# Composition and origin of Particulate Matter in the Netherlands

This is a publication of the Netherlands Research Program on Particulate Matter

PBL Netherlands Environmental Assessment Agency

# BOP – report

# Composition and origin of Particulate Matter in the Netherlands

## Results from the Dutch Research Programme on Particulate Matter

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PBL Netherlands Environmental Assessment Agency

ECN
Energy research Centre of the Netherlands

TNO

rivm
National Institute
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and the Environment

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ECN Energy research Centre of the Netherlands
PBL Netherlands Environmental Assessment Agency
TNO Built Environment and Geosciences
RIVM National Institute for Public Health and the Environment

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# Abstract

## Composition and origin of Particulate Matter in the Netherlands: *Results from the Dutch Research Programme on Particulate Matter*

Particulate matter has a negative impact on human health and plays a role in climate change. To develop effective mitigation strategies to reduce the concentrations of both $PM_{2.5}$ and $PM_{10}$ one needs to establish the origin of particulate matter. The composition of particulate matter reveals a lot of information on sources. Here, we report the results of a measurement campaign to determine the composition of $PM_{10}$, $PM_{2.5}$ and $PM_{10-2.5}$ at 6 locations in the Netherlands. Generally, there is a considerable conformity in the chemical composition in the Netherlands. Secondary inorganic aerosol and carbonaceous matter are the most important components, followed by significant contributions of sea salt, mineral dust and metals. Through mass closure a considerable part of the PM mass could be explained. The application of a source apportionment technique complemented the analysis based on the interpretation of the chemical data. It confirmed independently a large number of species to be a tracer for a specific activity or source. As such, we have obtained more confidence in the interpretation of the data set. Based on the measured concentrations and estimates of the natural fraction per component it was established that about 75% of $PM_{10}$ and 80 % of $PM_{2.5}$ is man made.

Keywords:
Particulate Matter, origin, source apportionment, composition, mass closure, anthropogenic fraction

# Rapport in het kort

## Samenstelling en herkomst van fijn stof ($PM_{10}$ en $PM_{2.5}$) in Nederland: Resultaten van het nationale onderzoeksprogramma voor fijn stof (BOP).

Fijn stof heeft een negatieve invloed op de gezondheid en speelt een belangrijke rol in klimaatverandering. Om effectief mitigatiebeleid te kunnen formuleren is het noodzakelijk om de relatie tussen emissies, atmosferische omstandigheden en de concentraties van luchtverontreinigende stoffen te kennen. De samenstelling van fijn stof geeft belangrijke informatie over de herkomst ervan. In dit rapport worden de resultaten van samenstellingsmetingen van $PM_{10}$, $PM_{2.5}$ en $PM_{10-2.5}$ op zes locaties in Nederland gerapporteerd. Over het algemeen is er een redelijk grote conformiteit in de samenstelling van PM in Nederland. De belangrijkste componenten van fijn stof zijn de secundaire anorganische en koolstofhoudende componenten. Daarnaast zijn er significant bijdragen van zeezout, bodemstof en metalen. Een groot gedeelte van de gemeten massaconcentratie kon met behulp van de gemeten componenten verklaard worden. De toepassing van een bronherkenningstechniek complementeerde de analyse van de chemische samenstelling en bevestigde op een onafhankelijk manier dat vele componenten de impact van specifieke (groepen van) activiteiten representeren. Op die manier is de betrouwbaarheid van de analyse vergroot. Op basis van de gemeten concentraties en inschattingen van de natuurlijke bijdragen per component is afgeleid dat ca. 75 % van $PM_{10}$ en ca. 80% van $PM_{2.5}$ door menselijk handelen verklaard kan worden.

Trefwoorden:
Fijn stof, metingen, herkomst, bronherkenning, samenstelling, massasluiting

# Contents

# Summary

Although air quality in Europe has improved substantially over the past decades, air pollution still poses a significant threat to human health. Health effects of air pollution are dominated by particulate matter, both $PM_{2.5}$ and $PM_{10}$. At present, many countries in Europe, including the Netherlands, have problems adhering to the daily limit value for $PM_{10}$ at hot-spot locations. Recently, new $PM_{2.5}$ objectives were introduced, to reduce human exposure to $PM_{2.5}$. The origin of particulate matter in the Netherlands needs to be established, to develop mitigation strategies for meeting these new targets and to reduce concentrations of both $PM_{2.5}$ and $PM_{10}$.

For this purpose, existing gaps in knowledge about composition, distribution and origin of particulate matter needed to be reduced. This was the major goal of the study presented here, which is part of the Netherlands Research Program on Particulate Matter (BOP). It was facilitated by an intensive, one-year measurement campaign from August 2007 to August 2008. During this year, $PM_{10}$ and $PM_{2.5}$ were sampled, simultaneously, at five locations. Subsequently, the samples were chemically analysed to assess the composition of particulate matter. The chemically speciated PM data were used to assess the origin of particulate matter using knowledge on existing markers for several sources as well as a statistical technique.

The sum of all components measured in the collected filter samples explained 75 to 80% of the $PM_{10}$ mass concentration. Hence, a full analysis was not obtained, but existing knowledge could be used to partially close the remaining gap. In a sequence of steps, we performed such a mass closure study to account for not-analysed material. Simultaneously, we estimated source contributions based on (groups of) tracers. Metals were taken into account as their oxides. Total carbonaceous matter, including non-C atoms such as H, O and N, was estimated based on the total carbon content. In addition, the contributions of mineral dust and sea salt were estimated. Most importantly, uncertainties involved in mass closure are conversion factors for total carbonaceous matter, and if and how to correct for the displacement of chloride by nitrate in the coarse fraction. After the procedure, 85 to 90% of the $PM_{10}$ mass was explained.

Generally, there is a considerable conformity in the chemical composition of PM in the Netherlands. From all the constituents that are part of $PM_{2.5}$ the secondary inorganic aerosol – the sum of sulphate, nitrate and ammonium – was the most dominant (42-48%). The secondary inorganic aerosol contributions were higher at the rural locations, whereas lower contributions were found at urban locations in the Rotterdam area. The second dominant contribution to $PM_{2.5}$ came from total carbonaceous matter and ranged between 22 and 32%. The lower values were found at rural locations, whereas the maximum values were found at the traffic location in Rotterdam, illustrating the impact of traffic emissions. Sea salt, mineral dust and metals each comprised about 5% of total $PM_{2.5}$. For $PM_{2.5}$ the unexplained part varied between 0 and 16 per cent.

For the first time, a detailed overview is presented of the composition of the coarse fraction of PM in the Netherlands. Compared to the fine fraction, the presence of secondary inorganic aerosol and total carbonaceous matter became less dominant with contributions lower than 29 and 25%, respectively. Comparable (relative) contributions originated from mineral dust (<23%) and sea salt (<30%). The contribution of metals added up to 17% at the traffic location. Hence, the composition shows a more even distribution among the components present in PM. The unexplained mass in the coarse fraction ranged between 3 and 21 per cent.

The contributions of the different components to $PM_{10}$ showed a large resemblance with the $PM_{2.5}$ findings above. The reason for this is that the mass contribution of $PM_{2.5}$ is about two thirds of total $PM_{10}$. The contribution of secondary inorganic aerosol (SIA) and total carbonaceous matter (TCM) to $PM_{10}$ is slightly lower than in $PM_{2.5}$ (SIA: 35-43%; TCM: 21-29%). As sea salt (SS) and mineral dust (MD) are mainly found in the coarse mode, their contributions to $PM_{10}$ (SS: 7-17%; MD: 6-9%) are twice that to $PM_{2.5}$.The metal contribution (4-9%) to $PM_{10}$ is also slightly higher. For $PM_{10}$,the unexplained part varies between 6 and 13 per cent. Days with high $PM_{10}$ concentrations are of particular interest, as the EU enforces a daily limit value. On days with high concentrations, all components, except sea salt, show higher concentrations. Relatively speaking, the nitrate and unexplained contributions increase most on these types of days, while the relative contribution of the remaining components is mostly stable as a function of PM concentration. Sea salt maximises in marine air masses associated with clean air conditions. To identify source categories and to apportion the observed PM concentrations to those categories, a statistical receptor model (Positive Matrix Factorization (PMF)) was applied to the data set. The technique groups the different components that behave similarly in time. Seven source groups were identified, using this procedure. In order of decreasing mass

contribution to $PM_{2.5}$ these were 1) nitrate-rich secondary aerosol, 2) sulphate-rich secondary aerosol, 3) traffic and re-suspended road dust, 4) metal from industrial activity/incineration, 5) sea salt, 6) mineral dust, and 7) particles from residual oil combustion. The technique only provides general categories relevant for the country as a whole, without the identification of local sources, as all data from all locations were combined in the PMF procedure.

A disadvantage of this statistical procedure is that it cannot cope with non-linear components. Consequently, the secondary aerosols ($SO_4$, $NO_3$, $NH_4$, OC) were mainly grouped together and no source information was obtained. The main separation was obtained in the primary components. For example, the tracers for sea salt (Na, Mg, Cl) as well as those for mineral dust (Al, Si, Ti) and traffic abrasion (Cu, Ba, Fe) were separated from a group that contained a host of different metals and elements. The application of PMF complemented the analysis based on the interpretation of the chemical data. Independently, it confirmed a large number of species to be tracers for a specific activity or source. As such, we obtained more confidence in the interpretation of the data set at hand.

From a literature study, the potential contribution from natural sources to the main PM components was estimated. The most important natural contributions came from sea salt and organic material. Using a natural contribution of 50% to organic material as an upper limit for its natural contribution to $PM_{10}$ and $PM_{2.5}$, this was estimated to be about one third. Central estimates for the natural contribution were one fourth for $PM_{10}$ and one fifth for $PM_{2.5}$. Although this analysis was relatively pragmatic, it clearly illustrates that the majority of PM in the Netherlands is of anthropogenic origin.

Major gaps in knowledge were identified with respect to composition and origin. Characterisation of the unexplained mass was obviously needed and the role of water had to be addressed. The experimental set-up did not allow a detailed characterisation of the increment between urban and rural background locations. New, future measurements should tackle this issue to address the sources within urban areas. These should include measurements of EC and OC, as well as mineral dust. Also, the inability to correctly differentiate EC and OC influences results. The statistical technique (PMF) does not provide detailed source information and is unable to differentiate sources for the secondary components. For the traditional PM components, such as SIA and primary material, it is recommended to perform a detailed source attribution with a chemistry transport model to identify source contributions at sector level, and to provide insight into national versus foreign sources. The origin of carbonaceous matter is one of the biggest challenges in PM research, and knowledge on this aspect is still basic. Therefore, a scenario study is advised, to test the plausibility of potential source strengths and formation routes. Such a modelling exercise should be evaluated with state-of-the-art measurements.

Although experimental research on PM is complicated and a number of compromises will always have to be made, the data set obtained in the Netherlands Research Program on Particulate Matter (BOP) is more complete than those obtained in earlier studies in the Netherlands. The data set as well as the analysis of the results is documented extensively. Our overview study has benefited largely from the thematic reports that were produced within the BOP programme. Similarly, the well documented results from this study are expected to be highly beneficial to further research and successful exploitation of the data.

# 1

# Introduction

## 1.1 Background

Although air quality in Europe has improved substantially over the past decades, air pollution still poses a significant threat to human health (EEA, 2007). Health effects of air pollution are dominated by particulate matter, both $PM_{2.5}$ and $PM_{10}$. Short-term exposure to $PM_x$ has frequently been associated with increased human morbidity and mortality (e.g., Brunekreef and Holgate, 2002). Effects of long-term exposure to PM are much more uncertain than short-term effects, but are believed to have a much greater effect on health loss (Dockery et al., 1993; Pope et al., 1995). Recent estimates arrive at an average loss of life expectancy in the Netherlands of about 6 to 12 months (EEA, 2007). So far, there is no conclusive evidence of which component or components are most relevant to deteriorating human health, although some suggestions have been made, such as soot, by Hoek et al. (2002). Therefore, the European air quality standards currently focus on the total mass of the unspecified combined particles smaller than 10 and 2.5 µm in diameter ($PM_{10}$ and $PM_{2.5,}$ respectively), covering the inhalable size fraction of PM.

At present, many European countries, including the Netherlands, have problems adhering to the daily limit value for $PM_{10}$ at hot-spot locations. In the new Directive (2008/50/EC) on ambient air quality and cleaner air for Europe (EU, 2008), new air quality standards for fine particulate matter ($PM_{2.5}$) have been established. An average annual $PM_{2.5}$ concentration of 25 µg/m³ has been set as target value to be achieved in 2010, and as limit value to be adhered to by 2015. The new directive further has introduced additional $PM_{2.5}$ objectives that aim to reduce human exposure to $PM_{2.5}$. Standards have been set at national level, based on the average exposure indicator (AEI). The AEI is a three-year averaged $PM_{2.5}$ level measured at urban background locations throughout each European Member State. A reduction target of achieving 15% of the AEI between 2010 and 2020 might be reached in the Netherlands under current legislation (Mathijssen et al., 2009). A reduction of 20% will almost certainly not be reached under current legislation, nor with outlined additional measures (Mathijssen et al., 2009). To develop mitigation strategies to meet these targets and to reduce the concentrations of both $PM_{2.5}$ and $PM_{10,}$ in general, one needs to establish the origin of particulate matter in the Netherlands.

Important information on the origin of particulate matter can be obtained through chemical analysis to establish its composition. Many components can be used as tracers for specific sources (see Table 1.1). For example, sodium (Na) is a tracer that is almost exclusively associated with sea salt. Likewise, Silicon and aluminium are tracers for mineral dust, whereas elemental carbon particles mainly derive from combustion. Finally, the secondary components (sulphate, nitrate and ammonium) can be attributed to their gaseous precursors. A number of issues, however, complicate the assessment. First of all, one is usually not able to analyse the full composition of the particulate mass. Hence, a significant portion is not analysed. Using assumptions on the relation between a (group of) tracers and major components, one can attribute the mass to mayor components, the so-called chemical mass balance approach (Harrison et al., 2003). In this way, an estimate can be derived for the major source contributions to PM. Nonetheless, also these approaches usually do not explain all of the mass. Hence, mass closure is not attained. The (relative) magnitude of the unexplained mass is an indicator for the uncertainty in the mass attribution. To independently address these issues, one can also apply statistical techniques to the observation data set to address the possible source categories for PM. Techniques, such as positive matrix factorisation (PMF), can be used to search for groups of components with the same behaviour in time, which are than assumed to derive from a single source or group of similar sources. Because of the complexity of PM composition, the uncertainty in the data, and the relatively small data sets at hand, one can normally differentiate only a small number (4-8) of different source profiles. On the other side of the spectrum, one can also use chemistry transport models to address the importance of source categories. In principle, a very detailed assessment can be made depending on the detail provided by the emission database. However, one assumes the emissions estimates are correct and that there are no large modelling errors. As these assumptions are clearly not valid for all components of PM, chemistry transport models cannot provide a full picture. Hence, the use of the measured data using a mass closure approach, as well PMF, will provide independent insights from an empirical point of view into the actual PM sources. This report provides such an analysis, based on a measurement campaign performed in the Netherlands within the BOP programme.

## 1.2 Objectives

This study was set up to reduce gaps in our knowledge about the composition, distribution and origin of particulate matter in the Netherlands. We grouped the research questions

**Main and secondary tracers for a number of sources** **Table 1.1**

| Source | Main | Secondary |
|---|---|---|
| *Sea salt* | Mg, Na | Na, Cl, Mg |
| *Mineral dust* | Si, Al, Fe | Si, Al, Ca, Fe, Ti |
| *Traffic related:* | | |
| *Exhaust diesel* | S | |
| *Exhaust petrol* | (Pb) | |
| *Tyre wear* | Zn | |
| *Brake wear* | Cu | Cu, Zn, Fe, Ba |
| *Industry:* | | |
| *Combustion, incineration* | Cd | Cd, Zn, Cu |
| *Steel production* | Mn | Fe, Mn |
| *Cement production* | Cd | Cd, Cu |

that are addressed in the report, into three categories: mass closure, source apportionment and policy relevant interpretation. The main research questions, per category, are:

Mass closure
1. What is the composition of particulate matter in the Netherlands?
2. What is the variation in composition as a function of location type?
3. Is the composition on exceedance days different from that on non-exceedance days?
4. What are the characteristics of the unexplained mass?

Source apportionment
5. What are the most important source categories of $PM_{10}$ and $PM_{2.5}$ in the Netherlands?
6. What is the value of PMF compared to chemical mass closure?
7. How do the source attributions based on PMF compare to those obtained from prognostic models?

Policy Relevant Interpretation
8. Can we make an estimate of the natural versus anthropogenic contribution to PM?
9. Which combination of factors causes a day of exceedance?
10. What are the main knowledge gaps and recommendations?

## 1.3 Approach

The research conducted within the national programme to improve our understanding of the composition, distribution and origin of particulate matter in ambient air was facilitated by an intensive, one-year measurement campaign, from August 2007 to August 2008, and also meant as an effort to improve the modelling capabilities with respect to PM

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

*This study is conducted partly under the auspices of the Netherlands Research Program on Particulate Matter (BOP), a national programme on* $PM_{10}$ *and* $PM_{2.5}$*, funded by the Netherlands Ministry of Housing, Spatial planning and the Environment (VROM). The programme 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 programme are published in a special series of reports. The subjects in this series, in general terms, are: sea salt, mineral dust, secondary inorganic aerosol, elemental and organic carbon (EC/OC), and mass closure and source apportionment (this report). Some BOP reports concern specific PM topics: shipping emissions, PM trend, urban background, EC/OC emissions from traffic, and attainability of* $PM_{2.5}$ *standards. Technical details of the research programme 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.*

(Schaap et al., 2009). The results presented in this report were based on an analysis of the measurement campaign regarding the full composition of $PM_{10}$ and $PM_{2.5}$. Hence, a detailed component-wise interpretation of the data is not provided, as this is presented in separate reports. For these interpretations we refer to Ten Brink et al. (2009), Manders et al. (2009), Denier van der Gon et al. (2010) and Weijers et al. (2010), for EC and OC, Sea salt, mineral dust, and SIA, respectively.

Below, first a short overview is provided on the measurement campaign and the source apportionment technique used (Chapter 2). Second, the mass closure of particulate matter in ambient air is described, as derived from the measurement campaign (Chapter 3). Third, the results are presented from the source apportionment using PMF (Chapter 4). Subsequently, all research questions are discussed, separately, and the results are interpreted in comparison to other studies (Chapter 5). Finally, the main findings are summarised per research question (Chapter 6).

# 2

# Methodology

## 2.1 Measurement campaign

### Monitoring locations

The objective of the measurement campaign was to construct a database that would help to improve the understanding of the composition of particulate matter and its sources. As the composition of PM varies per region, locations were selected in urban areas where traffic and domestic sources are the main source, as well as in rural background areas. In total, five locations were selected for the monitoring of particulate matter composition (see Figure 2.1). Three rural background locations (Hellendoorn, ~150 km from Rotterdam; Cabauw ~50 km from Rotterdam; Vredepeel, ~100 km from Rotterdam ) were selected. Cabauw represents the rural background for the western part of the country, whereas Hellendoorn and Vredepeel were selected to add information from the eastern part of the country. The Vredepeel location is characteristic of the intensive agricultural activity in its direct surroundings. The urban background location of Schiedam is a measurement location in the Dutch National Air Quality Monitoring Network (LML). In Rotterdam, a traffic location was chosen: Rotterdam-Bentinckplein, constituting part of the DCMR network. Another traffic location was chosen in Breda for $PM_{10}$ only. Local characteristics of all locations are given in Table 2.1.

### Measurement campaign and instrumentation

The filter collecting routine ($PM_{10}$ and $PM_{2.5}$) took place every second day between 15 August 2007 and 4 September 2008. The chemical analysis was done every fourth day. For each of the five locations, the following components in both mass fractions were determined: sodium, chloride, sulphate, nitrate, ammonium, organic carbon, elemental carbon and metals (and silicon). By subtraction the $PM_{2.5}$ levels from those measured in $PM_{10,}$ an estimation was made of the composition of the coarse fraction ($PM_{10\text{-}2.5}$).

The filters were collected according to the reference method described in the European Standards (EN12341: 1998 and EN14907:2005). The measurement instrument was the SEQ47/50 (Leckel GmbH, Germany). In the BOP programme's experimental set-up this sequential low-volume system (LVS) used a flow of 2.3 $m^3$/h. Four of these reference samplers were placed at every location for a paired measurement of $PM_{10}$ and $PM_{2.5}$. The sampling period was 24 hours and ran from midnight to midnight. The filters were changed once every fortnight. All filters were protected during storage and transport. The logistic and operational (QA/QC) procedures were those used in the LML network.

Two types of filter media, quartz (QMA) and teflon (PTFE), were used. The aim was to have parallel simultaneous measurements of $PM_{10}$ and $PM_{2.5}$ on two types of filter media

**Location characteristics of the five measurement locations** **Table 2.1**

| Location | Characteristics |
|---|---|
| *Cabauw* | Background location<br>Centre of the Netherlands, rural surroundings<br>Urban areas at a 20 to 40 km distance |
| *Hellendoorn* | Background location<br>In the eastern part of the Netherlands, rural surroundings<br>No anthropogenic sources nearby |
| *Vredepeel* | Background location<br>In the south-eastern part of the Netherlands, rural surroundings<br>Intensive livestock (pigs) breeding nearby |
| *Schiedam* | Urban background location<br>In the western part of the Netherlands<br>Part of Rotterdam agglomeration (around 600,000 inhabitants)<br>Residential areas surrounded by motorways<br>Close (<5 km) to industrial activity (refineries, oil industry) and harbour |
| *Rotterdam-Bentinckplein* | Traffic location<br>Part of the Rotterdam agglomeration<br>Less than 5 m from the kerb; traffic junction at 80 m<br>Heavy traffic |
| *Breda* | Traffic location<br>5 - 10 m from the kerb<br>$PM_{10}$ only |

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

*Locations of the monitoring stations*

(teflon and mixed quartz fibre filter). The teflon filters were chosen to quantify silicon in suspended particulate matter. The quartz fibre filter media is the material commonly used in gravimetric PM monitoring in the Netherlands.

## Chemical analyses

### *Secondary inorganic aerosols*

Ammonium that was captured on the filters was analysed on the AMFIA (AMmonia Flow Injection Analyser, a flow injection system built at ECN). This analysis system is based on the selective diffusion of $NH_4^+$ at reduced pH by conductivity. The detection level is 0.2 µg per filter (<0.5%).

Sulphate and nitrate were measured in aqueous solutions with the Dionex IC25. This system combines a Ion Chromatography System with a conductivity detector and a high performance dual-piston pump, combined into one compact package. Samples were eluted through an ion-exchange column using a diluted sodium hydroxide solution. The eluent is passed through self-regenerating suppressors that neutralise eluate conductance, ensuring that electrochemical detectors (conductivity or pulsed amperometric) can detect the ions down to sub-ppm concentrations. Detection level is 0.7 µg per filter (<1%).

### *Elemental carbon/Organic carbon (EC/OC)*

Analysis of the presence of carbon is based on thermography ('Cachier-method'). This means that a filter sample is heated in an oven resulting in the release of carbon. For quantitative determination of the amount of released carbon, the evolved gases are oxidised to $CO_2$ in a post-combustor oven. The discrimination of carbon in OC and EC is operationally defined. The OC is the carbon that is released during the first step (8 minutes at 340 °C); the remainder gives an estimate for EC, after combustion for 6 minutes at 750 °C. The analysis occurred in a Coulomat 702, manufactured by JUWE (Viersen, Germany).The total amount of carbon (TC) is directly proportional to the total amount of $CO_2$ produced. The detection system, in principle, is an absolute method. Monthly calibrations with a standard were performed. Cleaning of the instrument occurred once a month (after a full month of operation). Several samples were in the oven for a longer period and also at a higher temperature, to check for complete combustion and proper assessment of the EC. The lower detection limit of the method was around 5 µg per filter, corresponding to a concentration of 0.1 µg $m^{-3}$. An average experimental blank of 1.2 µgOC/$m^3$ was found during the campaign (Ten Brink et al., 2009), consisting of a filter blank of 0.5 µg/$m^3$, and a field blank of 0.7 µg/$m^3$ (due to gas adsorption on the filter material). As the latter contribution normally occurs in the PM determination that follows the reference method, we only subtracted the filter blank from the measured OC values.

### *Elemental composition*

Elemental composition of particulate matter in ambient air provides clues on the contribution from different sources. ICP-MS was employed to analyse the elemental composition of the collected $PM_{10}$ and $PM_{2.5}$ masses. In short, ICP-MS (Inductively Coupled Plasma Mass Spectrometry) is capable of determining a range of metal and non-metal concentrations, with high sensitivity. It is based on combining an inductively coupled plasma to produce ions with a mass spectrometer as a method of separating and detecting the ions. ICP-MS is the standard operational procedure in the Dutch National Air

**Detection limit, recovery and correction factor for oxide weights for all elements** **Table 2.2**

| Element | Detection limit (ng/m³) | Recovery (%) | correction factor for oxide weights |
|---|---|---|---|
| *Li* | 1 | 70 | 1 |
| *Be* | 1 | 70 | 1 |
| *Na* | 100 | 100 | 1 |
| *Mg* | 10 | 70 | 1 |
| *Al* | 100 | 70 | 1.89 |
| *Si* | 100 | 50 | 2.14 |
| *P* | 100 | 70 | 1 |
| *K* | 100 | 70 | 1.2 |
| *Ca* | 100 | 90 | 1.4 |
| *Ti* | 1 | 70 | 1.51 |
| *V* | 1 | 80 | 1.15 |
| *Cr* | 100 | 100 | 1.41 |
| *Mn* | 1 | 100 | 1.29 |
| *Fe* | 100 | 80 | 1.43 |
| *Co* | 1 | 80 | 1 |
| *Ni* | 10 | 70 | 1 |
| *Cu* | 10 | 100 | 1.13 |
| *Zn* | 10 | 100 | 1.23 |
| *As* | 1 | 100 | 1 |
| *Se* | 1 | 70 | 1 |
| *Sr* | 1 | 70 | 1.14 |
| *Y* | 0.1 | 70 | 1 |
| *Mo* | 1 | 100 | 1 |
| *Cd* | 0.1 | 100 | 1 |
| *Sn* | 1 | 90 | 1 |
| *Sb* | 1 | 100 | 1 |
| *Ba* | 10 | 90 | 1 |
| *Pb* | 1 | 90 | 1 |

Quality Monitoring Network (LML). The selected elements are summarised in Table 2.2, together with the corresponding detection limits and recoveries.

Although the measuring of these elements is relatively straight forward, the associated oxygen has to be estimated indirectly by assuming a certain oxidation state. To estimate their contributions to $PM_{10}$ and $PM_{2.5}$, a correction for the oxidised form was therefore necessary (e.g., Si is usually present as $SiO_2$). In the data interpretation in this study all elemental weights were recalculated to their respective oxide concentrations, which is the most probable form in the PM mass fractions. These correction factors are listed in Table 2.2.

## 2.2 Positive Matrix Factorisation

To identify sources and to apportion the observed pollutant concentrations to them, it is necessary to use receptor or receptor-oriented models (Hopke, 1991). These models are focused on the behaviour of the ambient environment at the point of impact, the so-called receptor location. The models search for correlation between the different (groups of) components in time and use these to find an optimal solution to define the total observed concentrations for all components. Hence, the data are interpreted on a pure statistical basis without pre-formulated assumptions, providing an independent source of information. Receptor modelling consists of the following objectives: to determine (i) the number of aerosol sources, (ii) the chemical composition profile of each source, and (iii) the amount that each of the sources contributes to the measured concentration. To do so one decomposes a matrix of PM speciation data. To decompose the speciation matrix, we used a multivariate factor analysis tool called Positive Matrix Factorization (PMF) (Paatero and Tapper, 1994). A publication (Mooijbroek et al., 2010) is available that describes in detail the methodology followed, such as the technical background, factor selection, uncertainties and technical issues, for example, rotational freedom. Below, a general description is provided of how the data was handled.
In earlier work (Bloemen *et al.*, 2008), it has been assumed that there would not be much variability between the composition of the sources on each location; most variability was expected to be found in the contribution from each individual source on each location. For example, the contribution from traffic has to be predominately higher at a traffic location compared to a rural location. Under this assumption we constructed a full data set. This also ensures that the number of observations is large enough for the statistical procedure to produce robust results. From the constructed data set, the analysis could provide insight into sources affecting all five receptor locations, and was most likely to focus on the global sources instead of the local contributions. It should be noted that PMF is based on a linear combination of factors and cannot cope with non-linear components. Consequently, the main separation was obtained in the primary components.
For application of PMF, one needs to have a data set where all components have a valid concentration value. As most

of the different tracers were supplied by the ICP-MS, only sampling days with a complete set of ICP-MS analysis were used. Both validated and rejected data were used. The rejected data were given a lower weight in the analysis (see Appendix B). For the data below the minimum detection limit (MDL) a general approach was followed (Pollisar *et al*., 1998) by replacing the data below the MDL with values of half the MDL and setting the corresponding uncertainty to 5/6 times the MDL. After this procedure, approximately 6% of the total number of samples still contained missing data, especially for chloride, ammonium, nitrate, sulphate, organic carbon and elemental carbon (see Appendix B). Multiple imputation (MI: Rubin, 1976; 1977; Hopke *et al*, 2001) was used to estimate missing values. The MI technique provides estimates for missing values based on statistical relations between the data.

Not every chemical species in the speciated PM database may provide valuable information to solve the PMF problem. In the literature (Paatero and Hopke, 2003), it was found that when all species in factor analytical models were included the solution would degrade. It was suggested to use the signal-to-noise ratio (S/N) as an indicator for qualifying species. For this study, we used only components with a signal-to-noise ratio greater than 1.5 (see Appendix B). Also, we removed beryllium, lithium and yttrium, primarily due to the fact that they are not considered tracer species.

The results from the EPA-PMF analysis reproduced the data and ensured, among other things, that both the source profiles and the source contributions would be non-negative. However, they did not take the total mass into account. The easiest way to estimate the total mass contributions is by calculating the sum of the species contributions. By using this method the assumption is made that the total mass is fully represented by the species, also known as mass closure. However, actual mass closure is rarely achieved (see Chapter 3), and a fraction of the PM mass mostly remains unidentified. Another way to estimate the total mass contributions is the inclusion of the total measured mass as an independent variable in the EPA-PMF modelling, effectively forcing the model to apportion the total mass for each profile as part of the solution. As this total variable should not have a large influence on the solution, it is given a high uncertainty by categorising it as a weak variable. This procedure also provides an indirect means to verify, to a certain extent, if the PMF worked properly, by comparing the apportioned mass to the sum of the components.

When applying this statistical PMF technique to the data set one has to select the number of factors that will provide the best description of the data set. This selection is always a compromise: when too few factors are selected, they are likely to combine sources in one source profile, whereas too many factors may dissociate a real factor into additional but non-existing sources. A number of statistical measures can be used for the selection. The resulting selection is presented in Chapter 4.

# 3

# Mass closure

## 3.1 Introduction

This chapter presents the (average) chemical composition of the daily $PM_{10}$ and $PM_{2.5}$ filter samples collected at the five BOP measurement locations. For each location, only samples with complete characterisation were used in the results. Completeness was interpreted very strictly. If the concentration value of at least one component (including metals) would be absent, the corresponding sample was excluded from the data set. This implies that the number of samples and sample dates partially differ per location.

The chapter first presents a comparison of the average total mass of the three PM fractions as measured at the locations. This is followed by an enumeration of the chemical components in PM, in terms of absolute concentration value. Next, the various conversion algorithms used for estimating the contributions of secondary inorganic aerosols, total carbon matter, mineral dust, sea salt and metals (and silicon) are introduced. Finally, the mass closure is given for every location and discussed, both for days with high and low PM concentrations.

## 3.2 PM mass concentrations at the five BOP locations

The average mass concentrations of the samples with complete characterisation from each of the locations in the BOP campaign are shown in Figure 3.1. The overall averages were 22.1 µg/m$^3$ ($PM_{10}$), 14.8 µg/m$^3$ ($PM_{2.5}$) and 7.3 µg/m$^3$ ($PM_{10-2.5}$). The highest levels were observed at Rotterdam ('traffic') while the lowest occurred at Hellendoorn ('rural') as expected. The difference in $PM_{10}$ concentrations between these locations was considerable: near 9 µg/m$^3$ (originating from almost equal differences in the corresponding fine and coarse fractions: 4 to 5 µg/m$^3$).

Note that the (average) concentration levels at Cabauw were relatively high compared to those at Schiedam. One reason for this is that the data presented in Figure 3.1 were obtained on different days. This issue is further discussed in the box below.

## 3.3 Chemical composition

The average concentrations of the various chemical components analysed in this study are presented in Figures 3.2 and 3.3 for the various PM fractions (NA='not analysed'). For the data, we refer to Appendix A. The following observations were made:

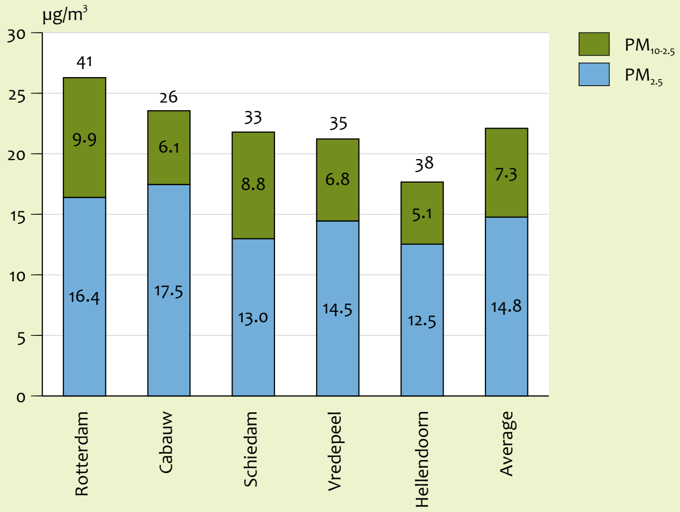
- In general, considerable similarity existed in the chemistry of PM filters at the various locations. In both fine and coarse mass, the largest contributions (in absolute value) came from nitrate and 'not-analysed' (NA). The only exception was observed at Rotterdam where elemental carbon (in $PM_{2.5}$) and (summated) metals (in $PM_{10-2.5}$) were important. Both could be ascribed to nearby traffic emissions. For the remaining locations, the next important component in $PM_{2.5}$ (and $PM_{10}$) was sulphate, followed by elemental carbon, and in different order organic carbon, ammonium, metals, chloride and sodium. The major part of the secondary inorganic components was found in the fine fraction, as was also the case for elemental and organic carbon, and NA. Dominant contributions of metals and sea salt related components (sodium and chloride) came from coarse-sized particles.
- Elevated ammonium and nitrate levels were seen in the $PM_{10}$ data set collected at Cabauw (2.0 and 5.6 µg/m$^3$). As a comparison, at Vredepeel (influenced by livestock-activity nearby) the respective concentrations were 1.5 and 4.3 µg/m$^3$. Although the Cabauw location was less suspect in this respect, local emissions of ammonia can happen and would explain the elevated PM mass noted above at this location. As a consequence, the presumption that Cabauw could serve as a background location for the urban Rotterdam and Schiedam regions is not valid for this data set.
- It is further notable that at urban locations (Schiedam and Rotterdam) nitrate still appeared as one of the important components in $PM_{10}$ (with levels near or above 4 µg/m$^3$). In addition, in the coarse mass, nitrate appeared not negligible, with levels ranging from 1.5 to 1.8 µg/m$^3$. At the rural locations, levels were lower, but still above 1 µg/m$^3$. A similar behaviour could be seen for sulphate, but with lower concentrations. It is known that at coastal environments coarse sea salt particles act as reactive sinks for nitric acid ($HNO_3$) and sulphuric acid, via the reactions $NaCl + HNO_3 \rightarrow NaNO_3 + HCl$ and $NaCl + H_2SO_4 \rightarrow Na_2SO_4 + HCl$, providing the principal source of the gas phase HCl.
- The contributions of sea salt components, such as sodium and chloride, and the (summated) metals were relatively larger. The highest metal contributions to the coarse fraction were observed at Rotterdam and Schiedam (from industrial sources and resuspension of traffic dust). Further notable is the relatively high concentration at Cabauw (which should originate from a different source).
- The range of OC concentrations in $PM_{10}$ was 1.6 µg/m$^3$ (Hellendoorn, Cabauw), 1.8 µg/m$^3$ (Vredepeel and Schiedam)

and 2.3 µg/m$^3$ (Rotterdam). It is unlikely that the higher levels at the last two locations came from the same source. A recent study by Ten Brink et al. (2009) indicated that 70% of the OC in the Netherlands is contemporary (emissions originating from living material and wood combustion); the remainder comes from fossil-fuel sources (diesel traffic). OC in the coarse fraction was highest at Vredepeel, Cabauw and Rotterdam (compared to Hellendoorn). At the first two locations this was probably related to emissions originating from nearby living material.

- The 'not-analysed'(NA) part was the largest 'component' in PM$_{10}$ at each of the five locations. There was no systematic difference between urban and rural locations. NA was highest at Cabauw (6.7 µg/m$^3$), followed by Rotterdam (6.4 µg/m$^3$), Vredepeel (5.5 µg/m$^3$), Schiedam (5.3 µg/m$^3$) and Hellendoorn (4.6 µg/m$^3$). Within the fine fraction, the NA parts at rural locations appeared somewhat larger than in the coarse fraction (2.6-4.9 µg/m$^3$ versus 2.4-3.3 µg/m$^3$), while for the coarse fraction it is the opposite (1.6-2.1 µg/m$^3$ versus 2.9-3.0 µg/m$^3$). Note further the similarity in the concentration distributed over the five locations, of nitrate and sulphate with the NA part suggesting a relationship between these parameters.

**Average PM mass for each of the five measurement sites**

**Figure 3.1**



*Average PM mass for each of the five BOP locations; also given are the number of samples per location.*

*Somewhat unexpected, Figure 3.1, were the relatively low and high (average) PM$_{2.5}$ levels at Schiedam and Cabauw, resulting in a PM$_{10}$ value at Cabauw (23.6 µg/m$^3$) that is higher than that at Schiedam (21.8 µg/m$^3$). One reason for this is that the corresponding data were obtained on different days. Table 3.1 summarises the average levels for each location using only filter samples collected on the same days. This resulted in a rather small data set of six days. The reason for this low number is the different sampling schedule at Cabauw during part of the campaign and the strict quality control performed in the weighing procedure. This way, the levels of the fine fraction were comparable at the five locations (in the order of 8-9 µg/m$^3$·). At the urban locations, PM$_{10}$ levels were elevated, compared to those at the rural locations (as expected), which was caused by the difference in coarse fractions measured at the urban and rural locations.*

*Further notable is that the fine and coarse fractions at both urban locations appeared of equal magnitude in terms of mass. This can be explained by the dominance of medium and long-range transport of rather clean marine air on these six days; the wind direction always was between 170 and 280°. These conditions will lead to SIA levels below average and sodium levels above average at the two (marine) urban locations. As a consequence, averages summarised in this table are systematically lower than those shown in Figure 3.1 (which were derived from the 'complete' data sets).*

**PM levels for each location using only filter samples collected on the same days**

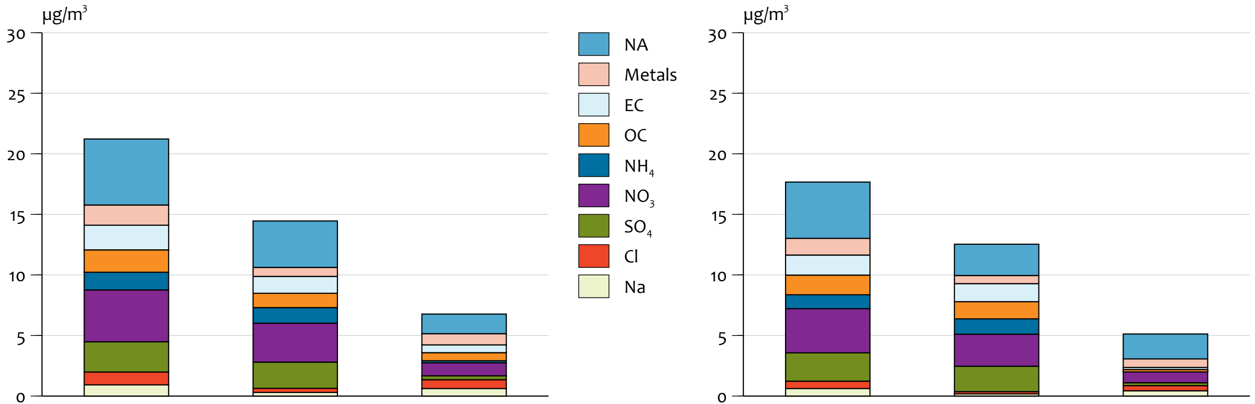
**Table 3.1**

| same days (6 in total) | Rotterdam | Cabauw | Schiedam | Vredepeel | Hellendoorn | average |
|---|---|---|---|---|---|---|
| *fine* | 8.7 | 8.8 | 8.3 | 9.1 | 9.0 | 8.8 |
| *coarse* | 8.6 | 4.9 | 7.9 | 4.9 | 3.5 | 6.0 |
| *PM$_{10}$* | 17.2 | 13.8 | 16.2 | 14.0 | 12.6 | 14.8 |

**Absolute concentrations of the components present in the $PM_{10}$ and $PM_{2.5}$ filter samples** **Figure 3.2**

Vredepeel

Hellendoorn

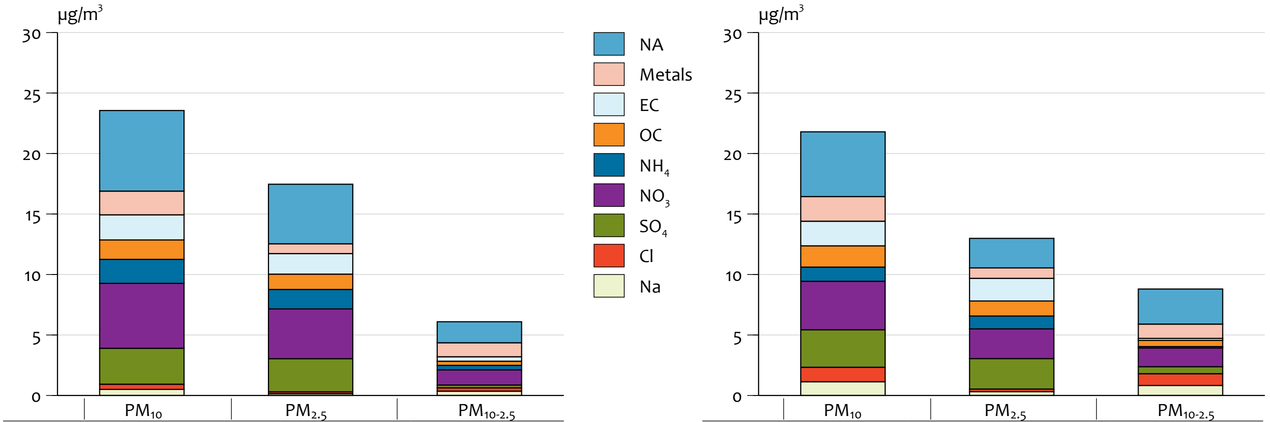


| | $PM_{10}$ | $PM_{2.5}$ | $PM_{10-2.5}$ |
|---|---|---|---|
| NA | 5.5 | 3.8 | 1.6 |
| Metals | 1.7 | 0.7 | 0.9 |
| EC | 2.0 | 1.4 | 0.6 |
| OC | 1.8 | 1.2 | 0.7 |
| NH4 | 1.5 | 1.3 | 0.2 |
| NO3 | 4.3 | 3.2 | 1.1 |
| SO4 | 2.5 | 2.2 | 0.3 |
| Cl | 1.1 | 0.3 | 0.7 |
| Na | 0.9 | 0.3 | 0.6 |

| | $PM_{10}$ | $PM_{2.5}$ | $PM_{10-2.5}$ |
|---|---|---|---|
| NA | 4.6 | 2.6 | 2.1 |
| Metals | 1.4 | 0.7 | 0.7 |
| EC | 1.7 | 1.5 | 0.2 |
| OC | 1.6 | 1.4 | 0.2 |
| NH4 | 1.2 | 1.3 | -0.1 |
| NO3 | 3.6 | 2.6 | 1.0 |
| SO4 | 2.3 | 2.1 | 0.2 |
| Cl | 0.6 | 0.2 | 0.4 |
| Na | 0.6 | 0.2 | 0.4 |

Cabauw

Schiedam

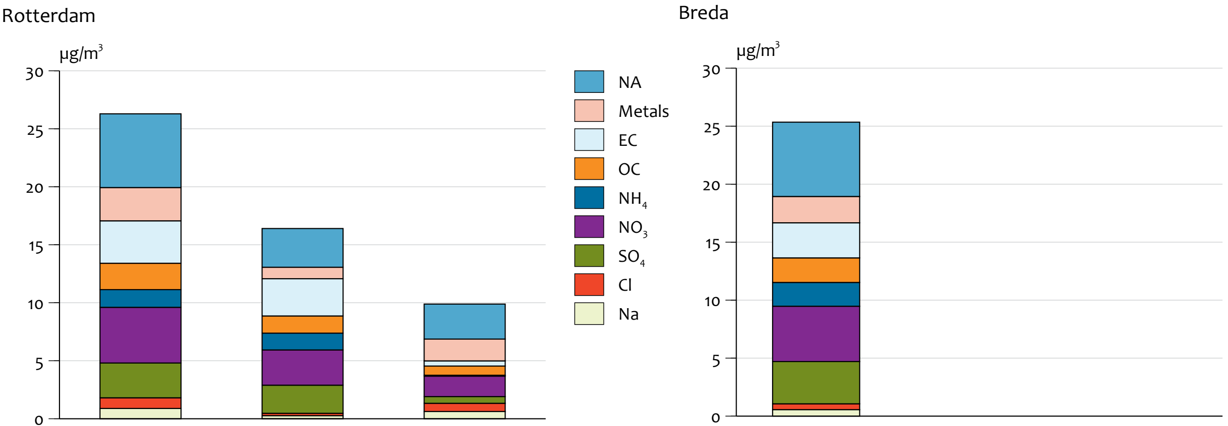


| | $PM_{10}$ | $PM_{2.5}$ | $PM_{10-2.5}$ |
|---|---|---|---|
| NA | 6.7 | 4.9 | 1.7 |
| Metals | 2.0 | 0.8 | 1.2 |
| EC | 2.1 | 1.7 | 0.4 |
| OC | 1.6 | 1.3 | 0.3 |
| NH4 | 2.0 | 1.6 | 0.4 |
| NO3 | 5.4 | 4.1 | 1.3 |
| SO4 | 3.0 | 2.7 | 0.2 |
| Cl | 0.4 | 0.2 | 0.3 |
| Na | 0.5 | 0.1 | 0.4 |

| | $PM_{10}$ | $PM_{2.5}$ | $PM_{10-2.5}$ |
|---|---|---|---|
| NA | 5.3 | 2.4 | 2.9 |
| Metals | 2.0 | 0.9 | 1.2 |
| EC | 2.0 | 1.9 | 0.2 |
| OC | 1.8 | 1.2 | 0.5 |
| NH4 | 1.2 | 1.1 | 0.1 |
| NO3 | 4.0 | 2.5 | 1.5 |
| SO4 | 3.1 | 2.5 | 0.6 |
| Cl | 1.2 | 0.2 | 1.0 |
| Na | 1.1 | 0.3 | 0.8 |

*Absolute concentrations of the components present in the $PM_{10}$ and $PM_{2.5}$ filter samples collected at the BOP locations. NA: not analysed.*

**Absolute concentrations of the components present in the $PM_{10}$ and $PM_{2.5}$ filter samples** **Figure 3.2 continued**



Rotterdam

| | $PM_{10}$ | $PM_{2.5}$ | $PM_{10-2.5}$ |
|---|---|---|---|
| NA | 6.4 | 3.3 | 3.0 |
| Metals | 2.9 | 1.0 | 1.9 |
| EC | 3.7 | 3.2 | 0.4 |
| OC | 2.3 | 1.5 | 0.8 |
| NH4 | 1.5 | 1.4 | 0.1 |
| NO3 | 4.8 | 3.0 | 1.8 |
| SO4 | 3.0 | 2.4 | 0.6 |
| Cl | 0.9 | 0.2 | 0.7 |
| Na | 0.9 | 0.3 | 0.6 |

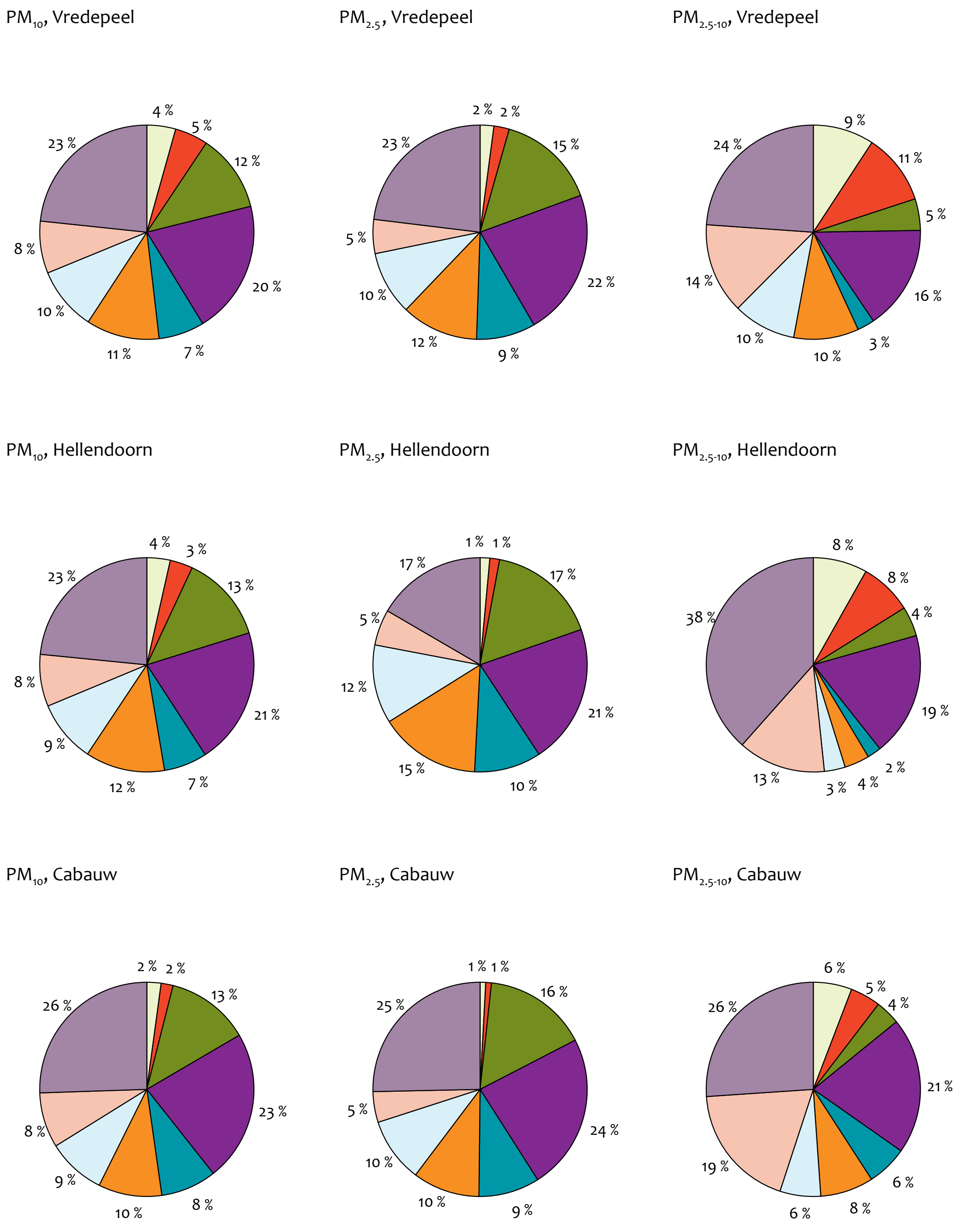
Breda

| | $PM_{10}$ |
|---|---|
| NA | 6.4 |
| Metals | 2.3 |
| EC | 3.0 |
| OC | 2.1 |
| NH4 | 2.1 |
| NO3 | 4.8 |
| SO4 | 3.6 |
| Cl | 0.5 |
| Na | 0.6 |

*Absolute concentrations of the components present in the $PM_{10}$ and $PM_{2.5}$ filter samples collected at the BOP locations. NA: not analysed.*

- At the traffic location of Breda, only $PM_{10}$ was measured. In general, these results corresponded with the above findings: a high contribution of nitrate and a substantial NA part (both similar to what was observed at Rotterdam). Notable are the maximum concentrations of sulphate and ammonium measured at this location (probably due to industrial and/or agricultural emissions to the east and south (Antwerp industrial agglomeration) of this location. Levels of EC and OC were of the same order as those measured at the Schiedam location.

**Relative distribution of the components in the $PM_{10}$ and $PM_{2.5}$ filter samples collected at the five BOP-locations** **Figure 3.3**


$PM_{10}$, Vredepeel

$PM_{2.5}$, Vredepeel

$PM_{2.5-10}$, Vredepeel

$PM_{10}$, Hellendoorn

$PM_{2.5}$, Hellendoorn

$PM_{2.5-10}$, Hellendoorn

$PM_{10}$, Cabauw

$PM_{2.5}$, Cabauw

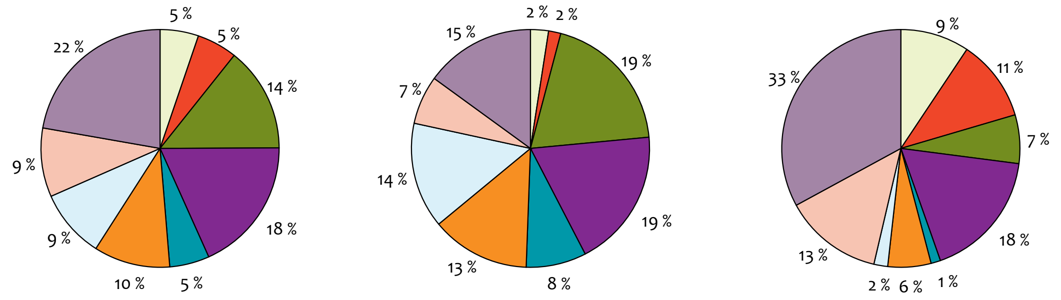
$PM_{2.5-10}$, Cabauw

*Relative distribution of the components in the $PM_{10}$ and $PM_{2.5}$ filter samples collected at the five BOP locations.*
*NA: not analysed*

PM$_{10}$, Schiedam

PM$_{2.5}$, Schiedam

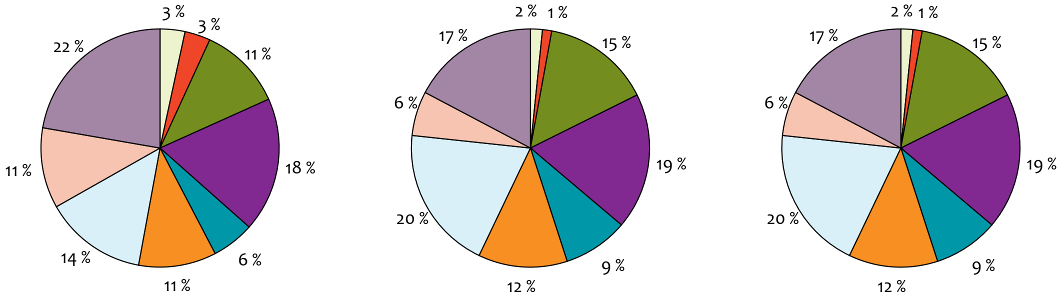
PM$_{2.5-10}$, Schiedam



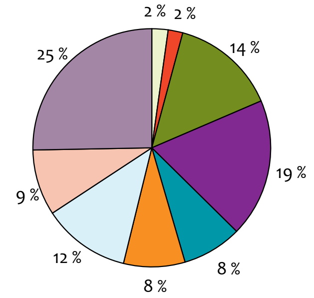
PM$_{10}$, Rotterdam

PM$_{2.5}$, Rotterdam

PM$_{2.5}$, Rotterdam



PM$_{10}$, Breda



*Relative distribution of the components in the PM$_{10}$ and PM$_{2.5}$ filter samples collected at the five BOP locations. NA: not analysed*

**Elemental and 'oxidised' concentrations and associated change in NA** **Table 3.2**

| $PM_{2.5}$ | Vredepeel | Schiedam | Hellendoorn | Rotterdam | Cabauw | Average |
|---|---|---|---|---|---|---|
| *elemental* | 0.7 | 0.9 | 0.7 | 1.0 | 0.8 | 0.8 |
| *oxide* | 1.0 | 1.2 | 1.0 | 1.4 | 1.2 | 1.2 |
| *increase* | 0.3 | 0.4 | 0.3 | 0.4 | 0.4 | 0.4 |
| *% decrease in 'NA'* | 2% | 3% | 2% | 3% | 2% | 2% |
| | | | | | | |
| $PM_{10-2.5}$ | | | | | | |
| *elemental* | 0.9 | 1.2 | 0.7 | 1.9 | 1.2 | 1.2 |
| *oxide* | 1.4 | 1.8 | 1.1 | 2.8 | 1.9 | 1.8 |
| *increase* | 0.5 | 0.6 | 0.4 | 1.0 | 0.7 | 0.6 |
| *% decrease in 'NA'* | 7% | 7% | 8% | 10% | 12% | 9% |
| | | | | | | |
| $PM_{10}$ | | | | | | |
| *elemental* | 1.7 | 2.0 | 1.4 | 2.9 | 2.0 | 2.0 |
| *oxide* | 2.4 | 3.0 | 2.1 | 4.3 | 3.1 | 3.0 |
| *increase* | 0.8 | 1.0 | 0.7 | 1.4 | 1.1 | 1.0 |
| *% decrease in 'NA'* | 4% | 4% | 4% | 5% | 5% | 4% |

## 3.4 Algorithms used for source attribution and mass closure

The chemical analysis of the particulate mass performed for this study provides a characterisation of a major part of the total mass. A substantial part of the mass was not analysed. This includes the non-measured oxides present in PM, as well as the contribution of non-carbon atoms (e.g. H, O, N) in organic material. Furthermore, it is possible to use specific tracers to provide insight into the sources of particulate matter, such as sea salt and mineral dust. The next section describes the procedure used for defining the observed total mass concentration. The outcome of this procedure effectively reduces the 'not-analysed' fraction to an 'not explained' or 'unknown' part in the mass closure. The following steps were investigated:

1. Correction for associated oxygen inmetals
2. Sea salt contribution (SS)
3. Non sea-salt sulphate ($nssSO_4$)
4. Mineral dust (MD)
5. Total carbon matter (TCM)

Below, we document the results from each of these steps have been documented, and the impact of the assumptions on the mass closure quantified.

### 3.4.1 Correction for associated oxygen

The result from recalculation of all elemental concentrations to their respective oxides is given in Table 3.2, where the correction factors numerated in Table 3.1 have been applied. This correction yielded a rather small increase in the elemental contributions to $PM_{2.5}$ (0.3-0.4 µg/m$^3$). The increase in the coarse fraction was between 0.4 (Hellendoorn) and 1.0 µg/m$^3$ (Rotterdam). As a result, the change in the $PM_{10}$ mass concentration could be as high as 1.4 µg/m$^3$ (Rotterdam). Roughly, the 'oxidised' contribution was a factor 1.4 to 1.5 higher than the summated elemental concentrations.

In conclusion, the incorporation of the 'oxidised' contribution had the largest effect on the mass closure of the coarse fraction. On average (i.e., for the five BOP locations), the additional mass concentration was 0.6 µg/m$^3$, yielding a decrease of the order of 9% (range: 7-12%) in the not-analysed part. In case of $PM_{2.5}$ and $PM_{10}$, (average) changes are +0.4 and +1.0 µg/m$^3$, improving the mass closure by 2 and 4%, respectively.

### 3.4.2 Sea salt contribution (SS)

The sea salt aerosol is generated from sea water through surf water spraying when waves break on the seashore and out at sea. Hence, the composition of pure sea salt aerosol reflects that of sea water. In the case of the sea salt analysed for this report, there are two common tracers: sodium and chloride. Sodium was used, as it has the advantage that there are no losses due to depletion, and measurements are reliable. In the case of chloride, reactions in the atmosphere may occur with any present sulphuric and nitric acid, resulting in the loss of $Cl^-$ in the aerosol. Hence, the presence of sea salt (SS) was estimated from:

$$SS = 3.26 * [Na^+].$$

The factor 3.26 follows from the composition of sea water (i.e. 1 l sea water contains 0.308 g sodium). The resulting sea salt estimation is given in Table 3.3, which also includes the decrease in the not-analysed part (compared to the sum of Na and Cl). The minor contributions of magnesium have been neglected here.

Generally, the application of the sea salt algorithm has a similar effect on mass and unexplained fraction as has the usage of oxidised elemental concentrations. In particular, the coarse fraction is affected. The average concentration rises with 1.0 µg/m$^3$ ($PM_{10}$), 0.3 µg/m$^3$ ($PM_{2.5}$) and 0.7 µg/m$^3$ ($PM_{10-2.5}$). The associated changes in the NA part are -5, -2 and -9%, respectively.

### 3.4.3 Non-sea salt sulphate ($nssSO_4$)

In the final estimation, the sulphate concentrations were corrected for a sea salt contribution ($ssSO_4^{2-}$), as follows:

$$nssSO4 = SIA - ssSO_4^{2-}$$

**Estimation of the sea salt contribution (SS) and the associated change in the amount of NA** **Table 3.3**

| **$PM_{10}$** | **Vredepeel** | **Schiedam** | **Hellendoorn** | **Rotterdam** | **Cabauw** | **Average** |
|---|---|---|---|---|---|---|
| *Na+Cl* | 2.0 | 2.3 | 1.2 | 1.8 | 0.9 | 1.7 |
| *SS* | 3.0 | 3.7 | 2.0 | 2.9 | 1.6 | 2.7 |
| *increase* | 1.0 | 1.4 | 0.8 | 1.1 | 0.7 | 1.0 |
| *% decrease in 'NA'* | 5% | 6% | 5% | 4% | 3% | 5% |
| $PM_{2.5}$ | | | | | | |
| *Na+Cl* | 0.6 | 0.5 | 0.4 | 0.5 | 0.3 | 0.4 |
| *SS* | 1.0 | 1.0 | 0.6 | 0.9 | 0.5 | 0.8 |
| *increase* | 0.4 | 0.5 | 0.2 | 0.4 | 0.2 | 0.3 |
| *% decrease in 'NA'* | 2% | 4% | 2% | 2% | 1% | 2% |
| $PM_{10\text{-}2.5}$ | | | | | | |
| *Na+Cl* | 1.4 | 1.8 | 0.9 | 1.3 | 0.6 | 1.2 |
| *SS* | 2.0 | 2.7 | 1.4 | 2.0 | 1.2 | 1.9 |
| *increase* | 0.6 | 0.9 | 0.6 | 0.7 | 0.5 | 0.7 |
| *% decrease in 'NA'* | 10% | 10% | 11% | 7% | 9% | 9% |

**Estimation of sea salt contribution to sulphate and associated change in the amount of NA** **Table 3.4**

| **$PM_{10}$** | **Vredepeel** | **Schiedam** | **Hellendoorn** | **Rotterdam** | **Cabauw** | **average** |
|---|---|---|---|---|---|---|
| $ssSO_4$ | 0.2 | 0.3 | 0.2 | 0.2 | 0.1 | 0.2 |
| *% increase in 'NA'* | 1 | 1 | 1 | 1 | 1 | 1 |
| $PM_{2.5}$ | | | | | | |
| $ssSO_4$ | 0.1 | 0.1 | 0.0 | 0.1 | 0.0 | 0.1 |
| *% increase in 'NA'* | 1 | 1 | 0 | 0 | 0 | 0 |
| $PM_{10\text{-}2.5}$ | | | | | | |
| $ssSO_4$ | 0.2 | 0.2 | 0.1 | 0.2 | 0.1 | 0.1 |
| *% increase in 'NA'* | 2 | 2 | 1 | 2 | 2 | 2 |

with $ssSO_4^{2-}$ = Na*(7.68/30.60), where the ratio is determined by the molar weights of sulphate and sodium as found in sea water. The resulting $ssSO_4^{2-}$ concentrations are presented in Table 3.4.

The estimated sea salt contributions in relation to sulphate are negligible: these are, on average, of the order of, or less than, 0.2 µg/m³. The separation into non-sea salt sulphate and sea salt sulphate slightly increases the 'NA', in particular for the coarse fraction.

### 3.4.4 Mineral dust (MD)

Various algorithms are used to estimate the contribution of mineral dust to the levels of $PM_{10}$ and $PM_{2.5}$. With 'mineral dust' is meant all fugitive wind-blown and mechanically resuspended soil dust with a composition comparable to that of the earth's crust. Mineral dust originates both from natural and anthropogenic sources, with diameters smaller than 10 µm. A number of elements are known to be present in mineral dust, the most important being Si, Al, Ca, K, Fe and Ti. In the BOP database, the correlation between Al and Si is very good ($r^2$=0.96; Denier van der Gon, 2010), suggesting that both elements originate from the same source. Moreover, it indicates that quartz and aluminium silicates are present in similar ratios in PM throughout the Netherlands.

The manner of estimating the contribution of MD is by focusing on the most abundant elements (Si and Al) according to the following algorithm (Denier van der Gon, 2010):

$$MD = 0.49 * Si + (2.36*Si + 2.7*Al)$$

In the data interpretation, all elemental weights were recalculated first to their respective oxide concentrations, which is the most probable form in the PM mass fractions. This formula was based on the average mass contribution from quartz and aluminium silicates in Dutch top soil (Denier van der Gon, 2010).

Since chemical analyses of PM samples present many elements, another approach is to sum over those elements known to be present in mineral dust. This approach is simply provided by taking the sum of silicon, aluminium, iron, calcium and potassium concentrations, and was used in the Bronstof study. Again, weights were recalculated to correct for their oxidised form. One should bear in mind here that particular elements may originate from other sources, as well, whereas minor contributions could also be due from other (additional) elements (not included) , which may result in either an overestimation or an underestimation of the MD contribution.

The calculated MD contribution is subtracted from the total elemental mass. Hence, the final mass balance (and the unexplained part therein) will not be affected. Here, only the differences between both approaches were considered.

The result from both algorithms is given in Table 3.5 for the five BOP locations. The BOP approach tended to lead to a slightly higher MD contributions than the one used in Bronstof (4 out of 5 locations). The largest difference was noted for Cabauw in $PM_{10}$ (+0.6 µg/m³) which was due to a relatively large abundance of Si when using the BOP algorithm. The exception was Rotterdam, where a relatively

**Estimations of mineral dust according to the BOP algorithm and the Bronstof algorithm** **Table 3.5**

| **$PM_{10}$** | **Vredepeel** | **Schiedam** | **Hellendoorn** | **Rotterdam** | **Cabauw** | **average** |
|---|---|---|---|---|---|---|
| *MD (BOP)* | 1.2 | 1.6 | 1.2 | 1,8 | 2,1 | 1,6 |
| *MD (Bronstof)* | 1.2 | 1.5 | 1.0 | 2.3 | 1.5 | 1.5 |
| *difference* | 0.0 | 0.2 | 0.3 | -0.5 | 0.6 | 0.1 |
| *$PM_{2.5}$* | | | | | | |
| *MD (BOP)* | 0.5 | 0.6 | 0.5 | 0.6 | 0.7 | 0.6 |
| *MD (Bronstof)* | 0.5 | 0.5 | 0.4 | 0.7 | 0.5 | 0.5 |
| *difference* | 0.0 | 0.1 | 0.1 | -0.1 | 0.2 | 0.1 |
| *$PM_{10\text{-}2.5}$* | | | | | | |
| *MD (BOP)* | 0.8 | 1.0 | 0.7 | 1.2 | 1.4 | 1.0 |
| *MD (Bronstof)* | 0.7 | 0.9 | 0.6 | 1.6 | 1.0 | 1.0 |
| *difference* | 0.0 | 0.1 | 0.1 | -0.4 | 0.4 | 0.0 |

**Increase in mass when estimating TCM from TC and the associated decrease in NA** **Table 3.6**

| **$PM_{10}$** | **Vredepeel** | **Schiedam** | **Hellendoorn** | **Rotterdam** | **Cabauw** | **average** |
|---|---|---|---|---|---|---|
| *TC* | 3.9 | 3.8 | 3.3 | 5.9 | 3.8 | 4.1 |
| *increase* | 1.2 | 1.1 | 1.0 | 1.8 | 1.1 | 1.2 |
| *% decrease in 'NA'* | 6% | 5% | 6% | 7% | 5% | 6% |
| *$PM_{2.5}$* | | | | | | |
| *TC* | 2.6 | 3.1 | 2.9 | 4.7 | 3 | 3.3 |
| *increase* | 0.8 | 0.9 | 0.9 | 1.4 | 0.9 | 1.0 |
| *% decrease in 'NA'* | 5% | 7% | 8% | 9% | 5% | 7% |
| *$PM_{10\text{-}2.5}$* | | | | | | |
| *TC* | 1.3 | 0.7 | 0.4 | 1.2 | 0.9 | 0.9 |
| *increase* | 0.4 | 0.2 | 0.1 | 0.4 | 0.3 | 0.3 |
| *% decrease in 'NA'* | 6% | 2% | 2% | 4% | 4% | 4% |

high Fe level was measured in both fine and coarse fraction (most likely not related to resuspended soil dust).

On average, the difference in the contribution estimated appears rather small, if not negligible. However, at the individual locations differences could be substantial.

### 3.4.5 Total carbonaceous matter

Carbonaceous constituents in PM contain other elements that contribute to the mass of PM (e.g., oxygen). The US EPA includes these associated elements in their approach to estimate the amount of mass that components contribute to PM. The parameter thus obtained is TCM, Total Carbonaceous Matter. Here, TCM was chosen to be equivalent to 1.3 times the amount of Total Carbon based on work by Frank (2007), who compared the mass on teflon filters with the summated contributions of the components analysed for a very large number of filters. The reason why we used the total carbon in the mass closure, and not convert OC to OM, is due to the issues regarding the OC-EC split in the chemical analysis. The available analysis procedures correspond well for total carbon, but yield very different EC/OC ratios. (Ten Brink et al., 2004). The procedure used here ('Cachier') is not subject to charring, as the full analysis is performed under oxygen. However, refractory OC was not combusted in the first but in the second step, and was attributed to EC. Thus, it may provide an upper estimate for EC and a lower estimate for OC (Ten Brink et al., 2009). The application of one of the SUNSET analysis procedures would yield in much lower EC/OC ratios. Within BOP it was established that the SUNSET method would yield only 40% of the EC levels reported here (Ten Brink et al., 2009). Consequently, the OC contribution would be about 50% higher using the SUNSET method. Hence, the lack of a clear separation between EC and OC works through in the interpretation of the data, and we chose to use the TC data in which we had confidence, for the TCM correction. Note that besides sampling issues the conversion factor from OC to organic material (OM) is uncertain. Literature data vary between 1.2 and 2 and it may very well be possible that the factor varies with lower values near sources and higher values after processing in aged air masses. The effect on the not-analysed part in the mass closure is given in Table 3.6.

Concluding, the largest effect on the mass closure (and the corresponding decrease in the unexplained part) is given by the estimation of total carbonaceous matter from the total carbon concentration. Not surprisingly, the largest change was observed for PM$_{2.5}$ as TC is predominantly measured in the fine fraction. Here, the decrease in the unexplained part was, on average, some 7% (1.0 $\mu g/m^3$) with the maxima observed in the urban region (Schiedam and Rotterdam; 7 and 9 %). This is more than what was found in the case of PM$_{10}$ and the coarse fraction (6 and 4%, respectively).

### *Coarse nitrate fraction*

*The role of nitrate in the chemical mass closure procedure needs special attention. In the Netherlands, most of the nitrate is found in the fine mode as ammonium nitrate. However, the coarse nitrate fraction is a substantial part of the analysed coarse mode mass (see Figures 3.2 and 3.3). In particular, the coarse-to-$PM_{10}$ ratio was near 40% at the urban locations (and some 26% at the rural locations). This has implications for the mass closure. According to the formation pathways, ammonia gas reacts reversibly with $HNO_3$ to form its ammonium salt, $NH_4NO_3$, which is semi-volatile and may release its gas phase precursors under conditions of low atmospheric $NH_3$ levels or high temperature:*

$NH_3 + HNO_3 \leftrightarrows NH_4NO_3$

*In marine and coastal atmospheres, nitric acid is also converted into particulate nitrate ($NaNO_3$) through reaction with sea salt (NaCl) particles, resulting in the release of HCl:*

$NaCl + HNO3 \rightarrow NaNO3 + HCl$

*In contrast to $NH_4NO_3$, $NaNO_3$ is a non-volatile compound under atmospheric conditions. Therefore, partitioning of nitric acid in sea salt is irreversible.*

*It is this formation pathway that poses a complication with respect to the chemical mass closure approach. However, in the chemical mass balance, we used sodium as a tracer of sea salt and multiplied its concentration with a factor to obtain an estimate of fresh sea salt aerosol, including all the chloride. Hence, when one would keep both the fresh sea salt estimate and the full coarse mode nitrate in the chemical mass balance, sea salt and nitrate cannot simply be added as the nitrate replaces chloride Consequently, one needs to make a correction in the chemical mass balance approach for this double counting.*

*In principle, there are two options for removing the double counting. The first is to remove the lost chloride mass from the sea salt estimate and to keep the coarse nitrate as it is. The second option is to assign only the net mass addition to the coarse nitrate part. The first option reflects the measured chemical composition of the particles. The second option reflects the sources and especially the associated reduction potential. Though both choices are valid and defendable, it can be argued that the second option suits better if we are after the source apportionment. Reduction of $NO_x$ emissions may cause a reduction in coarse mode nitrate, which is partly compensated by the fact that chloride is no longer lost. Such a reduction would yield a net result of $((NO_3\text{-}Cl)/NO_3 = (62\text{-}35)/62 =)\ 27/62$ times the nitrate reduction (where the numbers involved are molar weights of the respective components). Hence, the same factor could be used to scale back the coarse nitrate fraction in the chemical mass balance. The motivation is that when all anthropogenic sources would be non-existing, one still has the sea salt left, as it is given in the pie charts. The resulting effect on the not-analysed part (for $PM_{10}$) is given in Table 3.7.*

*As this correction is uncommon (as yet) in current chemical mass closure studies this correction was not implemented in this study to retain comparability.*

**Change in the NA part due to a correction for coarse nitrate**

**Table 3.7**

| | Vredepeel | Schiedam | Hellendoorn | Rotterdam | Cabauw | average |
|---|---|---|---|---|---|---|
| *$PM_{10}$ (ug/m$^3$)* | 21.2 | 21.8 | 17.7 | 26.3 | 23.6 | 22,1 |
| *coarse $NO_3$ (ug/m$^3$)* | 1.1 | 1.5 | 1.0 | 1.8 | 1.3 | 1,3 |
| *scaling back coarse nitrate* | 0.4 | 0.6 | 0.4 | 0.8 | 0.5 | 0,6 |
| *% increase in 'NA".* | 3 | 4 | 3 | 4 | 3 | 3,5 |

## 3.5 Chemical mass closure

The analytical results from the chemical speciation are presented in Figures 3.4-5 and 3.6-7, in terms of absolute and relative mass contributions for every BOP location.

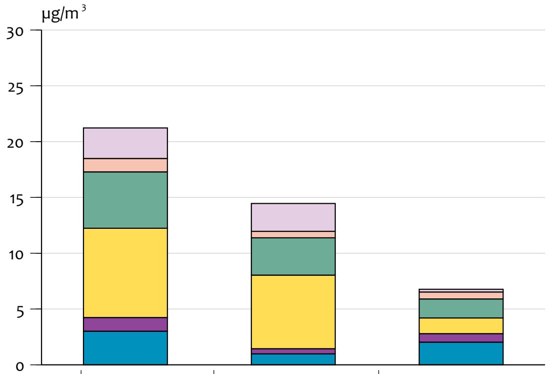
The following observations could be made:

- The most complete mass closure was obtained for the $PM_{2.5}$ filter samples. The closure was around 93 to 94% for the urban locations of Schiedam and Rotterdam, and 90% for rural Hellendoorn. The unexplained part in $PM_{2.5}$ appeared largest for the rural locations of Vredepeel (17%) and Cabauw (20%). In contrast, the mass closure for the coarse mass appeared relatively incomplete for the urban locations (12 and 16%) and Hellendoorn (21%), but was much more complete for Cabauw and Vredepeel (3-4%). Obviously, the mass closure in the $PM_{10}$ filter samples was between those of $PM_{2.5}$ and $PM_{10\text{-}2.5}$, with unknown 'contributions' between 9 (Rotterdam) and 16% (Cabauw).
- Further analysis revealed that the best chemical closure for $PM_{2.5}$ was achieved when both SIA and TCM contributions were substantial, which was the case at the urban locations. The SIA in the chemical distribution of $PM_{2.5}$ did not differ largely between BOP locations (42-48%). As the contributions of the remaining components such as sea salt (3-8%), mineral dust (3-5%) and metals (3-5%) are relatively unimportant in $PM_{2.5}$ and also rather independent of the type of location, the decrease in TCM as observed at the rural locations (22-23% versus 31-37% at the urban locations) resulted in a larger part of PM that was

## Average chemical composition of $PM_{10}$, $PM_{2.5}$ and the coarse fraction

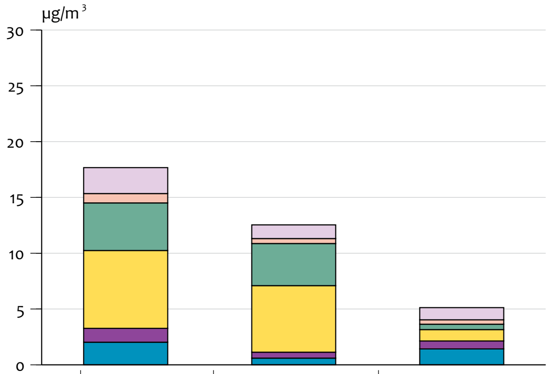
**Figure 3.4**

Vredepeel



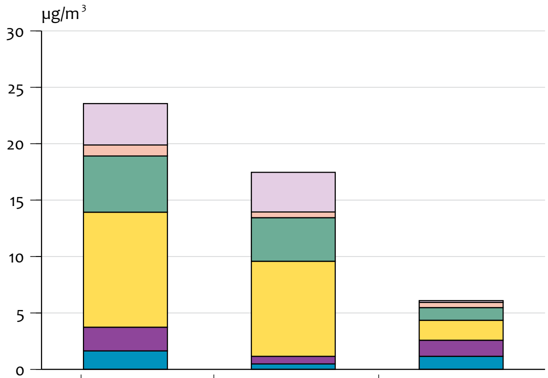
| | $PM_{10}$ | $PM_{2.5}$ | $PM_{10-2.5}$ |
|---|---|---|---|
| Unknown | 2.7 | 2.5 | 0.2 |
| Metals | 1.2 | 0.6 | 0.6 |
| TCM | 5.0 | 3.3 | 1.7 |
| SIA | 8.0 | 6.6 | 1.4 |
| MD | 1.2 | 0.5 | 0.8 |
| SS | 3.0 | 1.0 | 2.0 |

Hellendoorn



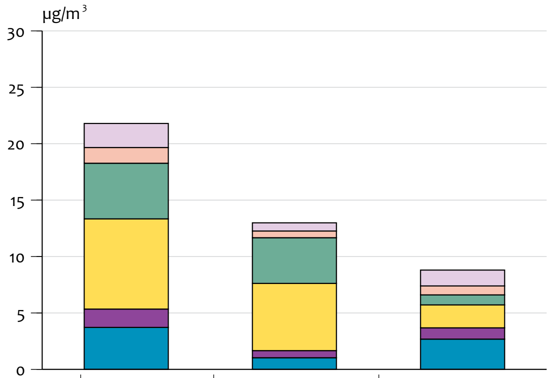
| | $PM_{10}$ | $PM_{2.5}$ | $PM_{10-2.5}$ |
|---|---|---|---|
| Unknown | 2.3 | 1.2 | 1.1 |
| Metals | 0.8 | 0.4 | 0.4 |
| TCM | 4.3 | 3.8 | 0.5 |
| SIA | 7.0 | 6.0 | 1.0 |
| MD | 1.2 | 0.5 | 0.7 |
| SS | 2.0 | 0.6 | 1.4 |

Cabauw



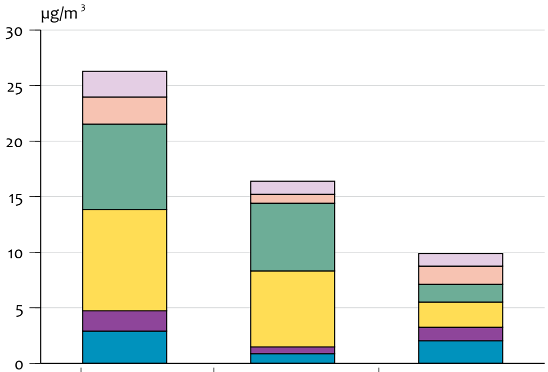
| | $PM_{10}$ | $PM_{2.5}$ | $PM_{10-2.5}$ |
|---|---|---|---|
| Unknown | 3.7 | 3.5 | 0.2 |
| Metals | 1.0 | 0.5 | 0.5 |
| TCM | 5.0 | 3.9 | 1.1 |
| SIA | 10.2 | 8.4 | 1.8 |
| MD | 2.1 | 0.7 | 1.4 |
| SS | 1.6 | 0.5 | 1.2 |

Schiedam



| | $PM_{10}$ | $PM_{2.5}$ | $PM_{10-2.5}$ |
|---|---|---|---|
| Unknown | 2.1 | 0.7 | 1.4 |
| Metals | 1.4 | 0.6 | 0.8 |
| TCM | 4.9 | 4.0 | 0.9 |
| SIA | 8.0 | 6.0 | 2.0 |
| MD | 1.6 | 0.6 | 1.0 |
| SS | 3.7 | 1.0 | 2.7 |

Rotterdam

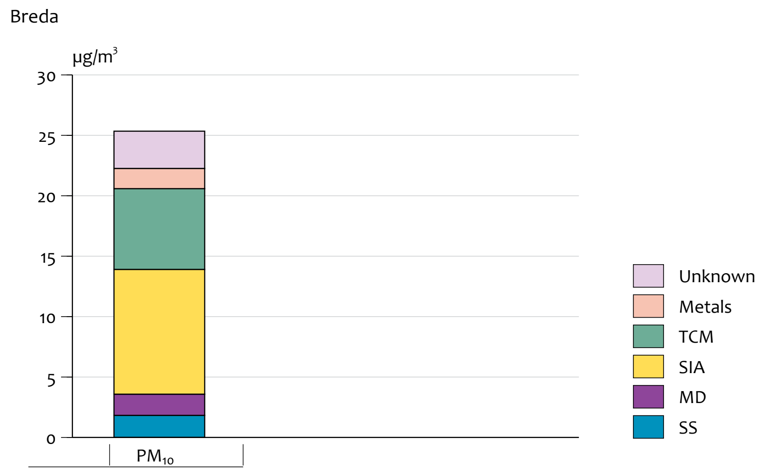


| | $PM_{10}$ | $PM_{2.5}$ | $PM_{10-2.5}$ |
|---|---|---|---|
| Unknown | 2.3 | 1.2 | 1.1 |
| Metals | 2.4 | 0.8 | 1.6 |
| TCM | 7.7 | 6.1 | 1.6 |
| SIA | 9.1 | 6.8 | 2.3 |
| MD | 1.8 | 0.6 | 1.2 |
| SS | 2.9 | 0.9 | 2.0 |

Unknown
Metals
TCM
SIA
MD
SS

*Average chemical composition of $PM_{10}$, $PM_{2.5}$ and the coarse fraction, at the BOP measurement locations*

**Average chemical composition of $PM_{10}$** **Figure 3.5**



|  | $PM_{10}$ |
|---|---|
| 🟪 Unknown | 3.1 |
| 🟧 Metals | 1.7 |
| 🟩 TCM | 6.7 |
| 🟨 SIA | 10.3 |
| 🟪 MD | 1.8 |
| 🟦 SS | 1.8 |

*Average chemical composition of $PM_{10}$ at the Breda location.*

unexplained (and not 'filled in' by any of the other known components).

- The presence of SIA and TCM was (far) less dominant in the coarse fraction, with contributions no higher than 29 and 25%, respectively. The various constituents were distributed more evenly. Comparable contributions came from mineral dust (<23% , maximum at Cabauw) and sea salt (<30%, Vredepeel and Schiedam). The contribution of the metals could be as high as 16% (Rotterdam). Remarkable is that the presence of TCM in the coarse mass was considerably higher (20-25%) at Cabauw and Vredepeel than at Schiedam (10%) and Rotterdam (16%). This was caused by rather high TC levels at Vredepeel (1.3 µg/m³) and Cabauw (0.7 µg/m³), comparable to those at Rotterdam (1.2 µg/m³) and Schiedam (0.7 µg/m³), while weighted PM levels were considerably lower at the two rural locations. The reason for the increased TC levels in the coarse fraction is not clear.
- Levels at Breda with respect to TCM and mineral dust were in line with those observed at the urban locations in the city of Rotterdam. As noted earlier, the contribution of SIA was the highest measured in the BOP data for $PM_{10}$.

The two measurement locations in the Rotterdam urban area allowed investigating of the components emitted by traffic, by comparing measured concentrations at the traffic location (Rotterdam) with those at the urban background location (Schiedam). In Figure 3.8 concentration differences were plotted for the main components in the three mass fractions. The difference in $PM_{10}$ between the two locations was 3.5 µg/m³ (based on 27 corresponding days). This difference can be attributed to carbonaceous material (2.5 µg/m³) and metals (1 µg/m³). The increment in carbonaceous material was largely due to elemental carbon. The increased amounts of metals consisted of copper, iron, barium and molybdenum, resulting from exhaust emissions (TCM) and brake and tire wear. Surprisingly, there was no increment in the concentrations of mineral dust. This would indicate that, at Rotterdam, resuspension is not a significant source, however, this is not in keeping with findings of other studies (e.g. Amato et al., 2009).

A lack of data prohibited a similar analysis of the increment in concentration between the urban background and rural background locations. Because of an operational error, a part of the data from Cabauw, which at about 35 km is the closest to Rotterdam, was obtained on different days than that from the other locations. Therefore, the number of complete, simultaneous samples was too low for analysis (see Section 3.2). Using the average of all concentrations, from each location, was also not possible, as $PM_{10}$ and $PM_{2.5}$ averages for Cabauw turned out to be higher than for Schiedam. This demonstrated that the variability in time was such, that using a limited number of data points to assess an average gradient was not possible. Local agricultural sources, as well as expected concentration gradients in the rural background (from the west to the (south)-east), suggest that Vredepeel is not a suitable rural background location for Schiedam. Similarly, we could not compare Schiedam to Hellendoorn, the location farthest away from Rotterdam. Unfortunately, this meant that we could not characterise the gradient from the rural to urban background.

**Average chemical distribution of the $PM_{10}$, fine and coarse mass fraction at the BOP-locations** **Figure 3.6**

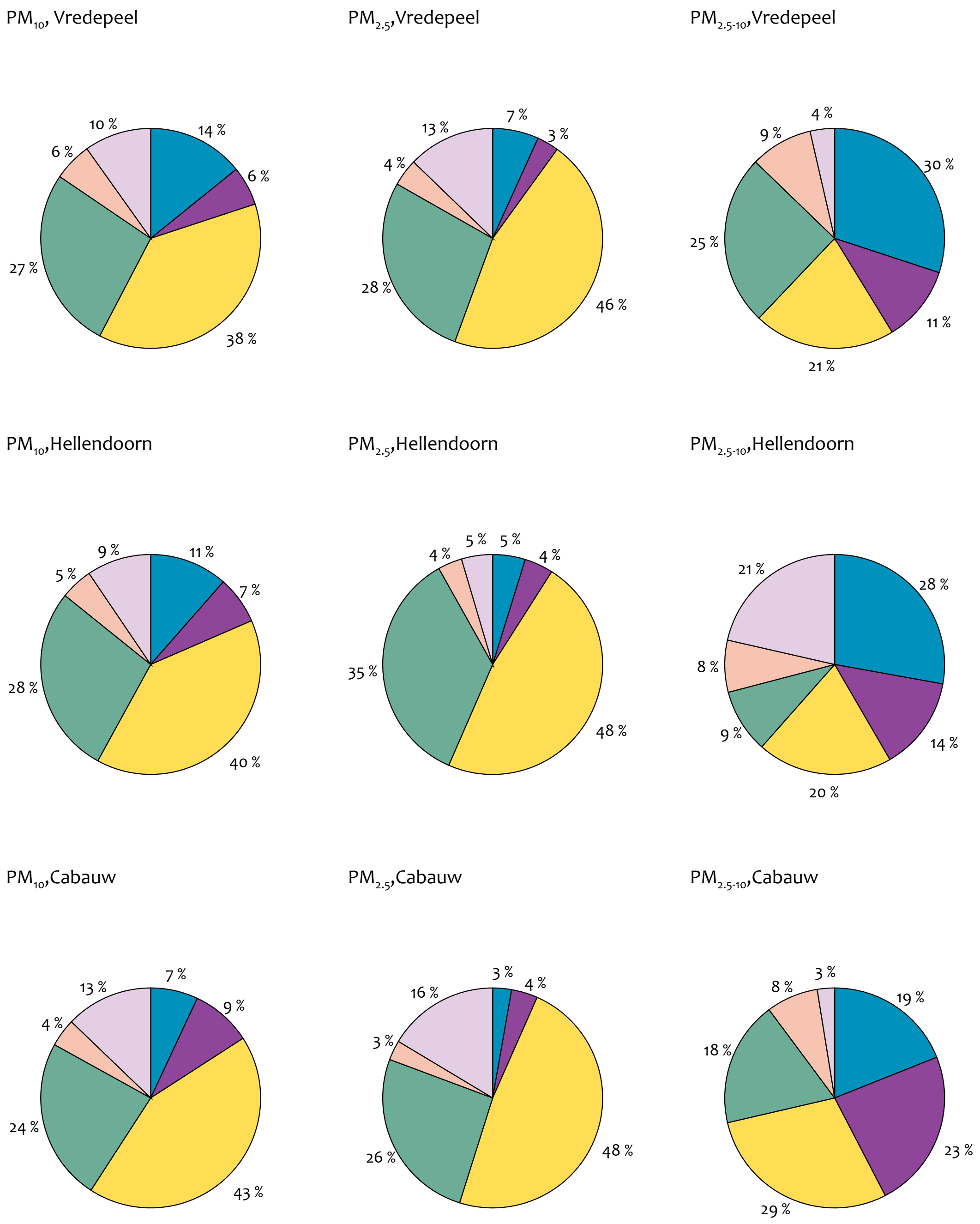
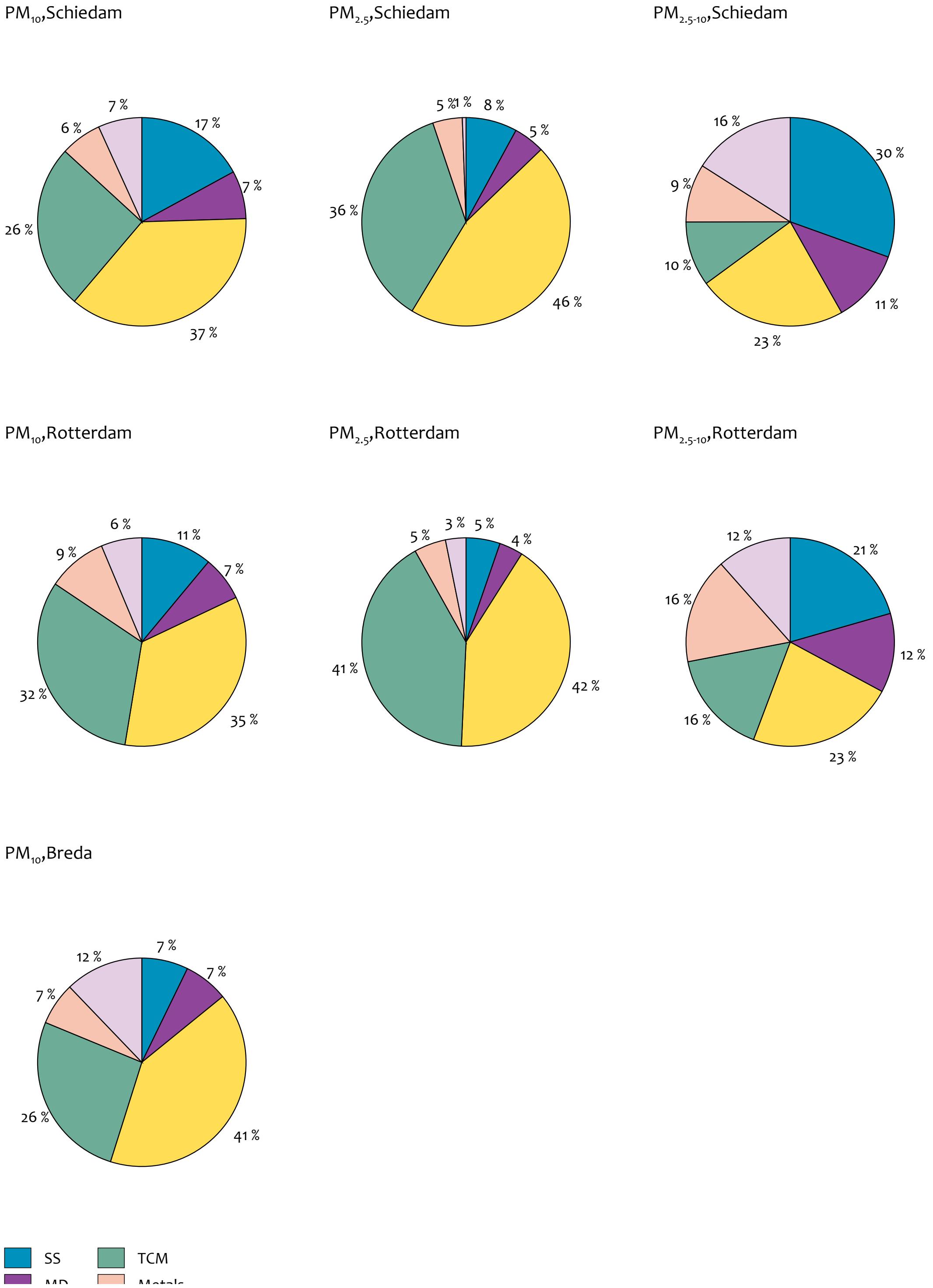
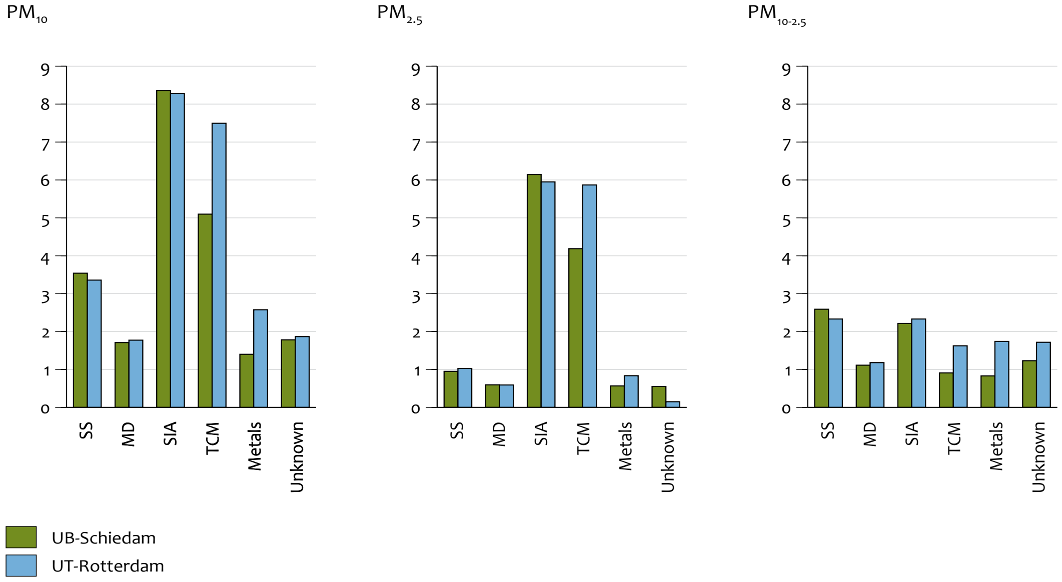


Figure 3.7



*Average chemical distribution of the PM$_{10}$, fine and coarse mass fraction at the BOP locations (Breda only PM$_{10}$).*

**Differences in concentrations for the main chemical constituents** **Figure 3.8**



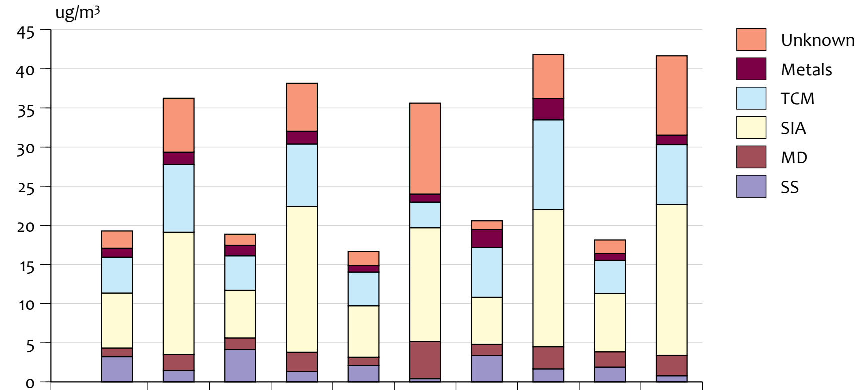
*Differences in concentrations between Rotterdam and Schiedam for the main chemical constituents in the three mass fractions.*

## 3.6 Chemical composition on days with high PM concentration

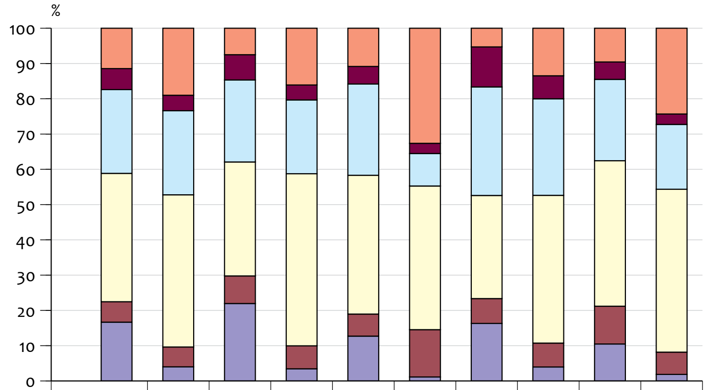
Figure 3.9 and 3.10 demonstrates the change in absolute concentrations and their relative distribution, for the various fractions at the five locations, after the data set had been partitioned into two subsets, that is, subsets containing only days with $PM_{10}$ ($PM_{2.5}$) concentrations of less or more than 30 (25) µg/m³. The reason for such an analysis was to determine which of the components played an important role in the occurrence of the high PM levels (e.g., on exceedance days).

Not surprisingly, the absolute contributions of most constituents rose when PM increased, when we compared the sets of high and low PM mass concentrations (average increase in $PM_{10}$ was 20 µg/m³). The largest changes in absolute concentrations were observed for SIA (+10.5 µg/m³ on average in $PM_{10}$) and for the unknown part (+6.4 µg/m³), followed by smaller or negligible changes for TCM (+3.0 µg/m³), MD (+1.5 µg/m³) and metals (<0.5 µg/m³). The only exception was sea salt, which decreased at higher PM levels (-1.8 µg/m³). As a consequence, the relative chemical distribution changed, which has been summarised in Figure 3.11 as the averages for the BOP locations, for both $PM_{10}$ and $PM_{2.5}$. Both SIA and the unknown part were more dominant at higher PM concentrations, whereas the contributions of the remaining constituents (MD, TCM and SS), when expressed in percentages, decreased.

**Absolute and relative chemical composition of $PM_{10}$ <= 30 µg/m$^3$ and $PM_{10}$ > 30 µg/m$^3$** **Figure 3.9**

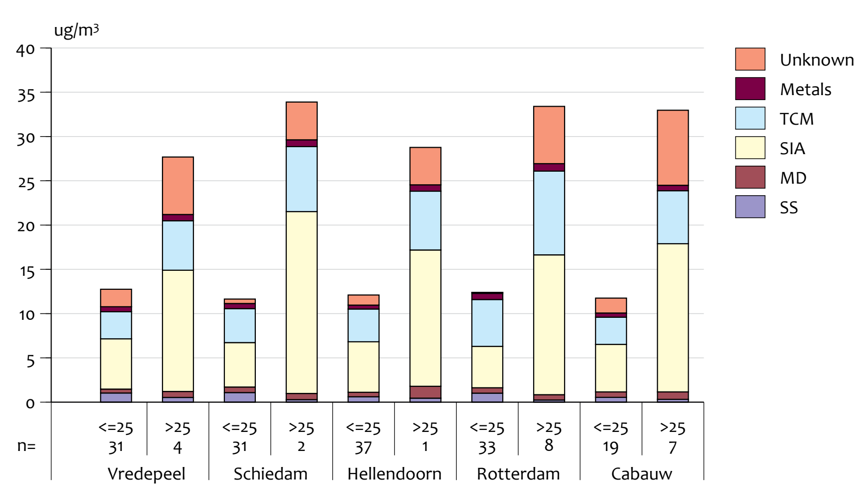


| | Vredepeel | | Schiedam | | Hellendoorn | | Rotterdam | | Cabauw | |
|---|---|---|---|---|---|---|---|---|---|---|
| | <=30 | >30 | <=30 | >30 | <=30 | >30 | <=30 | >30 | <=30 | >30 |
| n= | 31 | 4 | 28 | 5 | 36 | 2 | 30 | 11 | 20 | 6 |
| Unknown | 2.2 | 6.9 | 1.4 | 6.1 | 1.8 | 11.6 | 1.1 | 5.6 | 1.7 | 10.1 |
| Metals | 1.1 | 1.6 | 1.4 | 1.6 | 0.8 | 1.0 | 2.3 | 2.7 | 0.9 | 1.2 |
| TCM | 4.6 | 8.6 | 4.4 | 8.0 | 4.3 | 3.3 | 6.3 | 11.5 | 4.2 | 7.7 |
| SIA | 7.0 | 15.6 | 6.1 | 18.6 | 6.6 | 14.5 | 6.0 | 17.5 | 7.5 | 19.2 |
| MD | 1.1 | 2.0 | 1.5 | 2.5 | 1.0 | 4.8 | 1.5 | 2.8 | 1.9 | 2.6 |
| SS | 3.2 | 1.5 | 4.1 | 1.3 | 2.1 | 0.4 | 3.4 | 1.7 | 1.9 | 0.8 |

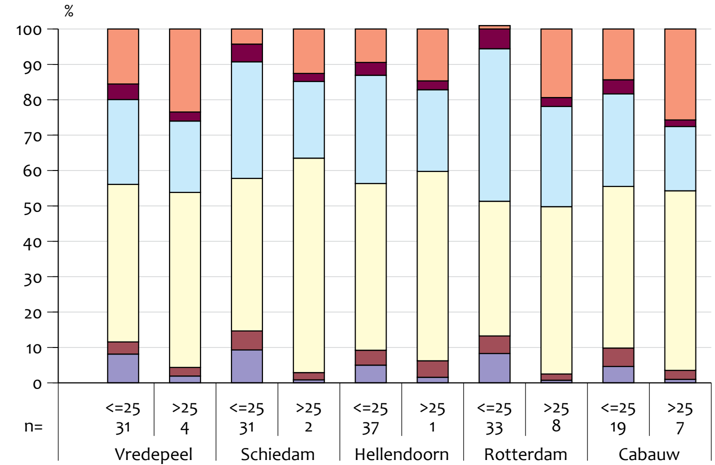


| | Vredepeel | | Schiedam | | Hellendoorn | | Rotterdam | | Cabauw | |
|---|---|---|---|---|---|---|---|---|---|---|
| | <=30 | >30 | <=30 | >30 | <=30 | >30 | <=30 | >30 | <=30 | >30 |
| n= | 31 | 4 | 28 | 5 | 36 | 2 | 30 | 11 | 20 | 6 |
| Unknown | 11% | 19% | 8% | 16% | 11% | 33% | 5% | 13% | 10% | 24% |
| Metals | 6% | 4% | 7% | 4% | 5% | 3% | 11% | 7% | 5% | 3% |
| TCM | 24% | 24% | 23% | 21% | 26% | 9% | 31% | 27% | 23% | 18% |
| SIA | 36% | 43% | 32% | 49% | 39% | 41% | 29% | 42% | 41% | 46% |
| MD | 6% | 6% | 8% | 7% | 6% | 13% | 7% | 7% | 11% | 6% |
| SS | 17% | 4% | 22% | 3% | 13% | 1% | 16% | 4% | 10% | 2% |

**Absolute and relative chemical composition of $PM_{2.5}$ <= 25 µg/$m^3$ and $PM_{2.5}$ > 25 µg/$m^3$** **Figure 3.10**



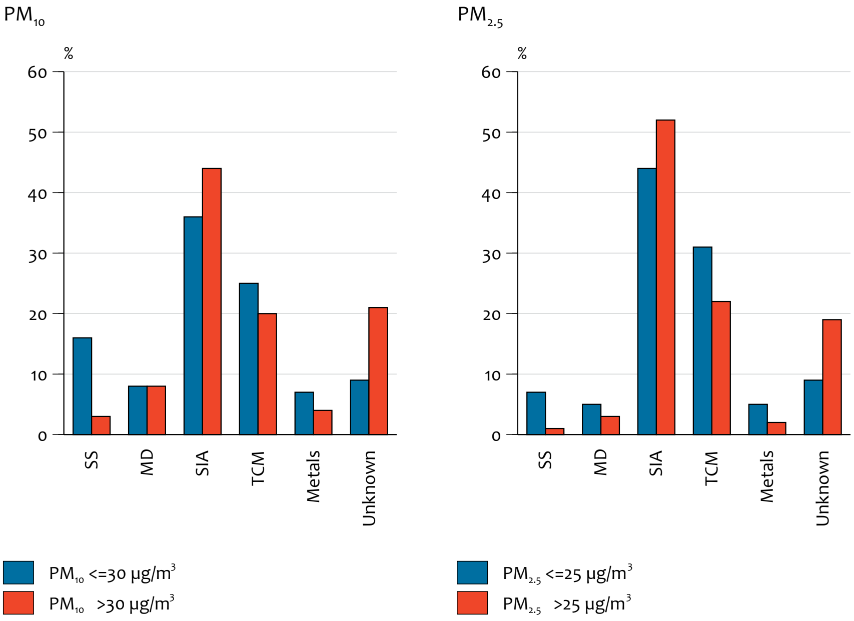
| | Vredepeel <=25 (n=31) | Vredepeel >25 (n=4) | Schiedam <=25 (n=31) | Schiedam >25 (n=2) | Hellendoorn <=25 (n=37) | Hellendoorn >25 (n=1) | Rotterdam <=25 (n=33) | Rotterdam >25 (n=8) | Cabauw <=25 (n=19) | Cabauw >25 (n=7) |
|---|---|---|---|---|---|---|---|---|---|---|
| Unknown | 2.0 | 6.5 | 0.5 | 4.3 | 1.1 | 4.2 | -0.1 | 6.5 | 1.7 | 8.5 |
| Metals | 0.6 | 0.7 | 0.6 | 0.8 | 0.4 | 0.7 | 0.8 | 0.8 | 0.5 | 0.6 |
| TCM | 3.1 | 5.6 | 3.8 | 7.3 | 3.7 | 6.6 | 5.3 | 9.5 | 3.1 | 6.0 |
| SIA | 5.7 | 13.7 | 5.0 | 20.5 | 5.7 | 15.4 | 4.7 | 15.8 | 5.4 | 16.7 |
| MD | 0.4 | 0.7 | 0.6 | 0.7 | 0.5 | 1.3 | 0.6 | 0.6 | 0.6 | 0.8 |
| SS | 1.0 | 0.5 | 1.1 | 0.3 | 0.6 | 0.4 | 1.0 | 0.5 | 0.5 | 0.3 |



| | Vredepeel <=25 (n=31) | Vredepeel >25 (n=4) | Schiedam <=25 (n=31) | Schiedam >25 (n=2) | Hellendoorn <=25 (n=37) | Hellendoorn >25 (n=1) | Rotterdam <=25 (n=33) | Rotterdam >25 (n=8) | Cabauw <=25 (n=19) | Cabauw >25 (n=7) |
|---|---|---|---|---|---|---|---|---|---|---|
| Unknown | 16% | 23% | 4% | 13% | 9% | 15% | -1% | 19% | 14% | 26% |
| Metals | 4% | 3% | 5% | 2% | 4% | 2% | 7% | 3% | 4% | 2% |
| TCM | 24% | 20% | 33% | 22% | 31% | 23% | 43% | 28% | 26% | 18% |
| SIA | 45% | 49% | 43% | 61% | 47% | 54% | 38% | 47% | 46% | 51% |
| MD | 3% | 2% | 5% | 2% | 4% | 5% | 5% | 2% | 5% | 3% |
| SS | 8% | 3% | 9% | 1% | 3% | 2% | 8% | 1% | 5% | 1% |

## Change in chemical distribution in percentages for data subsets

Figure 3.11



*Change in chemical distribution, in percentages, in data subsets for* $PM_{10}$*<=30 (*$PM_{2.5}$*<=25) and* $PM_{10}$*>30 (*$PM_{2.5}$*>25). Averages over the five BOP locations.*

# 4

# Source apportionment using Positive Matrix Factorization (PMF)

## 4.1 Estimation of source factors

To estimate the number of source factors, the behaviour of the PMF solution was studied for a range of 3 to 14 factors, for both $PM_{2.5}$ and $PM_{10}$, separately. Although the selection of the number of factors was somewhat arbitrary, the evaluation showed that a 7 factor solution would yield the most tangible comprehensible results for the $PM_{2.5}$ data set. For $PM_{10}$, the statistical analysis of the results was not conclusive. Therefore, we physically examined the results for a 5 to 9 factor solution. Both the 8 and 9 factor solution yielded several factors without a contribution to the total mass. The 7 factor solution yielded the most physically understandable results. In addition, it is our belief that the number of factors should not deviate much from the 7 factor solution for the $PM_{2.5}$ data set, primarily since the $PM_{10}$ data set also contains the $PM_{2.5}$ data. Hence, for both components a 7 factor solution was found to be the most suitable.

For both data sets, an additional 250 runs were performed, using random seeds, to ensure the convergence of the PMF problem. Furthermore, several sensitivity runs with different settings were performed to gain a better understanding of the rotational freedom of the solution. However, little improvement was found compared to the central solution. Hence, this study presents the results for the 'central solution'.

The results from the PMF for $PM_{2.5}$ and $PM_{10}$ are given in Figures 4.1 and 4.2, respectively. The graphs, for each of the 7 source profiles, show the apportioned mass concentrations per component, per profile. In addition to the components, the total $PM_{2.5}$ and $PM_{10}$ mass was also apportioned. The factors (1 to 7) are given in order of decreasing $PM_{2.5}$ total mass contribution. For $PM_{10}$, the factors with a corresponding composition as found for $PM_{2.5}$ were given the same number. The PMF does not interpret source profiles, so the next step was to provide an interpretation of these profiles, based on expert knowledge.

## 4.2 Identification of factors based on chemical constituents

In this section, the calculated source profiles are named (previously only identifiable by an arbitrary number), based on the chemical constituents attributed to the profile. We identified the profiles as follows:

1. Nitrate-rich secondary aerosol
2. Sulphate-rich secondary aerosol
3. Traffic and resuspended road dust
4. Industrial (metal) activities / incineration
5. Sea spray
6. Mineral dust
7. Residual oil combustion

It should be noted that the same sources were identified for both $PM_{2.5}$ and $PM_{10}$ data sets. Below, the characteristics of the 'named' source profiles are described. Furthermore, the identified source groups were visually compared to well-known sources found in other (literature) studies, with similar chemical compositions (e.g., Bloemen *et al.*, 2008). Also, the total mass, apportioned by the PMF, was compared with the measured PM mass concentrations.

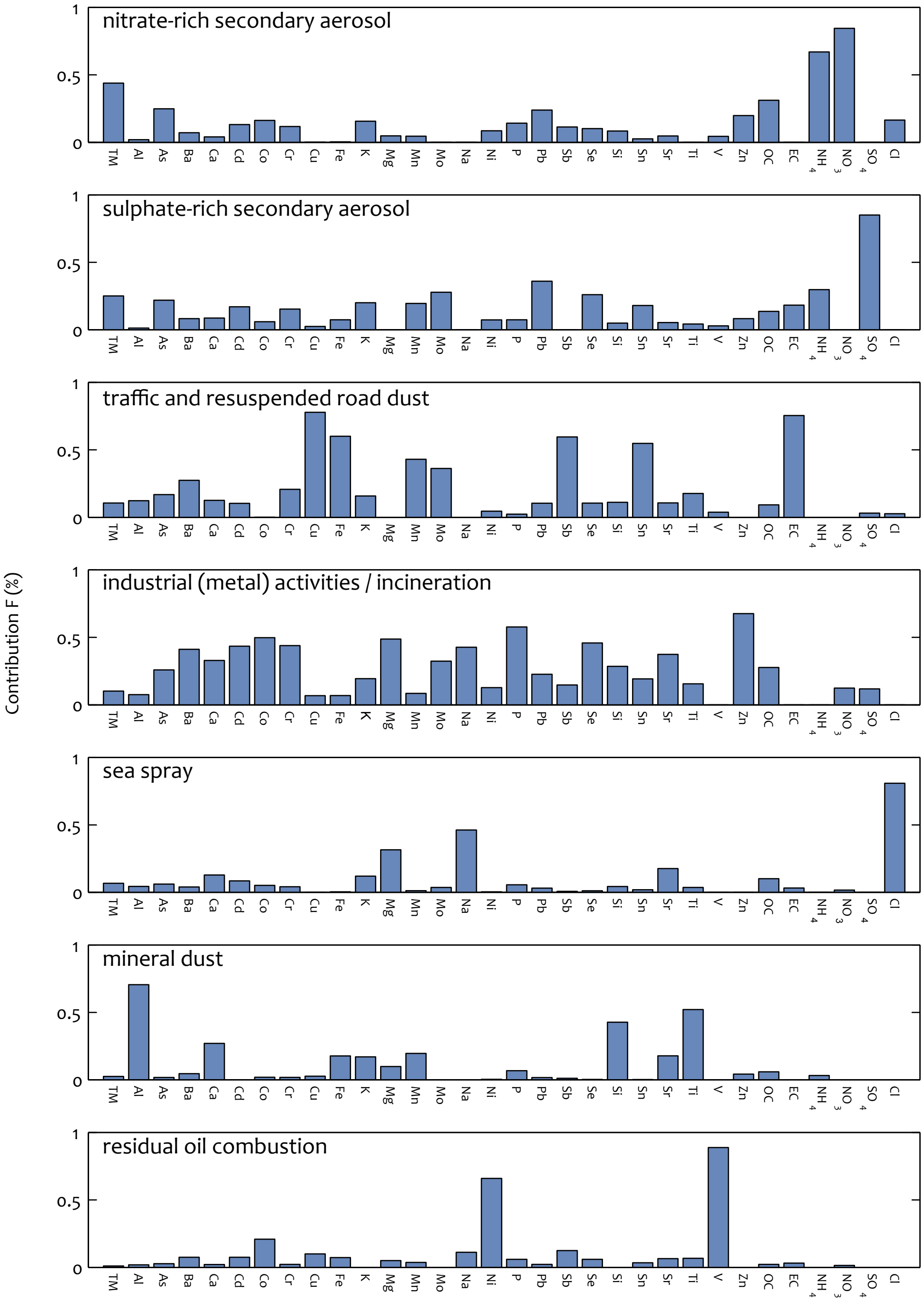
### 4.2.1 Identification of factors

#### Factor 1 (nitrate-rich secondary aerosol)

Factor 1 consists mainly of the secondary aerosol components nitrate and ammonium and is thought to be mostly the semi-volatile ammonium nitrate. A seasonal pattern in the mass concentration in this factor was expected, as temperature greatly affects the equilibrium of ammonium nitrate, ammonia, and nitric acid. Low temperatures during winter favour formation of the particulate form. Figure 4.3 shows the seasonal contributions in both the $PM_{2.5}$ and $PM_{10}$ data sets for this factor. The expected seasonal variation with a summer minimum was indeed found.

The concentration of ammonia in the Dutch atmosphere is such that, when sulphate is fully neutralised, a considerable amount is left to stabilise the ammonium nitrate. The origin of nitrate is the oxidation of $NO_2$ emitted by combustion

**Source compositions for the $PM_{2.5}$ data set** **Figure 4.1**



*Calculated source profiles for $PM_{2.5}$. The bars indicate the relative contribution (%) of the profile to the total mass of each component. Note that, in terms of percentage, a small contribution may be associated with a larger mass contribution rather than with a large relative contribution, depending on the respective concentrations.*

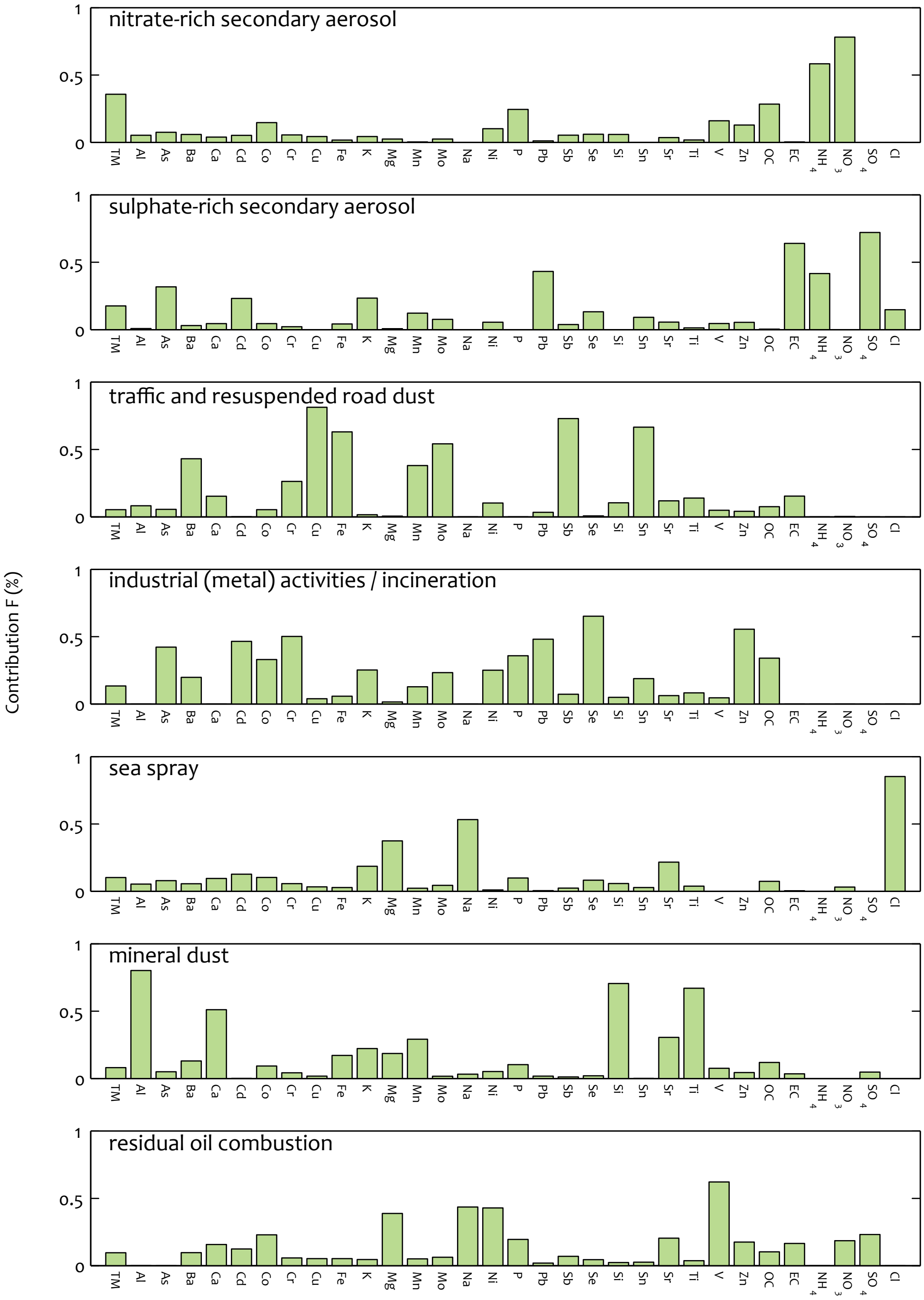
processes, mainly from traffic. Although sources that emit nitrogen oxides generally also emit carbonaceous material, they are not closely coupled, as the primary carbonaceous and secondary nitrate are expected to behave quite differently. Only some OC is associated with this profile. This is not unrealistic, as some of the OC is thought to be semi-volatile, similar to ammonium nitrate. In our study, factor 1 was categorised as 'nitrate-rich secondary aerosol'.

### Factor 2 (sulphate-rich secondary aerosol)

Factor 2 contains secondary aerosol, mainly sulphate. Furthermore, this factor contains substantial amounts of OC

### Source compositions for the PM$_{10}$ data set

**Figure 4.2**

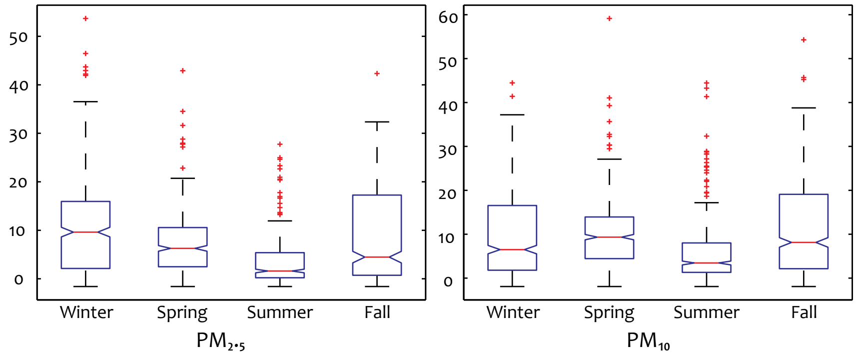


*Calculated source profiles for PM$_{10}$. The bars indicate the relative contribution (%) of the profile to the total mass of each component. Note that, in terms of percentage, a small contribution may be associated with a larger mass contribution rather than with a large relative contribution, depending on the respective concentrations.*

and EC, and the indicators for oil combustion V and Ni are also present (Olmez *et al, 1988*). The origin of the sulphate is the atmospheric oxidation of $SO_2$ and is associated with long-range transport. The $SO_2$ originates from the combustion of sulphur-containing fuels. The concurrence of the secondary aerosol and the indicators for oil combustion suggest that oil combustion contributes as a source of the precursor $SO_2$. As expected, the seasonal variation of factor 2 resembles the long-term average of sulphate (Weijers et al., 2010). Factor 2 was categorised as ‘sulphate rich’.

## Seasonal contributions for "nitrate-rich secondary aerosol" (full dataset)

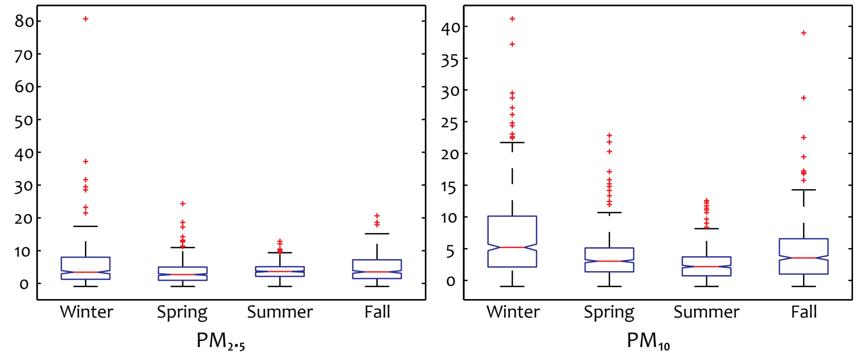
**Figure 4.3**



*Seasonal contributions for the factor identified as "nitrate-rich secondary aerosol'. Results for the $PM_{2.5}$ (left) and $PM_{10}$ (right) data set are given.*

## Seasonal contributions for "sulphate-rich secondary aerosol" (full dataset)

**Figure 4.4**



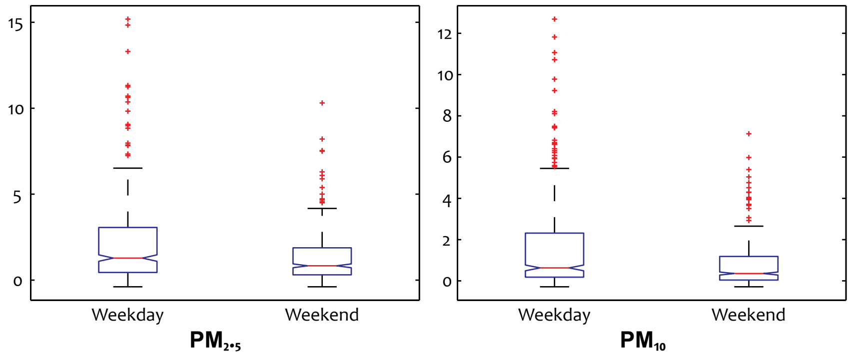
*Seasonal contributions for the factor identified as 'sulphate-rich secondary aerosol'. Results for the $PM_{2.5}$ (left) and $PM_{10}$ (right) data sets are given.*

The sulphate factor for the $PM_{10}$ data set, surprisingly, contains a larger amount of EC than that for $PM_{2.5}$. Previous studies have shown that carbon and tracer elements typically become associated with the secondary sulphate-rich aerosol, in both fine and coarse fractions (Ramadan *et al.*, 2000; Song *et al.*, 2001; *Kim et al.*, 2003; Lui *et al.*, 2003).

### Factor 3 (traffic and resuspended road dust)

Factor 3 consists mainly of elemental carbon (EC), a small amount of organic carbon (OC), and is associated with a range of metals (e.g. Fe, Cu, Ba, Mn, Mb, Sb, Sn). The large contribution of EC, a component released during combustion, along with these metals, suggests that factor 3 can be labelled as traffic emissions. The EC represents the exhaust emissions. Metals, such as iron, are associated with mechanical wear (Hildemann et al., 1991). Several studies have linked high concentrations of copper to brake wear (Sternbeck et al., 2002; Laschober et al., 2004; Denier van der Gon et al., 2008), whereas Barium (Ba) emissions are linked to tyre wear (Fernández-Espinosa and Ternero-Rodríguez, 2004). Molybdenum (Mb) is used as an additive in lubricants and is also released in the environment during the combustion of fossil fuels, explaining the contribution of molybdenum in this factor (Salminen et al., 2005). Thus, factor 3 was categorised as 'traffic and resuspended road dust'. Specific weekday/weekend variations were observed, as expected of a traffic source (See Figure 3.8). It should be noted that the enrichment of this factor with crustal elements is low, suggesting that dust resuspension from traffic is not a major source. This may be due to the fact that only one street location at a busy intersection was used here, which may not be representative of general conditions. In short, the low contribution of mineral dust at the street location needs to be verified, in the future.

**Seasonal contributions for "traffic and resuspended road dust" (full dataset)** **Figure 4.5**



*Weekday and weekend contributions for the factor identified as 'traffic and resuspended road dust'. Results for the* $PM_{2.5}$ *(left) and* $PM_{10}$ *(right) data set are given.*

Similar source composition is found for the $PM_{10}$ data set, except for the lower fraction of EC, as observed above. A low contribution of the resuspended road dust is present, but the fractions for the tracers associated with CRM are lower. Barium seems to be a more specific tracer in the $PM_{10}$ data set compared to in the $PM_{2.5}$ data set.

### Factor 4 (industrial (metal) activities / incineration)

Factor 4 contains large fractions of a host of metals that could not be identified as a single source. High concentrations of zinc, lead, nickel, cobalt and arsenic are mainly contributed by industrial activities, such as coal and waste combustion (Marcazzan et al., 2001; Salminen et al., 2005; Pacyna, 2001). Chromium, zinc, cobalt and strontium are also associated with steel processing and other metallic industrial activities (Salminen et al., 2005; Song et al., 2001; Lee et al., 1999). The main sources of calcium are cement factories, dust and fertilisers. Phosphorus, potassium, magnesium and cobalt in this factor could also be associated with fertilisers (Salminen et al., 2005). Based on the elemental composition of this source, it seemed to be a mixture of many different sources, not limited to waste incineration, (coal) combustion, metallic industrial activities and fertilisers. The profile is summarised as industrial activities and incineration

The $PM_{2.5}$ profile contained some nitrate and sulphate, suggesting at least part of this source could be considered global. The $PM_{10}$ profile did not contain these elements, suggesting primarily a local contribution. The latter may be from enrichment of the short-lived coarse mode particles with metals, not present in the finer fraction.

### Factor 5 (sea spray)

Factor 5 contains increased fractions of sodium, magnesium, chloride and, to a lesser extent, potassium. These tracers are mainly associated with sea salt particles. Hence, labelling this factor was straightforward and factor 5 was categorised as 'sea spray'.

It should be noted that sea salt also contains some sulphate. However, no sulphate was ascribed to this factor, in both the $PM_{2.5}$ and $PM_{10}$ profile, although in factor 7 there is an impact of sea salt (Na) in the $PM_{10}$ profile. Some nitrate and sulphate was ascribed to that factor, and this may include sea salt sulphate. The fact that these components are not included in the corresponding $PM_{2.5}$ profile could indicate that it is coarse mode material, as could be expected for sea salt. Taking these matters into account, we felt that it would be difficult for a statistical method based on correlations to differentiate in 5% of the sulphate associated with sea salt, when sea salt and sulphate show a distinct anti-correlation in time.

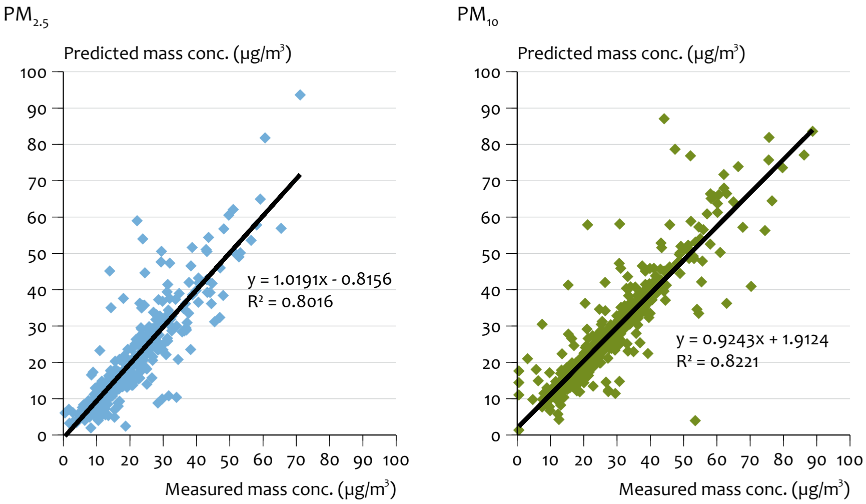
### Factor 6 (mineral dust)

Factor 6 contains the typical elements of mineral dust. These are particularly silicon, aluminium, and titanium, but also calcium and iron. We refer to Denier van der Gon et al. (2010) for a detailed discussion on mineral dust indicators. They showed an excellent correlation between silicon, aluminium and titanium. The factor also includes some organic carbon (OC), as is reported by many authors (Lewis *et al.*, 2003; Lee *et al.*, 2006) and points to detritus from vegetation and other organic soil constituents. Factor 6 was categorised as 'mineral dust (MD)'.

### Factor 7 (residual oil combustion)

Factor 7 contains significant fractions of measured vanadium and nickel concentrations, especially in the fine fraction of PM. Together with EC and OC, these are the tracers for oil combustion and incineration,. Typically, sources of oil combustion are shipping, municipal district heating power plants, and industrial power plants using heavy oil. A recent study by Vallius (2005) showed inland shipping via canals can also be considered a source of particulate matter. The $PM_{10}$ source profile also contains sea salt aerosol elements (sodium and magnesium), although the profile lacks chloride. Furthermore, a small amount of nitrate and sulphate were found in this profile. In other studies, this factor is not always part of the series of source profiles. Factor 7 was categorised as 'residual oil combustion'. As some of the

**Measured PM mass versus calculated PM mass (7 profiles, for all receptor sites)** **Figure 4.6**



*Comparison of measured mass and apportioned mass at all receptor locations ($PM_{2.5}$: 5 locations; $PM_{10}$: 6 locations) for both the $PM_{2.5}$ (left, in blue) and the $PM_{10}$ (right, in green) data sets, based on the contributions of all factors. The solid black lines are the linear regression results.*

species in the $PM_{10}$ profile are of marine origin, this would suggest that contribution from residual oil combustion would mainly be found in marine air masses transported to the various locations. Hence, the sources are located offshore or somewhere between coast and measurement location.

### 4.2.2 Check of apportioned mass by EPA PMF

By using the measured total mass in the PMF analysis as a total variable, albeit one with high uncertainty to prevent much influence on the solution, we calculated the predicted mass contributions for each source. These contributions could be summed up to give the predicted total mass for each day, and the resulting value could then be compared with the measured mass for a particular day. By making a simple plot of the predicted mass versus the measured mass, and calculating the correlation coefficient (Figure 4.6), we were able to determine whether the 7 factor model used in this case would  accounts for an accurate description of the total measured PM mass. The correlation coefficients for this 7 factor model are 0.8016 and 0.8221 for the respective $PM_{2.5}$ and $PM_{10}$ data sets, revealing that this model indeed describes the apportionment of measured mass to sources reasonably well. The correlation coefficients correspond well with results from the Bronstof study (Bloemen et al., 2008).

## 4.3 Location-specific source apportionment

This section first examines the results from the source apportionment for all locations, separately. Subsequently, more detailed results are illustrated for the urban background location of Schiedam.

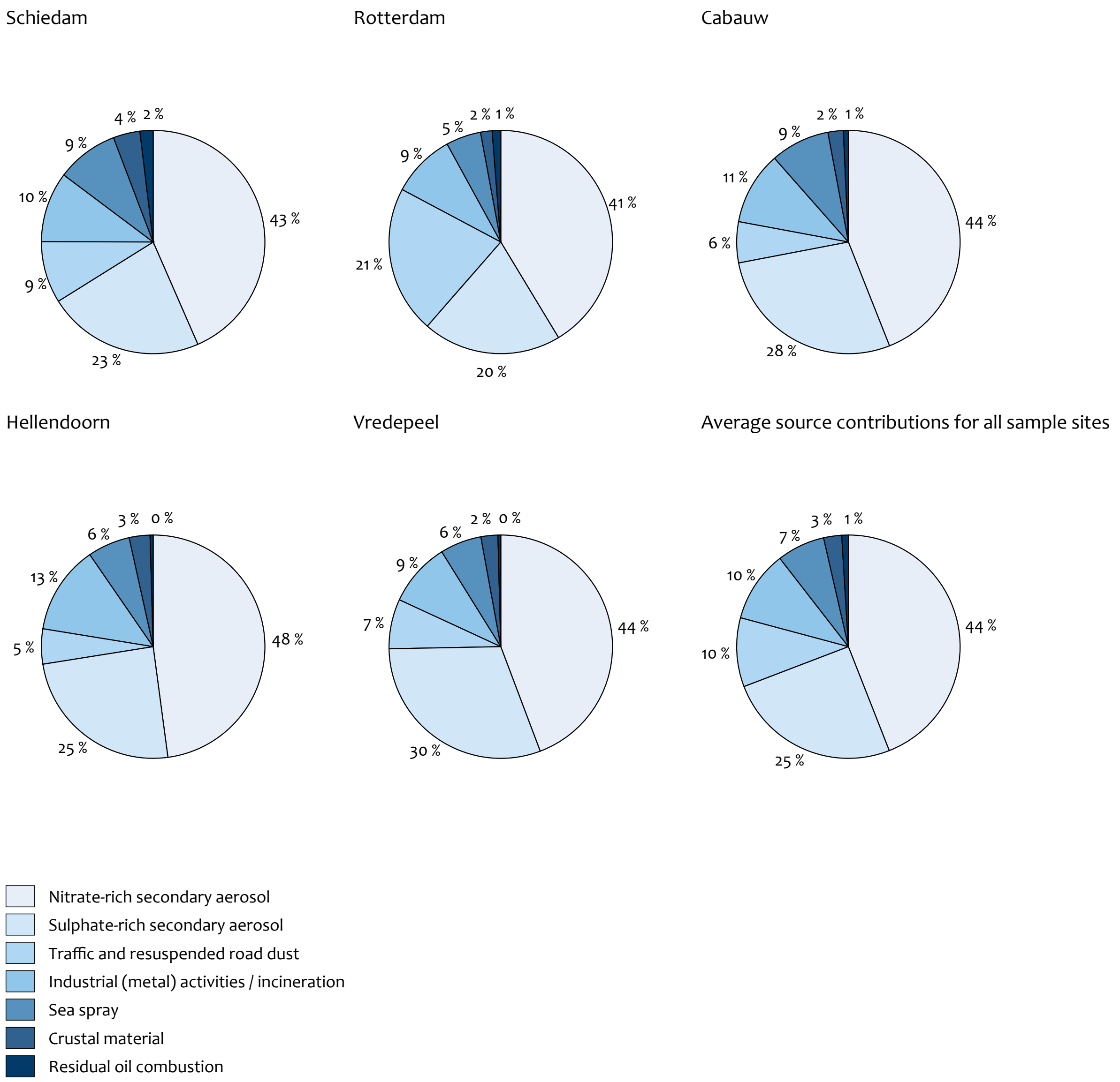
### 4.3.1 Overview of all locations

We assumed there to be little variance between the elemental compositions of the source profiles within the Netherlands, and all data were pooled prior to the PMF analysis. Hence, the main variability was expected to be found in the contribution of each factor at the different locations. Thus, following the PMF analysis, the source contributions once more were separated into the original five locations. The resulting contribution of each factor to the $PM_{2.5}$ and $PM_{10}$ mass is shown in the respective Figures 4.7 and 4.8.

The largest part of the $PM_{2.5}$ mass consisted of the first two factors: nitrate- and sulphate-rich secondary aerosol. Together, these two factors represented on average 69% of the $PM_{2.5}$ mass. The nitrate-rich factor dominated, with on average 44%, compared to 25% for the sulphate-rich factor. The highest contribution was found at the rural locations, located away from the coast. The lowest contribution was found at the traffic location in Rotterdam, explained by contributions from other, local sources in the form of traffic-related emissions. At Rotterdam, they contributed about 21% to the fine particulate mass, whereas at the rural locations a contribution of 5 to 7% was found. Industrial metallic activities and incineration contributed about 10 % at all locations. Sea salt showed a rather steady, relative contribution, as well, although the absolute concentrations a Rotterdam and Schiedam were higher than in the rural locations. Again, the additional sources in the urban environment explain the low observed variability in the relative contribution. The final contribution, from residual oil combustion, was low at all locations, although a maximum was observed at the urban background location of Schiedam.

The secondary inorganic factors contributed relatively less to $PM_{10}$ than to $PM_{2.5}$. On average, these factors explained slightly more than half (54%) the $PM_{10}$ mass. Similarly, the lowest contributions were found at Schiedam and Rotterdam. The relatively high contribution of these factors to $PM_{10}$ at the traffic location of Breda may have been due to the fact

**Calculated source contributions for $PM_{2.5}$** **Figure 4.7**



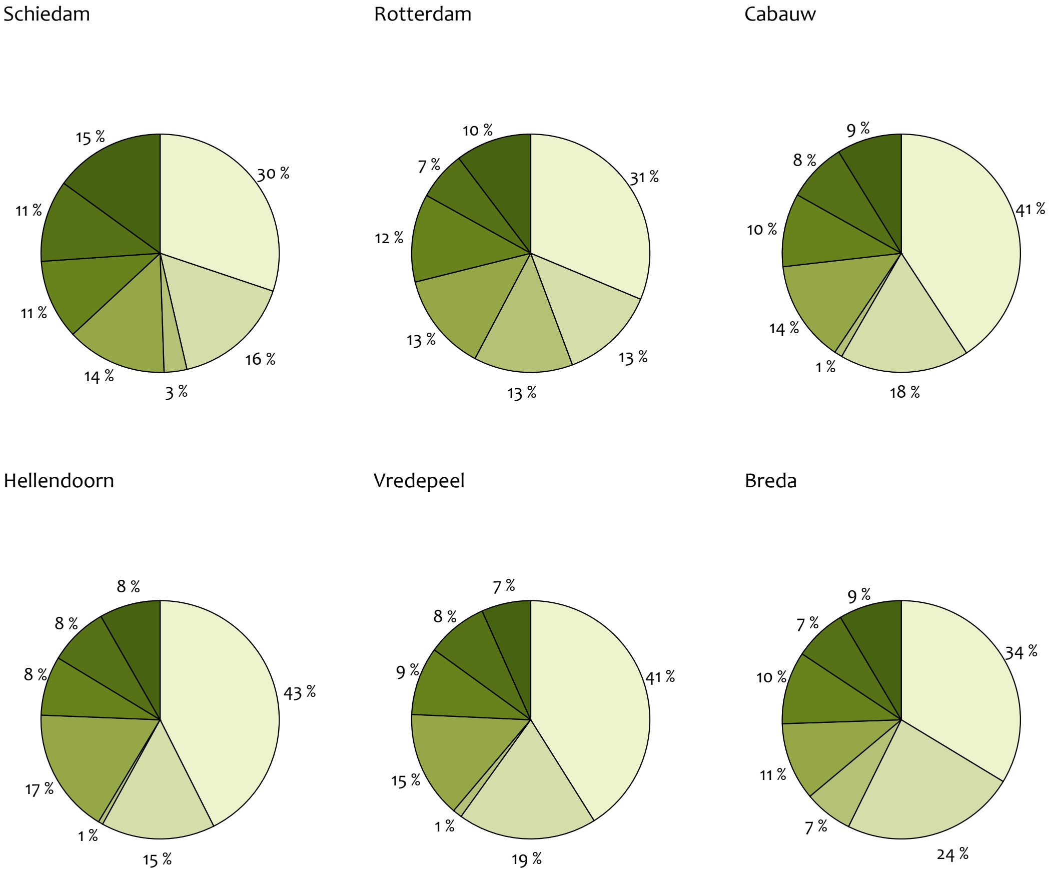
*Source apportionments for $PM_{2.5}$, at selected locations (top left diagram is urban background, mid-top diagram is traffic-related and remaining diagrams are rural background locations).*

that the city is located further inland. At both traffic locations, the traffic factor was increased, as expected. Industrial metallic activities and incineration contributed about 14% at all locations. Sea spray, mineral dust and residual oil combustion contributed between 24 and 28% to $PM_{10}$. The higher contribution in $PM_{10}$ compared to $PM_{2.5}$ reflects the dominant presence of the related tracers in the coarse mode. The three factors contributed about evenly to $PM_{10}$, although a slight increase towards the coast was observed for sea salt. Residual oil combustion showed a maximum contribution in the urban background location of Schiedam. The increase in importance of this factor compared to $PM_{2.5}$ may be explained by the significant contribution of sea salt and associated secondary inorganic aerosol to this factor for $PM_{10}$.

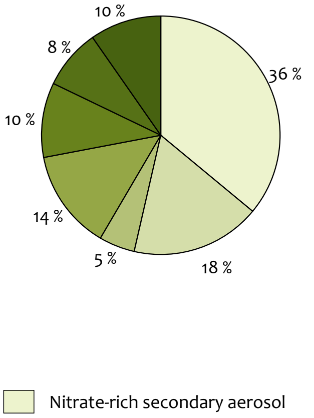
In general, the contributions of all factors showed a consistent picture over all locations. To further address the spatial distribution of the calculated source contributions we calculated the coefficients of divergence (COD). The COD is a coefficient used for determining the resemblance between objects or the variables describing these objects. Several studies have used the COD to provide information on the degree of uniformity of source profiles between monitoring locations (Kim et al., 2005; Kim and Hopke, 2008). For the spatial distribution, the COD approaches zero if the source contributions at the two locations are similar. In case the source contributions are very different, the COD approaches unity. The calculated CODs for $PM_{2.5}$ and $PM_{10}$ are shown in Figure 4.9.

The factor sulphate-rich secondary aerosol in $PM_{2.5}$ showed small spatial variability. All combinations of locations yielded almost the same CODs. This behaviour has also been found by several previous studies into the sulphate-rich secondary

**Calculated source contributions for PM$_{10}$ at the different sample sites** **Figure 4.8**



Average source contributions for all sample sites



*Source apportionments for PM$_{10}$, at selected locations (top left diagram is urban background, mid-top diagram is traffic-related and remaining diagrams are rural background locations).*

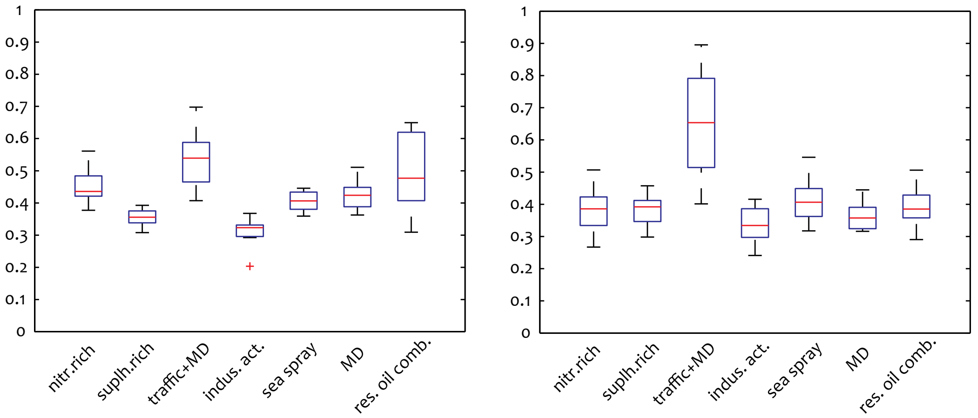
**Overview of the contributions from the $PM_{2.5}$ data set for each location, as used in this study** **Table 4.1**

| Source | Schiedam | Vredepeel | Rotterdam | Cabauw | Hellendoorn |
|---|---|---|---|---|---|
| *nitrate-rich secondary aerosol* | 43% | 44% | 41% | 44% | 48% |
| *sulphate-rich secondary aerosol* | 23% | 30% | 20% | 28% | 25% |
| *traffic and resuspended road dust* | 9% | 7% | 21% | 6% | 5% |
| *Industrial (metal) activities / incineration* | 10% | 9% | 9% | 11% | 13% |
| *sea spray* | 9% | 6% | 5% | 9% | 6% |
| *mineral dust* | 4% | 3% | 2% | 2% | 3% |
| *residual oil combustion* | 2% | 0% | 1% | 1% | 0% |

**Overview of the contributions from the $PM_{10}$ data set for each location, as used in this study** **Table 4.2**

| Source | Schiedam | Vredepeel | Rotterdam | Cabauw | Hellendoorn | Breda |
|---|---|---|---|---|---|---|
| *nitrate-rich secondary aerosol* | 30% | 41% | 31% | 41% | 43% | 34% |
| *sulphate-rich secondary aerosol* | 16% | 19% | 13% | 18% | 15% | 24% |
| *traffic and resuspended road dust* | 3% | 1% | 13% | 1% | 1% | 7% |
| *municipal solid waste incineration, (coal) combustion, metallic industrial activities fertilizers* | 14% | 15% | 13% | 14% | 17% | 11% |
| *sea spray* | 11% | 9% | 12% | 10% | 8% | 10% |
| *mineral dust* | 11% | 8% | 7% | 8% | 8% | 7% |
| *residual oil combustion* | 15% | 7% | 10% | 9% | 8% | 9% |

**Coefficients of divergence (COD) for identified $PM_{2.5}$ sources (left; N=5) and $PM_{10}$ sources (right; N=6)** **Figure 4.9**

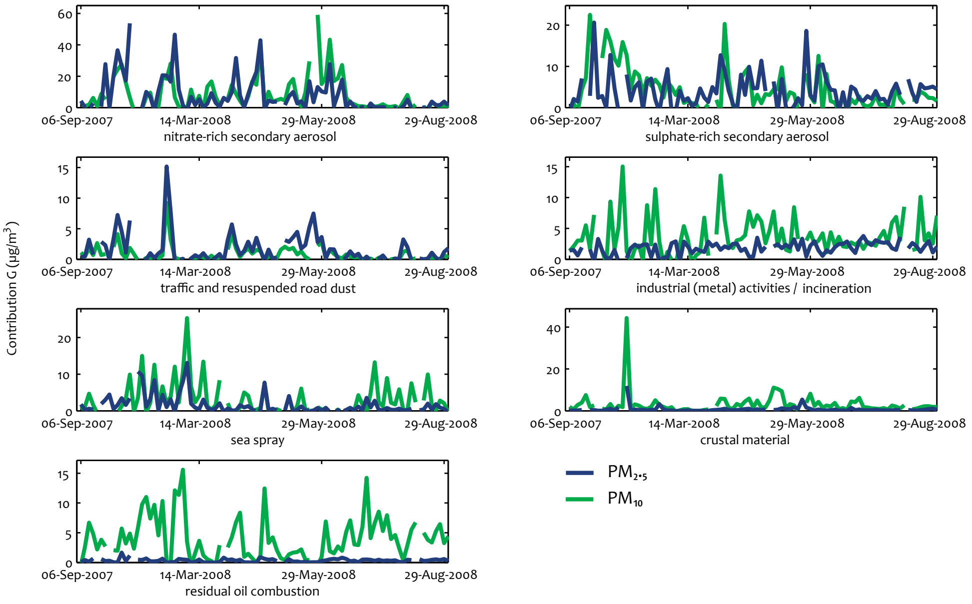


*Coefficients of divergence (COD) for identified $PM_{2.5}$ sources (left) and $PM_{10}$ sources (right), obtained from 5 and 6 monitoring locations, respectively.*

aerosol profile (Kim et al., 2005; Kim and Hopke, 2008). The importance of long-range transport into and across the monitored area is reflected in the small spatial variability. The factor nitrate-rich secondary aerosol in $PM_{2.5}$, on average, also showed a relatively small spatial variability. However, The COD for nitrate tended to increase as a function of distance. Hence, the highest COD value was found between Hellendoorn and Schiedam (0.56). The larger range in COD values indicated a larger gradient and a smaller correlation distance within the Netherlands than that of the sulphate-rich factor. This can be explained by the nature of ammonium nitrate, a semi-volatile component, and therefore more variable depending on ambient conditions and precursor gas concentrations.

A significant larger spatial variability was found for the traffic factor. As expected, the largest CODs for this factor were found between the urban/traffic locations and the rural locations, confirming that the contribution from this source is local in the urban environment. The increase in COD values from $PM_{2.5}$ to $PM_{10}$ highlights the effect of traffic-induced, (coarse mode) metal concentrations (i.e. Fe, Cu, Ba). The $PM_{10}$ COD between Rotterdam and the rural locations was much larger than between Breda and the rural locations. The reason may have been that the measuring location of Breda was located in the middle of a street with flowing traffic, whereas in Rotterdam it was located in a large traffic junction with associated heavy braking and accelerating, yielding more wear and abrasion emissions. Interestingly, the low COD values at the rural locations indicated that in the

**Schiedam: Time series contribution plots for 7 profiles** **Figure 4.10**



*Time series contribution plots for 7 profiles for the location at Schiedam. The blue line represents the results for $PM_{2.5}$ and the green line for $PM_{10}$.*

rural background the source contribution behaved similarly. This may indicate a traffic-related background across the Netherlands originating from distant sources. In our opinion, the PM did not originate from a distant source, but rather was due to the diffuse but highly correlated nature of traffic emissions over time. This also had been suggested earlier by Schaap et al. (2007), who found a very strong correlation for measured black smoke concentrations at rural background locations between different regions in the Netherlands. With the use of model calculations, the authors proved that most of the traffic emissions (for EC) had a national origin. It is expected that the same would apply to this factor.

As for the sulphate-rich secondary aerosol, the industrial (metal) activities / incineration profile had a small spatial variability. This may indicate a distant origin and long-range transport into and across the monitored area. However, the profile probably reflects a host of different sources that may have been very diffuse. Also, none of the locations reflected an industrial area where these sources could have been located. Hence, with respect to this source, all locations could be regarded as background, which could also explain the low spatial variability in behaviour of this factor.

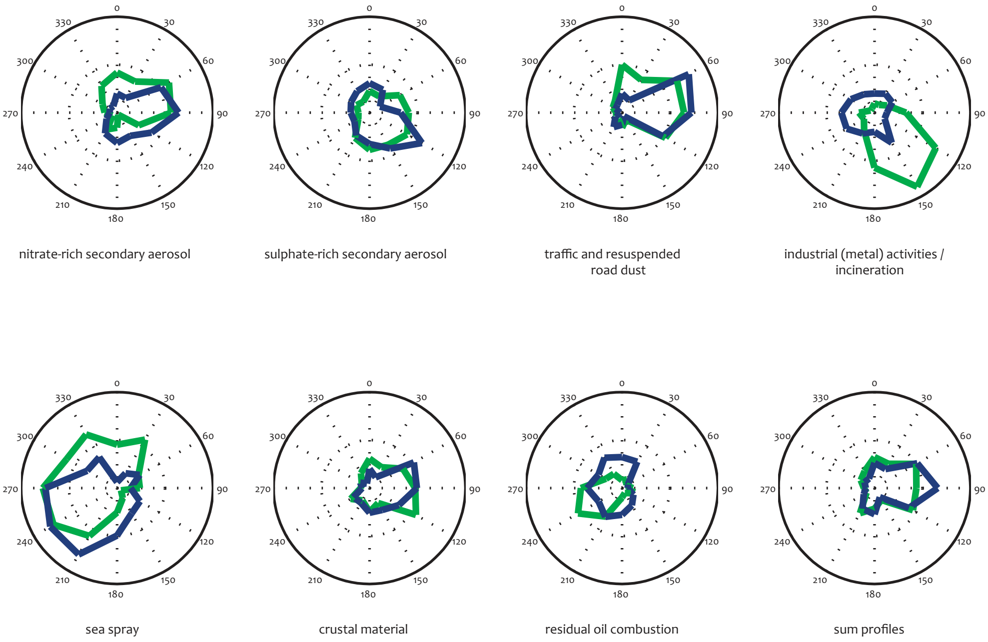
Factor 5, sea salt, also showed a small spatial variability with not much of a COD gradient from west to east. This was to be expected, as all locations were relatively close to the coast (<100 km), and sea spray aerosols would have been high at all locations, because of transport from the sea. The high correlation as observed by Manders et al. (2009) explains the low COD values found here. The COD values for mineral dust were very similar to those of sea spray. This result was surprising, as the sources for mineral dust are many compared to the single distinct source for sea salt. It was postulated that COD values could have been dominated by a Saharan dust episode that was observed during the sampling period, which yielded peak concentrations on the same day for all the locations. However, removing these episode days from the analysis did not impact the COD value, falsifying this hypothesis.

Finally, the second-largest spatial variability was found for the residual oil combustion source in $PM_{2.5}$. The variability between combinations of locations for this factor was also large. The COD between Schiedam and Rotterdam was the lowest, at 0.31. The difference between the Rotterdam area and the measuring locations in the eastern part of the Netherlands was almost twice as high. The higher source contribution in the area, as well as the low COD between Schiedam and Rotterdam indicated that the sources for the Rotterdam area could be considered mostly local. Considering the harbour activities nearby, this seemed quite plausible. The shift to lower COD values in the $PM_{10}$ fraction could be explained by the dominating mass contribution of aged marine air in the $PM_{10}$ source factor.

### 4.3.2 Further analysis: Schiedam

The interpretation of the results from the Positive Matrix Factorization (PMF) could be extended by investigating the temporal behaviour in the source profiles, as well as their variability according to meteorological conditions. Below, the result from such an exercise is illustrated for the urban background location of Schiedam. Schiedam provides an interesting case as the urban background location is situated within the Rotterdam area, which has almost 600,000 inhabitants and is influenced by refineries and harbour-related activities.

**Schiedam: CPF plots for 7 profiles, threshold: upper 25th percentile** **Figure 4.11**



nitrate-rich secondary aerosol; sulphate-rich secondary aerosol; traffic and resuspended road dust; industrial (metal) activities / incineration

sea spray; crustal material; residual oil combustion; sum profiles

*CPF plots for the seven profiles and for the sum of the profiles, using the wind data from meteorological station 344 at Rotterdam Airport. The blue line represents the results for $PM_{2.5}$ and the green line for $PM_{10}$.*

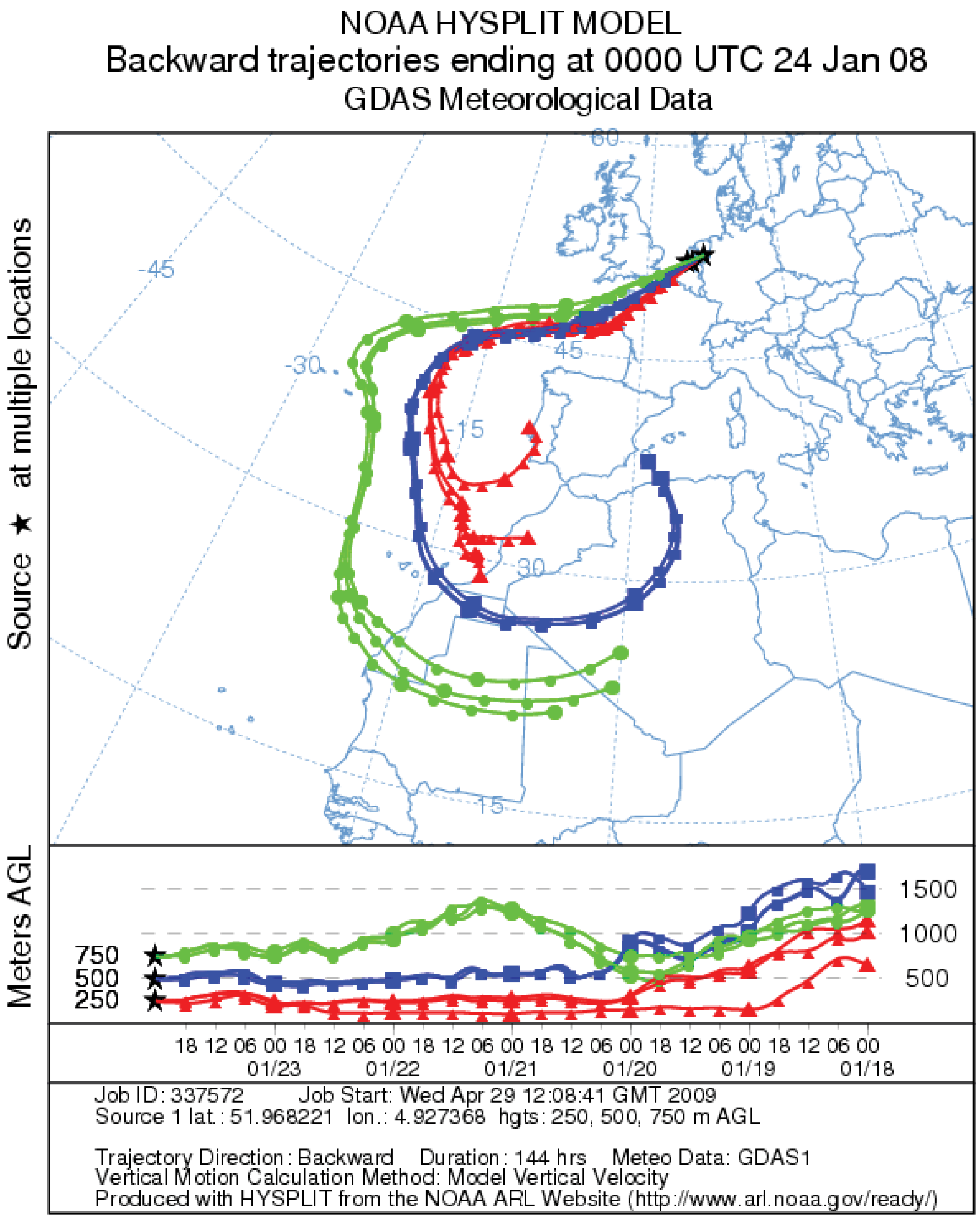
Figure 4.10 presents the time series contribution plots for the 7 profiles for both data sets. Besides providing information about certain events on several days for the sources, the plots also provide some information about the contributions of each source in each fraction. When the time series for a specific source are more or less similar, this could indicate that the majority of the contribution from this fraction would be present in the $PM_{2.5}$ fraction. For example, in the plot below, the lines for both $PM_{2.5}$ and $PM_{10}$ are fairly similar for the factor labelled ‘nitrate-rich secondary aerosol’. This is an indication of this source being primarily found in the $PM_{2.5}$ fraction and not in the $PM_{2.5\text{-}10}$ fraction. Examples of the contrary are the ‘sea spray’ and ‘mineral dust’ factors. Although there seemed to be a fair amount from both sources in the $PM_{2.5}$ fraction, the majority of the contributions from these sources could be found in the $PM_{2.5\text{-}10}$ fraction, as was found in the mass closure.

The Conditional Probability Function (CPF) was used to determine the directions in which sources were likely to have been located. The CPF was calculated using the source contributions from the PMF analysis and the wind direction values measured at a meteorological station nearby. For the measuring location at Schiedam, the nearest meteorological station is that of the Royal Netherlands Meteorological Institute (KNMI, station no. 344), near Rotterdam Airport. To match PM data and hourly wind data, all the daily average source contributions were assigned to the 24 hours in the corrsponding day, as proposed by Kim *et al,* 2003.

As can be seen in Figure 4.11, the contribution from the industrial (metal) activities / incineration source seemed to be coming predominately from the south-east and west. The highest contributions to the PM mass were from sources located east of the measuring location at Schiedam. This seemed a general feature of PM in the Netherlands. Most of the anthropogenic sources pointed in that direction. Transport from (south)easterly directions is associated with stagnant and strong accumulating conditions and brings continental, polluted air to the measuring locations. As expected, the contribution from sea spray was found in a south-western direction pointing to the Atlantic Ocean and the North Sea. Contributions from residual oil combustion came from west of the measuring location, but a dominant source may have been located in a north-western direction. From a south-western direction, contributions seemed to be coming from the ‘Botlek/Pernis’ area. Contributions from residual oil combustion sources were high on 21 and 29 December 2007, at the measuring locations at Schiedam and Rotterdam, for $PM_{2.5}$. For 21 December, several refineries in that area reported gas flares and problems with their installations, which indicates that the area may have contributed significantly. When taking into account that the $PM_{10}$ profile associated with this factor was dominated by aged marine air that came from the same direction as the contributions from residual oil combustion, this would explain the large difference between the two size fractions.

As $PM_{2.5}$ is also included in $PM_{10}$, wind roses were used to compare results for both components, as an indirect quality check on the PMF result. In other words, when the fine mode dominated, or the sources of the fine and coarse mode were the same, the wind rose for both situations should be quite similar. This was indeed the case for most factors. The residual oil combustion factor was different for both fractions, which showed a shift towards the south-west

**Backwards trajectories ending at 0000 UTC 24 January 2008** **Figure 4.12**



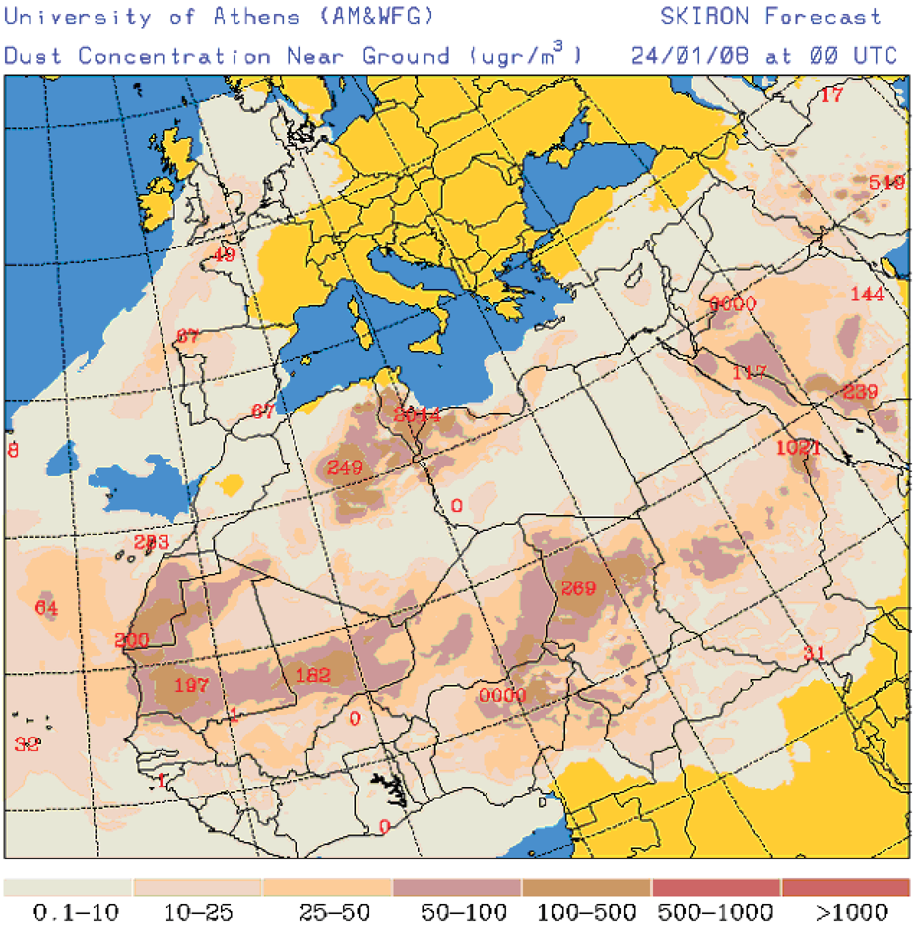
*Back trajectories ending at 0000 UTC on 24 January 2008, using heights of 250, 500 and 750 metres, providing dust forecasts calculated with HYSPLIT (upper) and SKIRON, generated by the University of Athens (Lower).*

in $PM_{10}$ compared to $PM_{2.5}$. This may have been associated with the additional contribution from sea spray to the factor for $PM_{10}$, which itself was associated with south-westerly winds. Another difference was observed, related to the metal activities and incineration. The fine mode did not show a marked variability as a function of wind direction, except for a small increase at 150 degrees. For the factor in $PM_{10}$, the origin points indicates the exact same direction of 150 degrees. Hence, the coarse mode may have been associated with a local important source, whereas the metals in the fine mode may have derived from more diffuse or distant sources.

A high contribution from the mineral dust source was observed at all locations from 23 to 25 January 2008. It was difficult to discriminate between contributions from long-range PM transport, because these are frequently masked by local sources (Nicolás *et al.*, 2008). The mineral dust profile used in this study is a mixture of these local sources, as well as long-range sources. We successfully identified the Saharan desert as one of the long-range sources for mineral dust.

We used the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model for calculating back trajectories for air mass during this period. These back trajectories were used for determining the possible locations of both local

**SKIRON dust forecasts, generated by the University of Athens, for 24 January 2008** **Figure 4.13**



*Back trajectories ending at 0000 UTC on 24 January 2008, using heights of 250, 500 and 750 metres, providing dust forecasts calculated with HYSPLIT (upper) and SKIRON, generated by the University of Athens (Lower)*[1].

and rural sources. We calculated the back trajectories for 3 measuring locations (Schiedam, Cabauw and Hellendoorn) with 3 different end heights (250, 500 and 750 m ), for a time period of 6 days. The back trajectories for both the 500 and 750 metres originated from the Sahara Desert (See Figure 4.12). Hence, the high contributions from the mineral dust source found during the January episode were caused by sandstorms originating from the Sahara Desert. This is substantiated by the dust forecast, as generated by the University of Athens, which forecasted Saharan dust over the Netherlands and north-western Europe for 24 January 2008.

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[1] http://forecast.uoa.gr/dustindx.php (last visited 13 May 2009)

# 5

# Policy relevant interpretation and discussion

This chapter discusses the answers to the research questions as defined at the start of the project. The questions related to mass closure are discussed first, followed by those related to source apportionment. Finally, it presents our main findings.

## 5.1 What is the composition of particulate matter in the Netherlands?

Generally, there was considerable conformity in the chemical composition of particulate matter at different locations in the Netherlands. The dominant constituent were the secondary inorganic components (SIA). In particular, this was the case in $PM_{2.5}$ filter samples for which the relative SIA contributions at the various locations ranged between 42 and 48%, on average (6.0-8.4 µg/m³). SIA levels tended to be (slightly) higher at the rural locations, especially in the presence of local agricultural activity (at Cabauw). The second important contribution to $PM_{2.5}$ came from total carbonaceous matter (TCM) which showed a larger variation over the measurement locations: 22 to 37%. In contrast to SIA, TCM in $PM_{2.5}$ was higher at the urban locations, with a maximum of 41% at Rotterdam (6.1 µg/m³). Other constituents, such as sea salt (SS), mineral dust (MD), and metals, contributed considerably less: below 8% (maximum at Schiedam), and concentrations (much) smaller than 1 µg/m³. The unexplained part in the $PM_{2.5}$ mass fraction varied between 6 (Schiedam) and 20% (Cabauw). In absolute value, this was 0.7 and 3.5 µg/m³, respectively.

The average mass contribution of $PM_{2.5}$ to $PM_{10}$ was about two thirds. The contributions of the different chemical parts in $PM_{10}$ showed a resemblance with the $PM_{2.5}$ findings. Relatively speaking, the contributions of SIA and TCM to $PM_{10}$ were slightly lower than to $PM_{2.5}$ (SIA: 35-43%; TCM: 21-29%). Because of the dominance of sea salt and mineral dust in the coarse mode, their contributions were sometimes even twice as high (SS: 9-17%; MD: 4-9%; metals 4-9%) compared to $PM_{2.5}$. Their respective concentrations in $PM_{10}$ increased to 2.9 µg/m³ (SS, Rotterdam), 0.7 µg/m³ (MD, Cabauw) and 0.8 µg/m³ (metals, Rotterdam).

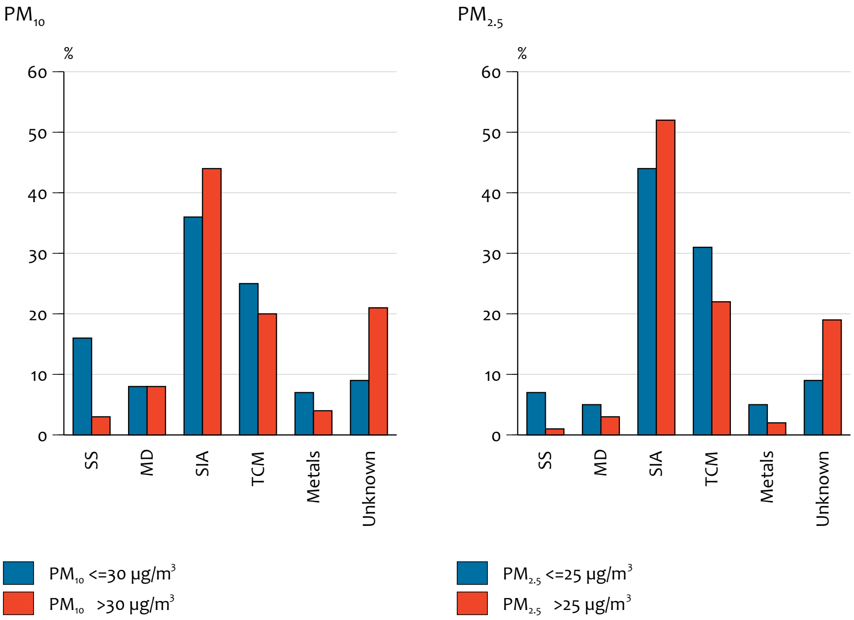
For the first time, a detailed overview of the chemical composition of the coarse fraction has been determined for the Netherlands. The composition in the coarse fraction showed a more even distribution of species. Compared to the fine fraction, SIA and TCM were less dominant with contributions of no higher than 29 and 25%, respectively. Larger contributions originated from mineral dust (23%, maximum at Cabauw) and sea salt (30%, Vredepeel and Schiedam). The metals summed to 16% (at Rotterdam). The unexplained mass in the coarse fraction was considerable, with amounts of between 3 and 21%, ( being lowest at Vredepeel and Cabauw).

## 5.2 What is the variation in composition as a function of location type?

Considering the role of location type on ambient chemistry, nitrate and ammonium showed clearly increased levels at the rural locations at Cabauw and Vredepeel, compared to the Hellendoorn location. The influence of local emissions is apparent here. For example, for $PM_{2.5}$, the following nitrate values were observed: 4.1 µg/m³ (Cabauw), 3.2 µg/m³ (Vredepeel), 3.0 µg/m³ (Rotterdam), 2.6 µg/m³ (Hellendoorn), and 2.5 (µg/m³) (Schiedam). The concentration at Rotterdam, to some extent, could be attributed to the formation of sodium nitrate The variation in sulphate in $PM_{2.5}$ was less (2.1-2.7 µg/m³), but we did observe a trend of slightly higher values in the western part of the country (Cabauw, Schiedam, Rotterdam), compared to locations in the east (Hellendoorn) and south (Vredepeel).

The TCM contribution at the traffic location at Rotterdam ($PM_{2.5}$: 6.8 µg/m³) was clearly higher than at its associated urban background location (Schiedam: 4.0 µg/m³), and at the rural locations in the BOP campaign (3.3-3.9 µg/m³). The increment in $PM_{2.5}$ was due to elemental carbon (3.2 versus 1.4-1.9 µg/m³), and, to a lesser extent, to organic carbon (2.8 versus 2.1-2.3 µg/m³), indicating that traffic emissions included OC. Further notable was the fact that part of TCM was also found in the coarse fraction, this was particularly the case at Vredepeel and Rotterdam, with concentrations around

**Change in chemical distribution in percentages for data subsets** **Figure 5.1**



*Change in chemical distribution, in percentages, in data subsets for PM$_{10}$<=30 (PM$_{2.5}$<=25) and PM$_{10}$>30 (PM$_{2.5}$>25). Averages over the five BOP locations.*

1.7 µg/m$^3$. The OC contribution to this coarse part appeared substantial (>50%), at these location, and likely related to local agricultural sources.

A gradient was observed for sea salt contributions, with maximum values at Rotterdam and Schiedam (PM$_{10}$: 2.9-3.7 µg/m$^3$), and low values at Hellendoorn and Cabauw (<2.0 µg/m$^3$). The change was most prominent for the coarse fraction, although the fine fraction still contained an average of between 25 and 30% of sea salt aerosol. The rather high value at Vredepeel could not be well understood, but coincided with the increased TCM level and was therefore probably of local origin. Mineral dust hardly varied in the fine fraction (0.5-0.7 µg/m$^3$) over the five locations; its average fine-to-coarse ratio (0.35) was only slightly larger than that of sea salt. Differences were more prominent in the coarse fraction between urban (>0.9 µg/m$^3$) and rural (<0.8 µg/m$^3$) locations. A maximum value observed at Cabauw (1.4 µg/m$^3$) was likely due to a local effect (resuspension of natural dust). It is further noted that the increments in MD in PM$_{10}$ between Breda and Rotterdam, and Breda and Schiedam, were negligible (< 0.2 µg/m$^3$).

## 5.3 Is the composition different on exceedance days, compared to non-exceedance days?

It was not possible to evaluate exceedance days, as their number in the data set was too small to allow a statistical evaluation. The PM$_{10}$ and PM$_{2.5}$ data sets were therefore each divided into two subsets, separating concentration values below and above 30 µg/m$^3$ for PM$_{10}$ and 25 µg/m$^3$ for PM$_{2.5}$. As anticipated, absolute contributions of most constituents rose as PM levels went up. However, this did not occur at the same rate for each constituent (see Figure 5.1). The largest increase was observed for SIA, most notably nitrate, and the missing part of the mass. Only sea salt levels decreased at higher PM levels. As a consequence, the chemical was ere different at higher PM concentrations: SIA and the ununknown part were more dominant, the contribution of mineral dust remained the same, while the importance of TCM and sea salt decreased (in a relative sense).

The variability in PM concentrations was largely influenced by the variability in large-scale meteorological situations. High concentrations of PM$_{2.5}$ and PM$_{10}$ occurred on days with stagnating weather conditions or under slow transport coming from the south, south-east or east. In such situations, weather conditions are fair and removal from the atmosphere is low, due to the absence of rain. As emissions are diluted less, due to low wind speeds, removal from the air is low and pollution starts to build up. During the winter period, the effect is strengthened, due to shallow planetary boundary layers. All components rise on a day with high PM concentrations, with the exception of sea salt, as continental air masses are transported over the Netherlands during these days. Model studies show high contributions from national sources to concentrations of primary material and ammonium nitrate (Schaap and Denier van der Gon, 2007; Denier van der Gon et al., 2009). Special events also contribute to a (small) number of exceedance days or days with high concentration levels. In the data set, we identified a substantial contribution of desert dust at the end of January 2008. Other events included fireworks on New Years Eve, fires at Easter, long-range transport of dust, and fire plumes.

## 5.4 What are the characteristics of the unexplained mass?

In this study, some 75% of the $PM_{10}$ and $PM_{2.5}$ mass could be identified, according to the components in the filter samples analysed in the chemical closure. To correct for known underestimations, we applied a number of algorithms to estimate various constituents. In addition to the correction from elemental concentrations to oxide concentrations, conversions were used for sea salt, sea-salt sulphate, total carbon matter, and mineral dust. Most of these recalculations (oxide concentrations, sea salt, total carbon material) improved the mass closure. For example, in case of $PM_{2.5,}$ the conversion from TC to TCM resulted in a decrease in unexplained mass of 5 to 9%. The closure was better for the urban locations, demonstrating this approach's sensitivity to location characteristics. As a result, the unexplained mass in $PM_{2.5}$ turned out to be rather small (<7%) at urban locations. At the rural locations (Hellendoorn, Vredepeel and Cabauw) this was 10, 17 and 20%, respectively. As the absolute SIA levels were more or less comparable at the five measurement locations, the closure seemed to correlate with the amount of (the next important constituent) TCM, which is predominantly present at locations influenced by traffic. However, dependence on the conversion factor (here 1.3) is moderate. Changing this factor with ±0.1 led to a change in unexplained mass of ±2 to 3% at the most.

In contrast to the fine fraction, the mass closure in the coarse fraction seemed better at rural locations (Cabauw and Vredepeel): here, the unexplained parts were less than 4% of the total mass (which, in absolute mass units, is negligible). However, at another rural location (Hellendoorn) it was 21% (1 $\mu g/m^3$), therefore, it appeared that the variability was rather large. Indeed, in the urban environment, 12% (Rotterdam) to 16% (Schiedam) of the coarse mass could not be accounted for; in absolute terms, this would be 1 to 1.5 $\mu g/m^3$. Obviously, the closure in the $PM_{10}$ filter samples was somewhere in between those of the fine mass and coarse mass, namely, 9% (Rotterdam) and 10% (Cabauw).

It was also found that the size of contribution of the unexplained mass would increase as the PM concentration levels rose. This was not only the case in absolute concentration units, but also in the (relative) chemical distributions. It could be established (at Rotterdam and Hellendoorn) that the unexplained mass fraction correlated with the SIA mass, which was no surprise as SIA is the main responsible constituent for the increase in PM. A possible reason for this may have been the amount of water attached to SIA. However, such a relation appeared absent in the coarse mass. There is no reason to believe that associated water should prefer the coarse mass over fine mass.

Water is a natural component of particulate matter. Hygroscopic salts on particles, such as ammonium nitrate and ammonium sulphate, attract water. Hence, water that is bound to particles also contributes to the PM mass measurements. Ideally, this water is removed by pre-heating the air sample or by conditioning the filters under dry (50% RH) circumstances, following the reference method (NEN12341). However, heating or drying only partly removes the particle-bound water, due to hysteresis (e.g. Speer et al., 2003). They report molar ratios of between 0.5 and 1.0 for water on particles of ammonium nitrate and ammonium sulphate, at a RH of 50% and 75%, respectively. $PM_{10}$ reference measurements are to be performed at a temperature of 20 °C and a relative humidity of 50%. We applied a molar ratio of 0.5 for water on particles of ammonium nitrate and ammonium sulphate. As such, we estimated the amount of water on $PM_{10}$ due to the presence of SIA to be about 10% of the SIA mass. This resulted in an estimated 4 to 5% of the $PM_{10}$ mass concentration. Such a contribution is possible as it is lower than the total unexplained mass. In short, water is expected to be an important, though not the sole, contributor to the unexplained mass.

A similar water uptake may be associated with sea salt. However, as the contribution of sea salt to the total mass is low, its water contribution would be much less than that of SIA. Likewise, the amount of water on organic carbon (OC) is unlikely to have played an important role, as hygroscopic OC is a fraction of the total OC amount and the amount of water bound to a unit of OC would be less than of SIA (Speer et al., 2003).

## 5.5 What are the most important source categories for $PM_{10}$ and $PM_{2.5}$ in the Netherlands?

In this study, five $PM_{2.5}$ and six $PM_{10}$ locations were used to estimate contributions and their sources. With the use of Positive Matrix Factorization (EPA PMF), seven sources for both fractions could be identified. These sources are:

1. Nitrate-rich secondary aerosol
2. Sulphate-rich secondary aerosol
3. Traffic and resuspended road dust
4. Industrial (metal) activities / incineration
5. Sea spray
6. Mineral dust
7. Residual oil combustion

The order of the factors reflects the mass of their contribution to $PM_{2.5}$. Nitrate-rich and sulphate-rich secondary aerosol profiles contributed most to the total $PM_{2.5}$ mass, at all locations. The contribution for both sources was relatively constant, although higher absolute contributions for both sources were found in the eastern part of the Netherlands, and lower relative contributions were found at the traffic location in Rotterdam. As expected, the profile for traffic and resuspended road dust was present at all locations, although contributions fluctuated. The highest contribution was found at the Rotterdam traffic location. Significant lower concentrations were found in urban and rural background locations. The contribution from industrial (metal) activities / incineration was also highest in Rotterdam. The wind rose plots suggested that the coarse mode of this factor may have been associated with a local important source, whereas the metals in the fine mode may have derived from more diffuse or distant sources. Sea spray clearly showed a west-to-east gradient, with higher concentrations in the western part of the country, near the North Sea, and lower concentration in the east. For mineral dust, a relatively constant contribution was found at all locations. A detailed examination of its daily contributions revealed specific contributions during a Saharan dust episode, as confirmed by back trajectories from the HYSPLIT model. The contribution from residual oil combustion showed high contributions nearby the highly industrialised Rotterdam harbour area. Contributions were also found at other locations, but to a much lesser extent. Wind rose analysis clearly placed the source to the south-west of the measuring locations. Considering that some of the species in the $PM_{10}$ profile were of marine origin, this would suggest the contribution from the residual oil combustion to be mainly found in marine air masses transported to these locations. Hence, these particular sources would have been located offshore, or in the Rotterdam harbour area.

## 5.6 What is the value of PMF compared to chemical mass closure?

Comparing results from the PMF to results from the chemical mass closure revealed a very similar picture at first glance. The majority of the mass was defined as the secondary inorganic fraction, which confirmed the important role of emissions of $NO_x$, $So_x$ and $NH_3$ in PM formation. Furthermore, sea salt and mineral dust were both also identified.

Finally, both approaches yielded a metal group. However, where the chemical mass balance would yield groups of components, the PMF provided insight into the combinations of components that have the same temporal variation. For example, the PMF combined soot with the components of copper and iron, and, as such, exhaust and wear emissions from traffic. Hence, chemical mass balance aims to define the total mass using information on the presence of components, whereas PMF provides insight into common origins of the different components. As such, the techniques are complementary and the added value of PMF is further discussed below.

In principle, PMF is independent and objective. No assumptions enter the procedure. Hence, the combinations of components are grouped together based on their correlated abundance in the atmosphere. Many components that are expected to stem from the same source, such as sodium, magnesium and chloride in the sea spray factor, are grouped together. As such, the technique confirms existing knowledge on source tracers, which is the main advantage of the procedure. However, a degree of subjectivity is introduced as the number of resulting source profiles depends on the interpretability of the factors. At some point, the information content is not strong enough to allow more factors, which results in factors with unrealistic features. Of course, there is always the danger that an unexpected or unidentified source is qualified as unrealistic.

Another disadvantage of the PMF is that it is based on a linear combination of factors and cannot cope with non-linear components. Consequently, the main separation is obtained in the primary components. The secondary aerosols are mainly grouped together and no source information is obtained. The same applies to the direct interpretation of the measured components, where gradients in primary components are used to identify sources, which is actually a common sense approach of the formal PMF. The origin of the specific secondary components, such as sulphate and nitrate, can only be addressed by using chemistry transport models with proper emission data.

Local sources were not identified in this study, as all data were combined in the PMF procedure. We believe that a PMF application on data sets obtained within a city or a limited region in the vicinity of different large industries or activities would yield a more effective use of the PMF technique. In our study, with locations spread over the whole of the country, we identified all mayor source categories. However, these could also be identified based on chemical composition and appreciation of the tracers. An exception was the separation of the traffic induced resuspension factor from total mineral dust and identification of the residual oil combustion.

Especially, the last with its relatively high contribution in the Rotterdam area illustrates the potential for the identification of local sources. It should be noted that a larger data set that used in this study (e.g. of a full year from one location) could yield much more interpretable information as the uncertainties would be reduced.

In short, the application of PMF complements the analysis based on the interpretation of the chemical data and independently confirms a large number of species as tracers for a specific activity or source. As such, we obtained more confidence in the interpretation of the data set at hand.

## 5.7 How do the source attributions based on PMF compare to those obtained from prognostic models?

Applying Positive Matrix Factorization (PMF) to the data set, in principle, provides independent and objective results, and confirms existing knowledge on source tracers, which is the main advantage of the procedure. In our study, with locations spread over the whole of the country, we identified only the mayor source categories. However, these could also be identified based on the chemical composition and the appreciation of the tracers. Furthermore, as PMF is based on a linear combination of factors, it yields source profiles with the secondary aerosols for which no further source separation is obtained.

Chemistry transport models (CTMs), however, use detailed emission information as input and are used to calculate concentration levels of specific species. The results are typically available in hourly maps over a region such as the Netherlands, or for Europe as a whole. In cases where there is confidence in the emission database, next to the ability of the model to correctly describe the formation, transport and removal of the pollutants, then the model could be used for assessing source contributions. For this purpose, scenarios could be used, in which certain activities are left out of the emission database to estimate their contribution. As such, it is possible to differentiate activities on a subsectoral level, for example, for different industrial activities, or as a function of fuels used in traffic. As such, one can differentiate many contributions in both primary and secondary components. Hence, the ability to address source contributions by using a model is much larger than when using PMF. Results from PMF are too general to make a detailed comparison.

The two techniques should therefore be used in conjunction. Chemistry transport models are only capable of assessing the source contribution of an activity when their emissions are characterised well. For example, up to a few years ago, the copper emission inventories regarded the metal industry as the largest source of copper emissions. Using these emissions, the models severely underestimated the observed concentrations. The inventories were revised once it became clear that copper is also emitted in brake wear. This fact was deduced from the high copper content of road run-off into the sewer system and was confirmed by our own and many other PMF studies linking copper to traffic emissions. Hence, for components with large uncertainties, PMF may provide additional indications regarding their origin. Also, using a CTM would only be warranted when the verification against measurements is such that the model can be used with confidence. In case of large uncertainties or components that are not included in the model, PMF may be a valuable asset. For example, within the BOP programme, we tested several sources of mineral dust for the first time in the LOTOS-EUROS model (Denier van der Gon et al., 2010). The results showed that traffic-induced resuspension could be a significant source. The PMF also yielded indications that the mineral dust was associated with traffic and confirmed the model analysis. Hence, applications of PMF could be used to some extent to verify modelled source contributions.

To assess the ability of national measures to reduce particulate matter concentrations it would be necessary to assess the contribution from national sources to the PM levels in the Netherlands. The information on the spatial distribution of such a source may provide some indications. The rather low coefficients of divergence (COD) between the rural locations indicated that, in the rural background, most of the source contributions behaved similarly. This could indicate a background across the Netherlands originating from distant sources. However, distant source origins are hard to distinguish from sources that are present everywhere, with emissions that are highly correlated in time, such as those from traffic. Both possibilities would show low COD values between pairs of rural locations. Though some components (i.e. sulphate) are commonly thought to be derived mostly from long-range transport, a model calculation would be needed to make a proper assessment of national versus foreign contributions. The need for a model for this purpose is further illustrated by the fact that the national contributions are dependent on atmospheric conditions and may be different under different pollution levels. Under stagnant conditions, national emissions play a more important role than under other conditions (Schaap and Denier van der Gon, 2007).

These considerations show that a model is able to provide valuable insights into the origin of air pollution in the Netherlands, provided that the model is able to explain any observed variability in the concerning component. A dedicated model study, to this end, could yield valuable additional information, and such an exercise, therefore, would be recommended.

## 5.8 Could an estimate be made of natural versus anthropogenic contributions to PM?

An important question to answer for policymakers is that of how many of the observed particulate matter concentrations would be of anthropogenic origin. After all, it is this fraction that could be targeted by abatement strategies. A first-order assessment of natural versus anthropogenic contributions is presented below, based on current knowledge for each of the major components as identified in the mass closure.

### Sulphate

The sea is a source of particulate sulphate. In sea water the relative abundance of sulphate is ~23% of the sodium concentration. This value has been used to correct sulphate concentrations for sea salt contributions in the chemical mass balance approach described in section 3.4. As sea salt is mostly coarse mode aerosol, the same applies for this sulphate fraction. For the Dutch locations, this correction learned that ~5% of the particulate sulphate was of marine origin. Besides in sea salt and a few per cent of primary sulphate in anthropogenic emissions, sulphate is formed in the oxidation of sulphur dioxide.

Though aerosol sulphate may be emitted directly into the atmosphere, its mayor source is the oxidation of sulphur dioxide ($SO_2$). $SO_2$ originates from both natural and anthropogenic sources. Anthropogenic $SO_2$ emissions derive from the combustion of sulphur-containing fuels, such as coal and crude oil. The most important source group of $SO_x$ in north-western Europe is power generation (11 Mt). International shipping (2 Mt) is significant compared to the total land based European emissions (16 Mt), and very relevant for the Netherlands.

Natural sources of $SO_2$ emissions include volcanoes, oxidation of dimethylsulfide (DMS) from the sea, and wild fires. Of these sources, volcanoes are estimated to be the most important for Europe, where significant volcanic emissions are currently limited to those from Italy and Iceland. For Italy, the time-averaged $SO_2$ output rate from Mt Etna was estimated at around 2.0±0.4 Mt/yr, for the 1987-2000 period (Caltabiano et al., 2004). Similarly, emissions from the Icelandic volcanoes were estimated at 1.0±0.2 Mt/yr (Friedrich et al., 2008). Volcanoes, currently contribute about 20% to the total European $SO_x$ emissions. As anthropogenic emissions are to be significantly reduced under the Gothenburg protocol, the relative contribution from volcanoes is expected to grow in the future (Friedrich et al., 2008). However, given the volcano locations, the height at which compounds are emitted, the distance to the Netherlands, and limited transport from southern Europe to the north, we concluded that the contribution to ground level sulphate from volcanoes, at the most, would be a 1-2 per cent, in the Netherlands.

Globally, an important source for background sulphate concentrations in remote areas is related to dimethylsulfide (DMS). DMS is produced biologically and photochemically in sea surface waters and subsequently emitted into the atmosphere by sea to air gas exchange. Rapid oxidation of DMS then follows, leading to the formation of $SO_2$ and methane sulphonic acid (MSA) (Bates et al., 1992). Other biogenic sources of $SO_2$ are the oxidation of $H_2S$ from swamps and COS from vegetation. For Europe, these contributions were found to be of minor importance. Wildfire emissions of $SO_2$ are thought to be a minor source and are normally not even included in estimations on land emissions from wildfires. In short, natural contributions to sulphate concentrations in the Netherlands have been estimated at 5 to 10%. Most of the natural contribution is thought to exist of sea salt sulphate.

### Nitrate

In general, aerosol nitrate is formed though oxidation of $NO_x$ to nitric acid ($HNO_3$), which forms particles as a result of a reaction with ammonia ($NH_3$) or with sodium chloride and dust. To estimate how much of the nitrate in Europe is anthropogenic, we examined the European emission strengths of $NO_x$. Nitrogen oxide emissions from semi-natural sources are caused by NO emissions from agricultural and forest soils, biomass burning and lightning activities. Estimates on soil NO emissions range between 59 and 190 Ktonnes in the EU15 (Simpson et al., 1999; Friedrich et al., 2008). This broad range indicates the high uncertainty associated with these numbers. Relative to the total inventoried emissions, the average value contributes 4%. From these emissions, about two thirds can be attributed to agricultural soils and one third to forest soils. However, soil $NO_x$ emissions cannot be regarded as totally natural, as they largely depend on the nutrient input (through fertilisation or atmospheric deposition). Hence, the 4% contribution is an upper limit and is most probably significantly lower in reality.
Lightning is a purely natural source of $NO_x$. $NO_x$ emissions from lightning scales linearly with the amount of convective precipitation (Meijer et al., 2001). Consequently, emissions tend to be highly variable in space and time, but mainly occur in the tropics. For Europe, the emissions are estimated at about 65 ktonnes, of which 80% is thought to occur at an altitude of 1 to 5 kilometres and mostly in southern Europe (Meijer et al., 2001; Friedrich, 2009). The contribution to the total emission is about 1% of the total anthropogenic emissions.
Emissions from wildfires, mostly anthropogenic, are highly uncertain. The available estimates range from 200 to 500 ktonnes (Friedrich, 2009; Hoelzemann et al., 2004). Note that the majority (90%) of emissions occur outside the EU27, in countries such as Russia, the Ukraine and Kazakhstan. The 20 to 50 ktonnes emitted inside the EU27 occur mostly in the Mediterranean countries. These emissions are less than one per cent of the total inventoried emissions. For the Netherlands, we assumed the contributions from wildfires to be negligible.
In short, the natural $NO_x$ emissions were considered to be a small fraction (5% or probably less) of present day $NO_x$ emissions that lead to nitrate formation in the EU27.

### Ammonium

Ammonium in aerosols derives from the neutralisation of sulphuric acid and nitric acid by ammonia. Ammonia is emitted from different sources, most notably animal manure, traffic and fertiliser application (Olivier et al., 1998). Ammonia emissions in Europe, for the largest part (80-95%), are associated with agricultural activities (Van der Hoek, 1998). Recently, Erisman et al. (2009) estimated the natural emissions at about 10% of the total emissions in Europe. This percentage includes contributions from wild animals and wetlands. We assumed the same percentage for ammonium in the Netherlands.

### Carbonaceous aerosol

Carbonaceous aerosols contain a host of chemical constituents, of which only a small fraction has been identified. Commonly, the elemental and organic aerosol fractions are distinguished. Elemental carbon is emitted from combustion processes and is a pure primary component. The main source is the (incomplete) combustion of fossil fuels. Wildfires are occasional sources of vast amounts of carbonaceous particles. Though wildfires may seem natural, the vast majority of present day wildfires is due to human behaviour. Hence, elemental carbon (EC) is almost exclusively anthropogenic.

Along with elemental carbon, organic carbon (OC) is also released through incomplete combustion of fuels. However, there are a number of additional sources of particulate organic carbon, complicating the picture. OC may be emitted during farming activities (both from stables and harvesting), as well as naturally. Anthropogenic combustion sources as well as stable emissions have been inventoried. Using models, with such an emission inventory as input, explain about half of the observed concentrations of OC. Hence, a significant contribution is expected from sources not included in present inventories that contain known anthropogenic sources, such as secondary formation, wildfires, harvesting and abrasion processes.
A source of OC is primary biological material, such as fungal spores and plant debris. Within the EU-CARBOSOL project, primary biological material was estimated to contribute up to 0.4 ug/m³ at rural background locations (Sanchez-Ochoa et al., 2008). These concentrations correspond to on average of about ~2% of $PM_{10}$ mass and ~6% of organic mass. Although this contribution is biogenic, agriculture and other landscaping activities may also contribute significantly. Hence, only part of the biological material is natural. As for the other components, we concluded that contributions from wildfires in the Netherlands are negligible.
The real complicating factor in the estimation of the natural part of OC is the uncertainty related to its secondary component. Secondary organic aerosol (SOA) is formed through the degradation of volatile organic compounds. Oxidation by hydroxyl or ozone yields products with low vapour pressures that may condense on existing aerosol. At present, the contribution of SOA to aerosol mass is uncertain, as the major formation routes are not well known. Similarly, the ratio of natural to anthropogenic SOA is under large scientific debate. Note that the oxidation pathways that yield SOA are largely influenced by hydroxyl and ozone in anthropogenic emissions. Currently, it is postulated that biogenic sources are a major contributor to atmospheric SOA. When using present-day emission inventories, it could be assumed that the unexplained OC, for the largest part, consists of SOA, with an upper limit of ~50% of natural OC. As part of the SOA may very well be anthropogenic, we postulate a second assumption, with half of the SOA as from natural sources, leading to 25% of natural OC.
In short, we estimated that EC is fully anthropogenic. For OC, the assessment is difficult to make, as the amount of natural derived SOA is under large scientific discussion. Potentially, up to 50% of OC may be of natural origin.

### Mineral dust

Despite the importance of mineral dust in total $PM_{10}$ mass, the sources are still poorly understood. Mineral dust may originate from distinctly different sources, for example, wind erosion of bare soils, agricultural land management, resuspension of road dust from paved an unpaved roads, road

**Analysis of the natural contribution (%), for all components, and $PM_{2.5}$ and $PM_{10}$ as a whole, for Hellendoorn. For each component, the relative contributions to $PM_{2.5}$ and $PM_{10}$ are listed as well as the estimated natural contributions. The last columns provide the resulting natural contribution, expressed in percentage of PM10 mass, for each component, for a high and low estimate of the natural OC content (see text).** **Table 5.1**

| | **$PM_{10}$ contrib** | **$PM_{2.5}$ contrib** | **Natural** | **Hellendoorn $PM_{10}$** | **Hellendoorn $PM_{2.5}$** |
|---|---|---|---|---|---|
| **Comp** | | | | **Low / high** | **Low / high** |
| *$NO_3$* | 21 | 21 | 5 | 1 | 1 |
| *$SO_4$* | 13 | 17 | 5 | 1 | 1 |
| *$NH_4$* | 7 | 10 | 10 | 0.5 | 1 |
| *MD* | 7 | 4 | 20 | 1.5 | 1 |
| *SS* | 11.5 | 5 | 100 | 11.5 | 5 |
| *Metals* | 5 | 4 | 0 | 0 | 0 |
| *EC*1.3* | 12 | 15 | 0 | 0 | 0 |
| *OC*1.3* | 12 | 14 | 25 / 50 | 3 / 6 | 3.5 / 7 |
| *Sum known* | | | | 18 / 22 | 12.5 / 16 |
| *Unknown* | 13 | 10 | # | 2.5 / 3 | 1.5 / 1.5 |
| *Total* | | | | 21 / 25 | 14 / 18 |

# The natural contribution is assumed to be the same as the total natural percentage of PM mass without the unknown fraction.

wear, handling of materials, and building and construction activities. This report provides a first-order estimate of the natural contribution to ambient dust concentrations that originate from the various sources in Europe. Considering sources, only wind erosion may contribute to the natural fraction. Its importance is discussed below.

Globally, present-day emission estimates for mineral dust are dominated by emissions from wind erosion. The global source is dominated by a few areas exceptionally susceptible to wind erosion. These areas are characterised by a fine soil texture, low soil moisture and sparse vegetation, as well as low precipitation levels, high wind speeds and wind gusts. For Europe, the Sahara Desert is relevant. Saharan dust is regularly transported to Mediterranean countries. In central and northern Europe, dust transport from the Sahara is infrequent and not considered a significant contribution to ambient dust concentrations. During the BOP programme, we could only identify one day with a significant contribution of Saharan dust to PM (~4% of the average annual concentration).

Recent studies have shown that, by using model routines in chemistry transport models for wind-blown dust, a large portion of the ambient dust concentrations in Europe cannot be explained (Vautard et al., 2005; Schaap et al., 2009). Korcz et al. (2009) and Denier van der Gon et al. (2010) have shown that wind-blown dust on the European continent is a smaller source of dust than traffic resuspension and agricultural land management. More importantly, the wind-blown dust source strength from soils other than arable land is low. Hence, wind-blown dust emissions are strongly related to anthropogenic changes in surface vegetation cover and are regarded as mostly anthropogenic. Consequently, the total mineral dust concentration in air is expected to be largely anthropogenic. To be on the safe side, we assumed that an upper limit of 20% of the mineral dust would be of natural origin.

### Sea salt

Sea salt is produced by the bursting of small air bubbles in the foam of breaking waves. This process generates mostly coarse-mode aerosols. The emission of sea salt is mainly dependent on wind speed. Sea salt is considered the second-largest contributor in the global aerosol budget, as a vast area of the earth consists of sea. Sea salt aerosols consist mainly of sodium chloride originating from sea spray; other constituents of atmospheric sea salt reflect the composition of sea water, and thus include magnesium, sulphate, calcium and potassium. Sea salt is the only pure natural aerosol component.

### Metals

Metals originate from a vast range of abrasion processes and the metallurgical industry. Though soils may contribute to metal concentrations, these are mostly accounted for in the mineral dust estimate. Hence, all metals are assumed to be anthropogenic.

### Unknown fraction

The anthropogenic fraction of the unknown part is by definition unknown. As water accounts for part of the unknown fraction and most of that water may be associated with SIA, it is likely that a significant part of the unknown fraction is anthropogenic. As we could not make an assessment we simply assumed that the anthropogenic and natural parts of the unknown fraction resemble those of the defined mass.

### Synthesis

Below, a crude assessment is presented of the natural contributions to $PM_{10}$ and $PM_{2.5}$, for Schiedam and Hellendoorn. Hellendoorn is the cleanest location and is situated in the eastern part of the Netherlands. Schiedam is representative for urban background locations in the west of the country. Table 5.1 presents the analysis for Hellendoorn. We applied the estimated natural contribution to each component and added all contributions together, to arrive at a total natural fraction of the known mass. To make an easy estimate, we used the relative mass contributions per component. For instance, in Hellendoorn, 11.5% of $PM_{10}$ was associated with sea salt which is purely natural. However, nitrate contributed 21%, 5% of which was assumed to be natural resulting in a natural contribution of 1% of total $PM_{10}$. Adding all contributions resulted in an estimated 25%

**Analysis of the natural contribution (%), for all components, and $PM_{2.5}$ and $PM_{10}$ as a whole, for Schiedam. For each component, the relative contribution to $PM_{2.5}$ and $PM_{10}$ is listed, as well as the estimated natural contribution. The last columns provide the resulting natural contribution expressed in percentage of $PM_{10}$ mass, for each component, for a high and low estimate of the natural OC content (see text).** **Table 5.2**

| **Comp** | **$PM_{10}$ contrib** | **$PM_{2.5}$ contrib** | **Natural** | **Schiedam $PM_{10}$ Low / high** | **Schiedam $PM_{2.5}$ Low / high** |
|---|---|---|---|---|---|
| *$NO_3$* | 18 | 19 | 5 | 1 | 1 |
| *$SO_4$* | 14 | 19 | 5 | 1 | 1 |
| *$NH_4$* | 5 | 8 | 10 | 0.5 | 1 |
| *MD* | 7.5 | 5 | 20 | 1.5 | 1 |
| *SS* | 17 | 8 | 100 | 17 | 8 |
| *Metals* | 6 | 5 | 0 | 0 | 0 |
| *EC*1.3* | 12 | 18 | 0 | 0 | 0 |
| *OM*1.3* | 10 | 13 | 25 / 50 | 2.5 / 5 | 3 / 6 |
| *Sum known* | | | | 24 / 27 | 15 / 18 |
| *Unknown* | 10 | 6 | # | 2.5 / 3 | 1 / 1 |
| *Total* | | | | 26 / 30 | 16 / 19 |

# The natural contribution is assumed to be the same as the total natural percentage of PM mass without the unknown fraction.

natural fraction of the known part of $PM_{10}$. The low estimate for carbonaceous particles contained a natural fraction of 21%. Hence, around one quarter of $PM_{10}$ was estimated to be natural. Performing the same exercise for $PM_{2.5}$ yielded estimates for the high and low cases of OC contribution, of 18 and 14% , respectively. For the urban background location of Schiedam, slightly higher values were found, with 26 to 30% for $PM_{10}$ and 16 to 29% for $PM_{2.5}$.The explanation for these slightly higher values is the higher relative contribution of sea salt at Schiedam.
The uncertainty in such a simple analysis is quite large. Hence, we rounded all data to the closest interval of half a per cent. As such, the uncertainty in the summation is around 2 to 3%. The largest challenge, however, was how to account for the total carbonaceous mass. Here, we chose the approach to multiply both EC and OC by 1.3 and apply the natural factors to these concentrations. This was a very arbitrary choice. The EC-OC analytical approach following Cachier is known to give high EC levels, as it does combust the non-refractory OC in the first step of the analysis. Hence, part of the OC may have been accounted for as EC and has not been taken into account in the estimation of the natural contribution. Therefore, we concluded that the application of the natural OC contributions to TCM would provide an upper limit for the natural contribution of the carbonaceous aerosol and PMx. Using a natural OC contribution of 50% in this assumption, an upper limit for the natural contribution to $PM_{10}$ and $PM_{2.5}$ was estimated at 31% and 26% at Hellendoorn and 35 and 28% at Schiedam. As a result, we conclude that the natural contribution to PM in the Netherlands is at maximum about one third of the observed mass, where the best estimates are one fourth for $PM_{10}$ and one fifth for $PM_{2.5}$.

## 5.9 Which combination of factors causes a day of exceedance?

The variability of PM concentrations is largely influenced by the variability in large-scale synoptic meteorological situations. High concentrations of $PM_{2.5}$ and $PM_{10}$ occur at days with stagnating conditions or slow transport from the south, south-east or east. During these conditions, the weather is fair and the removal from the atmosphere is low due to the absence of rain. As emissions are diluted less because of the low wind speeds, the removal is low, and air pollution builds up. During the colder half of the year, this effect is strengthened due to the occurrence of shallow planetary boundary layers. All components show higher than average concentrations on a day with high PM concentrations. The exception being sea salt, as continental air masses are transported over the Netherlands during these days. Nitrate and the unexplained part of PM increase disproportionally with PM10 mass and their contributions are relatively higher in the high concentration range. Model studies have shown high contributions from national sources to the concentrations of primary material and ammonium nitrate (Schaap and Denier van der Gon, 2007; Denier van der Gon et al., 2009).

Special events also contribute to a (small) number of exceedances or days with high concentrations. We identified a substantial contribution of desert dust at the end of January, 2008. Other events include fireworks at New Years Eve, bon fires during Eastern and long-range transport of dust and fire plumes.

## 5.10 What are the main knowledge gaps and recommendations?

This section highlights a number of gaps in knowledge concerning the PM composition and origin.

### Unexplained mass fraction

The first gap in knowledge is straightforward. The unexplained mass fraction of PM covers about 10 to 15% of the total mass. Many authors have pointed at the potential contribution of water as an explanation of the unexplained material. As the unexplained mass correlates with the hygroscopic secondary inorganic aerosols, in particular with nitrate, this assumption may be valid. However, to date, a quantitative measurement methodology to verify this assumption has not been identified and is highly needed to further characterise the PM mass concentration.

### Urban increment

The availability of the data prohibited a characterization of the increment between the urban background and rural background, on statistical grounds. Although increments are suggested, the number of simultaneous measurements at, for example, Cabauw and Schiedam, were too low for such an assessment. Moreover, expected concentration gradients in the rural background (from the west to the south-east and east) suggested that Vredepeel, Hellendoorn and potentially also Cabauw would not be suited to act as a rural background location for the urban area around Schiedam and Rotterdam. This was substantiated by observed local agricultural contributions to PM at Vredepeel and possibly Cabauw. Alternatively to our approach, the full BOP data base could be used for deriving first-order estimates for the rural to urban background gradient. Within the BOP programme this has been done for TC, SIA and mineral dust, in the thematic reports (Keuken and Ten Brink, 2009; Weijers et al., 2010; Denier van der Gon et al., 2010). These estimates, however, included the abovementioned uncertainties. Therefore, we recommend that a study be set up to quantify this increment in more detail, by using a rural background location at close proximity to the city involved.

### Organic carbon

The largest gaps in knowledge are associated with organic carbon. The largest uncertainties concern the concentrations themselves and their origins. A number of known issues are related to quartz filters, such as potential evaporative losses of organic carbon, on the one hand, and adsorption of organic vapours, on the other (Vecchi et al., 2009). Although the potential loss of OC is unknown, the adsorption of organic gases to the quartz filters can be quantified by measuring the field blanks. The importance of this was illustrated by the very high quantities of organic material in the field blanks observed during the BOP programme (Ten Brink et al., 2010). Such high field blanks make the sampling results less precise and obviously complicate interpretation. Another major issue in the analysis procedure is the split between EC and OC. The available analysis procedures correspond well for total carbon, but yield very different EC/OC ratios. During several available analysis procedures, part of the OC may be converted to EC, that is, by charring (Ten Brink et al., 2004). The temperature profile and the length of each step influence the degree of charring. Most methods try to correct for the charring by monitoring the blackness of the filter during the analysis, using optical measurements but this is only successful to a certain (limited) extent. However, during the Cachier analysis procedure, as was used in this study, refractory OC is not combusted in the first but in the second combustion step and is appointed to EC, thus providing an upper estimate for EC and a lower estimate for OC. The application of one of the SUNSET analysis procedures would yield much lower EC/OC ratios. Hence, the lack of a clear separation between EC and OC works through in the interpretation of the data. For instance, it yields uncertainties in the mass closure, the interpretation of gradients between locations and also in the source identification. Besides sampling issues, the conversion factor from OC to organic material (OM) is uncertain. Literature data vary between 1.2 and 2, and it may very well be possible that the factor varies geographically, that is, showing lower values near sources and higher values after processing in aged air masses.

The source apportionment applied in this study did not separate source contributions to the secondary inorganic aerosols or organic carbon. Especially for OC, the origin is subject to large scientific research and debate. Current chemistry transport models only explain about half of the observed OC mass concentration, considering the known (mainly combustion derived) anthropogenic sources (Schaap et al., 2004; Stern et al., 2008). Not included are possibly important contributions due to wood combustion, as identified in rural areas in Europe. Although being a substantial source in some Dutch regions during the winter period, it is expected that the contribution from wood burning in the Netherlands is less important than in other countries. Another source for OC is the emission of biogenic and anthropogenic gases and subsequent degradation to low volatility gases and secondary aerosol formation. Current understanding shows large deviations in the potential contributions from secondary organic aerosol, due to a lack of solid knowledge on formation routes. In the past, SOA formation was thought to be mainly due to the oxidation of biogenic organic vapours. Nowadays, also anthropogenic gases are under investigation. Consequently, the contribution from natural and anthropogenic sources to OC is not known. It is possible to assess the contribution of biogenic OC versus fossil-fuel derived OC through isotope analyses, as radioactive carbon (C14) is absent in fossil fuel, in contrast to modern (biogenic) material. However, these measurements are not conclusive with regard to the natural contribution, as also biofuel burning and primary biological material (e.g. agriculture) result in biogenic OC. Nonetheless, such measurements are highly needed in the Netherlands (and Europe) to shed more light on the OC problem.

Furthermore, the behaviour of OC in the atmosphere is uncertain. Recently, it has been established that OC emitted from fossil-fuel burning can be regarded as semi-volatile (Donahue et al., 2009). The implication of this is that, after emission, the OC may evaporate and only small local near-source contributions of OC would be observed. The volatilised primary material may return to the aerosol after one (or more) oxidation steps in the atmosphere. This would yield a rural anthropogenic contribution to OC. New measurements using aerosol mass spectrometers are now used for investigating and proposing SOA formation mechanisms. However, the uncertainty in the proposed mechanisms and source attribution is large. We advise to address the different mechanisms, as well as the different sources, in a modelling study that explores the different scenarios and evaluates the resulting patters in both space and time, compared against measurements. For example, anthropogenic and natural source areas are separated in space and should, therefore, yield different concentrations patters. Similarly, biological emissions occur mostly in summer, whereas anthropogenic emissions occur throughout the year. For evaluation purposes, the BOP and EMEP OC-EC data, novel Dutch isotope measurements, as well as AMS data (EUCAARI), should be used.

### Modelling SIA

As for OC, PMF and data interpretation give no indications of the source sectors that contribute to the SIA concentrations. In contrast to OC, however, there is a relatively good understanding of the processes leading to the formation of nitrate, ammonium and sulphate. Nevertheless, the modelling of especially nitrate is challenging, as its concentration is dependent on many parameters. The concentration of ammonium nitrate is sensitive to the sulphate concentration, to concentrations of precursor gases, as well as meteorological conditions (T, RH). Models need to accurately describe source strengths of precursors, chemical production of sulphate and nitric acid, the equilibrium between ammonium nitrate and its gaseous counterparts, as well as the sinks for all components involved. Furthermore, the coarse mode nitrate should be included, which is currently not the case. The higher than expected levels of SIA (Weijers et al., 2010) call for a renewed attention to the modelling of SIA in the Netherlands.

### Mineral dust

The mineral dust concentrations measured in this study were relatively low. Measured contributions to $PM_{10}$ were between 6 and 9%. Concerning the measurement methodology, the interpretation of the elemental composition was challenging, especially concerning the mineral dust tracers, Si and Al. The extraction of the Teflon filters was performed with a standard acid solution. These are known to not effectively solute all mineral components and the recovery was estimated to be between 50 and 70%. Because a comparison against the solution with a BOM-extraction was not successful, the actual percentage was not established, and only a recovery based on the use of standard material could be used. Hence, further attention is needed to establish the mineral dust concentration in PM samples. It is our recommendation to improve quantification of silicon by total dissolution combined with ICP-OES analysis techniques.

A second issue concerning mineral dust is its origin in urban areas. The increment from the urban background location Schiedam to the traffic location Rotterdam showed that the increase compared to the urban background could mainly be attributed to exhaust particles (carbonaceous material) and abrasion material (Fe, Cu, etc.). Though the PMF associated some of the mineral dust with traffic, the gradient of mineral dust between Schiedam and Rotterdam was near zero for mineral dust. The absence of a traffic contribution to mineral dust was unexpected and in contrast to findings elsewhere. For many cities, such a gradient has been observed (Denier van der Gon et al., 2010) and in southern Europe, 80% of the mineral dust has been attributed to traffic resuspension (Amato et al., 2009). Denier van der Gon et al. (2010) have shown that the mineral dust concentrations at urban locations were 30 to 60% higher than at rural locations, depending on which rural location was selected as rural background. This illustrates that an urban source is present. Using the complete data set, these authors also did not report a gradient between Rotterdam and Schiedam. A confirmation is needed that this picture is valid for other traffic locations, or that the situation at Rotterdam-Bentinkplein or Schiedam was exceptional. We propose to acquire a number of simultaneous samples with long sampling times at different locations within one city. The locations should encompass at least two urban background locations, three different traffic locations and preferably also locations near other potential sources, such as building and construction activities. Note, that some of the locations should be located close together so that gradients in the urban background can be neglected.

### Experimental uncertainties

Finally, assessing the mass, composition and origin of particulate matter is complicated by the difficulties around reliably sampling PM and those in the subsequent analysis of the composition. There is no approach for reliably sampling all components and for analysing the full composition of PM. Sampling and analysis strategies are chosen to fit the purpose of a study. In a study to provide the full composition of PM, compromises have to be made. Most delicate are the determination of the carbonaceous components, ammonium nitrate and the mass concentration, due to water uptake and artefacts in the previously mentioned components. To be able to perform the analysis for carbonaceous particles, quartz filters must be used in the sampling.

Quartz filters are known for a number of issues: 1) evaporative losses of ammonium nitrate and organic carbon; 2) adsorption of organic vapours (discussed above); 3) high field blank or a number of species; and 4) long equilibrium times in the weighing room with respect to water. Quartz filters are prone to evaporative losses of ammonium nitrate (Hering and Cass, 1999; Vecchi et al., 2009). These losses are thought to be significant at temperatures above 20 degrees Celsius (Schaap et al., 2004). Hence, the nitrate contribution should be interpreted as a minimum estimate. Although, in this study, the impact was estimated to be small, as temperatures were generally below 20 °C, daily monitoring with this approach may yield underestimations for warm (summer) days. In addition, quartz filters have a very long equilibrium timescale, with respect to adjustment to relative humidity. Short equilibrium times used in the first weighing, before the filters are brought into the field, may cause an artificial mass contribution due to the water uptake in the field (De Jonge, 2009).

From March 2008, in order to reduce this artefact, filters have been wetted thoroughly before being used in the field (Van Arkel et al., 2010). This procedure causes PM levels to be lower and may partly explain the differences in mass closure studies with respect to the unexplained mass. However, no influence in the BOP data set was observed. Unfortunately, the procedure and consequences have not been well documented and should be investigated in more detail.

# Appendix Concentration data

**Average concentration, standard deviation and number of samples for $PM_{10}$ total mass (TM) and all analysed species** **Table A.1**

| | | AVG ± STDEV | N | AVG ± STDEV | N | AVG ± STDEV | N | AVG ± STDEV | N | AVG ± STDEV | N | AVG ± STDEV | N |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Species** | **Unit** | **Schiedam** | | **Vredepeel** | | **Rotterdam** | | **Cabauw** | | **Hellendoorn** | | **Breda** | |
| *TM* | µg/m³ | 27.6 ± 14.5 | 71 | 25.6 ± 11.7 | 71 | 29.7 ± 11.9 | 87 | 23.0 ± 10.8 | 61 | 19.3 ± 8.1 | 73 | 28 ± 12.2 | 70 |
| *Al* | ng/m³ | 253.1 ± 444.3 | 76 | 161.5 ± 232.9 | 112 | 194.9 ± 341.6 | 116 | 139.8 ± 152.8 | 82 | 123.9 ± 134.2 | 69 | 186 ± 312.3 | 95 |
| *As* | ng/m³ | 0.8 ± 0.6 | 76 | 0.8 ± 0.4 | 112 | 0.8 ± 0.4 | 116 | 0.6 ± 0.4 | 82 | 0.5 ± 0.3 | 69 | 0.8 ± 0.5 | 95 |
| *Ba* | ng/m³ | 17.7 ± 71.7 | 76 | 7.2 ± 6.8 | 112 | 18.2 ± 8.1 | 116 | 6.7 ± 3.5 | 82 | 5.9 ± 2.8 | 69 | 12.6 ± 6.3 | 95 |
| *Be* | ng/m³ | 0.0 ± 0.1 | 76 | 0.1 ± 0.2 | 112 | 0.2 ± 0.3 | 116 | 0.1 ± 0.1 | 82 | 0.0± 0.0 | 69 | 0.1 ± 0.3 | 95 |
| *Ca* | ng/m³ | 385 ± 274.4 | 76 | 314.6 ± 204.9 | 112 | 396.1 ± 265.6 | 116 | 240.8 ± 156 | 82 | 200.7 ± 120.9 | 69 | 400.4 ± 330.7 | 95 |
| *Cd* | ng/m³ | 0.4 ± 0.2 | 76 | 0.4 ± 0.2 | 112 | 0.3 ± 0.3 | 116 | 0.3 ± 0.1 | 82 | 0.4 ± 0.1 | 69 | 0.4 ± 0.3 | 95 |
| *Co* | ng/m³ | 0.5 ± 0.3 | 76 | 0.3 ± 0.2 | 112 | 0.5 ± 0.3 | 116 | 0.3 ± 0.2 | 82 | 0.2 ± 0.2 | 69 | 0.4 ± 0.2 | 95 |
| *Cr* | ng/m³ | 4.7 ± 3.3 | 76 | 3.6 ± 2.1 | 112 | 8.4 ± 5.6 | 116 | 3.0 ± 1.2 | 82 | 3.5 ± 2.1 | 69 | 4.8 ± 2.2 | 95 |
| *Cu* | ng/m³ | 12.7 ± 14.4 | 76 | 6.7 ± 3.6 | 112 | 49.2 ± 25.1 | 116 | 5.6 ± 3.8 | 82 | 4.3 ± 2.8 | 69 | 22.9 ± 12.5 | 95 |
| *Fe* | ng/m³ | 490.9 ± 396 | 76 | 289 ± 204.7 | 112 | 1190 ± 642.2 | 116 | 246.6 ± 177.4 | 82 | 252.7 ± 259.6 | 69 | 723.9 ± 464.1 | 95 |
| *K* | ng/m³ | 311.8 ± 895.8 | 76 | 271.9 ± 150.3 | 112 | 217 ± 104.4 | 116 | 185.4 ± 74.0 | 82 | 148.0 ± 66.8 | 69 | 234.8 ± 112.2 | 95 |
| *Li* | ng/m³ | 0.6 ± 0.4 | 76 | 0.6 ± 0.3 | 112 | 0.8 ± 0.3 | 116 | 0.5 ± 0.3 | 82 | 0.5 ± 0.3 | 69 | 0.8 ± 0.3 | 95 |
| *Mg* | ng/m³ | 300.3 ± 243.6 | 76 | 183.5 ± 112.4 | 112 | 261.7 ± 194.8 | 116 | 185.5 ± 105.6 | 82 | 135.9 ± 85 | 69 | 216 ± 155.1 | 95 |
| *Mn* | ng/m³ | 12.2 ± 14.7 | 76 | 7.3 ± 5.2 | 112 | 18.8 ± 17.9 | 116 | 6.3 ± 4.8 | 82 | 5.5 ± 5 | 69 | 10.8 ± 7.2 | 95 |
| *Mo* | ng/m³ | 1.1 ± 0.6 | 76 | 1.0 ± 0.9 | 112 | 3.1 ± 1.6 | 116 | 0.7 ± 0.6 | 82 | 0.7 ± 0.6 | 69 | 1.9 ± 1.1 | 95 |
| *Na* | ng/m³ | 1202.1 ± 1080.6 | 76 | 690.8 ± 630.5 | 112 | 1090.9 ± 988.3 | 116 | 755.6 ± 625.8 | 82 | 532 ± 532.5 | 69 | 850.8 ± 784.5 | 95 |
| *Ni* | ng/m³ | 9.3 ± 5.5 | 76 | 3.5 ± 2.1 | 112 | 8.4 ± 5.5 | 116 | 4.4 ± 2.7 | 82 | 3.3 ± 2.1 | 69 | 4.9 ± 2.7 | 95 |
| *P* | ng/m³ | 137.5 ± 53.8 | 76 | 122.3 ± 77.1 | 112 | 122.5 ± 60.9 | 116 | 129.5 ± 46.8 | 82 | 127.7 ± 62.2 | 69 | 121.9 ± 70.7 | 95 |
| *Pb* | ng/m³ | 12.3 ± 13.6 | 76 | 12 ± 8.3 | 112 | 11.1 ± 7.3 | 116 | 11.8 ± 13.8 | 82 | 9.6 ± 14.0 | 69 | 12.8 ± 8 | 95 |
| *Sb* | ng/m³ | 1.9 ± 1.5 | 76 | 1.1 ± 0.6 | 112 | 5.6 ± 2.9 | 116 | 1.0 ± 0.7 | 82 | 0.9 ± 1.0 | 69 | 3.6 ± 2 | 95 |
| *Se* | ng/m³ | 4.6 ± 9.1 | 76 | 1.9 ± 1.2 | 112 | 3.5 ± 4.6 | 116 | 1.5 ± 1 | 82 | 1.2 ± 1.1 | 69 | 1.9 ± 1.8 | 95 |
| *Si* | ng/m³ | 544.6 ± 958.7 | 76 | 397.5 ± 560.7 | 112 | 519.9 ± 677.7 | 116 | 375.9 ± 377.5 | 82 | 331 ± 283.5 | 69 | 498.9 ± 802.7 | 95 |
| *Sn* | ng/m³ | 6.4 ± 14.4 | 76 | 2.0 ± 1.1 | 112 | 9.7 ± 4.7 | 116 | 1.7 ± 1.4 | 82 | 1.7 ± 3.5 | 69 | 5.4 ± 2.9 | 95 |
| *Sr* | ng/m³ | 5.6 ± 19.8 | 76 | 2.5 ± 1.8 | 112 | 3.5 ± 1.9 | 116 | 2.2 ± 1.0 | 82 | 1.7 ± 0.7 | 69 | 3.0± 1.8 | 95 |
| *Ti* | ng/m³ | 9.9 ± 11.5 | 76 | 6.0 ± 7.0 | 112 | 9.0 ± 9.0 | 116 | 5.4 ± 5.0 | 82 | 4.9 ± 4.2 | 69 | 7.3 ± 8 | 95 |
| *V* | ng/m³ | 12.8 ± 8.6 | 76 | 3.5 ± 2.9 | 112 | 9.5 ± 8.1 | 116 | 5.3 ± 4.5 | 82 | 2.8 ± 2.1 | 69 | 5.6 ± 4.6 | 95 |
| *Y* | ng/m³ | 0.1 ± 0.1 | 76 | 0.2 ± 0.3 | 112 | 0.2 ± 0.2 | 116 | 0.1 ± 0.1 | 82 | 0.0 ± 0.0 | 69 | 0.2 ± 0.1 | 95 |
| *Zn* | ng/m³ | 104.3 ± 39.9 | 76 | 86.8 ± 41.5 | 112 | 102.3 ± 42.8 | 116 | 102.9 ± 31.3 | 82 | 97.9 ± 32.5 | 69 | 91.3 ± 40.4 | 95 |
| *OC* | µg/m³ | 2.4 ± 1.5 | 43 | 2.6 ± 1 | 89 | 2.9 ± 1.2 | 73 | 2.1 ± 0.8 | 41 | 2.1 ± 0.9 | 54 | 3.0 ± 1.1 | 51 |
| *EC* | µg/m³ | 2.3 ± 1.5 | 43 | 2.4 ± 1.2 | 89 | 3.8 ± 1.8 | 73 | 1.9 ± 0.9 | 41 | 1.7 ± 1.0 | 54 | 3.4 ± 1.5 | 51 |
| $NH_4$ | µg/m³ | 1.3 ± 1.9 | 43 | 2.0 ± 1.8 | 91 | 1.6 ± 1.9 | 73 | 1.8 ± 1.7 | 42 | 1.4 ± 1.4 | 53 | 2.3 ± 2.2 | 51 |
| $NO_3$ | µg/m³ | 4.3 ± 3.9 | 43 | 5.2 ± 3.3 | 91 | 5.2 ± 4.6 | 73 | 5.0 ± 3.7 | 42 | 4.2 ± 3.4 | 54 | 5.5 ± 3.8 | 52 |
| $SO_4$ | µg/m³ | 3.4 ± 2 | 43 | 3.1 ± 2.2 | 91 | 3.0 ± 1.9 | 74 | 2.6 ± 1.6 | 42 | 2.5 ± 1.5 | 54 | 3.9 ± 2.6 | 52 |
| *Cl* | ng/m³ | 1405.6 ± 1770.5 | 43 | 924 ± 975.5 | 91 | 1291.9 ± 1287.5 | 74 | 789 ± 816.9 | 42 | 739.4 ± 958.6 | 53 | 798.1 ± 923.6 | 52 |

## Average concentration, standard deviation and number of samples for PM2.5 total mass (TM) and all analysed species

**Table A.2**

| | | AVG ± STDEV | N | AVG ± STDEV | N | AVG ± STDEV | N | AVG ± STDEV | N | AVG ± STDEV | N |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Species** | **Unit** | **Schiedam** | | **Vredepeel** | | **Rotterdam** | | **Cabauw** | | **Hellendoorn** | |
| *TM* | µg/m$^3$ | 16.8 ± 10.9 | 75 | 17.5 ± 9.2 | 65 | 19.1 ± 10.4 | 84 | 17.8 ± 10.4 | 63 | 14.0 ± 6.9 | 65 |
| *Al* | ng/m$^3$ | 88.2 ± 189.3 | 81 | 50.6 ± 78 | 112 | 50.7 ± 65.4 | 111 | 46.3 ± 47 | 80 | 51.9 ± 106 | 82 |
| *As* | ng/m$^3$ | 0.6 ± 0.5 | 81 | 0.7 ± 0.5 | 112 | 0.6 ± 0.4 | 111 | 0.5 ± 0.3 | 80 | 0.4 ± 0.4 | 82 |
| *Ba* | ng/m$^3$ | 12.3 ± 62.9 | 81 | 5.3 ± 6.6 | 112 | 11.7 ± 50.8 | 111 | 5.0 ± 2.5 | 80 | 6.7 ± 18.8 | 82 |
| *Be* | ng/m$^3$ | 0.0 ± 0.0 | 81 | 0.2 ± 0.2 | 112 | 0.2 ± 0.3 | 111 | 0.0 ± 0.1 | 80 | 0.0 ± 0.0 | 82 |
| *Ca* | ng/m$^3$ | 102.5 ± 82.7 | 81 | 84.7 ± 58.1 | 112 | 98.0 ± 65.6 | 111 | 77.5 ± 111.7 | 80 | 74.1 ± 65.9 | 82 |
| *Cd* | ng/m$^3$ | 0.3 ± 0.2 | 81 | 0.4 ± 0.2 | 112 | 0.3 ± 0.3 | 111 | 0.3 ± 0.2 | 80 | 0.4 ± 0.1 | 82 |
| *Co* | ng/m$^3$ | 0.3 ± 0.2 | 81 | 0.2 ± 0.2 | 112 | 0.3 ± 0.2 | 111 | 0.3 ± 0.2 | 80 | 0.3 ± 0.1 | 82 |
| *Cr* | ng/m$^3$ | 2.9 ± 1.3 | 81 | 3.1 ± 1.6 | 112 | 3.7 ± 2.3 | 111 | 2.7 ± 1.7 | 80 | 2.6 ± 1.2 | 82 |
| *Cu* | ng/m$^3$ | 5.4 ± 10.0 | 81 | 3.5 ± 2.3 | 112 | 10.7 ± 10.3 | 111 | 3.2 ± 3.3 | 80 | 2.8 ± 3.5 | 82 |
| *Fe* | ng/ m$^3$ | 142.8 ± 147.8 | 81 | 109.2 ± 94.2 | 112 | 253.9 ± 147.7 | 111 | 98.4 ± 80.3 | 80 | 90.1 ± 95.7 | 82 |
| *K* | ng/ m$^3$ | 185.6 ± 759.9 | 81 | 162.6 ± 144.9 | 112 | 182.1 ± 626.3 | 111 | 114.1 ± 65.8 | 80 | 142 ± 206.7 | 82 |
| *Li* | ng/ m$^3$ | 0.4 ± 0.3 | 81 | 0.5 ± 0.3 | 112 | 0.6 ± 0.2 | 111 | 0.4 ± 0.2 | 80 | 0.5 ± 0.2 | 82 |
| *Mg* | ng/ m$^3$ | 93.2 ± 124.8 | 81 | 59.7 ± 40.8 | 112 | 69.9 ± 103.1 | 111 | 79.7 ± 44.5 | 80 | 68.9 ± 47.3 | 82 |
| *Mn* | ng/ m$^3$ | 3.8 ± 3.1 | 81 | 3.7 ± 3.6 | 112 | 5.1 ± 3.6 | 111 | 3.0 ± 2.3 | 80 | 2.6 ± 2.3 | 82 |
| *Mo* | ng/m$^3$ | 0.6 ± 0.3 | 81 | 0.9 ± 1.2 | 112 | 1.0 ± 0.6 | 111 | 0.6 ± 0.5 | 80 | 0.5 ± 0.4 | 82 |
| *Na* | ng/m$^3$ | 340.9 ± 313.1 | 81 | 207.3 ± 208.4 | 112 | 253.9 ± 272.8 | 111 | 262.4 ± 241.5 | 80 | 206.5 ± 218.5 | 82 |
| *Ni* | ng/m$^3$ | 7.3 ± 4.6 | 81 | 3.0 ± 1.9 | 112 | 6.0 ± 4.6 | 111 | 3.8 ± 2.4 | 80 | 2.8 ± 1.6 | 82 |
| *P* | ng/m$^3$ | 126.6 ± 51.1 | 81 | 109.8 ± 62.0 | 112 | 122.7 ± 53.7 | 111 | 116.5 ± 47.4 | 80 | 107.5 ± 64 | 82 |
| *Pb* | ng/m$^3$ | 9.5 ± 12.6 | 81 | 11.1 ± 10.2 | 112 | 9.2 ± 13.2 | 111 | 13.5 ± 19.7 | 80 | 12.0 ± 20.4 | 82 |
| *Sb* | ng/m$^3$ | 1.0 ± 1.0 | 81 | 0.7 ± 0.5 | 112 | 1.6 ± 0.9 | 111 | 0.7 ± 0.6 | 80 | 0.6 ± 0.5 | 82 |
| *Se* | ng/m$^3$ | 3.8 ± 8.4 | 81 | 1.9 ± 1.2 | 112 | 2.7 ± 3.4 | 111 | 1.3 ± 1.0 | 80 | 1.0 ± 1.0 | 82 |
| *Si* | ng/m$^3$ | 193 ± 342.3 | 81 | 165.6 ± 202.8 | 112 | 153.1 ± 87.7 | 111 | 155.1 ± 123.8 | 80 | 174.6 ± 285.3 | 82 |
| *Sn* | ng/m$^3$ | 4.6 ± 12.6 | 81 | 1.6 ± 1.1 | 112 | 3.2 ± 1.8 | 111 | 1.3 ± 1.1 | 80 | 1.1 ± 0.9 | 82 |
| *Sr* | ng/m$^3$ | 3.2 ± 17.8 | 81 | 1.2 ± 1.6 | 112 | 2.4 ± 13.5 | 111 | 1.1 ± 0.9 | 80 | 1.5 ± 3.6 | 82 |
| *Ti* | ng/m$^3$ | 3.6 ± 4.2 | 81 | 2.4 ± 2.7 | 112 | 2.7 ± 1.5 | 111 | 2.1 ± 1.5 | 80 | 2.2 ± 2.8 | 82 |
| *V* | ng/m$^3$ | 10.6 ± 7.9 | 81 | 3.0 ± 2.7 | 112 | 7.8 ± 7.4 | 111 | 4.6 ± 4.2 | 80 | 2.7 ± 2.3 | 82 |
| *Y* | ng/m$^3$ | 0.0 ± 0.0 | 81 | 0.2 ± 0.3 | 112 | 0.1 ± 0.1 | 111 | 0.0 ± 0.0 | 80 | 0.0 ± 0.0 | 82 |
| *Zn* | ng/m$^3$ | 94.2 ± 35.9 | 81 | 92 ± 40 | 112 | 93.4 ± 34.5 | 111 | 96.5 ± 30.2 | 80 | 90.1 ± 33.9 | 82 |
| *OC* | µg/m$^3$ | 2.0 ± 0.9 | 45 | 2.0 ± 1.0 | 88 | 2.3 ± 1.1 | 78 | 1.8 ± 0.6 | 35 | 2.0 ± 0.8 | 62 |
| *EC* | µg/m$^3$ | 2.1 ± 1.2 | 45 | 1.9 ± 1.3 | 88 | 3.3 ± 1.6 | 78 | 1.7 ± 0.9 | 35 | 1.7 ± 1 | 62 |
| $NH_4$ | µg/m$^3$ | 1.1 ± 1.3 | 45 | 1.9 ± 1.5 | 85 | 1.5 ± 1.8 | 78 | 1.4 ± 1.3 | 35 | 1.6 ± 1.4 | 62 |
| $NO_3$ | µg/m$^3$ | 2.6 ± 3.1 | 45 | 4.2 ± 2.9 | 87 | 3.5 ± 3.7 | 78 | 3.7 ± 3.4 | 35 | 3.7 ± 3.1 | 62 |
| $SO_4$ | µg/m$^3$ | 2.5 ± 1.3 | 45 | 2.9 ± 2.2 | 87 | 2.4 ± 1.5 | 78 | 2.4 ± 1.4 | 35 | 2.5 ± 1.8 | 62 |
| *Cl* | ng/m$^3$ | 230.7 ± 230.9 | 45 | 391.1 ± 412.3 | 87 | 386.1 ± 521.4 | 78 | 275 ± 269.4 | 35 | 300.4 ± 337.3 | 62 |

# Appendix B Speciation data used in Positive Matrix Factorization (PMF)

**Table B.1**

**Overview of the species measured in PM2.5, with detailed information about S/N ratio, various statistics and the percentage of values below the minimum detection limit. The 'Category' field denotes the chosen category for the species used in the PMF analysis. The total mass (TM) is included in the analysis as a 'total variable' with a high uncertainty**

| Species | Category | S/N | Min | 25th | Median | 75th | Max | % below MDL |
|---|---|---|---|---|---|---|---|---|
| *TM* | Weak | 0.8 | 0.5000 | 10.8108 | 15.3679 | 23.9891 | 71.1580 | 0% |
| *Al* | Strong | 3.7 | 0.0014 | 0.0159 | 0.0234 | 0.0383 | 0.9589 | 0% |
| *As* | Strong | 2.5 | 0.0001 | 0.0003 | 0.0005 | 0.0008 | 0.0042 | 23% |
| *Ba* | Strong | 2.5 | 0.0014 | 0.0031 | 0.0044 | 0.0060 | 0.5142 | 18% |
| *Be* | Bad | 0.7 | 0.0001 | 0.0001 | 0.0001 | 0.0001 | 0.0006 | 91% |
| *Ca* | Weak | 0.3 | 0.0364 | 0.0364 | 0.0364 | 0.0997 | 0.9061 | 55% |
| *Cd* | Weak | 1.2 | 0.0002 | 0.0002 | 0.0002 | 0.0004 | 0.0019 | 63% |
| *Co* | Weak | 1.0 | 0.0001 | 0.0001 | 0.0001 | 0.0003 | 0.0016 | 66% |
| *Cr* | Strong | 2.1 | 0.0002 | 0.0021 | 0.0027 | 0.0035 | 0.0192 | 0% |
| *Cu* | Strong | 1.9 | 0.0003 | 0.0019 | 0.0034 | 0.0065 | 0.0906 | 5% |
| *Fe* | Weak | 1.3 | 0.0136 | 0.0459 | 0.0828 | 0.1674 | 0.7393 | 11% |
| *K* | Weak | 0.5 | 0.0182 | 0.0489 | 0.0689 | 0.1107 | 4.8413 | 14% |
| *Li* | Bad | 0.4 | 0.0004 | 0.0004 | 0.0004 | 0.0004 | 0.0011 | 98% |
| *Mg* | Strong | 2.7 | 0.0136 | 0.0285 | 0.0417 | 0.0569 | 0.7315 | 23% |
| *Mn* | Strong | 1.6 | 0.0003 | 0.0017 | 0.0030 | 0.0050 | 0.0271 | 8% |
| *Mo* | Strong | 1.6 | 0.0002 | 0.0002 | 0.0006 | 0.0010 | 0.0105 | 33% |
| *Na* | Strong | 2.4 | 0.0273 | 0.0870 | 0.1596 | 0.3045 | 1.7704 | 11% |
| *Ni* | Strong | 2.9 | 0.0002 | 0.0014 | 0.0023 | 0.0042 | 0.0272 | 1% |
| *P* | Weak | 0.3 | 0.0318 | 0.0318 | 0.0911 | 0.1107 | 0.2168 | 29% |
| *Pb* | Weak | 0.8 | 0.0009 | 0.0036 | 0.0065 | 0.0114 | 0.1157 | 11% |
| *Sb* | Strong | 2.0 | 0.0001 | 0.0005 | 0.0008 | 0.0013 | 0.0059 | 9% |
| *Se* | Strong | 2.5 | 0.0005 | 0.0005 | 0.0009 | 0.0016 | 0.0418 | 49% |
| *Si* | Weak | 0.3 | 0.0227 | 0.0468 | 0.0640 | 0.0924 | 1.5149 | 21% |
| *Sn* | Strong | 3.5 | 0.0003 | 0.0007 | 0.0012 | 0.0022 | 0.0876 | 18% |
| *Sr* | Strong | 3.7 | 0.0001 | 0.0005 | 0.0007 | 0.0009 | 0.1129 | 6% |
| *Ti* | Strong | 2.4 | 0.0001 | 0.0009 | 0.0014 | 0.0022 | 0.0243 | 3% |
| *V* | Strong | 3.5 | 0.0001 | 0.0012 | 0.0025 | 0.0065 | 0.0491 | 5% |
| *Y* | Bad | 1.7 | 0.0001 | 0.0001 | 0.0001 | 0.0001 | 0.0008 | 90% |
| *Zn* | Strong | 1.8 | 0.0036 | 0.0790 | 0.0956 | 0.1115 | 0.3309 | 1% |
| *OC* | Weak | 0.8 | 0.2797 | 1.4633 | 1.9137 | 2.6811 | 7.4079 | 0% |
| *EC* | Weak | 0.8 | 0.0440 | 1.2571 | 2.0102 | 2.9456 | 9.6238 | 1% |
| $NH_4$ | Weak | 0.8 | 0.0033 | 0.4966 | 1.1164 | 2.1687 | 19.8315 | 1% |
| $NO_3$ | Weak | 0.8 | 0.1085 | 1.4873 | 2.5763 | 5.3501 | 34.2003 | 0% |
| $SO_4$ | Weak | 0.8 | 0.1160 | 1.4450 | 2.2925 | 3.4582 | 19.2984 | 0% |
| *Cl* | Weak | 0.8 | 0.0067 | 0.1011 | 0.2209 | 0.4545 | 5.8882 | 1% |

**Table B.2**

**Overview of the species measured in $PM_{10}$, with detailed information about S/N ratio, various statistics and the percentage of values below the minimum detection limit. The 'Category' field denotes the chosen category for the species used in the PMF analysis. The total mass (TM) is included in the analysis as a 'total variable' with a high uncertainty.**

| Species | Category | S/N | Min | 25th | Median | 75th | Max | % below MDL |
|---|---|---|---|---|---|---|---|---|
| *TM* | Weak | 1.0034 | 0.5000 | 17.1113 | 23.6339 | 33.4588 | 88.7620 | 1% |
| *Al* | Strong | 5.7852 | 0.0014 | 0.0435 | 0.0765 | 0.1326 | 2.5359 | 0% |
| *As* | Weak | 1.0442 | 0.0001 | 0.0004 | 0.0006 | 0.0010 | 0.0065 | 14% |
| *Ba* | Weak | 1.1460 | 0.0014 | 0.0049 | 0.0073 | 0.0130 | 0.5699 | 4% |
| *Be* | Bad | 0.5885 | 0.0001 | 0.0001 | 0.0001 | 0.0001 | 0.0010 | 88% |
| *Ca* | Strong | 2.6703 | 0.0364 | 0.1612 | 0.2402 | 0.3502 | 1.7996 | 6% |
| *Cd* | Weak | 1.0623 | 0.0002 | 0.0002 | 0.0002 | 0.0005 | 0.0019 | 54% |
| *Co* | Weak | 1.2373 | 0.0001 | 0.0001 | 0.0003 | 0.0004 | 0.0017 | 49% |
| *Cr* | Strong | 1.5493 | 0.0002 | 0.0026 | 0.0037 | 0.0059 | 0.0341 | 0% |
| *Cu* | Strong | 1.6805 | 0.0003 | 0.0047 | 0.0096 | 0.0262 | 0.1390 | 1% |
| *Fe* | Strong | 2.3882 | 0.0136 | 0.1667 | 0.2901 | 0.6299 | 2.6543 | 2% |
| *K* | Strong | 1.6687 | 0.0182 | 0.0994 | 0.1396 | 0.1831 | 5.5588 | 1% |
| *Li* | Bad | 0.5149 | 0.0004 | 0.0004 | 0.0004 | 0.0004 | 0.0026 | 92% |
| *Mg* | Strong | 1.5485 | 0.0136 | 0.0752 | 0.1193 | 0.1840 | 0.9135 | 3% |
| *Mn* | Weak | 1.3750 | 0.0003 | 0.0043 | 0.0078 | 0.0135 | 0.1385 | 2% |
| *Mo* | Weak | 1.3405 | 0.0002 | 0.0006 | 0.0012 | 0.0021 | 0.0098 | 14% |
| *Na* | Strong | 1.7192 | 0.0273 | 0.2410 | 0.5877 | 1.1872 | 5.5433 | 1% |
| *Ni* | Weak | 0.9535 | 0.0002 | 0.0018 | 0.0031 | 0.0049 | 0.0294 | 1% |
| *P* | Weak | 1.0409 | 0.0318 | 0.0318 | 0.0952 | 0.1218 | 0.2041 | 31% |
| *Pb* | Weak | 1.0176 | 0.0009 | 0.0053 | 0.0083 | 0.0141 | 0.1012 | 5% |
| *Sb* | Weak | 1.1465 | 0.0001 | 0.0008 | 0.0015 | 0.0037 | 0.0167 | 2% |
| *Se* | Strong | 1.5371 | 0.0005 | 0.0005 | 0.0011 | 0.0017 | 0.0382 | 43% |
| *Si* | Strong | 3.3854 | 0.0227 | 0.0947 | 0.1522 | 0.2453 | 4.1462 | 4% |
| *Sn* | Strong | 2.0911 | 0.0003 | 0.0012 | 0.0023 | 0.0057 | 0.0916 | 6% |
| *Sr* | Weak | 1.3379 | 0.0001 | 0.0012 | 0.0017 | 0.0023 | 0.1225 | 1% |
| *Ti* | Strong | 1.8013 | 0.0001 | 0.0020 | 0.0037 | 0.0062 | 0.0659 | 1% |
| *V* | Weak | 0.9362 | 0.0001 | 0.0017 | 0.0030 | 0.0073 | 0.0494 | 1% |
| *Y* | Bad | 1.3648 | 0.0001 | 0.0001 | 0.0001 | 0.0001 | 0.0010 | 74% |
| *Zn* | Weak | 1.0359 | 0.0036 | 0.0778 | 0.0993 | 0.1184 | 0.4567 | 1% |
| *OC* | Weak | 1.0362 | 0.2797 | 1.7613 | 2.4619 | 3.4372 | 8.5922 | 1% |
| *EC* | Weak | 0.7733 | 0.0440 | 1.6150 | 2.5504 | 3.7634 | 13.8336 | 1% |
| $NH_4$ | Weak | 0.7774 | 0.0033 | 0.5468 | 1.1575 | 2.4135 | 25.6719 | 1% |
| $NO_3$ | Weak | 0.7806 | 0.0114 | 2.3867 | 3.9377 | 7.0954 | 56.9369 | 1% |
| $SO_4$ | Weak | 0.8014 | 0.0153 | 1.7110 | 2.7303 | 4.0468 | 23.2464 | 0% |
| *Cl* | Weak | 0.7947 | 0.0067 | 0.2674 | 0.5732 | 1.4812 | 9.7073 | 1% |

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## Composition of Particulate Matter determined for the Netherlands

Particulate matter has a negative impact on human health and plays a role in climate change. To develop effective mitigation strategies to reduce the concentrations of both $PM_{2.5}$ and $PM_{10}$ one needs to establish the origin of particulate matter. The composition of particulate matter reveals a lot of information on sources. Here, we report the results of a measurement campaign to determine the composition of $PM_{10}$, $PM_{2.5}$ and $PM_{10-2.5}$ at 6 locations in the Netherlands. Generally, there is a considerable conformity in the chemical composition in the Netherlands. Secondary inorganic aerosol and carbonaceous matter are the most important components, followed by significant contributions of sea salt, mineral dust and metals. Through mass closure a considerable part of the PM mass could be explained. The application of a source apportionment technique complemented the analysis based on the interpretation of the chemical data. It confirmed independently a large number of species to be a tracer for a specific activity or source. As such, we have obtained more confidence in the interpretation of the data set. Based on the measured concentrations and estimates of the natural fraction per component it was established that about 75% of $PM_{10}$ and 80 % of $PM_{2.5}$ is man made.

The Netherlands Research Program on Particulate Matter (BOP) is a national program on $PM_{10}$ and $PM_{2.5}$. It is a framework of cooperation involving 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.

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