/07 - Feb/08 | $PM_{10}$ | regional | 10.9 | 2.2 | 5.7 | 2.9 | Cabauw |
| | | $PM_{10}$ | urban | 12.4 | 2.4 | 6.0 | 4.1 | Schiedam |

## SIA overall, regional and urban averages for the LML, BOP and MARGA data sets

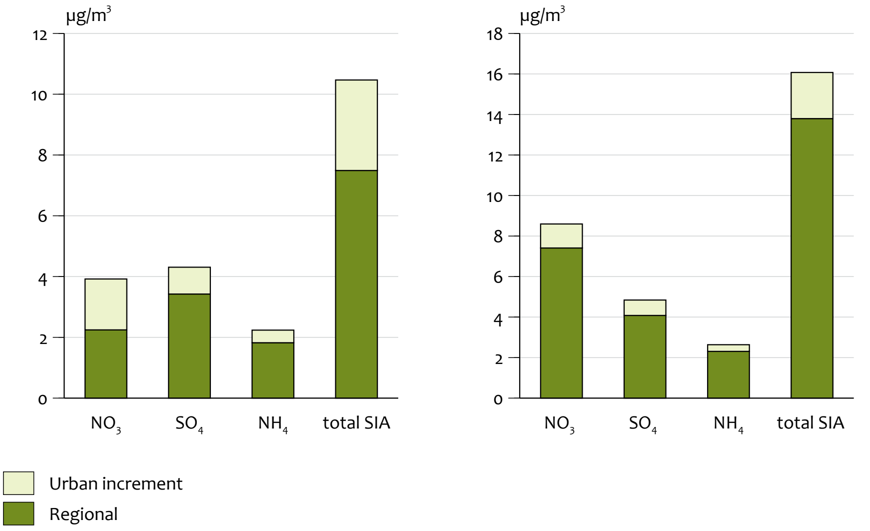
Figure 5.8



ammonium were 1 µg/m³, 1.3 µg/m³ and 0.8 µ/m³, respectively. In terms of percentage, the increase in SIA in Bilthoven, with respect to the network average, was 19%. It should be noted that the LML levels appeared fairly low (see Section 5.2).

Figure 5.8 clearly demonstrates that the highest SIA concentrations in the BOP campaign were measured by the MARGA systems: 10.9 µg/m³ (Cabauw) and 12.4 µg/m³ (Schiedam) of $PM_{10}$. This can be explained by the volatile character of ammonium nitrate, which evaporates from the

**Average $PM_{10}$ regional contribution and urban increment** **Figure 5.9**


IUTA dataset (Germany, 5-2-2008 / 28-9-2008)

Chemkar dataset (Belgium, 16-9-2006 / 11-9-2007)

*SIA concentrations in the IUTA (Germany) and Chemkar (Belgium) data sets.*

filter under influence of temperature. Based on the averages over the common measurement periods, the differences between the measurements by filter method and the MARGA system, at urban and regional locations, was estimated to be in the range of 2.0 to 2.2 µg/m³. For estimating the mass closure, ordinarily, filter measurements such as the reference method are used. From the observed differences, it is advised that – next to the filter collection – parallel measurements (using filter denuder packs or MARGA-like systems) would be carried out, to estimate the loss of volatile material from the filter.

Further indication of incremental SIA in the urban environment was derived from the Chemkar and IUTA data sets ($PM_{10}$), as presented in Figure 5.9. Here, increments between 2.3 and 3 µg/m³ were calculated. In both data sets, the largest contribution came from nitrate (1.2 and 1.7 µg/m³).

Going into more detail, based on the (synchronised) $PM_{10}$ and $PM_{2.5}$ subsets, average increments at urban locations were calculated for the BOP filter data set. In this data set, there were three stations (Hellendoorn, Cabauw and Vredepeel) considered to be 'regional' or 'background'. Hellendoorn exhibited the lowest concentrations, with an average SIA content in $PM_{10}$ of 8.0 µg/m³ and of 7.6 µg/m³ in $PM_{2.5}$ (Table 4.2). It is a typical background location, being unaffected by direct emissions from industry or traffic (in contrast with Vredepeel station, which is largely affected by nearby agricultural emissions). Cabauw showed higher SIA concentrations than Hellendoorn: 9.3 µg/m³ ($PM_{10}$) and 8.3 µg/m³ ($PM_{2.5}$). However, Cabauw may be considered a more representative regional background location for the Randstad area (where the city of Rotterdam is situated). With Schiedam and Rotterdam being the only urban background and traffic locations in the data set, the increments in $PM_{10}$ and $PM_{2.5}$ from the presence of SIA components were calculated for both Cabauw and Hellendoorn (see Figure 5.10).

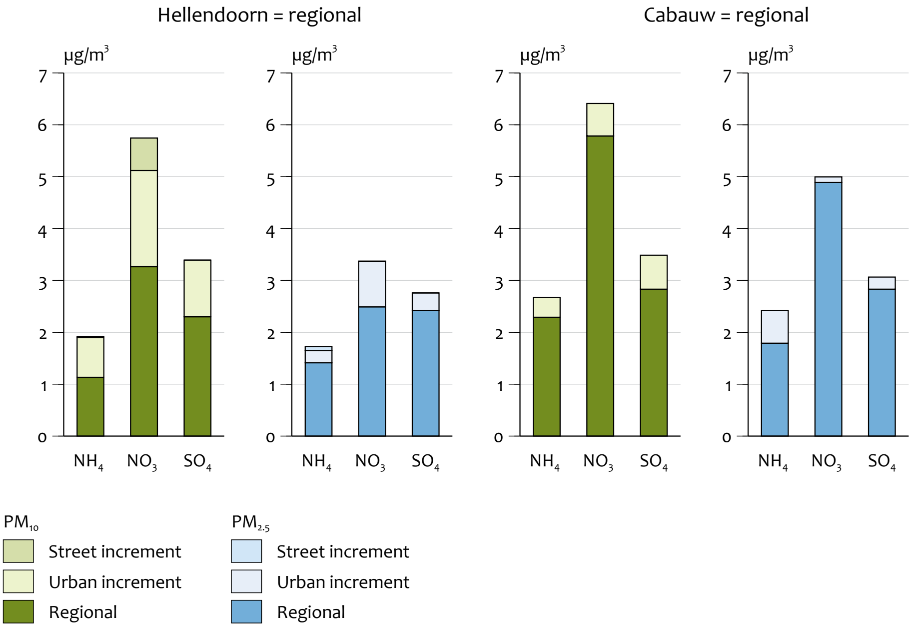
Out of the data points for $PM_{10}$ – 44 (Hellendoorn), 41 (Schiedam) and 70 (Rotterdam), only 18 days matched for $PM_{2.5}$ (mostly in the period from April to August). For Cabauw, the subset consisted of 14 days (between March and July). From the (synchronised) subsets, the incremental average concentrations were estimated. In a few cases, incremental concentrations at traffic locations appeared negative (not shown).

These two figures confirm the earlier observations above. As expected, the contribution of 'regional' SIA in urban Schiedam dominated, in particular, 'regional' nitrate added to $PM_{10}$ and $PM_{2.5}$. While 'regional' sulphate was entirely present in the form of $PM_{2.5}$ particles, part of 'regional' nitrate (13 to 25%) was found in the coarse fraction.

Increments at traffic locations due to SIA appeared mostly negligible, in both $PM_{10}$ and $PM_{2.5}$. The only exception was nitrate, for which an increment of 0.6 µg/m³ in $PM_{10}$ was observed (compared to Hellendoorn). Since the conversion of $NO_2$ into $NO_3$ takes a few hours, it is expected that $NO_2$ would dominate at the traffic site, and $NO_3$ would be formed elsewhere (further downwind).

Assuming that both selected regional locations represented background air conditions, the urban increments were estimated to be within the range of 1.7 to 3.8 µg/m³ ($PM_{10}$) and 0.9 to 1.4 µg/m³ ($PM_{2.5}$), indicating a coarse fraction for SIA in the urban background (0.8 to 2.5 µg/m³). The largest contribution to the urban increment again is from nitrate (0.6 to 1.9 for $PM_{10}$ and 0.1 to 0.9 µg/m³ for $PM_{2.5}$), followed by anthropogenic sulphate (0.7 to 1.1 and 0.2 to 0.3 µg/m³) and ammonium (0.4 to 0.8 and 0.2 to 0.3 µg/m³). The concentrations

**Incremental concentrations of ammonium, nitrate and anthropogenic sulphate** **Figure 5.10**



*Incremental concentrations of ammonium, nitrate and anthropogenic sulphate, at the urban background location (Schiedam) and at the traffic location (Rotterdam), compared to the regional concentration levels at Hellendoorn (left) and Cabauw (right).*

in the coarse fraction were 0.5 to 1 µg/m³ (nitrate), 0.5 to 0.8 µg/m³ (sulphate) and less than 0.5 µg/m³ (ammonium). Apparently, the presence of nitrate in the coarse fraction was a large-scale phenomenon (being present in the regional and urban contributions), while anthropogenic sulphate in $PM_{10}$ was restricted to the urbanised region around Rotterdam, and likely related to the $SO_2$ emissions nearby.

The explanation for a higher presence of both nitrate and sulphate in the coarse fraction of PM would be that, in a marine environment such as the western part of the Netherlands, coarse sea salt particles may act as a reactive sink for nitric and sulphuric acid via the reactions:

$$NaCl + HNO_3 \rightarrow NaNO_3 + HCl,$$

and

$$NaCl + H_2SO_4 \rightarrow Na_2SO_4 + HCl.$$

Hence, Cl can be removed by heterogeneous reactions with $HNO_3$ and $H_2SO_4$. Evidence for the depletion of Cl and the release of gas-phase HCl is shown in Figure 5.11, showing the daily cycle of the chloride deficit with respect to seawater and gaseous HCl (as measured with the MARGA instrument). Clearly, the ratios Cl/Na were consistently smaller than 1.8 (being the ratio in sea salt). The deficit was at a maximum in the afternoon, which coincided with a maximum of gaseous HCl.

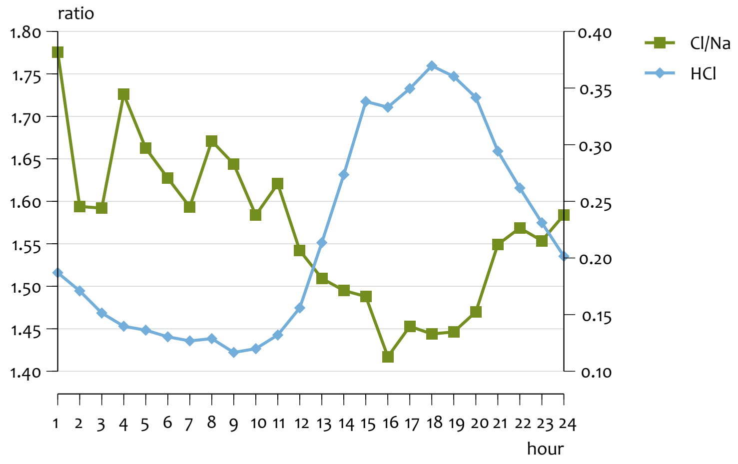
### 5.3.3 The role of SIA in the occurrence of high $PM_{10}$ levels

The MARGA data sets for Cabauw and Schiedam allowed a comparison between the presence of various components (SIA, sea salt) and associated $PM_{10}$. The Figure 5.12 shows the relative contributions of these components as a function of $PM_{10}$ (classes). In general, there is a clear relationship between $PM_{10}$ mass and the presence of ionic components. Ranging from low to high PM concentrations, the largest increase was measured for nitrate (from 15 to 25%), while for ammonium this was 4.5 to 12%. The sulphate contribution remained more or less unchanged, with varying $PM_{10}$ concentrations at 12 to 13%.

Clearly visible was that the sea salt contribution (Na+Cl) acted opposite to that of SIA: the relative contribution decreased from 20% to a level as low as 3%. Further notable was that the contribution of the 'unknown' part in $PM_{10}$ remained the same, at almost 50%. Considering the opposite behaviour of SIA and sea salt, it was concluded that on exceedance days ($PM_{10}$> 50 µg/m³) SIA (≥50%) was the most important constituent, while the presence of sea salt contribution decreased to less than 4%.

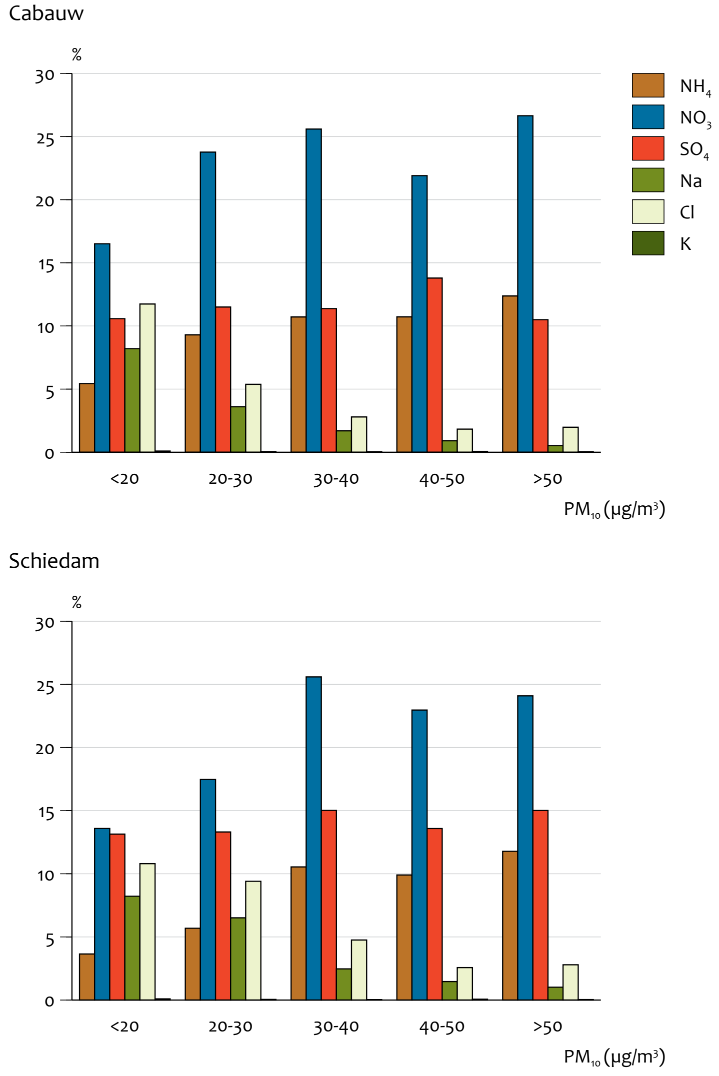
The opposing findings for SIA and sea salt reflected the influence from different sources and trajectories on the occurrence of high PM levels. This effect could already be identified in the original time series. As an example, Figures 5.13 contained two episodes with $PM_{10}$ concentrations far above 50 µg/m³ (9 to 12 October and 15 to 17 October). Visual inspection revealed a relationship between wind direction (measured at Rotterdam airport) and SIA (measured at Schiedam). The highest concentrations (up to 60 µg/m³) were measured when the wind direction was between 100° and 150° (on 10 October). Further notable was (i) the gradual decrease in the period between 9 and 11 October, corresponding with a backing of the wind from south to north, and (ii) the slow

**Daily cycles of Cl/NA and HCl as measured with the MARGA system at Schiedam** **Figure 5.11**



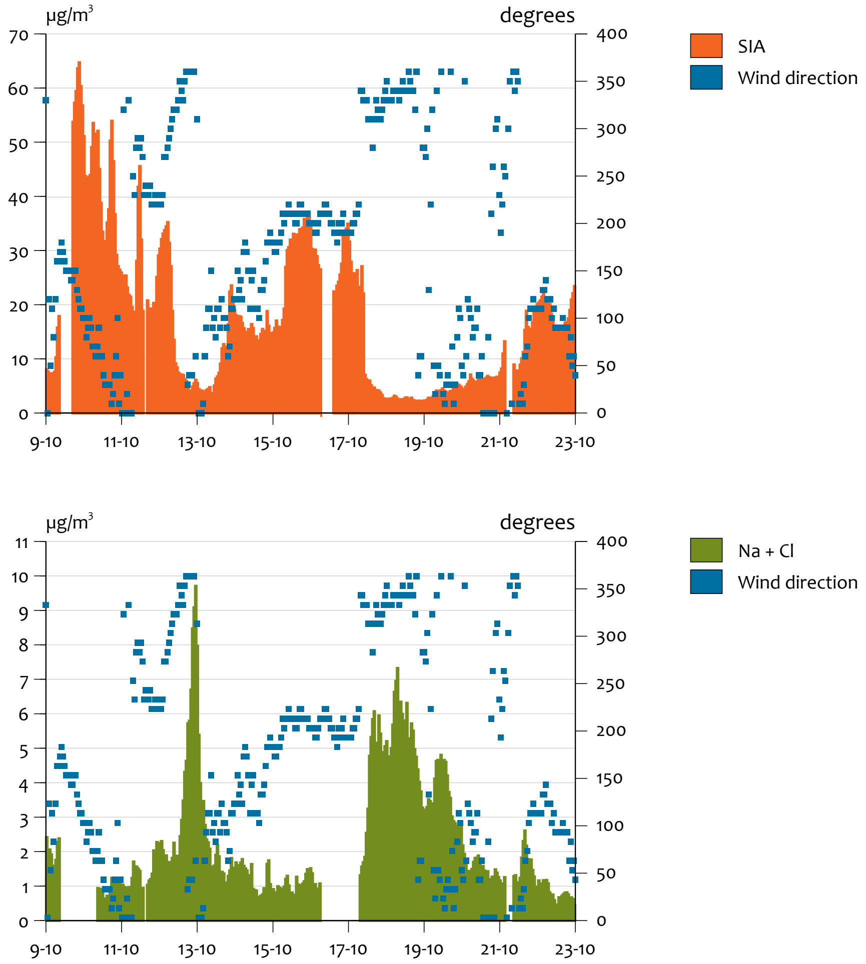
*Daily cycles of Cl/NA and HCl, as measured with the MARGA system at Schiedam.*

**Relative contribution of components as a function of $PM_{10}$** **Figure 5.12**



*Relative distributions of the various components as a function of PM concentration classes at Cabauw and Schiedam.*

**Hourly concentrations in Schiedam** **Figure 5.13**



*Hourly registrations of SIA and sea salt by the MARGA system in Schiedam.*

build-up between 13 to 16 October with a related veering. Also notable was the drastic decline in SIA concentrations on 12 and 17 October, when the wind direction rapidly veered within the sector south-west (going from 220° to 300°-350°). It was concluded that the maximum concentrations typically occurred when the wind direction was in the sector south to east (but obviously depended on backward trajectories). The contrasting variation in levels of sea salt was recognisable on 13 October and from 17 to 20 October. Note that during periods with SIA concentrations of above 30 µg/m³, the contribution of sea salt was less than 2 µg/m³.

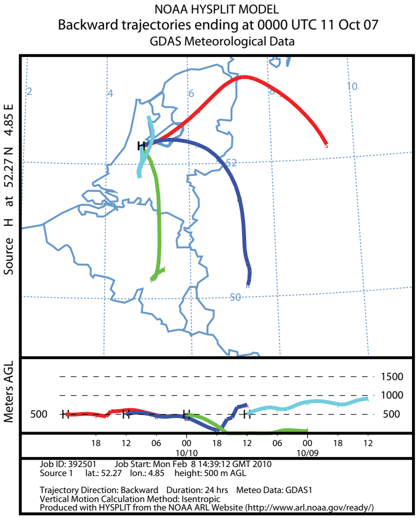
Summarising, the variability of air pollution levels bore a strong relationship with ambient meteorology. Prevailing wind direction (which related to specific conditions of wind speed, mixing height and temperature lapse rates) was of influence on the measured concentration levels at the experimental sites. Among these variables, wind direction was of interest, because it visually links measurements to areas of emissions elsewhere. A relationship between the dominant wind direction during certain periods (with exceedances) and atmospheric stability existed. In the Netherlands, under the influence of high pressure systems in winter, the supply of cold air from the European continent generally leads to the existence of a stable boundary layer (stagnant conditions). In such situations, the air masses transported to our regions usually carry large amounts of polluted air, due to the combination of pollution emitting sources (east and south of the Netherlands; see Figure 5.14), and stagnant (non-dispersive) weather conditions. Note the difference with the trajectory ending on 12 October (24:00), characterised by a rather high sea salt concentration (Figure 5.15).

It is clear that a large part of SIA in the Netherlands was due to long-range transport. The question remains which part of SIA was generated within the Netherlands. There was indication of such a production, as upward gradients were measured when moving towards urbanised areas.

### 5.3.4 Conclusions

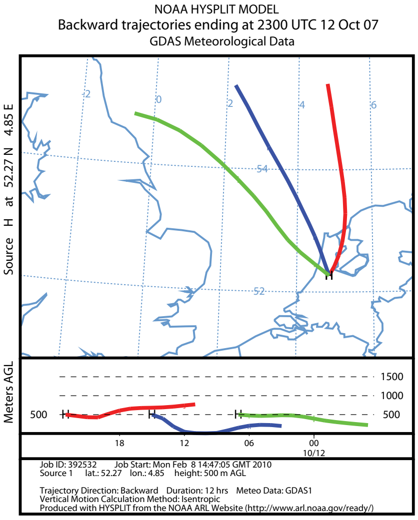
The various data sets suggested that SIA concentrations in PM were higher in the southern and western part of the Netherlands. In particular, higher levels were observed in the urbanised regions, such as Breda and Rotterdam and in source regions such as Vredepeel. The regional contribution

**Backward trajectories ending at 0000 UTC 11 October 2007** **Figure 5.14**



*Backward trajectories for 10 October 2007.*

**Backward trajectories ending at 2300 UTC 12 October 2007** **Figure 5.15**

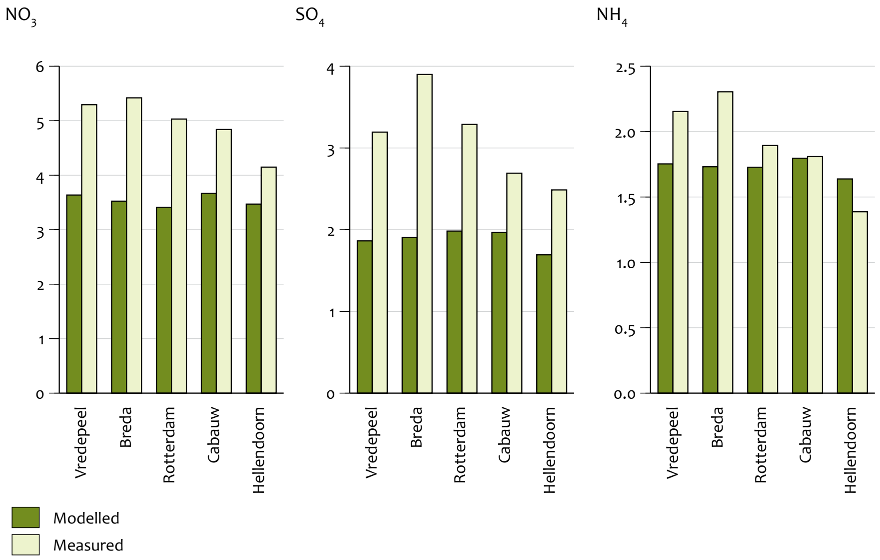


*Backward trajectories for 12 October 2007.*

dominated the presence of SIA at these urban locations. Urban increments in $PM_{10}$ were up to 3.8 µg/m³ (depending on which locations were compared). Similar results were calculated in German and Belgian data sets. The largest contribution to the urban $PM_{10}$ increment came from nitrate (2 µg/m³), followed by anthropogenic sulphate (1.2 µg/m³). Both these increments were partly measured in $PM_{10}$. The data suggested that coarse sea salt particles act as reactive sinks for nitric and sulphuric acid, resulting in Cl depletion and HCl gas release. Increments at traffic locations due to SIA appeared negligible in both $PM_{10}$ and $PM_{2.5}$.

The variability of SIA and sea salt in PM bore a strong relationship with ambient wind direction. On days with high PM concentrations, the increase in SIA was larger than the average increase in PM (or in any component therein). The SIA contribution on such days rose to 45 to 55%, making SIA (and nitrate, in particular) primarily responsible for these high PM concentration levels. A relationship with wind direction was established: high levels occurred when the wind direction was within 50° to 220°. Such directions usually coincided with the influence of high pressure systems (mainly in winter), when the supply of cold air from the European continent leads to stagnant (non-dispersive) conditions and lower mixing heights. However, next to the long-range contribution, an additional local production was suggested, needing further clarification.

**Averages modelled and measured concentrations** **Figure 5.16**



*Averages per component for each of the five BOP locations..*

## 5.4 Modelling of SIA by LOTOS-EUROS compared to the filter and MARGA measurements

### 5.4.1 Introduction

The complex formation pathways for SIA are represented in chemistry transport models in a simplified manner. In the Netherlands, the LOTOS-EUROS (LE) model is used to investigate the SIA levels in Europe and the Netherlands, in particular. The data from the BOP campaign provided a good test case for the LE model. This is especially true, because, for the first time, an hourly data set was available over the period of an entire year, in the case of Cabauw (August 2007 to August 2008). As described below, LOTOS-EUROS results were compared to measurements to assess the performance in the simulation of time series and to estimate the average levels of nitrate, sulphate and ammonium. Furthermore, possible explanations are given for the observed differences, together with directions for model improvements.

The experimental data used here were obtained from the reference filter method, as well as the MARGA system at the two BOP locations Rotterdam and Cabauw. The MARGA hourly data were also averaged to obtain synchronised daily concentration values. First, the comparison was made with the filter measurements. Next, a comparison was made with the daily average MARGA data, for both Rotterdam and Cabauw. Finally, we used the MARGA data for Cabauw to address the diurnal and seasonal cycle of SIA and its gaseous counterparts. Cabauw was selected for this purpose, as it was the only location for which a full year of MARGA data was available. The model validation for LML data (for 2005) was laid down in the technical background report by Schaap *et al.* (2009) and has not been included in this report.

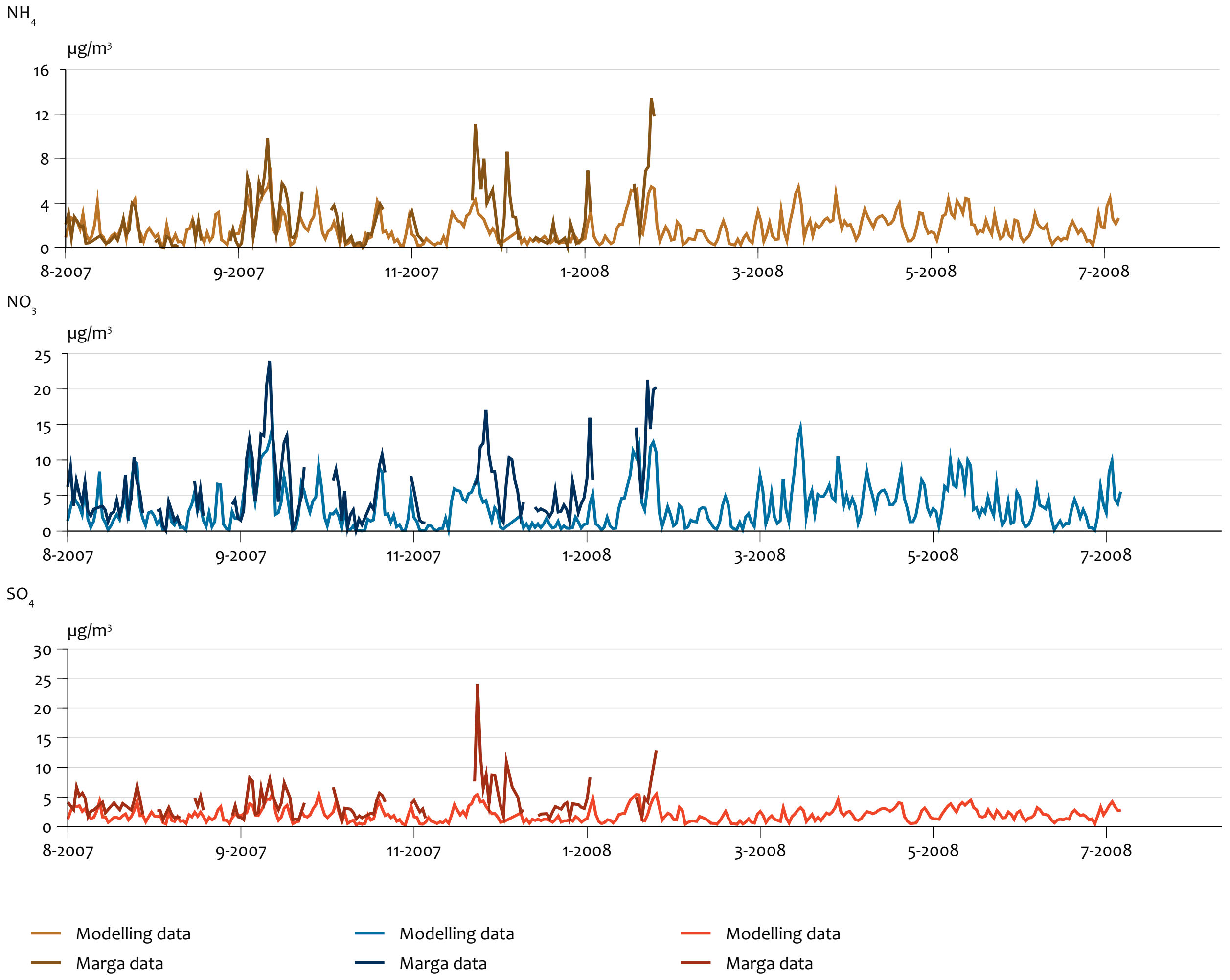
### 5.4.2 Simulation of SIA time series at the 5 BOP locations

Figure 5.16 gives the average modelled and measured concentrations for each of the five locations in the BOP measurement campaign. The time series modelled for these five locations and the three components looked very similar, yielding comparable average concentrations of ammonium sulphate and ammonium nitrate. After averaging over the entire period, the modelled differences between the concentrations at the locations were small and within the following ranges: 0.2 µg/m³ (NH$_4$), 0.3 µg/m³ (NO$_3$) and 0.3 µg/m³ (SO$_4$) (Figure 5.16). As a consequence, the upward gradient measured for the location series Hellendoorn - Cabauw - Rotterdam - Breda was almost absent. Also, the model considerably underestimated the average measured concentrations for all locations: for SO$_4$ this was -10 to -48%, for NO$_3$ it was -27 to -55%, and appeared more representative for NH$_4$ with -18 to +25%. Note, that the underestimation compared to the LML data, which has been used for validation over the past decade, was lower or absent (Schaap *et al.*, 2009). Hence, these measurements shed a new light on the model performance and need to be evaluated in more detail. Here, we further addressed the model to measurement comparison with the hourly MARGA data.

### 5.4.3 Comparison with the daily MARGA data

The comparison between the modelled and measured daily values for SIA (Figure 5.17) showed a considerable agreement at Cabauw and Rotterdam. The model was able to capture a large part of the day-to-day variability in the observed concentrations. The correlation coefficient values were about 0.6 for NO$_3$ and NH$_4$ and around 0.40 for SO$_4$. These coefficients were slightly higher than in the comparison with the filter measurements (not shown). As shown above, the LE modelling underestimated the SIA levels obtained by the MARGA instrument, especially at the Schiedam location, as can be seen in Table 5.4. Closer inspection revealed that

**Time series of the modelled data and measured Marga data for Schiedam** **Figure 5.17a**



*Time series of the modelling data and MARGA data for Schiedam..*

base line values appeared well estimated for ammonium and sulphate, and that the underestimation predominantly took place for the peak concentrations. For example, the four periods with sulphate concentrations of above 10 µg/m³ were not captured by the model. Hence, the formation of sulphate during these episodes, which occurred mostly in winter and spring, needed to be addressed. For nitrate, the variability towards high concentrations was much better captured and a systematic relative underestimation remained.

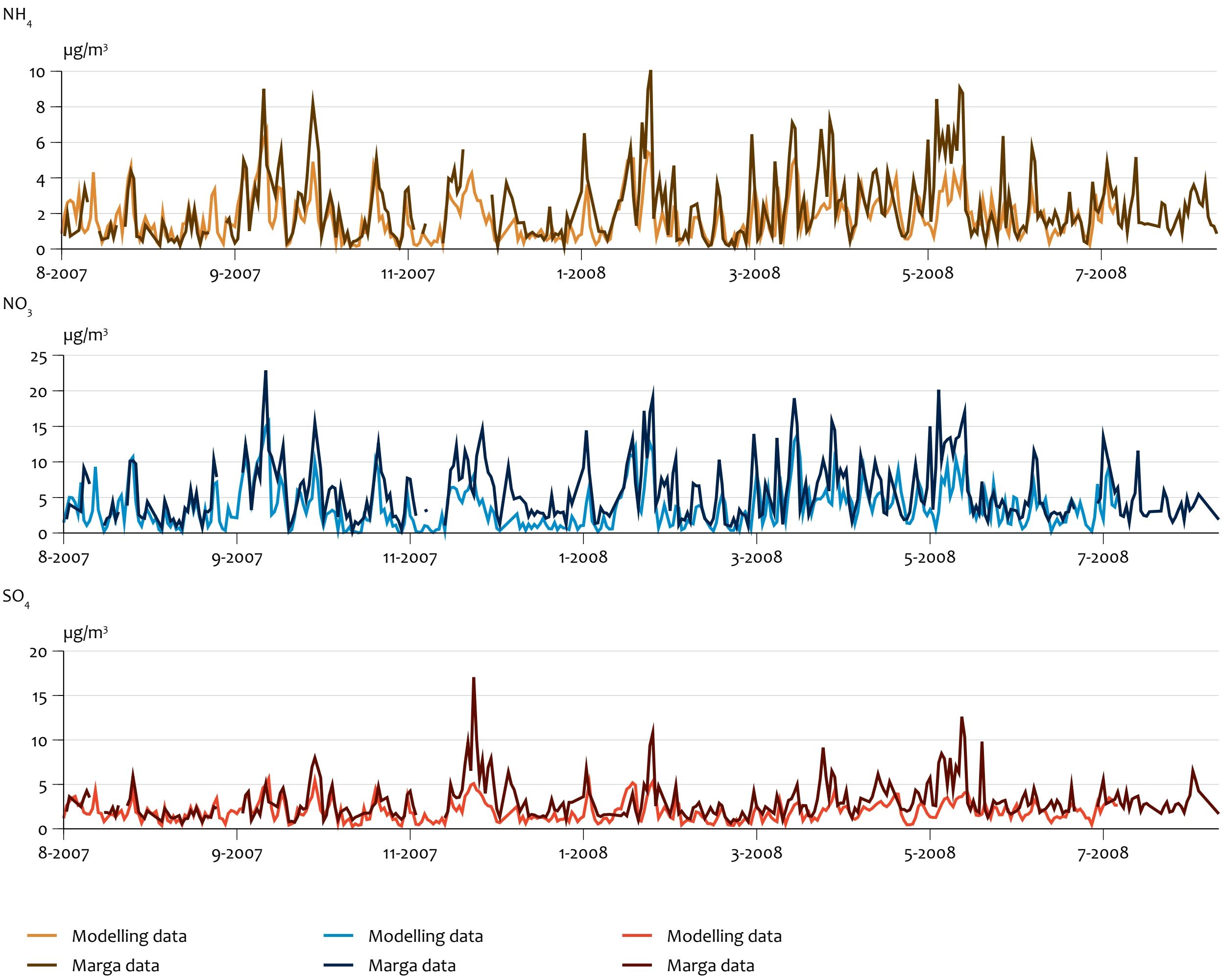
The day-to-day variability was condensed to the seasonal variation in Figure 5.19. Note that the figures show a year from January to December, meaning that the 2008 data are put before those of 2007 to arrive at a figure that is more easy to interpret. For nitrate, ammonium and, to a lesser extent, sulphate, the month-to-month variability was captured, although levels were underestimated, as noted before. Nitric acid showed a modelled distribution with a pronounced summer maximum, which, surprisingly, was not found in the measured data. Such a summer time maximum was observed in other countries, so the different behaviour in the Netherlands needs to be explained in the future. Furthermore, the observed ammonia levels were higher than those modelled.

As Cabauw is located in an agricultural area, local contributions may have affected the analysis. Hence, the scale at which LE was aimed, could have been too coarse to properly account for ammonia in source regions (as it also is not meant to reproduce $NO_2$ inside a city). Hence, the comparison for ammonia should be interpreted with care.

### 5.4.4 Comparison with the hourly MARGA data

The MARGA data provided a unique set to evaluate the temporal behaviour of the LOTOS-EUROS model. For the first time, the model could be evaluated on an hourly resolution with both the particulate components and their gas-phase counterparts, which together determine the equilibrium for ammonium nitrate. The comparison of the hourly data was illustrated in the form of time series in Figure 5.19 and 5.20. These time series show the general features as described above. In other words, they show the underestimation but good correlation for nitrate, as well as the sulphate episodes not captured in spring. However, much more detail was visible in the time series and we noticed that the model was able to reproduce many features, also at the intra-day scale.

**Time series of the modelled data and measured Marga data for Cabauw** **Figure 5.17b**



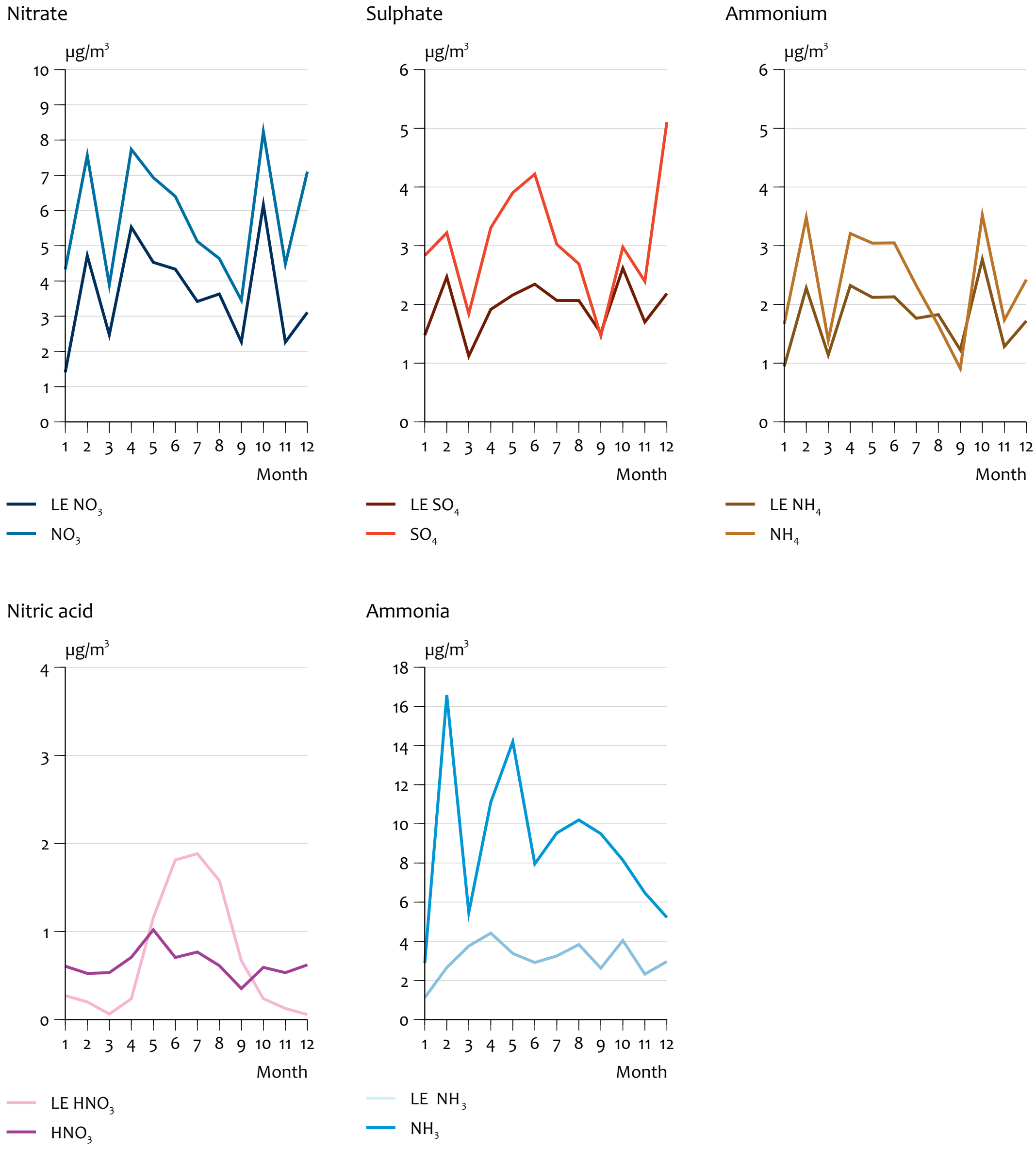
*Time series of the modelling data and measured MARGA data for Cabauw.*

**Average concentrations (LE modelled and MARGA measured) at Schiedam and Cabauw** **Table 5.4**

| $NH_4$ | measured | modelled |
|---|---|---|
| *Schiedam* | 2.5 | 1.7 |
| *Cabauw* | 2.4 | 1.8 |
| | | |
| $NO_3$ | | |
| *Schiedam* | 6.1 | 3.4 |
| *Cabauw* | 5.7 | 3.7 |
| | | |
| $SO_4$ | | |
| *Schiedam* | 4.1 | 2.0 |
| *Cabauw* | 3.1 | 2.0 |

To further investigate the behaviour of the model on an hourly basis, we compared the average diurnal variation against the measurements (Figure 5.21). Although the absolute level of nitrate was underestimated, the diurnal variation was rather well captured. Maximum concentrations occurred in the early morning after a night-time build up. Both the model and the observations showed a daytime minimum, which was driven in the model by the higher instability of ammonium nitrate at high temperatures. It appeared that the decrease in nitrate (and also ammonium) in the early morning started 1 to 2 hours earlier than in the observations. This may have been due to the three-hourly meteorological data used by the model, which were interpolated to acquire hourly values. However, the timing of the rise of the mixing layer was not well represented and occurred gradually, between 6 and 9 a.m. in summer, whereas, in reality, it may be characterised by a more rapid mixing layer growth that occurs later in the morning.

**Modelled and measured seasonal cycle** **Figure 5.18**



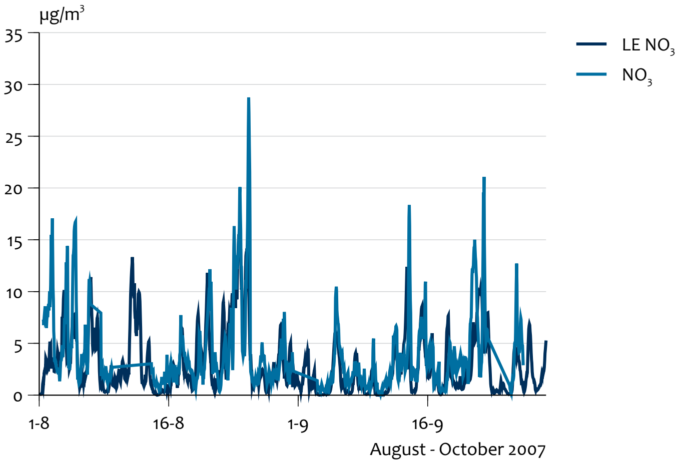
*Modelled and measured seasonal cycle for nitrate, sulphate, ammonium, nitric acid and ammonia. Note that for easy interpretation the data have been organised as if it was a year from January to December. Hence, the monthly averages of January to July 2008, were put before the period of August to December 2007.*

The measured sulphate variation over the day was relatively flat, with a tendency to a daytime maximum. LOTOS-EUROS yielded a flat distribution as well, but had a tendency to a slight daytime minimum. We concluded that the formation of sulphate, as well as the sinks, should be investigated to improve the absolute level and especially the peak values rather than investigating the diurnal variability.

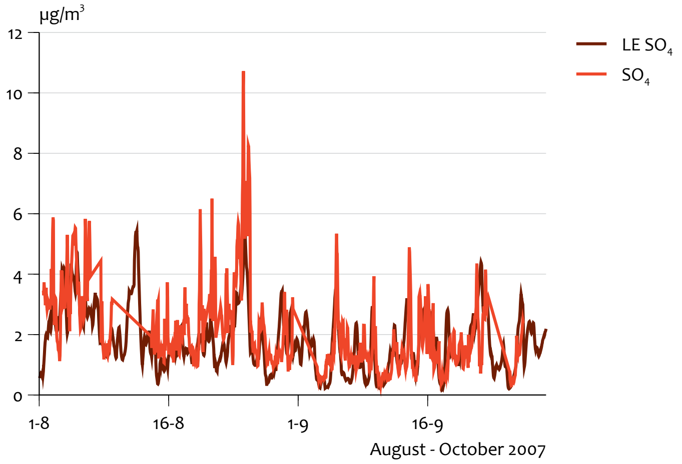
The comparison for nitric acid and ammonia revealed an interesting picture. The model predicted a strong diurnal variation of nitric acid. In summer, a strong daytime maximum was modelled up to an average concentration of about 3.5 µg/m³. During winter, the model simulated much lower values than in summer, with a daytime minimum, that was associated with a daytime maximum in ammonia. The measurements, however, yielded a much lower dependency on season. The measured concentrations in summer were only a little higher than in winter. Moreover, the measurements indicated a flat diurnal variation in winter and only a slight daytime maximum in summer. For ammonia, the diurnal variation was roughly in line with observations, albeit that the absolute concentrations were too low, as was discussed above. The discrepancies between modelled and measured variability on the seasonal and the diurnal scale need to be addressed taking into account several (interacting) processes that influence the concentrations and their dependencies.

**Comparison of hourly modeled and measured concentrations of nitrate and sulphate** **Figure 5.19**

Nitrate



Sulphate

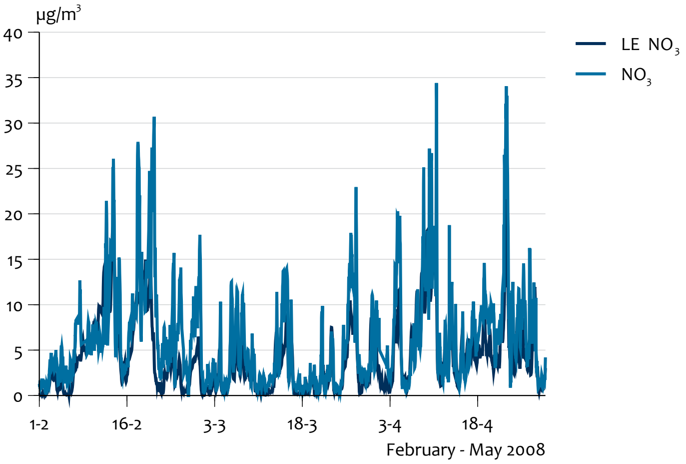


*Comparison of hourly modelled (black) and measured (red) concentrations of nitrate and sulphate for August to September, 2007.*

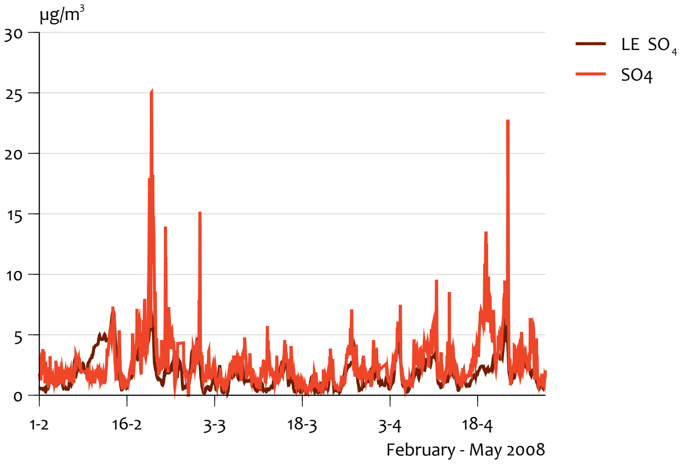
As for the observations, the correlation between the SIA components were calculated (Table 5.5). In the model, the anions were strongly correlated to ammonium with coefficients of 0.98 for nitrate and 0.88 for ammonium. Nitrate was more strongly correlated to ammonium than was sulphate. Also, nitrate and sulphate were less strongly correlated than each of them with ammonium. This pattern was also found for the MARGA data, adding to the conclusion that the model was able to reproduce many features of the SIA components. However, it appeared that the correlations were stronger in the model than in reality, which is explainable for the role of other cations than ammonium in the atmosphere, which were not accounted for in LOTOS-EUROS

**Comparison of hourly modeled and measured concentrations of nitrate and sulphate** **Figure 5.20**

Nitrate



Sulphate

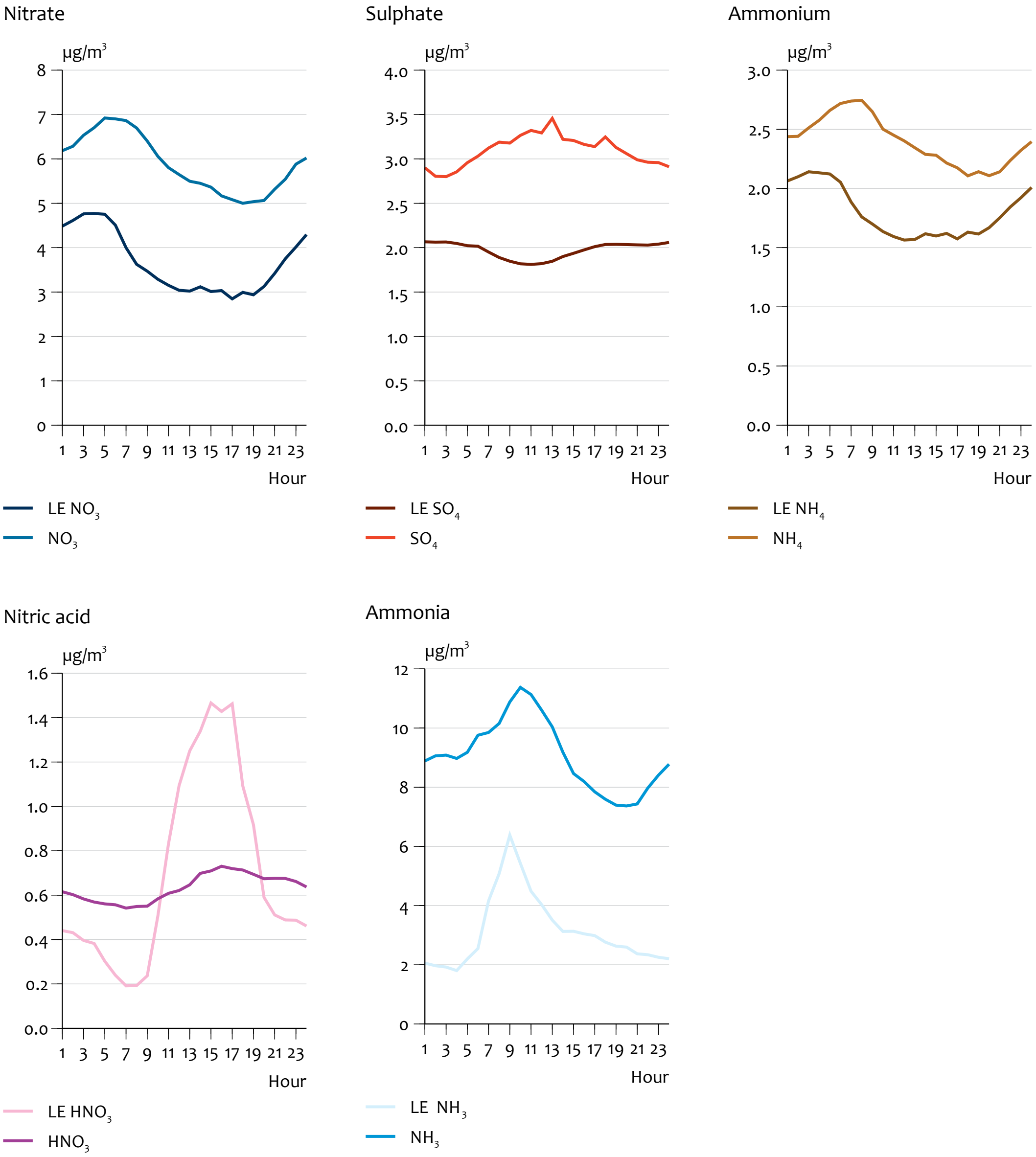


*Comparison of hourly modelled (black) and measured (red) concentrations of nitrate and sulphate for February to April, 2008.*

**Comparion of the correlation (R) between the SIA components** **Table 5.5**

| **LE** | $SO_4$ | $NO_3$ | **MARGA** | $SO_4$ | $NO_3$ |
|---|---|---|---|---|---|
| $NH_4$ | 0.88 | 0.98 | $NH_4$ | 0.75 | 0.93 |
| $NO_3$ | 0.75 | | $NO_3$ | 0.59 | |

**Modelled and measured diurnal cycle** **Figure 5.21**


Nitrate

Sulphate

Ammonium

Nitric acid

Ammonia

*Modelled and measured diurnal cycle for nitrate, sulphate, ammonium, nitric acid and ammonia.*

### 5.4.5 Conclusions

In the sections above has been described how the model performance against the BOP data for SIA and nitric acid and ammonia was investigated. Though it was not the purpose of the study to provide a detailed analysis, a few conclusions could be drawn, see below.

First of all, the MARGA data set provided a unique case for model validation. The detailed data provided new insights into the model performance and may provide a good basis for tackling a number of shortcomings indentified above. Note that the levels in BOP were consistently higher than those from the LML sites against which the model had always been evaluated. The higher than expected levels of SIA as well as the possibility to evaluate the diurnal behaviour calls for a renewed attention to the modelling of SIA in the Netherlands.

The MARGA data provided insight into the equilibrium between particulate ammonium nitrate and gaseous nitric acid and ammonia. As the nitrate levels were sensitive to the concentrations of the precursor gases, as well as the meteorological conditions (T, RH) the full picture was needed to assess why nitrate was underestimated systematically. Evaluation of the seasonal cycles showed that, for the particulates, they were generally captured by the model. Ammonia was severely underestimated and the seasonal variability of nitric acid in the model was much higher than in reality. The same applied to the diurnal variations. Hence, in winter the nitric acid concentrations were much lower than measured, even with an underestimation of ammonia levels. This means that the ammonium nitrate in the model was significantly more stable than in reality. For the summer, it was difficult to draw conclusions about this aspect, as the concentration product of the underestimated ammonia and the overestimated nitric acid may have been more inline with the measured values. To investigate the description of the equilibrium, a test of the equilibrium module is needed, by using the measured concentrations as input and to evaluate the calculated gas-aerosol partitioning against the one modelled. In the next step, the nitric acid formation in the model should be addressed.

The underestimation of ammonia needs further attention. As Cabauw is located in an agricultural area, local emission contributions can not be excluded. Therefore, a comparison to the observations in nature areas should be used for validation. Furthermore, ongoing activities at RIVM on the incorporation of the compensation point in the deposition routine for ammonia may yield a considerable improvement, and the impact on the particulate concentrations needs to be quantified.

The BOP filter measurements indicated that a significant part of the nitrate (up to 1 μg/m$^3$) was found in the coarse mode. The model did not incorporate the formation of coarse mode nitrate through reaction of nitric acid with sea salt (or dust). Incorporation of this process appears to be needed as it may contribute to lowering the underestimation of nitrate and the overestimation of nitric acid. Furthermore, the process would contribute to the lowering of the correlation between nitrate/ sulphate and ammonium, which was slightly too high in the model.

In short, the model was able to reproduce many features found in the observed data on the SIA components. A first analysis of the new data set revealed limitations of the model, which need to be addressed to further improve the model performance. The benefit of having the hourly data with both particulate and gas-phase concentrations is illustrated, and a continuation of these measurements may prove to be very useful in future model evaluation and improvement studies.

# References

Allen, D. and J.R. Turner (2008): Transport of Atmospheric Fine Particulate Matter: Part 1. Findings from Recent Field Programs on the Extent of Regional Transport within North America. J. Air Waste Manage. Assoc. 58, 254-264.

Andreae, M.O., H. Berresheim, T.W. Andreae, M.A. Kritz, T.S. Bates and J.T. Merrill (1998): Vertical-distribution of dimethylsulfide, sulphur-dioxide, aerosol ions, and radon over the Northeast Pacific-Ocean. J. Atmos. Chem. 6, 149–73.

Bauer, S.E., D. Koch, N. Unger, S.M. Metzger, D.T. Shindell and D.G. Streets (2007): Nitrate aerosols today and in 2030: a global simulation including aerosols and tropospheric ozone. Atmos. Chem. Phys. 7, 5043–5059.

Bergin, M., J. West, T. Keating, A. Russell and J. Comer (2005): Regional atmospheric pollution and Transboundary air quality management. Annual Review of Environment and Resources 30, 1–37.

Brink, H.M. ten, C. Kruisz, G.P.A. Kos and A. Berner (1997): Size, composition of the light-scattering aerosol in the Netherlands. Atmos. Environ. 31, 3955–3962.

Brink, H.M. ten, R. Otjes, P. Jongejan and S. Slanina (2007): An instrument for semi-continuous monitoring of the size-distribution of nitrate, ammonium, sulphate and chloride in aerosol. Atmos. Environ. 41, 2768-2779.

Christoforou, C.S., L.G. Salmon, M.P. Hannigan, P.A. Solomon and G.R. Cass (2000): Trends in fine particle concentration and chemical composition in Southern California. J. Air Waste Manage. Assoc. 50, 43–53.

Claes, M., K. Gysels, R. van Grieken and R.M. Harrison (1998): Inorganic composition of atmospheric aerosols. In: R.M. Harrison and E.E. van Grieken, Editors, Atmospheric Particles, Wiley, Chichester.

EMEP (2004): Assessment report - Part I European Perspective.

EPA(1997): PM-2.5 composition and sources. Prepared by Emissions, Monitoring and Analysis Division Office of Air Quality Planning and Standards.

Erisman, J.W. and M. Schaap (2004): The need for ammonia abatement with respect to secondary PM reductions in Europe. Environmental pollution 129, 159-163.

Fagerli H., Simpson D. and S. Tsyro (2003): Model Performance for Sulphur and Nitrogen Compounds for the Period 1980 - 2000 (In: Transboundary acidification, eutrophication and ground level ozone in Europe. Status Report 1/2003. Part II: Unified EMEP Model Performance, L. Tarrasón, ed.). Norwegian Meteorological Institute, Oslo, Norway.

IPCC (2007): Fourth Assessment Reports.

Khlystov, A., G.P. Wyers and J. Slanina (1995): The steam-jet aerosol collector, Atmos. Environ. 29, 2229-2234.

Magliano, K.L., V.M. Hughes, L.R. Chinkin, D.L. Coe, T.L. Haste, N. Kumar and F.W. Lurmann (1999): Spatial and temporal variations in PM10 and PM2.5 source contributions and comparison to emissions during the 1995 integrated monitoring study. Atmos. Environ., 33, 4757–4773.

Matthijsen, J. et al. (2002): Modelling of Particulate Matter on a European Scale. Proceedings 5th GLOREAM workshop, Wengen, Switzerland. Internet: http://people.web.psi.ch/keller_j/GLOREAM/WS2001/Final/Matthijsen.pdf

Nenes, A., C. Pilinis and S.N. Pandis (1999): Continued Development and Testing of a New Thermodynamic Aerosol Module for Urban and Regional Air Quality Models. Atmos. Environ.33 , 1553-1560.

Park, R.J., D.J. Jacob, B.D. Field, R.M. Yantosca and M. Chin (2004): Natural and transboundary pollution influences on sulphate–nitrate–ammonium aerosols in the United States: implications for policy. J. Geophys. Res.-Atmos. 109, D15204, 2004.

Pun, B.K. and C. Seigneur (2001): Sensitivity of particulate matter nitrate formation to precursor emissions in the California San Joaquin Valley. Environmental Science & Technology 35 2979-2987.

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

Putten, E.M. van, and M.G. Mennen (1998): Laboratory study of five methods for measuring ambient ammonium aerosol. RIVM report nr 722601004.

Quass, U.,T. Kuhlbusch and M. Koch (2004): Identifizierung von Quellgruppen für die Feinstaubfraktion. IUTA-Report, LP15.

Schaap, M. (2003): On the importance of aerosol nitrate over Europe, Thesis, University of Utrecht, December, 2003, Utrecht, the Netherlands.

Schaap, M., van Loon, M., ten Brink, H.M., Dentener, F.D., Builtjes, P.J.H. (2004): Secondary inorganic aerosol simulations for Europe with special attention to nitrate, Atmos. Phys. Chem., 4, 857-874.

Schaap, M., Timmermans, R.M.A., Sauter, F.J., Roemer, M., Velders, G.J.M., Boersen, G.A.C., Beck, J.P., and Builtjes, P.J.H. (2008). The LOTOS-EUROS model: description, validation and latest developments. Int. J. Environment and Pollution32, 270-289.

Schaap, M., A.A.M. Manders, E.C.J. Hendriks, J.M. Cnossen, A.J.S. Segers, H.A.C. Denier van der Gon, M.Jozwicka, F.J. Sauter, G.J.M. Velders, J. Matthijsen and P.J.H. Builtjes (2009): Regional Modelling of Particulate Matter for the Netherlands, Technical Background report. PBL report 500099008, Bilthoven, The Netherlands. (http://www.rivm.nl/bibliotheek/rapporten/500099008.pdf)

Seinfeld, J.H. and S.N. Pandis (1998): Atmospheric Chemistry and Physics: From Air Pollution to Climate Change. John Wiley & Sons, Inc., New York, NY, 1326.

Sillanpää, M., R. Hillamo, S. Saarikoski, A. Frey, A. Pennanen, U. Makkonen, Z. Spolnik, R. Van Grieken, M.Braniš, B. Brunekreef, M. Chalbot, T. Kuhlbusch, J. Sunyer, V. Kerminen, M. Kulmala and R.O. Salonen (2006): Chemical composition and mass closure of particulate matter at six urban sites in Europe. Atmos. Environ. 40 212-223.

Torfs, R., F. Deutsch, L. Schrooten, S. Broekx, J. Vankerkom, C. Matheeussen, E. Roekens, F. Fierens, G. Dumont and M. Bossuyt (2007): MIRA Milieurapport Vlaanderen.

Tsyro, S., M. Kahnert and L. Tarrasón (2003): Physical Characterisation of particulate matter across Europe in 2000 and 2001: In Transboundary particulate matter in Europe. EMEP CCC, MSC-W and CIAM Status Report 4, 2003.

Velders, G.J.M., J.M.M. Aben, W.F. Blom, H.S.M.A. Diederen, G.P. Geilenkirchen, B.A. Jimmink, A.F. Koekoek, R.B.A. Koelemeijer, J. Matthijsen, C.J. Peek, F.J.A. Rijn, M.W. de Schijndel, O.C. van der Sluis and W.J. de Vries (2009): Concentratiekaarten voor grootschalige luchtverontreiniging in Nederland. Rapportage 2009 (in Dutch), PBL report 500099005/2009, Bilthoven, the Netherlands. (http://www.rivm.nl/bibliotheek/rapporten/500088005.pdf)

Vestreng, V., G. Myhre, H. Fagerli, S. Reis and L. Tarrasón (2007): Twenty-five years of continuous sulphur dioxide emission reduction in Europe, Atmos. Chem. Phys. 7, 3663-3681.

Vestreng, V., L. Ntziachristos, A. Semb, S. Reis, I.S.A. Isaksen and L. Tarrasón (2008): Evolution of NOx emissions in Europe with focus on road transport control measures, Atmos. Chem. Phys. Discuss. 8, 10697–10747.

Visser, H., E. Buringh and P.B. van Breugel (2001): Composition and origin of airborne particulate matter in the Netherlands. RIVM report 650010029, RIVM, Bilthoven.

Visser, H. (2004): Estimation and detection of flexible trends, Atmos. Environ.38, 25, 4135-4145.

Weijers, E.P., R.P. Otjes, M. van Loon, M. Schaap, J.W. Erisman, J. Slanina, W.C.M. van den Bulk, P.B. Fonteijn, J.J. Mols and A.T. Vermeulen (2002): Concentration, size and origin of background particulate matter in the Netherlands. ECN report ECN-CX--02-010. .

Wieprecht, W., K. Acker , K. Muller, G. Spindler, E. Bruggemann, W. Maenhaut, X.G. Chi, R. Hitzenberger, H. Bauer and H.M. ten Brink (2004): INTERCOMP2000: ionic constitution and comparison of filter and impactor. Atmos. Environ. 38, 6477–6486.

Worobiec, A., J. De Hoog, J. Osán, I. Szalóki, C.U. Ro and R. van Grieken (2003): Thermal stability of beam sensitive atmospheric aerosol particles in electron probe microanalysis at liquid nitrogen temperature. Spectrochimica Acta B 58, 479–496.

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Secondary inorganic aerosol (SIA) form the major fraction of particulate matter (PM). SIA, containing ammonium nitrate and ammonium sulphate, is almost completely of anthropogenic origin, and can be influenced by abatement strategies. Precursor gases ($NO_x$, $SO_2$, $NH_3$) are emitted by traffic, energy production and agricultural sources. The report improves the existing knowledge on SIA, and its contribution to $PM_{10}$ and $PM_{2.5}$. The focus here is on the interpretation of measurements. Subjects studied are the climatology and variability in time and space, the contribution to urban background concentrations, and a comparison with modelling results.
The concentrations of secondary inorganic aerosol in the Netherlands is larger than previously thought. The average contribution to $PM_{10}$ was measured to be 30 to 40%. This increased to more than 50% during periods with high PM levels (i.e. 'exceedance days'). Long-range transport and adverse meteorology are the main reasons for these higher levels. For the period 1994 to 2007 SIA concentrations decreased. However, from 2001 onwards, the trends weakened which appears to be in line with changing (European) emissions of precursors. The various data sets acquired in the BOP Program provided a good test for the LOTOS-EUROS model.. It is concluded that the current policy tools (monitoring, modelling) need further improvement.

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