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Composition and Origin of Airborne Particulate Matter in the Netherlands

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Abstract

Particulate Matter (PM) in ambient air has consistently and coherently been associated with serious human health effects. The new EU air quality standards have, for the Dutch government, led to a number of questions concerning current levels, particle size and chemical composition of PM in the Netherlands, along with the sources influencing the Dutch ambient PM levels.

In 1998 and 1999 measurements were performed at six sites in the Netherlands. We measured PM_{10}, its fine and coarse fractions, the secondary inorganic aerosols, elemental and organic carbon, tracers for sea salt and the elemental composition of aerosol.

One conclusion of this study is that there is no significant difference between measured PM_{10} concentrations and modelled PM_{10} concentrations in combination with the contribution of natural sources. The average fraction of model estimates and measured concentrations is 0.94 or 0.91 (depending on the correction factors). Taking the uncertainty in the various estimates into account, we found a 1-σ confidence limit of ± 0.20 for the fraction.

After combining model calculations and results from this study to get an impression of what abatement could achieve, we found the maximum level of PM_{10} that can be influenced by domestic abatement measures within the Netherlands, to be highly variable: from 6 to 18 $\mu g/m^3$. The maximum level of PM_{10} that can be influenced by foreign abatement measures (EU) varies from 10 to 15 $\mu g/m^3$. The PM_{10} in the Netherlands from a natural origin is estimated between 7 and 9 $\mu g/m^3$. All these figures are indicative.

Preface

The project as such has been a huge undertaking, and could only succeed in close co-operation with a number of institutions, which made this work possible. First of all, we would like to name the support provided by the Ministry of Housing, Spatial Planning and Environment, the Province of Gelderland, which contributed within the framework of their research programme in Weurt – Nijmegen-West, and DCMR in the province of Zuid-Holland, operating from their research platform in Overschie. Secondly, the management of the project was assigned to the Air Research Laboratory of the National Institute for Public Health and the Environment, which was kindly assisted in the fieldwork by OMEGAM, Amsterdam.

The filter analyses were performed by the RIVM's Laboratory of Inorganic Chemistry (inorganic secondary aerosol) and Laboratory of Analytical Organic Chemistry (experimental analysis of organic compounds in particulate matter), and by the Micro- and Trace Analysis Centre (MiTac) at the Department of Chemistry of the University of Antwerp in Belgium. The National Exposure Research Laboratory of the US-EPA, Research Triangle Park, North Carolina (USA) performed the elemental analyses; the Netherlands Organisation for Applied Scientific Research (TNO) in Delft, the morphology of large particles, and the Sunset Laboratory in Oregon (USA) the analyses of carbonaceous aerosol – EC&OC.

Acknowledgements are due to H.J.T. Bloemen who devised the project and to both H.J.T. Bloemen and E.M. van Putten for the performance of the measurements and the management of the fieldwork, quality control and the data streams during this complex process. Without their efforts this report would not have been possible. Finally, we would like to thank A. Opperhuizen and H. Diederen (both of the RIVM), the first of whom managed the overall project on PM of which this project forms part, and, further, all those not mentioned by name who co-operated to make this project a success.

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Samenvatting

Fijn stof in de buitenlucht met een diameter kleiner dan 10 µm (PM_{10}) blijkt op een consistente wijze geassocieerd te zijn met ernstige humane gezondheidseffecten. Dergelijke gezondheidseffecten zijn over de hele wereld gevonden, inclusief in Nederland. Dit was voor de Wereld Gezondheids Organisatie (WHO) reden om fijn stof op te nemen in de ‘Air Quality Guidelines’. De Europese Unie wijdde een aparte dochter-richtlijn aan fijn stof (1999/30/EC, onderdeel van de kaderrichtlijn luchtkwaliteit 96/62/EC). Voor de EU is dit een dubbele norm geworden met een jaargemiddelde waarde van 40 $\mu g/m^3$ en een dagelijks gemiddelde van 50 $\mu g/m^3$ met 35 toegestane overschrijdingen per jaar (het 90-percentiel van de daggemiddelde waarden), beide in 2005. De indicatieve waarden voor 2010 zijn 20 $\mu g/m^3$ als jaargemiddelde met 7 toegestane overschrijdingen voor het daggemiddelde van 50 $\mu g/m^3$.

Voor de Nederlandse overheid leidden de nieuwe luchtkwaliteitsnormen tot een aantal vragen over de huidige niveaus van fijn stof, de deeltjesgrootte-verdeling, chemische samenstelling, en de bijdragen van natuurlijke en antropogene bronnen (zowel lokale als buitenlandse) aan de huidige PM-niveaus in Nederland. Meer in het bijzonder zou het in het verleden gevonden ‘gat’ van 50% tussen modellen en metingen beter verklaard en zo mogelijk verkleind moeten worden. De ratio tussen metingen en modellen (waarbij alleen het antropogene deel van de bronnen is meegenomen) bedroeg in 1995 slechts 0,50.

Dit rapport gaat in op de bovenstaande vragen. Op zes plaatsen in Nederland zijn gedurende de jaren 1998 en 1999 een groot aantal metingen uitgevoerd. We hebben naast PM_{10} ook de fijne fractie ($PM_{2.5}$) gemeten en de grove fractie (PM_{10} - $PM_{2.5}$). Verder zijn de concentraties van secundaire anorganische zouten: ammonium, nitraat en sulfaat; elementair koolstof en organisch koolstof, natrium en chloride als tracers voor zeezout en 16 verschillende chemische elementen bepaald. Ook werden er nog bronprofielen verzameld van wegverkeer in de IJ-tunnel in Amsterdam. De kwaliteitscontrole op het veldwerk werd uitgevoerd door OMEGAM. De kwaliteitscontrole op de filtermetingen werd uitgevoerd door het RIVM.

Een van de conclusies van deze studie is dat er geen significant verschil bestaat tussen gemeten PM_{10}-concentraties en gemodelleerde PM_{10}-concentraties in combinatie met de bijdrage van natuurlijke bronnen. De gemiddelde ratio van de gemodelleerde versus gemeten concentraties bedraagt 0,94 (bij een uniforme correctiefactor voor de FAG-meetinstrumenten) of 0,91 (bij een locatie-specifieke correctiefactor). Wanneer ook rekening gehouden wordt met de verschillende onzekerheden, bedraagt één keer de standaardafwijking van de bovengenoemde ratio 0,20. Daaruit concluderen we dat het ‘gat’ tussen metingen en modellen adequaat is gesloten.

Aan de hand van de berekeningen met OPS/SIGMA en de resultaten van deze studie hebben we ons een indruk kunnen vormen van datgene wat met behulp van maatregelen te verbeteren zou zijn aan de concentraties van fijn stof. We vonden daarbij dat het maximale deel van PM_{10} dat door binnenlandse maatregelen te beïnvloeden zou zijn in Nederland, variabel is: 6 tot 18 $\mu g/m^3$. Het maximale deel dat door buitenlandse maatregelen (EU) te beïnvloeden is, varieert van 10 tot 15 $\mu g/m^3$. Jaargemiddeld is ongeveer 7 tot 9 $\mu g/m^3$ van het fijn stof in Nederland van natuurlijke oorsprong. Deze cijfers zijn indicatief: ze kunnen van jaar tot jaar variëren ten gevolge van meteorologische condities.

Summary

Particulate Matter (PM) in ambient air has consistently and coherently been associated with serious human health effects. Such effects have been found over the whole world, including the Netherlands. These health effects have constituted the reason for WHO providing guidelines for PM and for the EU to provide standards for PM in a daughter directive (1999/30/EC) of the EU 'Framework directive' on air quality (96/62/EC). For the EU this represents a combined PM_{10} standard with an annual average value of 40 µg/m^3 and a daily average value of 50 µg/m^3 in **2005**, with 35 permitted exceedances per year (90 percentile daily values). The indicative values for **2010** are 20 µg/m^3 as the annual average and 7 exceedances for a daily average of 50 µg/m^3.

The new EU air quality standards have, for the Dutch government, led to a number of questions concerning current levels, particle size and chemical composition of PM in the Netherlands, along with the contribution of natural and anthropogenic sources (both local and foreign) influencing the Dutch ambient PM levels. More specifically, the 50% 'gap' found between modelled concentrations (in which only the anthropogenic part of the sources were included) and measurements should be closed as far as possible.

This reports addresses the questions raised above. A great number of measurements were performed on six sites in the Netherlands in 1998 and 1999. Substances measured were PM_{10} – both its fine fraction ($PM_{2.5}$) and coarse fraction (PM_{10} - $PM_{2.5}$), the secondary inorganic aerosols - NH_4^+, SO_4^{2-} and NO_3^-, elemental and organic carbon - Cl^- and Na^+ as tracers for sea salt, and the elemental composition of aerosol (16 elements). Source profiles of traffic were gathered at the IJ-tunnel in Amsterdam. OMEGAM carried out the quality control of the fieldwork and the RIVM performed the quality control on the filter analyses.

One conclusion of this study is that there is no significant difference between measured and modelled PM_{10} concentrations in combination with the contribution of natural sources. The average ratio between model estimates and measured concentrations [modelled / measured] is 1:0.94 (uniform correction factors for the FAG instruments) or 1: 0.91 (location-specific correction factors for the FAG instruments). In earlier studies a 'gap' of approximately 50% was found. Taking the uncertainty in the various estimates into account, we found that the 1-σ confidence limits in the ratio [modelled / measured] to be ± 0.20. Hence, we could conclude the 'gap' between measurements and model estimates to be adequately closed.

Combining OPS/SIGMA model calculations and results from this study to get an impression of what abatement could achieve led us to discover that the maximum level of PM_{10} that can be influenced by domestic abatement measures within the Netherlands, is highly variable: from to 6-18 µg/m^3. The maximum PM_{10} level that can be influenced by foreign abatement measures (EU) varies from 10 to 15 µg/m^3. PM_{10} in the Netherlands from a natural origin is estimated between 7 and 9 µg/m^3. Due to year-to-year variations in meteorological conditions these values may differ for other sampling periods.

1. Introduction

Particulate Matter (PM) in ambient air has been consistently and coherently associated with serious human health effects. Such effects have been found over the whole world (US-EPA, 2001), including the Netherlands (Hoek et al., 1997; Vonk and Schouten, 1998).

These health effects have been the reason for WHO in providing guidelines for PM (WHO, 2000) and for the EU in providing standards for PM in a daughter directive (1999/30/EC) of the EU Air Quality Directive (96/62/EC). For the EU this represents a combined standard for PM_{10} in **2005**, with an annual average value of 40 $\mu g/m^3$ and a daily average value of 50 $\mu g/m^3$, as well as 35 permitted exceedances per year (90 percentile daily values). Indicated for **2010** are values of 20 $\mu g/m^3$ as an annual average and 7 exceedances for a daily average of 50 $\mu g/m^3$. The **current** PM_{10} standard is based on the less severe annual average value of 40 $\mu g/m^3$ and daily average value of 140 $\mu g/m^3$ (no exceedances allowed). It should be noted that annual and daily thresholds hold for *any* location in the Netherlands.

Both present and future standards are difficult to maintain in the Netherlands, as shown by Visser and Römer (1999), Wal and Janssen (2000) and Hammingh (2001). Therefore the new air quality standards have led to a number of issues posed by the government concerning PM in the Netherlands, like PM levels, particle size and chemical composition, and the contribution by natural and anthropogenic sources (both local and foreign) to Dutch ambient PM levels. More specifically, the 50% ‘gap’ found between modelled concentrations and measurements should to be closed as far as possible.

Epidemiology has provided us with concentration –response relationships (Hoek et al., 1997; Hoek and Brunekreef, 1999) for a PM risk assessment. Epidemiology also provided us with the conclusion that judging by the criteria of Hill (1965), one should accept a causal relationship between the ambient PM levels and observed health effects in populations. An extra complicating factor with PM and health effects is that there does not seem to be a threshold for those effects (US-EPA, 2001; Hoek et al., 1997; Vonk and Schouten, 1998; WHO, 2000).

For risk assessment and risk management purposes the concentrations of PM in ambient air are, therefore, essential pieces of information. The RIVM National Air Quality Monitoring Network regularly monitors the PM_{10} concentrations in the Netherlands (Den Hartog, 1999). The annual average PM_{10} concentrations in the Netherlands in ambient air have also been modelled with Gaussian dispersion models (Jaarsveld, 1995) on the basis of national and European emission inventories (Wesselink et al., 1998).

Neither of the methods led to matching results (Bloemen et al., 1998; Buringh et al., 1998). Generally speaking, only half the annual average of 40 $\mu g/m^3$ of the PM_{10} that was measured during the early nineties in the Netherlands could be calculated with the models, taking the emissions for these years as an input parameter. However, the gap is probably not a modelling problem as the dispersion model has been validated for gases (Jaarsveld, 1995) but is mainly caused by unaccounted sources of PM.

A number of natural sources contributing to primary ambient PM levels like sea salt and wind-blown crustal material, was originally not modelled. They are not included as sources in the existing emission inventories, which only cover anthropogenic emissions. These and maybe even some currently unknown other sources, seem important in understanding the PM mass balance in the Netherlands.

A project to measure the particle size and chemical composition of PM for one year was started up at six different locations in the Netherlands. These locations are representative for different exposure situations in the country e.g. busy streets, urban backgrounds, and rural and seaside locations. Armed with the knowledge of chemical composition and particle sizes of specific sources and tracers, we had as objective to find out which natural and anthropogenic sources were contributing to PM (**Figure 1**). The project was also started to be able to estimate the level of the contribution of these currently still unknown or non-quantified sources to Dutch ambient PM levels by way of source apportionment. We note that a completely different approach, based on 'rule of thumb', was reported by Janssen et al. (1999[b]).

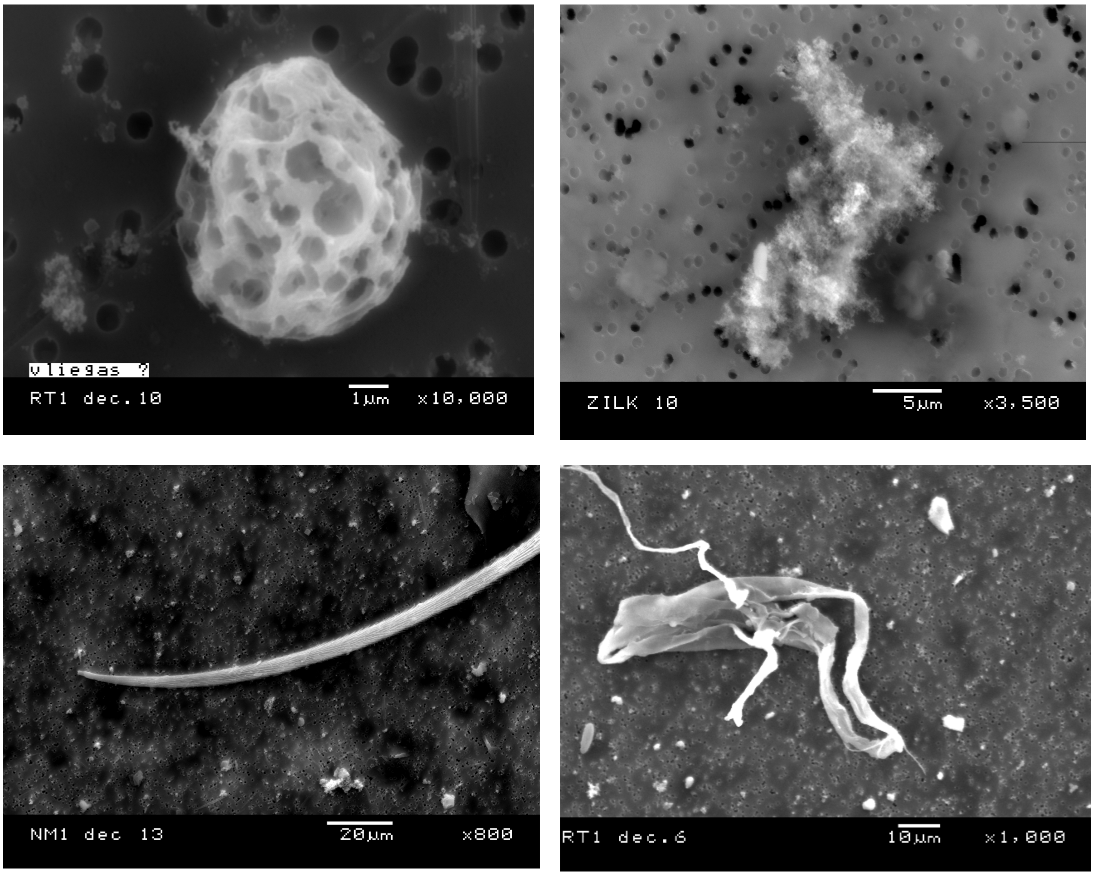


Figure 1 *SEM projections of particles from anthropogenic sources (upper left: fly-ash particle in a sample from the site, Rotterdam Overschie; upper right: soot from traffic emissions in a sample from the site, De Zilk), and natural sources (lower left: antenna of an insect in a sample from the site, Nijmegen; lower right: plant material in a sample from the site Rotterdam Overschie). Source: Timmner (2000[b]).*

In summary, the primary objectives of this PM study were:

- to identify relevant sources and quantify their contribution to ambient particulate matter concentration in the Netherlands
- to assess the degree of under- and overestimation of relevant sources by comparison of measured and modelled levels of PM_{10}
- to assess the contribution of sources not to be influenced by abatement measures (in particular the natural sources).

This report consists of seven Chapters. In Chapter 2 we describe the study design of the project, presenting the six monitoring sites and the sampling regime. We also give a short resume of the different instruments used for sampling and size classification of PM, as well as the various techniques used afterwards for the chemical analyses. The other algorithms used for the interpretation and the statistical techniques are also briefly presented.

Chapter 3 presents the results found during the course of the project. It gives the PM_{10} and $PM_{2.5}$ mass levels collected with the various instruments, VAPS, FAG and TEOM. The results for inorganic secondary aerosol measurements and sea salt concentrations (Cl^-) using a Dichote and LVS are presented next, followed by the carbonaceous aerosol (OC and EC) concentrations and elemental composition measured by VAPS. It concludes with the total PM mass of VAPS and FAG. Chapter 4 extends the results to the dispersion models (TREND/OPS and SIGMA) that have been used for the calculation of the annual average concentrations, the model uncertainties and the results of the modelling exercises for PM_{10}, secondary aerosol and tailpipe emissions of road transport. Maps of the modelling exercises have been included.

Chapter 5 presents the discussion, which starts with the instrumental differences for the concentrations of PM_{10} and $PM_{2.5}$, inorganic secondary aerosols and sea salt. Then the estimated contribution of traffic and of crustal material to PM_{10} is discussed, with a separate contribution on estimated sea salt. All the results are interpreted in the light of the scientific knowledge in especially the countries surrounding the Netherlands, such as Germany and the UK. Chapter 6 extends the discussion to the question of gap closure. For example is the mass of PM more in balance by the contributions of sea salt, crustal material and traffic? The final chapter, 7, presents the conclusions of the project.

2. Study design

2.1 Monitoring sites and sampling program

The objective of the measurement campaign was to collect data that would help to improve the understanding of the composition of particulate matter and its origin. As stated in Chapter 1, the hypothesis for the discrepancy between monitoring results and model calculations includes the underestimation of anthropogenic source categories and the absence in the emission data of biogenic, natural sources. To account for these types of sources, sites were selected that might be impacted by these sources at a different rate.

This calls for sites in urban areas where traffic and other domestic sources would be the main source. Furthermore, as the Netherlands is bordered by the sea in the north and west, a site mainly impacted by the sea with the wind blowing in certain directions is included in the set. Since industry and agricultural activities are expected to be an important source for particulate matter, two sites near these sources are included as well.

Temporal variation of particulate matter levels can be considerable. Several observations in the NAQMN and a series of investigations show the PM composition to vary substantially over time (Visser, 1999). A period of one year was considered minimal to capture these variations and to allow for comparison of measurement data with annual averaged model calculations. Logistic and operational considerations led to a sampling regime that only partially covered this period for most of the measurements. Details on timing of sampling and analysis are given below.

Particulate matter can be divided into the groups: inorganic secondary aerosol, organic secondary aerosol, primary emitted aerosol and organic material (detritus). Rationale for the selection of the parameters is elaborated in the respective sections.

Six sites were selected for monitoring particulate matter parameters. See **Figures 2A and 2B**. We selected two regional background sites (De Zilk and Vredepeel), which constituted part of the National Air Quality Monitoring Network (NAQMN). De Zilk was included in the set for its proximate vicinity to the sea, and Vredepeel for its agricultural surroundings. In Amsterdam two sites were selected, both of them forming part of the Amsterdam Air Quality Monitoring Network, operated by OMEGAM Amsterdam. These sites represented the urban background site, Overtoom, and the street site, Stadhouderskade, the latter site surrounded by heavy traffic.

The Rotterdam-Overschie site was added on request of and on behalf of DCMR. This site has been included in several epidemiological studies and forms part of the local DCMR air quality monitoring network. An industrial site at Nijmegen was added to the project for the Province of Gelderland. This site is situated in an industrial area, surrounded by residential areas, where, in the last few years, several investigations have been conducted .

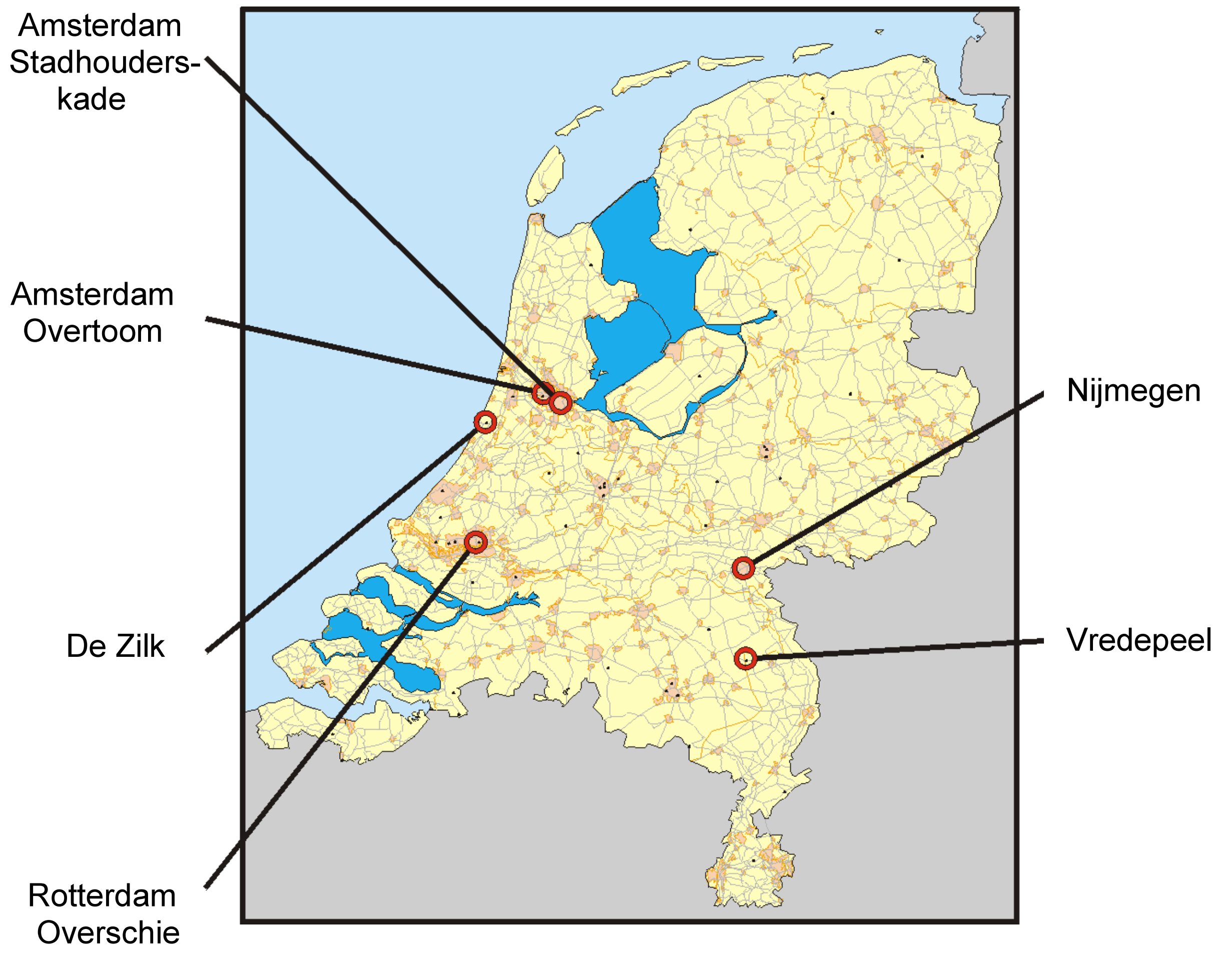


Figure 2A Location of the six sampling sites within the Netherlands.

Table 1 gives the specifications of the sites.

The project ran from September 1998 to August 1999. Continuous monitoring of PM_{10} and $PM_{2.5}$ was conducted during the entire period. The basic measurement frequency for filter methods was every sixth day. The 24-hour measurement period ran from midnight to midnight. The filters were changed the day after sampling except for the Friday or Saturday sample (when filter was changed on the following Monday). The measurement frequency was increased once to every other day for two periods (half January 1999 to half February 1999 and July 1999). A calendar is given of all the sampling days in Van Putten et al. (2001^c). The database consists of 79 days in total.

Table 1 Characteristics of the six sampling sites.

	1 **Nijmegen**	**2** **Rotterdam Overschie**	**3** **Amsterdam Overtoom**
Classification	Industrial	Urban background	Urban background
Co-ordinates	51°51'09", 5°50'00"	51°56'11", 4°26'06"	52°21'40", 4°52'00"
Housing	On the roof of a three-storey building; VAPS and Dichotomous sampler outside	Non-climate-controlled concrete housing	Climate-controlled housing, contains TEOMs
Inlet height	14 m	3 m	3 m
Operator	Province of Gelderland, City of Nijmegen	DCMR	OMEGAM
Monitoring methods	TEOM $PM_{2.5}$ TEOM PM_{10} VAPS Dichotomous sampler	TEOM $PM_{2.5}$ TEOM PM_{10} VAPS Dichotomous sampler	TEOM $PM_{2.5}$ TEOM PM_{10} VAPS Dichotomous sampler
Remarks	Incineration plant, coal-fired power plant and various other industrial plants nearby	Residential area surrounded by motorways	West of City park (Vondelpark) and separated by 3 story building from street.

	4 **Amsterdam Stadhouderskade**	**5** **Vredepeel**	**6** **De Zilk**
Classification	Street	Rural agricultural	Rural seashore
Co-ordinates	52°21'30", 4°54'15"	51°32'28", 5°51'13"	52°17'53", 4° 30'37"
Housing	Climate-controlled advertising column	Climate controlled portacabin (standard monitoring network housing)	Climate controlled portacabin (standard monitoring network housing)
Inlet height	4 m	3.2 m	3.2 m
Operator	OMEGAM	OMEGAM RIVM	OMEGAM RIVM
Monitoring methods	TEOM $PM_{1.0}$ TEOM PM_{10} VAPS Dichotomous sampler	TEOM $PM_{2.5}$ ß-dust PM_{10} VAPS Dichotomous sampler LVS	TEOM $PM_{2.5}$ ß-dust PM_{10} VAPS Dichotomous sampler LVS
Remarks	20,000 vehicles per 24 h.	Nearby farm growing potato and flowers; Region – factory-farm pig breeding NAQMN station (NAQMN-131)	Surroundings in use as glider field. Approx. 2 km east of seashore. NAQMN station (NAQMN-444)

2.2 Instrumentation

2.2.1 PM_{10} and $PM_{2.5}$

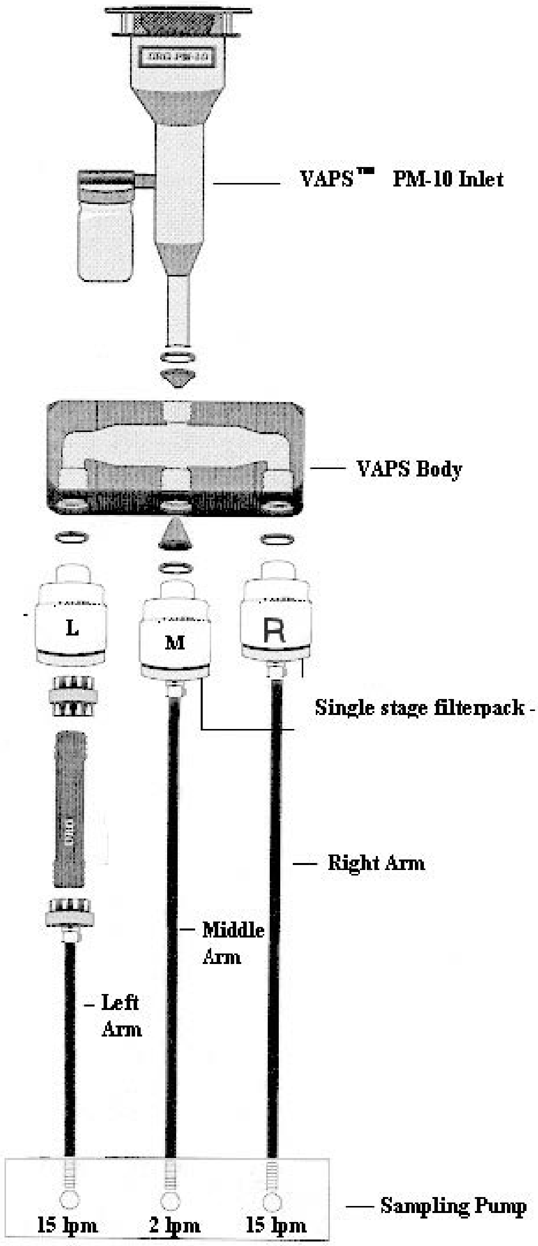
PM_{10} and $PM_{2.5}$ concentrations were measured on a continuous (hourly) basis and were time integrated (daily). *Continuous* PM_{10} concentrations were measured with either TEOM 1400 monitors, equipped with a Sierra-Andersen 246b PM_{10} inlet (all stations except the rural background station De Zilk and Vredepeel) or FAG/Eberline monitors. The inlet and the oscillating filter were kept at 50°C. Filters were changed at filter loads higher than 90%. At the rural background stations a FAG/Eberline fh62I-N monitor, equipped with an identical inlet on top of a heated inlet line (50°C), were used. Filters were changed automatically every 25 hours. This monitor is further on known as a 'FAG'.

$PM_{2.5}$ was *continuously* monitored with a TEOM 1400 equipped with a URG $PM_{2.5}$ cyclone. Operation conditions were identical to those for the PM_{10} measurements with the TEOM 1400 except at the De Zilk and Vredepeel stations, where a 3 $l.min^{-1}$ sample flow inlet was used. At the street station in Amsterdam (Stadhouderskade) the TEOM 1400 was equipped with an URG $PM_{1.0}$ cyclone. All instruments present the concentrations as hourly averaged values at Standard Conditions (20°C and 1 atm).

The data were collected at the stations or through the data network of the NAQMN, and validated at the RIVM on the basis of technical parameters supplied by the instrument (operation quality parameters; omitting first value after filter change). After inspection of the remaining data by the operator, hourly data were converted to daily averaged values only when more than 75% (= 18 hourly values) of the data was available.

Integrated samples were collected over a day with the Versatile Ambient Particle Sampler (VAPS URG 3000K) as in **Figure 3A**. This sampler has been used for collecting samples for source apportionment studies (e.g. Mukerjee et al., 1993). It consists of a Teflon-coated PM_{10} inlet and a $PM_{2.5}$ virtual impactor separating two side streams ($PM_{2.5}$) from a main stream ($PM_{coarse} = PM_{10} - PM_{2.5}$) in the ratios of 15:15:2 l/min (mass flow controller). Besides the coarse mode the main stream contains approximately 6.3% (2/32) of the $PM_{2.5}$ particles. Particulate matter in the main stream and in one of the side streams is collected on Gelman, Teflo R2PJ047 filters (pores size 2 μm). The particles in the second side stream were collected on a pre-fired quartz filter. The filters, diameter 47 mm, were mounted in Teflon filter holders. A timer controlled the sample time.

After sample collection, the filter holders, along with the filters, were changed in the field and transported to the laboratory. The quartz filters were removed from the holders, packed in coded plastic petri dishes, wrapped in aluminium foil and stored at –15°C until transhipment in blue ice to Sunset Laboratories for analysis. The Teflon filters were removed from the holder, placed in coded petri dishes and stored in a conditioned room (temperature 23 ± 1°C; RH% 53 ± 2%). Teflon filters were weighed at the institute before and after sampling at a Mettler AT 261 analytical balance (resolution 10 μg) after conditioning for at least 48 hours.



The VAPS is equipped with a Teflon coated 32 l/min PM_{10} sampling inlet.

The VAPS body separates $PM_{2.5}$ (fine) and $PM_{2.5}$ - PM_{10} (coarse) particles.

The left and right arms collect fine particles.

The middle arm collects the coarse particles.

Three pumps maintain the desired flows, controlled by mass flow controllers and followed by gas meters.

Figure 3A The URG 3000K VAPS. Throughout the project the Teflon filters from the VAPSs were weighed both before and after sampling to determine the mass of the particulate material collected. The filters were weighed in the RIVM-LLO weighing room. This room has climate control and is kept at a temperature of 23 °C (± 1°C) with a relative humidity of 53% (± 2%). Weighing was done using a Mettler AT 261 analytical balance.

2.2.2 Secondary aerosols and sea salt

Inorganic secondary aerosol samples for measuring sodium chloride, NO_3, SO_4 and NH_4 in both the fine ($PM_{2.5}$) and coarse (PM_{10} - $PM_{2.5}$) fractions were collected with the Dichotomous Sampler (Dichote - Sierra Instruments model 244), equipped with a 246b PM_{10} inlet. It further consists of a $PM_{2.5}$ virtual impactor separating a $PM_{2.5}$ side stream and a PM_{coarse} main stream. Chloride and sodium concentrations were also measured using the Dichote.

Particles were collected on Gelman, Teflo R2PJ047 filters (pores size 2 μm), placed between two Teflon rings. Filters were transported in a holder to and from the measurement location between these rings. Filters were removed from the rings in the laboratory with a pair of tweezers and placed in a sample jar. The day before analysis, 40 ml of de-mineralised water was added to the jar and placed in a (unheated) ultrasonic bath for fifteen minutes.

Ammonium was determined with photometry as its indofenol complex, sodium analysed using ICP-AES and chloride, nitrate and sulphate with ion-chromatography and a pulsed electrochemical detector. Details of the methods are described in Van Putten et al. (2001^c).

The inorganic secondary aerosols NO_3, SO_4 and NH_4 as well as Cl^- are also measured on a daily basis within the NAQMN, using Low Volume Samplers (LVS) as in **Figure 3B**. A volume of air (2500 l per 24 hours) is sucked through the PM filter with a constant flow. Concentrations of sulphate, nitrate, ammonium and chloride are then determined with the aid of ion-chromatography.

For two sites the NAQMN coincided with our sampling sites, De Zilk and Vredepeel. The results using the Dichote were to be compared with those of the LVS for these two particular sites.

2.2.3 Carbonaceous aerosol

Carbonaceous aerosol was measured as the sum of two parameters: elemental carbon (EC) and organic carbon (OC). The samples, collected at quartz filters prefired (700°C, 1 hour by Sunset Laboratories) using the VAPS, were send to Sunset Laboratories (Oregon, USA), packed in blue ice. The OC/EC instrument and analysis procedures are described by Birch and Cary (1996).

Briefly, the method consists of three phases. In phase 1 all the organic carbon is removed from the filter by heating in steps to 700°C in oxygen-free helium. Part of the organic carbon might be pyrolitically converted to elemental carbon (char), indicated by a decrease of the transmission of the filter, and monitored continuously by laser. In phase 2 the organic compounds are oxidised to carbon dioxide and reduced to methane, which is detected with FID. After cooling, 2% oxygen is added to the helium atmosphere and the filter oven is heated to 850°C in order to oxidise elemental carbon.

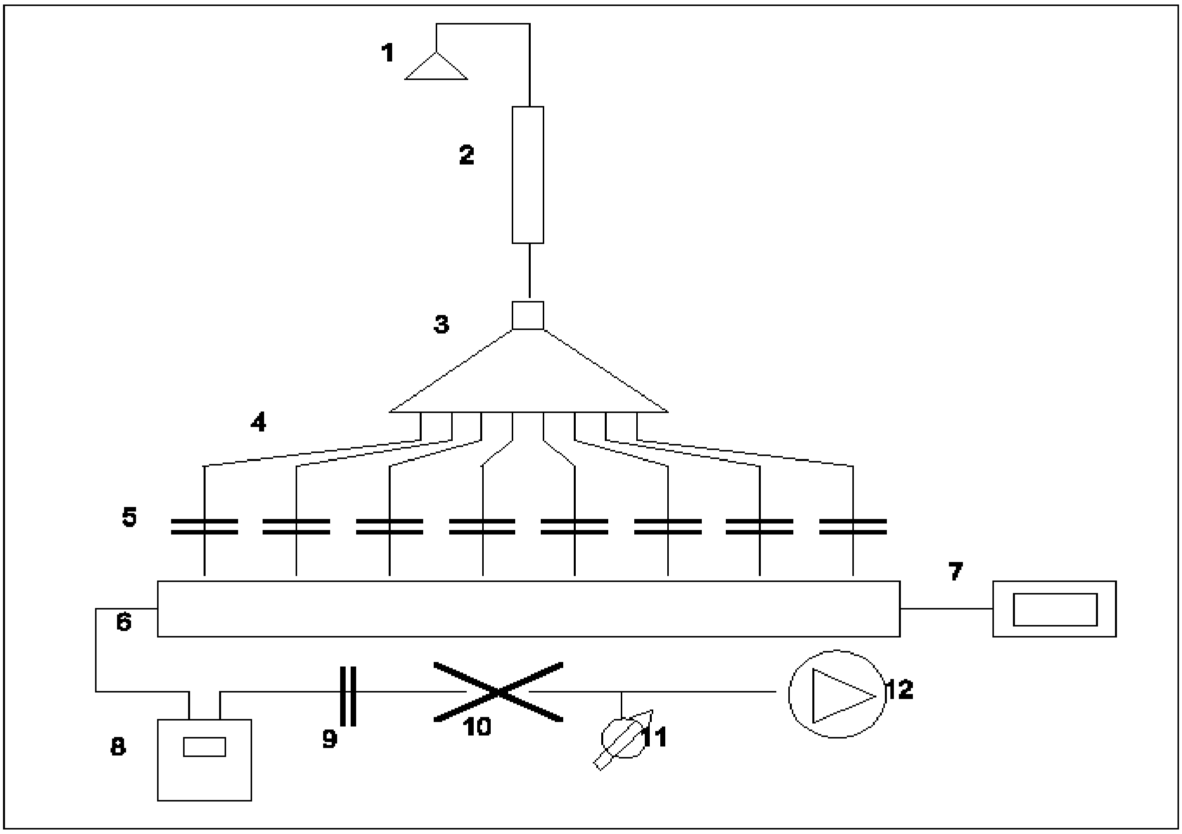


Figure 3B Schematic view of the Low Volume Sampling (LVS) for sulphate, nitrate, ammonium en chloride in ambient aerosol.

1:	*sucking funnel*	*7:*	*electronic steering clock*
2:	*coal denuder*	*8:*	*gas meter*
3:	*allocation part*	*9:*	*protection filter*
4:	*sucking hose*	*10:*	*critical opening*
5:	*filter head*	*11:*	*underpressure monitor*
6:	*manifold and valve box*	*12:*	*vacuum pomp*

In phase 3 each sample is followed by its own calibration with a known volume of methane. Only a 1.5 x 1.0 cm punch of the filter is used, allowing a repeat.

Precision and accuracy as claimed by Sunset Laboratories is 4-6% and 5% (standard deviation) for the range of 5 – 400 $\mu g/m^3$ OC and 1 – 15 $\mu g/m^3$ EC. There were 46 repeats carried out during the project. The average results differ less than 2% for both OC and EC with a pair-wise maximum deviation of 10% and 20% for OC and EC, respectively. The analysis results expressed in $\mu g/cm^2$ were converted to $\mu g/m^3$, assuming equal distribution over the quartz filter, and based on the measured flow and sampling time of the VAPS.

2.2.4 Elemental composition

During the project, samples were analysed by MiTac (Antwerp, Belgium) and the National Exposure Research Laboratory of the US Environmental Protection Agency, Research Triangle park (NC, USA)[1]. Intercomparison exercises were included at the start and mid-term of the project.

The weighed Teflon filters were transported to the MiTac laboratory (Antwerp, Belgium) for EDXRF elemental analysis. Measurements were performed by an automated Tracor Spectrace 5000 EDXRF system (Tracor X-Ray, CA USA), coupled to a PC controlling the spectrometer and the data acquisition. The whole white spectrum generated by a low power Rh-anode X-ray tube (17.5W, operational range 6 – 50keV, current 50mA) was used for excitation of the samples under vacuum conditions. Emergent rays were detected at 90^o relative to the incident X-ray beam by a Si(Li) detector.

The standard operation procedure followed the guidelines of USEPA/NERL. A series of thin film reference standards (Micromatter, Seattle, WA, USA) were used to derive sensitivity factors. Besides the intercomparison with EPA, MiTac participates in world-wide intercomparisons organised by the International Atomic Energy Agency (IAEA, Vienna, Austria). Further, it does intercomparisons with the ‘Vlaamse Milieumaatschappij’ (VVM), the Flemish Environmental Agency in Antwerp, Belgium, using a wavelength-dispersive XRF for a limited number of elements. Accuracy of the MiTac analysis was on average 14% depending on the element and concentration. Precision was less than 5%. Background levels of Teflon filters were measured and subtracted from measured intensities of the aerosol samples. Homogeneity was tested on ten randomly selected samples. Three repeated measurements each after rotating the filter 40^o gave an average standard deviation of 5%.

The method used by EPA/NERL is comparable with the MiTac method and is described in more detail in Dzubay and Stevens (1988).

The results of the intercomparisons with USEPA/NERL showed good agreement (average relative difference 10-20%, depending on element and concentration). Special attention was given to potential losses due to transport; however, based on the results, no (trampoline–) effect could be identified. Accuracy of the MiTac analysis was on average 14%, depending on element and concentration. Precision was less than 5%. Background levels of Teflon filters were measured and subtracted from the measured intensities of the aerosol samples. Homogeneity was tested on 10 randomly selected samples. Three repeated measurements after rotating the filter over 40^o each gave an average standard deviation of 5%. The method is described in detail in Van Putten et al. (2001^c).

The method used by EPA/NERL is described in detail in Dzubay and Stevens (1988). Both methods of MiTac and EPA/NERL were intercompared before and during the project and showed good agreement (Van Putten et al., 2001^c). Hence, the results are considered interchangeable.

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[1] Courtesy of Dr. Charles Lewis, NERL/USEPA

2.2.5 Notes on sampling characteristics of different instrumentation

Ambient aerosol consists out of a mixture of particles with a broad spectrum of sizes, shapes, chemical composition and physical characteristics. Apart from very arid conditions a considerable fraction of the mass of ambient aerosol is water. With the exception of in situ measurements it is almost impossible to analyse ambient aerosol unbiased.

Measurements of PM_{10}, $PM_{2.5}$ and chemical constituents of aerosol in this study are carried out with various instruments. Especially the presence of water can disturb automatic sampling and detection systems. Necessarily, the instruments have a device to avoid this disturbance but they will have also unwanted interferences on the aerosol. Additional interferences are caused by inlet systems and by pre-concentration of aerosol on filter media. The interference of an instrument varies with the amount and composition of the aerosols sample and thus it is a function of time and location.

The samples of a FAG instrument will contain still some water and will show losses of volatile organic compounds and ammonium nitrate. In the NAQMN PM_{10} measured by FAG is multiplied by 1.3 as a standard correction procedure for this losses. TEOM has a more fierce system to dry the sample leading to even more losses of volatile constituents. Although, VAPS, Dichote and LVS methods are relatively ‘mild’, some losses will still be possible.

FAG, TEOM, VAPS and Dichote are equipped with inlet systems or virtual impactors with well defined cut off points for aerosol particles. The LVS method has no such device. The 50% cut off point will be somewhere in between 2.5 and 10 micrometer. So, all instruments but LVS will sample the larger particles in the PM_{10} range.

2.3 Additional data

Meteorology
To evaluate the observed levels of the various parameters meteorology is essential. As the sites are spread over the Netherlands from west to east data from three meteorological observation stations were gathered from the NAQMN database (collected by KNMI at Rotterdam airport, Schiphol airport and Volkel airport).

Source profiles for traffic
In addition to the routine sampling programme that continued for a year, special samples were collected in order to draw up a source profile for motor traffic. These samples were obtained in the IJ Tunnel in Amsterdam, between 13 and 17 December 1999. The tunnel under the IJ is a double tunnel, one for each two-lane carriageway. The samples were collected a hundred metres from the end of the tunnel. Particulate material concentrations were collected during the morning rush hour only, when traffic on the city-bound carriageway is at its heaviest.

The sampling procedure was comparable to the routine programme, except for the sampling period which was much shorter, on account of the higher concentrations. Five morning rush hour samples were collected using the VAPS with same set-up as the standard measurements. Using a second VAPS, samples were collected on five occasions with a Nuclepore filter fitted in the coarse stream and dummy filters in the $PM_{2.5}$ streams. Sampling periods varied from five to fifteen minutes. The Nuclepore filters were subjected to SEM/XRF analysis by MiTac.

VOC measurements were also made in the tunnel using carbon tubes, in accordance with the following procedures. The universal sampler consists of a pump, three capillaries, a case with 32 programmable valves and a computer unit. Sampling was programmed for the times indicated below. Over a period of five days, a total of 32 tubes were exposed.

To get an impression of the source profiles of traffic, three samples were collected in one of the tubes of the IJ-Tunnel. During three consecutive days the VAPS was run for different periods. The filters were treated analogue to the ambient air samples. No background samples outside the tube were collected.

Morphology of large particles
Eleven samples were collected on open-face gold Nucleopore filters (sample volume 3.4 m^3, sample time: 7 hours). The diameter of the pores in these filters is 0.8 μm. The filters were transported to TNO for morphological and elemental examination. At the laboratory the filters were removed from the holder and fixed to a SEM-stub using conducting silver-paste. Morphology and elemental composition were examined with stereo light microscopy and SEM/RMA (ScanningElectronMicroscopy/RőntgenMicroAnalysis).

SEM/RMA is a technique for simultaneous research of the surface structure (morphology) and (local) elemental composition of material. All elements with atom numbers of 6 and higher are detectable. In some cases the shape of a particle is sufficient for determination of its origin. Examples are conglomerates of soot (compare Figure 18) or plant material (compare Figure 21). But in most cases morphology and the use of Rőntgen spectra go hand in hand. An example is the fly-ash particle in Figure 18. In some cases only the use of the Rőntgen spectra are conclusive as in the case of the Fe-oxide particle in Figure 11 or the Al particle in Figure 22. Details are given in Timmner (2000[a,b,c]).

In this report we use the SEM/RMA technique only for illustrative purposes. Unfortunately, the technique is not able to quantify the weight of various particles in a sample in a statistical sense. At best, one can get a qualitative estimate of particle frequencies or weights.

Speciation of organic particulate matter
Samples for the speciation of organic particulate matter were collected at all sites on three days at the end of the project (26, 28 and 30 September 1999) on a pre-treated quartz filter and a poly-urethane-foam filter (PUFF) in series in the VAPS. Sampling time was 24 hours resulting in a volume of approximately 22 m^3. Filter and PUFF were ultrasonic extracted with dichloromethane. The extracts were concentrated and analysed using GC/MS for selected compounds as tracers for significant sources based on Cass (1998). The selected tracers included: 5-α-cholestane, coronene, benzo[ghi]perylene (petrol and diesel fuelled engines), benz[a]anthracene-7,12-dione (gas combustion), tetratriacontane (road and tire dust), octacosane and triacontane, dotriacontane (vegetation), cholesterol (meat processing). Recovery ranges from 70-100%. Quantification was based on the use of selected on deuterated internal standards.

2.4 Quality control

Monitoring, sampling and analysis were performed according to standard operation procedure (SOP) for all field operations and the analysis in the certified laboratories of the institute. Quality officers of the institute performed an audit of the fieldwork mid-term of the project. Flows and volumes of sampling equipment were checked at regular intervals if not for each sample. Various trails were conducted to test sample blanks, reproducibility of weighing and analysis. The obtained results were examined for internal consistency. All these tests were used to validate the results that were used for the final data exploration and examination.

Operators
OMEGAM controlled the quality of the fieldwork by instructing all operators in the field. They also performed several checks throughout the project. An RIVM-quality manager made an audit by visiting all sites and checking the fieldwork. The working method, quality, archiving and safety of the operators was carefully checked and reported (Van Putten et al., 2001[c]).

The instruments
One of the concerns in the field of the instruments is the sampled volume.

- The dichotomous samplers were all equipped with identical electronic timers that were very accurate. The flow is controlled by a pressure drop system, which maintains the flow even if the filters are loaded. The dichotomous sampler has no gas meters so a regular control with a BOIS DryCal DC-1 flow calibrator was needed. Because of the low temperatures during the winter period the BOIS did not function well. Therefore, it was impossible to measure the flows accurately in this period. The dichotomous samplers were tested and adjusted before placing them in the field.
- The VAPSs have build-in timers. Three mass-flow meters control the three flows and the flows are recorded by three gas meters. The VAPSs were tested before placing in the field on stability of the flow, timers and overall performance.
- The TEOM has a mass-flow controller.

The second concern is the cleaning of the sampling inlet. The PM_{10} sampling head and the $PM_{2.5}$ cyclone were cleaned every 3 months.

Weighing
The Mettler AT261 analytical balance, which was used for the weighing of the VAPS filters, has been calibrated once a year and operated according the manual. Some filters were weighed twice after loading with a few weeks in between. The results show that the followed procedure was accurate.

Filter blanks
A number of filter blanks was sent to each laboratory along with other filters. If necessary, these values were used to correct the actual values.

Intercomparison of laboratories
The Teflon filters of the VAPS were analysed in two laboratories MiTac (Belgium) and EPA (USA). Before the start of the project some filters, analysed by EPA, were also analysed by

MiTac. Because of the satisfactory results, the nearby MiTac was chosen as the element analyses laboratory. When troubles arouse within the project because of the time consuming analyses, EPA was asked to analyse several batches. Some filters already analysed by MiTac were sent with these batches. This was possible because XRF analyses are non-destructive. The results were satisfactory (Van Putten et al., 2001[c]).

Data transport and control

OMEGAM was in control of the data transports. Because OMEGAM sent the filters to the different laboratories, they received the results. Then, all results of the analysed filters were sent to the RIVM-LLO. At the RIVM a database was constructed in which the measured volumes, mass and analyses results were coupled by their sample code.

2.5 Other analyses

2.5.1 Crustal contribution

Two separate algorithms are used to present an estimate of the contribution of crustal material to the levels of PM in the Netherlands. With the term 'crustal material' we mean all wind-blown and re-suspended dust with a composition comparable to the earth's crust. Crustal material is both from natural and anthropogenic sources, and has diameters smaller than 10 μm.

In the first approach the concentrations of Al and Si that have been measured, are used as an input parameter. As a measure for the composition of the earth's crust page F-195 from the Handbook of Chemistry and Physics (56th ed.) is used. For Si this is 277200 ppm and for Al it is 81300 ppm. The annual average concentrations of each of these two elements are divided by the number of ppm's and multiplied by 1,000,000, which leads to the average contribution of the earth's crust based on the specific element as a tracer. As both elements give different values for the contribution of crustal material because both tracers are subject to a number of random processes producing errors of measurement, the mean of both elements is presented as the crustal contribution (see equation 1a):

$$[\text{Crustal1}] = ([\text{Si}]^* 10^6/277200 + [\text{Al}]^*10^6/81300) / 2$$

$$= 1.80 [\text{Si}] + 6.15 [\text{Al}] \qquad (1a)$$

Smeets et al. (2000) report in their Table 2.3 an average concentration of elements in soil and crustal material (their concentrations are not specific for the Netherlands). For Si they report 330,000 ppm in soil and 277,000 – 311,000 ppm in crustal material, while for Al their figures are 71,300 ppm for soil and 77,000 – 81,000 ppm for crustal material. If their values for soil were taken from Equation (1a), a difference of 16% for Si and of 12% for Al would hold. If their values of crustal had been taken, even smaller differences would arise. Since the values of Smeets et al. (2000) are so close to those presented in Equation (1a), we will use this tracer equation throughout this report.

In the second approach we estimate the crustal contribution in a different way. Using an equation based on the average concentrations of a number of elements: Si, Al, Fe, Ca, K. This second estimate of the crustal material has been presented by Van Loy et al. (2000):

$$[\text{Crustal2}] = 2.14\ [\text{Si}] + 1.89\ [\text{Al}] + 1.43\ [\text{Fe}] + 1.4\ [\text{Ca}] + 1.2\ [\text{K}] \tag{1b}$$

The numerical weighing factors in Equation (1b) are simply based on the corresponding oxides. The results of both approaches will be presented in Section 3.7.

2.5.2 Traffic contribution by tailpipe emissions

Similar to the previous contribution, the traffic contribution of the Dutch ambient PM levels can be calculated in a number of ways. In this section two methods will be explored. The first method leads to an overestimation and the second to an underestimation. Therefore, both methods will be used to present a bandwidth for the traffic contribution by tailpipe emissions (traffic_t). The contribution by resuspension of crustal and plant material by traffic (traffic_c) will be treated in the discussion in Section 5.2.

- The first method interprets all the measured ambient EC concentration as a marker of the tailpipe emissions by traffic. As traffic does not only emit EC but also OC, the ratio of OC to EC from traffic was measured during the project (compare Section 3.4) with the same instruments. For the time being the traffic contribution may be calculated using the following equation by giving this ratio a value of α:

$$[\text{Traffic1}_t\,] = [\text{EC}] + \alpha * [\text{EC}] \tag{2a}$$

- The second method tries to take into account the fact that not all EC emissions are from traffic. Other combustion sources also contribute to the EC emissions; unfortunately, the exact value of the EC emissions is not known, as the emission inventories for PM are not chemically specified. However, by taking the emission of the traffic by its tailpipe and dividing this by the emissions of the other combustion sources (the energy sector in industry and for electricity production in combination with that of traffic), the fraction of EC that may be attributed to traffic can be calculated. In 1995 Dutch traffic tailpipe emissions were x kT, energy in industry was y kT and energy for electricity was z kT. The traffic fraction for EC would therefore be $x / (x + y + z) \equiv \beta$. The estimate with this second method will be an underestimate because the emissions from the energy generation tend to be emitted from high stacks and therefore contribute less to the concentrations of EC at noise levels in cities. In the equation the second estimate becomes:

$$[\text{Traffic2}_t\,] = \beta * ([\text{EC}] + \alpha * [\text{EC}]) \tag{2b}$$

2.6 Data processing and statistical approach

Raw data files were used with only little or no formatting as input for a relational database in Microsoft Excel using method, compound, site and date as keys. Calculation of control variables were incorporated in the database and used for validation., along with logbook entries. Extracted subsets were Excel spreadsheet, formatted for use in the statistical software (S-PLUS 2000).

The final Excel database, containing six sheets, one for each of the six sites: ‘Stadhouderskade’, ‘Overtoom’, ‘Overschie’, ‘Nijmegen’ , ‘DeZilk’ and ‘Vredepeel’ is called BSDATABASE-ORI.XLS. Missing values are denoted by ‘#N/A’. Furthermore, the following convention is used in variable names: ‘f’ for a concentration in the fine fraction ($PM_{2.5}$), ‘c’ for a concentration in the coarse fraction (PM_{10} - $PM_{2.5}$), and ‘d’ for the error made in the analysis. It is important to note that elemental measurements below the detection limit are presented as 'missing' in the Excel database!

We imported the Excel database into S-PLUS 2000. In S-PLUS the data for the six sites were split into six individual *data frames*: ‘stadkade’, ‘overtoom’, ‘oversch’, ‘nijmegen’ , ‘dezilk’ and ‘vredep’. In the S-PLUS data frames we removed the data for 31-12-1998/1-1-1999. Due to fireworks, the extremely high concentrations of PM are not taken into account in Chapter 3. No specific corrections for volatile losses or moisture were applied to TEOM- and VAPS-PM measurements in either the Excel database or S-PLUS. The FAG-PM_{10} data have the standard correction of 1.3.

By using the function *f.make.data,* we have made a number of data frames where variables of all six sites are placed in one new data frame. For some variable X the function uses the following notation: X.1= variable X measured at Nijmgen (site 1, compare Figure 2), X.2= variable X, measured at Rotterdam Overschie, etc. We made the following data frames for separate analyses in Chapter 3 (by repeated application of *f.make.data*):

- ‘PMall’, containing all PM_{10} and $PM_{2.5}$ measurements (fine fraction, coarse fraction and PM_{10}) using TEOM and VAPS instruments. In PMall we also added PM_{10} measurements from the NAQMN (FAG instruments). The NAQMN stations coded 724 (Wageningen), 418 (Rotterdam Schiedamse Vest), 520 (Amsterdam Florapark), 131 (Vredepeel), and 444 (De Zilk) were taken as representative for the sites of Nijmegen, Rotterdam Overschie, Amsterdam, Vredepeel and De Zilk, respectively. By inspection of matrix-scatter plots we have identified three outliers. These data have been set to 'missing'. The data are the $PM_{2.5}$ measurement with TEOM at site De Zilk in record 46, coarse PM with VAPS at the Nijmegen site in record 47, and VAPS-$PM_{2.5}$ at the Amsterdam Stadhouderskade site in record 6
- ‘Secondary’, containing all measurements for secondary aerosol (both Dichote and LVS, fine, coarse and PM_{10})
- ‘ClTOT’, containing all chloride measurements (VAPS, Dichote and LVS)
- ‘OCEC’, containing all OC and EC measurements (VAPS). We set one measurement to ‘missing’: the OC measurement at site Nijmegen in record 74
- ‘Cr’, containing the elemental concentrations Al, Si, Fe, Ca and K, which are needed to calculate the concentration of crustal material. In this data frame measurements below the detection limit are set to 10 ng/m^3.

All statistical calculations, such as averages, correlations, and regression lines, have been performed in S-PLUS. (Matrix-) scatterplots were also calculated within S-PLUS.

3. Results

3.1 Particulate Matter

3.1.1 PM_{10} concentrations

Spatial variation

In all the analyses to follow we analysed both concentrations measured at the *same site* using different instruments and concentrations of the *same instrument* over the six sampling sites. This approach serves two goals. First, we could analyse the presence of outliers. Second, we could get an impression of the spatial coherence of the data.

Figure 4 shows the spatial coherence for the daily averaged VAPS-PM_{10} concentrations over the six sampling sites. Each rectangle in this so-called *scatter-plot matrix* shows a scatter plot between two stations. Concentrations are in µg/m^3 throughout the matrix. The figures show good correspondence between sites. The largest scatter is shown for station De Zilk (site 6).

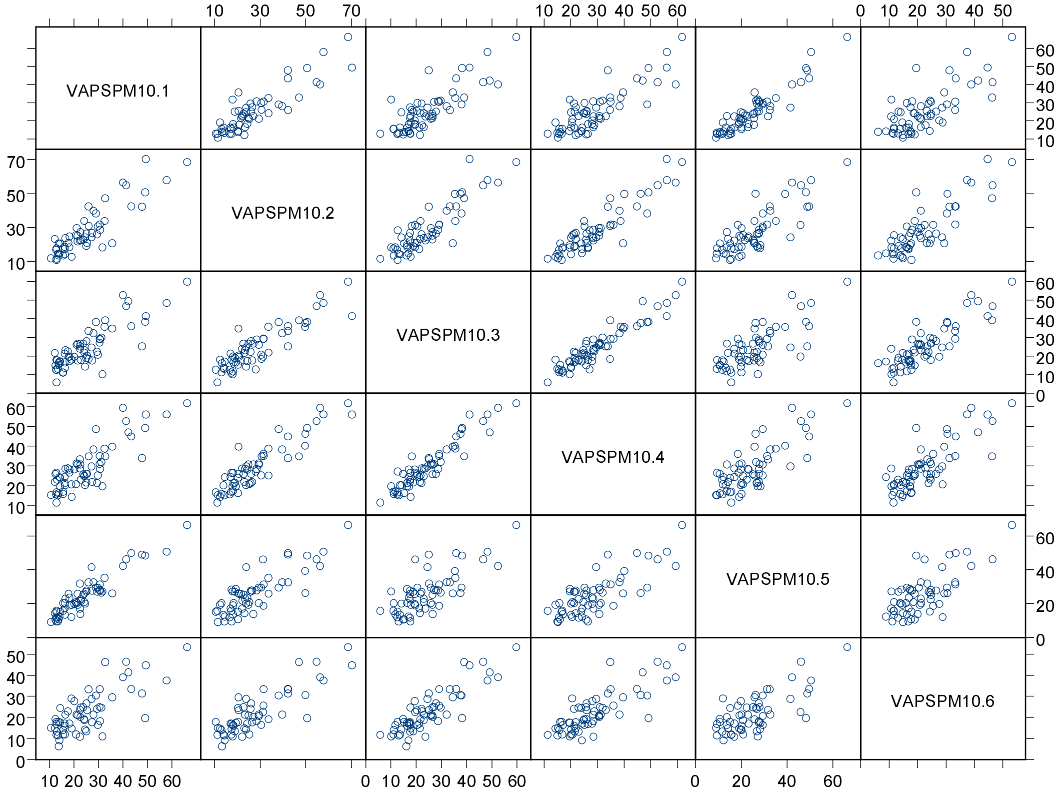
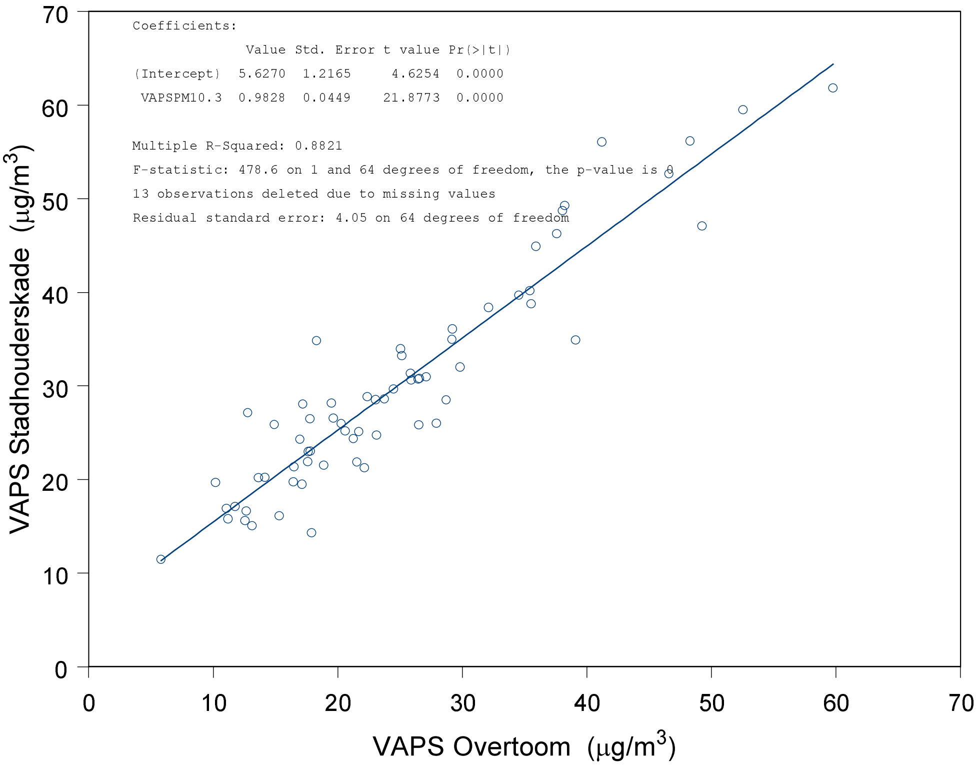


Figure 4 Daily VAPS-PM_{10} concentrations, expressed in µg/m^3, in a scatter-plot matrix for six sampling sites (1= Nijmegen, 2= Rotterdam Overschie, 3= Amsterdam Overtoom, 4= Amsterdam Stadhouderskade, 5= Vredepeel and 6= De Zilk).

The correlation between paired stations varied from R = 0.79 (stations Nijmegen and De Zilk, distance: 106 km) to R = 0.96 (stations Amsterdam Overtoom and Amsterdam Stadhouderskade, distance 2 km). Analogous results were found for FAG and TEOM.

Figure 5A shows the daily PM_{10} concentrations using two VAPS instruments at locations close to each other: Amsterdam Overtoom and Amsterdam Stadhouderskade. The correspondence is good, with a correlation of R = 0.94. It is also interesting to look at the residual standard error: 4.1 $\mu g/m^3$. This standard error gives an upper boundary for the σ_{VAPS} accuracy of the VAPS instruments: $\sigma_{VAPS} \approx 4.1/\sqrt{2} = 2.9\ \mu g/m^3$.

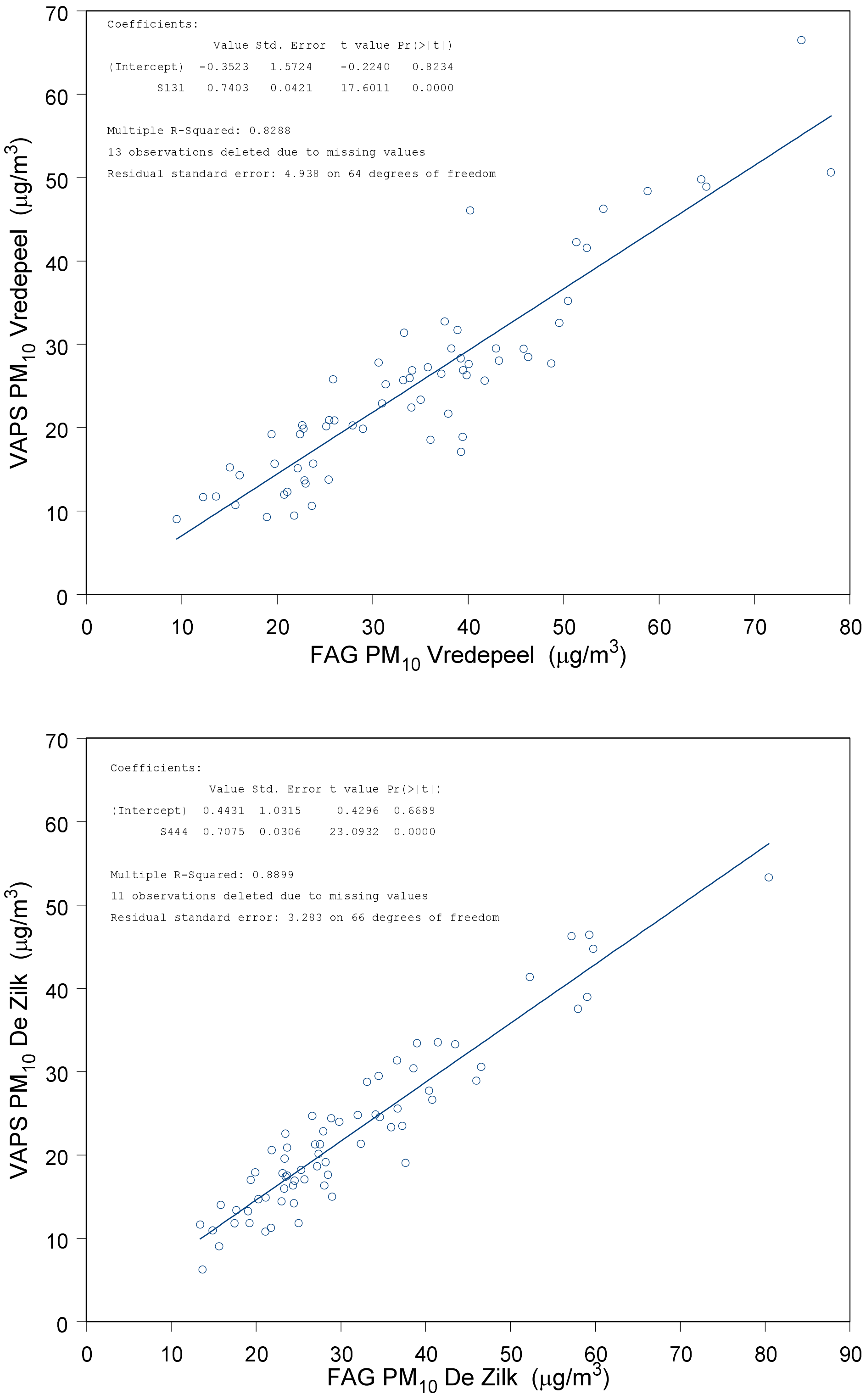


```
Coefficients:
               Value Std. Error t value Pr(>|t|)
(Intercept)  5.6270  1.2165     4.6254  0.0000
 VAPSPM10.3  0.9828  0.0449    21.8773  0.0000

Multiple R-Squared: 0.8821
F-statistic: 478.6 on 1 and 64 degrees of freedom, the p-value is 0
13 observations deleted due to missing values
Residual standard error: 4.05 on 64 degrees of freedom
```

Figure 5A *Scatterplot of daily VAPS-PM_{10} concentrations at Amsterdam Overtoom and Amsterdam Stadhouderskade (sites 3 and 4).*

Figure 5B shows the comparison of daily PM_{10} concentrations using two different instruments, VAPS and FAG, on the same sites (Vredepeel in the upper panel and De Zilk in the lower panel). In general, the comparison is good. For station Vredepeel we find R = 0.91 and for station De Zilk we find R = 0.94. Remarkable is that the residual standard error for Vredepeel is larger than that of De Zilk: 4.9 $\mu g/m^3$ and 3.3 $\mu g/m^3$, respectively.



```
Coefficients:
             Value Std. Error  t value Pr(>|t|)
(Intercept)  -0.3523   1.5724    -0.2240   0.8234
       S131   0.7403   0.0421    17.6011   0.0000

Multiple R-Squared: 0.8288
13 observations deleted due to missing values
Residual standard error: 4.938 on 64 degrees of freedom
```

```
Coefficients:
             Value Std. Error t value Pr(>|t|)
(Intercept)  0.4431  1.0315     0.4296  0.6689
       S444  0.7075  0.0306    23.0932  0.0000

Multiple R-Squared: 0.8899
11 observations deleted due to missing values
Residual standard error: 3.283 on 66 degrees of freedom
```

Figure 5B A comparison of daily PM$_{10}$ concentrations using VAPS and FAG for Vredepeel (site 5, upper panel) and De Zilk (site 6, lower panel).

Table 2 shows a summary of the linear relationships per site between daily VAPS measurements on the one hand and daily measurements using TEOM and FAG on the other. We chose the FAG station at Wageningen (NAQMN code 724) as a proxy for the Nijmegen site, idem for the Rotterdam Schiedamse Vest station (NAQMN code 418) and Rotterdam Overschie and idem for the FAG station, Amsterdam Florapark (520), for both Amsterdam sites. Only FAG measurements were taken at the Vredepeel and De Zilk monitoring sites of the project. Rotterdam Overschie and Amsterdam Stadhouderskade are urban street stations, while the FAG stations are urban background.

The regressions show that not all relationships go through the origin (intercept unequal zero). This is particularly true for the Rotterdam Overschie site. Furthermore, as none of the slopes equals 1.00, it is suggested that correction factors are needed. We will discuss this point in Section 5.1.

Table 2 *Linear relationships between VAPS PM_{10} measurements on the one hand and TEOM and FAG PM_{10} measurements on the other. FAG stations are: $X_{1,t}$ = Wageningen (724), $X_{2,t}$ = Rotterdam Schiedamse Vest (418), $X_{3,t} = X_{4,t}$ = Amsterdam Florapark (520), $X_{5,t}$ = Vredepeel (131) and $X_{6,t}$ = De Zilk (444). VAPS and TEOM data have not been corrected. The regressions for Vredepeel and De Zilk are shown Figure 5B. Uncertainty bands represent 1-standard error, or, assuming normal distributed errors, 68% confidence limit.*

Y_t = VAPS	**X_t = TEOM**	**X_t = FAG**
1 Nijmegen	$Y_{1,t} = 0.3 + 1.19 \bullet X_{1,t}$ ±2.2 ±0.10 **$R^2 = 0.72$**	$Y_{1,t} = 5.3 + 0.62 \bullet X_{1,t}$ ±1.7 ±0.05 **$R^2 = 0.71$**
2 Rotterdam Overschie	$Y_{2,t} = -6.3 + 1.44 \bullet X_{2,t}$ ±2.8 ±0.11 **$R^2 = 0.74$**	$Y_{2,t} = -4.5 + 0.84 \bullet X_{2,t}$ ±2.0 ±0.05 **$R^2 = 0.84$**
3 Amsterdam Overtoom	$Y_{3,t} = -4.0 + 1.32 \bullet X_{3,t}$ ±2.1 ±0.07 **$R^2 = 0.75$**	$Y_{3,t} = 1.7 + 0.68 \bullet X_{3,t}$ ±1.0 ±0.05 **$R^2 = 0.79$**
4 Amsterdam Stadh. kade	$Y_{4,t} = -2.7 + 1.30 \bullet X_{4,t}$ ±2.3 ±0.07 **$R^2 = 0.76$**	$Y_{4,t} = 5.0 + 0.74 \bullet X_{4,t}$ ±2.0 ±0.05 **$R^2 = 0.76$**
5 Vredepeel	-	$Y_{5,t} = -0.4 + 0.74 \bullet X_{5,t}$ ±1.6 ±0.04 **$R^2 = 0.83$**
6 De Zilk	-	$Y_{6,t} = 0.4 + 0.71 \bullet X_{6,t}$ ±1.0 ±0.03 **$R^2 = 0.89$**

Annual and seasonal averages

Annual averages for the six sampling sites and three instruments are summarised in **Table 3A**. Again, we chose the FAG station as denoted in Table 2. Data from TEOM and VAPS have not been corrected for volatile losses or moisture. FAG data have been corrected with the standard correction factor of 1.3.

Uncertainty bands in the table represent 1-standard error, or, assuming normal distributed errors, 68% confidence limit. We note that the confidence intervals should not be used for hypothesis testing. The *paired* t-test should be used for testing equality of averages. In this way day-to-day variation due to meteorological conditions is ruled out.

Table 3A Annual average PM_{10} concentration measurements with three instruments at six sampling sites. The confidence intervals represent 68% confidence limits. TEOM and VAPS data have not been corrected for possible losses of semi-volatile compounds or for the influence of moisture. All averages within the same column are calculated over the same days (see column headings). FAG stations are chosen as in Table 2.

Annual average PM_{10} concentrations	**1 Nijmegen N=66 (µg/m^3)**	**2 Rotterdam Overschie N=65 (µg/m^3)**	**3 Amsterdam Overtoom N=71 (µg/m^3)**	**4 Amsterdam Stadh. kade N=70 (µg/m^3)**	**5 Vredepeel N=68 (µg/m^3)**	**6 De Zilk N=68 (µg/m^3)**
TEOM	21.1 ± 1.1	23.9 ± 1.0	21.6 ± 0.9	24.7 ± 0.9	-	-
VAPS	25.0 ± 1.4	28.1 ± 1.7	24.5 ± 1.3	29.3 ± 1.4	25.3 ± 1.4	22.4 ± 1.2
FAG	31.1 ± 1.9	38.7 ± 2.0	34.3 ± 1.9	33.9 ± 1.9	34.5 ± 1.8	31.1 ± 1.6

The ratios between VAPS and TEOM, and VAPS and FAG, are given in **Table 3B**. The table shows the VAPSs measure at 12% to 21% *higher* than TEOMs, and 10% to 29% *lower* than FAGs. We note the ratios to differ from the division of annual averages shown in Table 3A. The same holds for the error bounds for the ratios. The general reason for this is that if we have a relation $y_t = x_t / z_t$, and we average y_t, x_t and z_t, we may not conclude that $E[y_t] = E[x_t]/E[y_t]$. In the table we calculated $E[y_t] = E[x_t / z_t]$.

Table 3B *Ratios for six sampling sites of between VAPS PM_{10} concentrations on the one hand and TEOM- and FAG-PM_{10} concentrations on the other,. On should note that these ratios differ from division of the corresponding averages in Table 3A.*

Annual average PM_{10} concentrations	**1 Nijmegen N=66 (µg/m^3)**	**2 Rotterdam Overschie N=65 (µg/m^3)**	**3 Amsterdam Overtoom N=71 (µg/m^3)**	**4 Amsterdam Stadh. kade N=70 (µg/m^3)**	**5 Vredepeel N=68 (µg/m^3)**	**6 De Zilk N=68 (µg/m^3)**
Ratio VAPS / TEOM	1.21 ± 0.03	1.16 ± 0.04	1.12 ± 0.03	1.18 ± 0.03	-	-
Ratio VAPS / FAG	0.84 ± 0.03	0.71 ± 0.02	0.74 ± 0.02	0.90 ± 0.03	0.74 ± 0.01	0.72 ± 0.01

In **Table 4** we calculated the summer and winter averages based on TEOM, VAPS and FAG data. The table shows concentrations of ~5 µg/m^3 higher in winter than in summer for the heavy traffic sites of Rotterdam Overschie and Amsterdam Stadhouderskade (sites 2 and 4). The winter-summer differences are not significant for the other sites. .

Table 4 *Average PM_{10} concentrations for 5 summer months (May through September) and 5 winter months (November through September) at six sampling sites. Error bounds represent 68% confidence limits. TEOM and VAPS data have not been corrected for possible losses of semi-volatile compounds or for the influence of moisture. The number of days varies with the instrument used, period and site. We have not added these numbers to the table. The number of days varies from 27 to 35.*

Annual average PM_{10} concentrations	**1 Nijmegen (µg/m^3)**	**2 Rotterdam Overschie (µg/m^3)**	**3 Amsterdam Overtoom (µg/m^3)**	**4 Amsterdam Stadh. kade (µg/m^3)**	**5 Vredepeel (µg/m^3)**	**6 De Zilk (µg/m^3)**
TEOM summer	22.8 ± 1.2	23.8 ± 1.1	21.8 ± 1.0	24.8 ± 0.9	-	-
TEOM winter	20.5 ± 1.7	23.4 ± 1.6	21.5 ± 1.5	24.7 ± 1.6	-	-
VAPS summer	22.5 ± 1.3	23.2 ± 1.6	22.0 ± 1.5	26.6 ± 1.4	23.1 ± 1.5	21.9 ± 1.6
VAPS winter	27.8 ± 2.6	32.0 ± 3.1	27.5 ± 2.4	31.9 ± 2.6	26.8 ± 2.6	23.3 ± 2.1
FAG summer	30.5 ± 1.7	35.9 ± 2.0	33.4 ± 1.8	30.8 ± 2.6	35.5 ± 1.7	30.9 ± 1.9
FAG winter	32.2 ± 3.4	40.4 ± 3.2	35.1 ± 3.1	35.1 ± 3.1	33.4 ± 3.4	32.5 ± 2.6

Representativity of sampling period
In Chapter 6 we will compare PM_{10} measurements with model calculations. These model calculations are annual averages. Therefore it is of great importance that the 79 measuring days in this project give annual averages which are representative for the *whole* year. We tested this by calculating FAG-PM_{10} concentrations for all days available in the September 1998 through August 1999 (N=350) period, and for the sampling period only (N=68). The results are given in **Table 5**.

Table 5 *Annual average FAG PM_{10} concentrations based on two samples (N= 350 and N= 68 days) at six sampling sites. All days fall within the September 1998 through August 1999 period. Error bounds are 1-σ.*

Annual average PM_{10} concentrations	**1 Nijmegen ($\mu g/m^3$)**	**2 Rotterdam Overschie ($\mu g/m^3$)**	**3 Amsterdam Overtoom ($\mu g/m^3$)**	**4 Amsterdam Stadh. kade ($\mu g/m^3$)**	**5 Vredepeel ($\mu g/m^3$)**	**6 De Zilk ($\mu g/m^3$)**
FAG 350 days	33.2 ± 0.9	39.0 ± 0.9	36.6 ± 0.9	36.6 ± 0.9	35.1 ± 0.8	30.5 ± 0.7
FAG 68 days	31.1 ± 1.9	38.7 ± 1.7	34.3 ± 1.7	33.9 ± 1.9	34.5 ± 1.8	31.1 ± 1.6
Difference Δ	2.1 ± 2.1	0.3 ± 1.9	2.3 ± 1.9	2.7 ± 2.1	0.6 ± 2.0	0.6 ± 1.7

The table shows the six differences as not being statistically different from zero if tested with $\alpha = 0.05$ (differences greater than two standard errors would lead to a rejection of the null hypothesis of equal annual averages).

3.1.2 Fine and coarse fractions of PM_{10}

The concentrations of $PM_{2.5}$ (the fine fraction of PM_{10}) and the concentrations of PM_{10} - $PM_{2.5}$ (the coarse fraction of PM_{10}) are given in **Table 6A** for two instruments and the six sampling sites (upper panel VAPS, lower panel TEOM). Both VAPS and TEOM concentrations have no corrections for volatile losses or moisture.

The ratios $PM_{2.5}$ / PM_{10} are presented in **Table 6B**. The ratios are reasonably constant both over the sites and the instruments. The VAPS ratios range from 0.60 to 0.71, and the TEOM ratios range from 0.65 to 0.71. The overall average ratio is 0.67. In other words, 67% of PM_{10} is in the fine fraction, on average, and 33% of PM_{10} is in the coarse fraction.

Table 6A *Annual average concentrations of the VAPS (upper panel) and TEOM instruments (lower panel) at the six sampling sites. Error bounds represent 68% confidence limit.*

Annual average concentrations with VAPS	**1 Nijmegen N=66 (µg/m^3)**	**2 Rotterdam Overschie N=65 (µg/m^3)**	**3 Amsterdam Overtoom N=71 (µg/m^3)**	**4 Amsterdam Stadh. kade N=70 (µg/m^3)**	**5 Vredepeel N=68 (µg/m^3)**	**6 De Zilk N=68 (µg/m^3)**
Fine fraction ($PM_{2.5}$)	17.6 ± 1.3	19.7 ± 1.6	16.5 ± 1.3	19.2 ± 1.3	18.4 ± 1.3	14.1 ± 1.1
Coarse fraction (PM_{10} - $PM_{2.5}$)	7.4 ± 0.4	8.5 ± 0.4	7.9 ± 0.4	10.1 ± 0.5	6.9 ± 0.4	8.3 ± 0.5
PM_{10}	25.0 ± 1.4	28.1 ± 1.7	24.5 ± 1.3	29.3 ± 1.4	25.3 ± 1.4	22.4 ± 1.2

Annual average concentrations with TEOM	**1 Nijmegen (µg/m^3)**	**2 Rotterdam Overschie (µg/m^3)**	**3 Amsterdam Overtoom (µg/m^3)**	**4 Amsterdam Stadh. kade (µg/m^3)**	**5 Vredepeel (µg/m^3)**	**6 De Zilk (µg/m^3)**
Fine fraction ($PM_{2.5}$)	14.4 ± 0.8	17.1 ± 0.9	14.2 ± 0.7	-	18.1 ± 1.1	19.9 ± 1.4
Coarse fraction (PM_{10} - $PM_{2.5}$)	6.7 ± 0.4	6.8 ± 0.4	7.4 ± 0.4		-	-
PM_{10}	21.1 ± 1.1	23.9 ± 1.0	21.6 ± 0.9	24.7 ± 0.9	-	-

Table 6B *Ratios between VAPS PM_{10} concentrations on the one hand and TEOM and FAG PM_{10} concentrations on the other hand, for six sampling sites. It should be noted that the ratios differ from the division of the corresponding averages in Table 6A.*

Annual average PM_{10} concentrations	**1 Nijmegen N=66 (µg/m^3)**	**2 Rotterdam Overschie N=65 (µg/m^3)**	**3 Amsterdam Overtoom N=71 (µg/m^3)**	**4 Amsterdam Stadh. kade N=70 (µg/m^3)**	**5 Vredepeel N=68 (µg/m^3)**	**6 De Zilk N=68 (µg/m^3)**
Ratio VAPS: $PM_{2.5}$ / PM_{10}	0.68 ± 0.02	0.66 ± 0.02	0.63 ± 0.02	0.62 ± 0.02	0.71 ± 0.02	0.60 ± 0.02
Ratio TEOM: $PM_{2.5}$ / PM_{10}	0.67 ± 0.01	0.71 ± 0.02	0.65 ± 0.01	-	-	-

3.2 Secondary inorganic aerosol

3.2.1 Secondary aerosol concentrations in PM_{10}

Spatial variation

As stated in Section 2.2.2 secondary inorganic aerosol is defined in this report as the sum of NO_3^-, SO_4^{2-} and NH_4^+. The spatial coherence between the six sites is reasonable, as illustrated for the Dichote in **Figure 6**. No aerosol was sampled with the Dichote at Amsterdam Stadhouderskade. Correlations range from R = 0.66 (sites Nijmegen and De Zilk) to R = 0.94 (sites: Amsterdam Overtoom and Rotterdam Overschie).

At the sites Vredepeel and De Zilk we measured secondary inorganic aerosol both with the Dichote and LVS methods. The linear relations are shown in **Figure 7**. For Vredepeel (upper panel), the relation is good: R = 0.70. The intercept is non-significant and the slope is 1.06 ± 0.08 (1-σ bounds). In other words, the slope does not differ from the expected 1.00. However, the relationship is not so good for De Zilk (lower panel): R = 0.55. The intercept is 2.0 ± 0.6 and the slope 0.67 ± 0.07. These values differ from the respective expected values 0.0 and 1.00. The explanation is unclear.

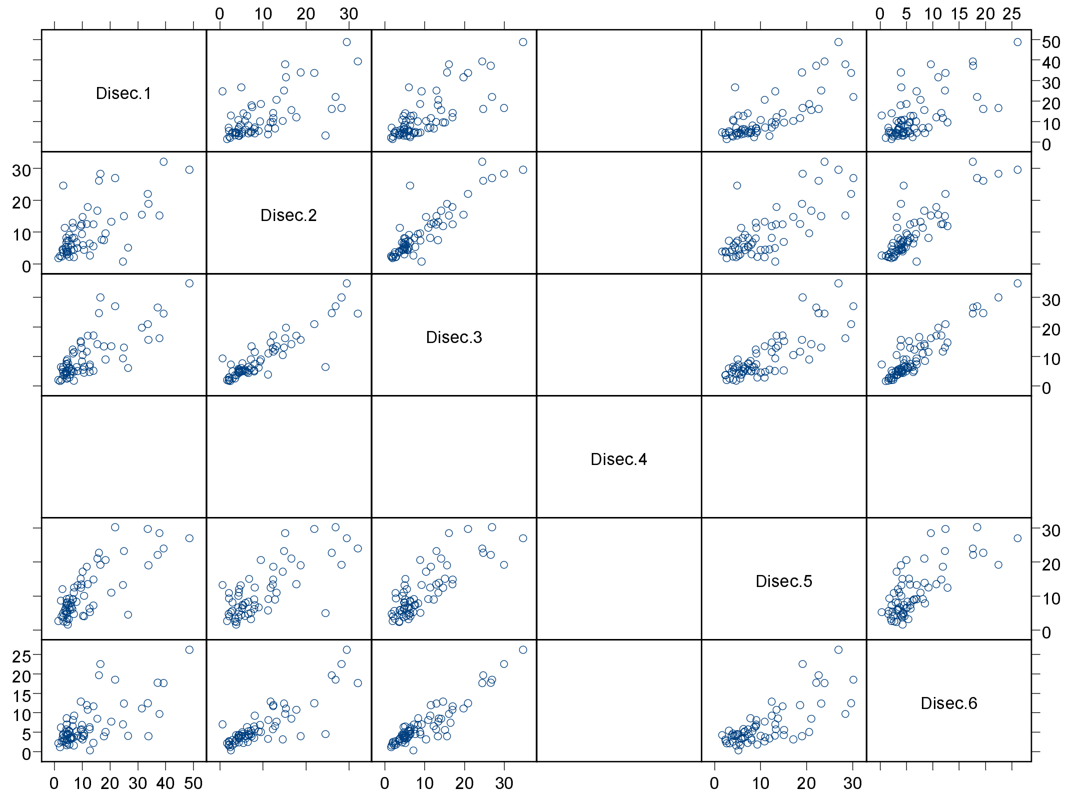
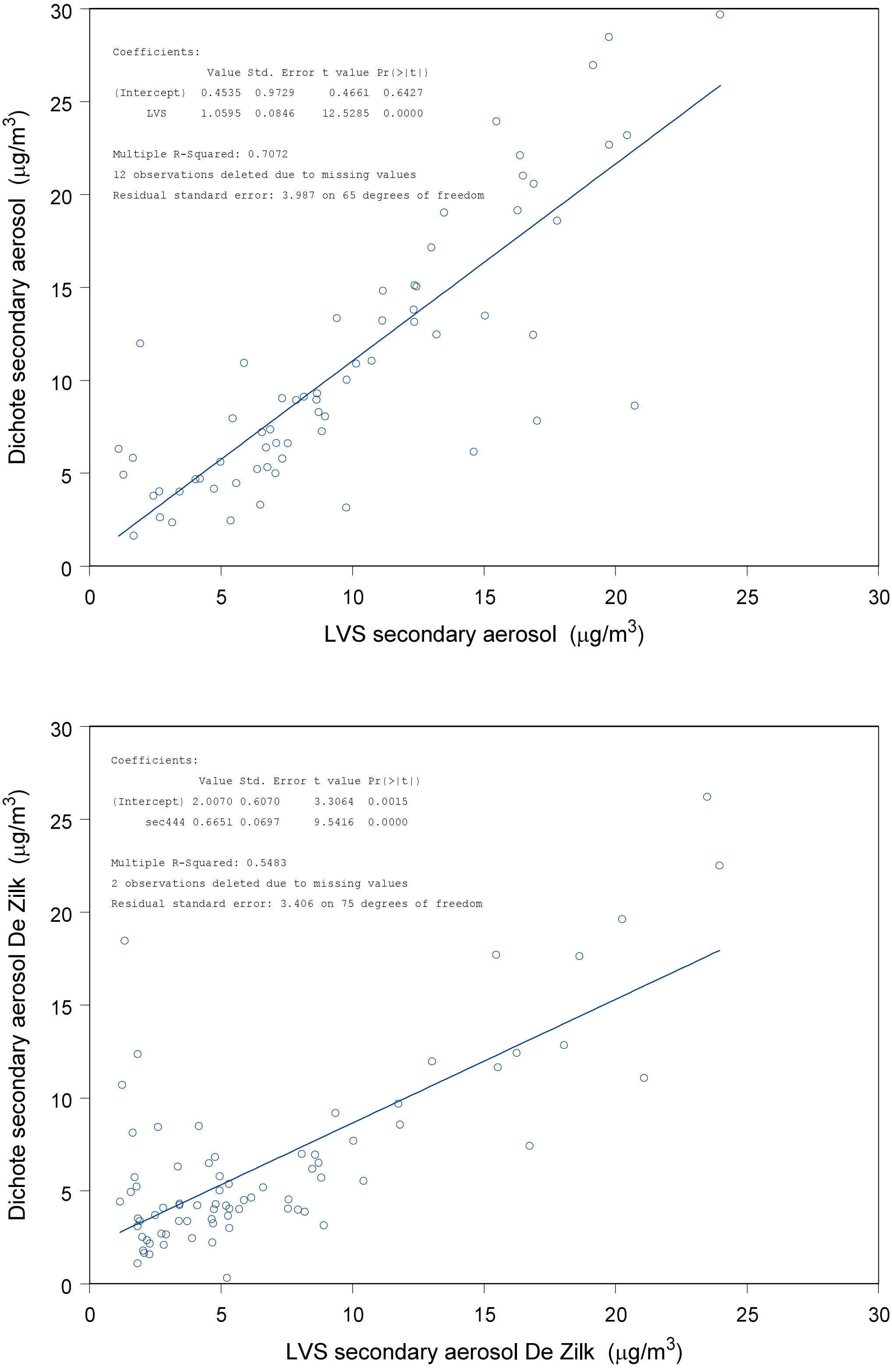


Figure 6 The daily totals of secondary aerosol with the Dichote and expressed in µg/m³, shown in a scatter-plot matrix for six sampling sites (1= Nijmegen, 2= Rotterdam Overschie, 3= Amsterdam Overtoom, 4= Amsterdam Stadhouderskade, 5= Vredepeel and 6= De Zilk).


```
Coefficients:
                Value Std. Error t value Pr(>|t|)
(Intercept)  0.4535  0.9729     0.4661  0.6427
     LVS     1.0595  0.0846    12.5285  0.0000

Multiple R-Squared: 0.7072
12 observations deleted due to missing values
Residual standard error: 3.987 on 65 degrees of freedom
```

```
Coefficients:
              Value Std. Error t value Pr(>|t|)
(Intercept) 2.0070 0.6070     3.3064  0.0015
     sec444 0.6651 0.0697     9.5416  0.0000

Multiple R-Squared: 0.5483
2 observations deleted due to missing values
Residual standard error: 3.406 on 75 degrees of freedom
```

Figure 7 *Comparison between daily secondary inorganic aerosol (NO_3^- + SO_4^{2-} + NH_4^+) with Dichote and LVS. The upper panel shows Vredepeel (site 5), and the lower panel De Zilk (site 6).*

Annual averages

Table 7 shows the annual averages for both Dichote and LVS. The highest estimates are found for Nijmegen and Vredepeel (sites 1 and 5). These stations are located in the eastern part of the Netherlands. The most western site, De Zilk, shows the lowest concentrations.

Table 7 Annual average secondary aerosol concentrations in PM_{10} at the six sampling sites. Data are compared for Dichote and LVS. Error bounds represent 68% confidence limits. Averages within each column are based on the same sampling days.

Annual average concentrations	**1 Nijmegen N=70 (µg/m^3)**	**2 Rotterdam Overschie N=67 (µg/m^3)**	**3 Amsterdam Overtoom N=73 (µg/m^3)**	**4 Amsterdam Stadh. kade N=0 (µg/m^3)**	**5 Vredepeel N=67 (µg/m^3)**	**6 De Zilk N=77 (µg/m^3)**
NH_4 Dichote	2.5 ± 0.3	1.8 ± 0.2	1.8 ± 0.2	-	2.2 ± 0.2	1.1 ± 0.2
SO_4 Dichote	4.4 ± 0.5	4.3 ± 0.4	3.9 ± 0.4	-	4.6 ± 0.4	3.4 ± 0.4
NO_3 Dichote	5.1 ± 0.5	3.4 ± 0.5	3.9 ± 0.4	-	4.2 ± 0.4	2.0 ± 0.4
Total Dichote	**11.9 ± 1.3**	**9.4 ± 0.9**	**9.6 ± 0.8**	**-**	**11.0 ± 0.9**	**6.5 ± 0.6**
NH_4 LVS	-	-	-	-	2.2 ± 0.2	1.4 ± 0.2
SO_4 LVS	-	-	-	-	3.0 ± 0.2	2.4 ± 0.2
NO_3 LVS	-	-	-	-	4.4 ± 0.3	2.7 ± 0.3
Total LVS	-	-	-	-	**9.6 ± 0.6**	**6.6 ± 0.6**

3.2.2 Fine and coarse fractions in PM_{10}

Table 8A shows the division of inorganic aerosol over the fine and coarse fractions of PM_{10}. We see from the table that secondary aerosol is largely found in the fine fraction, i.e. $PM_{2.5}$.

Table 8A *Concentrations of secondary aerosol for the fine and the coarse fractions, measured using the Dichote at the six sampling sites. Error bounds represent 68% confidence limits.*

Annual average concentrations Dichote	**1 Nijmegen (µg/m³)**	**2 Rotterdam Overschie (µg/m³)**	**3 Amsterdam Overtoom (µg/m³)**	**4 Amsterdam Stadh. kade (µg/m³)**	**5 Vredepeel (µg/m³)**	**6 De Zilk (µg/m³)**
NH_4 fine	2.5 ± 0.3	1.8 ± 0.2	1.8 ± 0.2	-	2.2 ± 0.2	1.1 ± 0.2
SO_4 fine	4.0 ± 0.5	3.9 ± 0.4	3.5 ± 0.3	-	4.0 ± 0.3	3.0 ± 0.3
NO_3 fine	4.5 ± 0.5	2.3 ± 0.4	3.3 ± 0.4	-	3.3 ± 0.4	1.5 ± 0.3
Total fine	11.0 ± 1.2	8.0 ± 0.9	8.6 ± 0.9	-	9.5 ± 0.9	5.6 ± 0.6
NH_4 coarse	0.0	0.0	0.0	-	0.0	0.0
SO_4 coarse	0.37 ± 0.09	0.43 ± 0.07	0.41 ± 0.06	-	0.58 ± 0.07	0.38 ± 0.07
NO_3 coarse	0.56 ± 0.07	1.06 ± 0.09	0.59 ± 0.06	-	0.91 ± 0.07	0.47 ± 0.07
Total coarse	0.9 ± 0.1	1.5 ± 0.1	1.0 ± 0.1	-	1.5 ± 0.1	0.8 ± 0.1

In **Table 8B** we calculated the exact ratio [secondary aerosol in $PM_{2.5}$ / secondary aerosol in PM_{10}], based on all daily ratios available, finding, on average, inorganic aerosol for 77% to 88% in the fine fraction.

Table 8B *Ratios between secondary aerosol in Dichote $PM_{2.5}$ and Dichote PM_{10} for six sampling sites. It should be noted that the ratios differ from the division of the corresponding averages in Table 8A.*

Annual average PM_{10} concentrations	**1 Nijmegen N=66 (µg/m³)**	**2 Rotterdam Overschie N=65 (µg/m³)**	**3 Amsterdam Overtoom N=71 (µg/m³)**	**4 Amsterdam Stadh. kade N=70 (µg/m³)**	**5 Vredepeel N=68 (µg/m³)**	**6 De Zilk N=68 (µg/m³)**
Ratio secondary aerosol: $PM_{2.5}$ / PM_{10}	0.88 ± 0.02	0.77 ± 0.02	0.84 ± 0.01	-	0.81 ± 0.02	0.81 ± 0.02

3.3 Sea salt

3.3.1 Chloride concentrations in PM_{10}

Spatial variation

Chloride was measured with the Dichote (five sites), VAPS (six sites) and LVS (two sites). The spatial coherence between sites is reasonably good. For Dichote the coherence is shown in **Figure 8**. Correlations range from R = 0.51 (sites Rotterdam Overschie and Vredepeel) to R = 0.94 (sites Nijmegen and Amsterdam Overtoom).

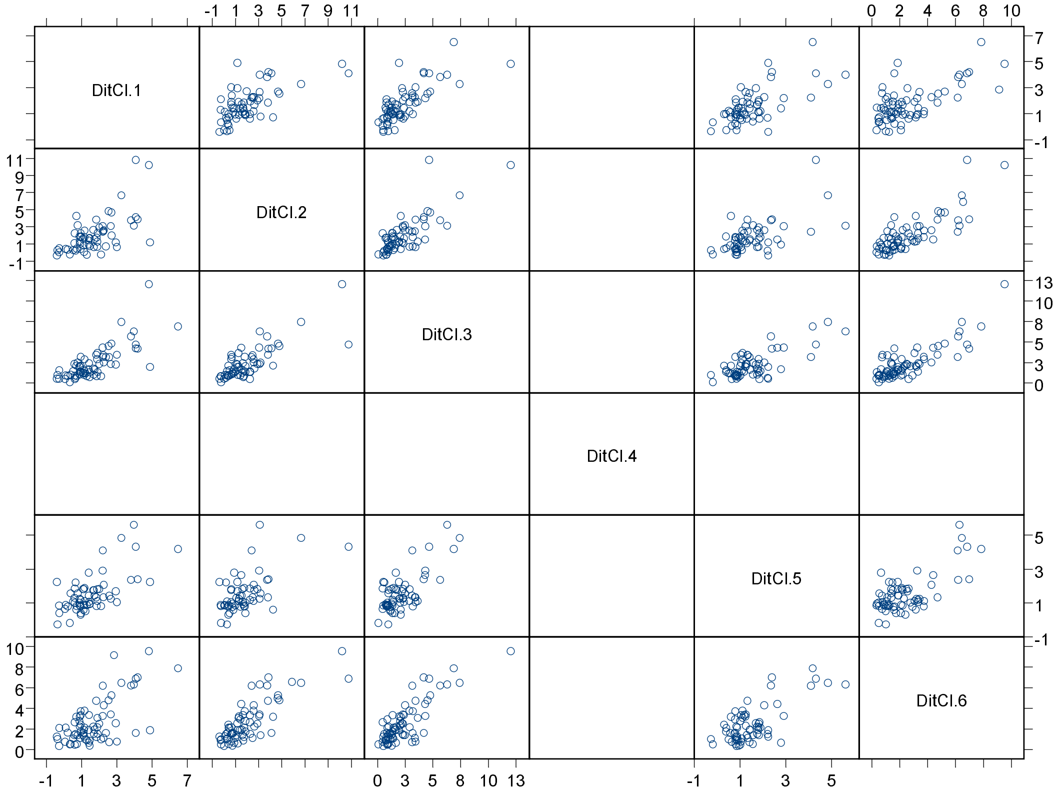


Figure 8 Daily averaged Cl^- concentrations, expressed in $\mu g/m^3$, in a scatter-plot matrix for six sampling sites (1= Nijmegen, 2= Rotterdam Overschie, 3= Amsterdam Overtoom, 4= Amsterdam Stadhouderskade, 5= Vredepeel and 6= De Zilk).

Annual averages

Annual averages for Chloride are shown in **Table 9A** for Dichote, VAPS and LVS. The table shows that annual averages for Dichote and VAPS are quite comparable for sites 1, 2, 3, 5 and 6. Values of LVS-Chloride, however, lie much lower. We will discuss these differences in Section 5.1.3. The values for the coastal site of De Zilk (site 6) are roughly double the estimates of the other sites.

We noted that the weight of sea salt could be obtained by multiplying all Cl^- concentrations by the factor 1.80 (assuming all sea salt to originate from the measured CL^- concentrations). For details we refer to Section 5.1.3.

Table 9A Annual average Cl^- concentrations in PM_{10}, measured with three instruments at six sampling sites. Error bounds represent 68% confidence limits.

Annual average Cl^- concentrations	**1 Nijmegen N=57 (µg/m^3)**	**2 Rotterdam Overschie N=51 (µg/m^3)**	**3 Amsterdam Overtoom N=60 (µg/m^3)**	**4 Amsterdam Stadh. kade N=62 (µg/m^3)**	**5 Vredepeel N=54 (µg/m^3)**	**6 De Zilk N=64 (µg/m^3)**
Dichote	1.8 ± 0.2	2.3 ± 0.3	2.4 ± 0.2	-	1.6 ± 0.1	3.0 ± 0.3
VAPS	2.0 ± 0.3	2.5 ± 0.3	1.8 ± 0.3	3.3 ± 0.4	1.2 ± 0.2	2.6 ± 0.3
LVS	-	-	-	-	0.7 ± 0.1	1.5 ± 0.2

Sodium concentrations have been measured with Dichote alone. Annual averages are given in **Table 9B**. The differences between De Zilk and the more inland sites are less pronounced if compared to the five other sites.

We note that the weight of sea salt is obtained by multiplying all Na^+ concentrations by the factor 3.24 (assuming all sea salt to originate from the measured Na^+ concentrations). For details we refer to Section 5.1.3.

Table 9B Annual average Na^+ concentrations in PM_{10} measured with three instruments at six sampling sites. Error bounds represent 68% confidence limits.

Annual average Na^+ concentrations	**1 Nijmegen N=70 (µg/m^3)**	**2 Rotterdam Overschie N=67 (µg/m^3)**	**3 Amsterdam Overtoom N=73 (µg/m^3)**	**4 Amsterdam Stadh. kade N=0 (µg/m^3)**	**5 Vredepeel N=67 (µg/m^3)**	**6 De Zilk N=67 (µg/m^3)**
Dichote	1.6 ± 0.1	2.3 ± 0.2	2.2 ± 0.2	-	1.9 ± 0.3	2.4 ± 0.2

3.3.2 Fine and coarse fractions in PM_{10}

In **Table 10A** the contribution of chloride to the fine and coarse fractions of PM_{10} is given both for Dichote and VAPS. There is a remarkable difference in Dichote and VAPS estimates. For Dichote the ratio [Cl^- in $PM_{2.5}$ / Cl^- in PM_{10}] varies between 0.35 and 0.56 (average 0.46). For VAPS this ratio is found between 0.12 and 0.23 (average 0.16). An explanation is not easy .

Table 10A Annual average Cl^- concentrations in the fine and coarse fractions of PM_{10} using two instruments at six sampling sites. Error bounds represent 68% confidence limits.

Annual average Cl^- concentrations	**1 Nijmegen N=57 (µg/m^3)**	**2 Rotterdam Overschie N=51 (µg/m^3)**	**3 Amsterdam Overtoom N=62 (µg/m^3)**	**4 Amsterdam Stadh. kade N=57 (µg/m^3)**	**5 Vredepeel N=54 (µg/m^3)**	**6 De Zilk N=64 (µg/m^3)**
Dichote fine	1.0 ± 0.1	0.8 ± 0.1	1.1 ± 0.1	-	0.6 ± 0.1	1.1 ± 0.1
Dichote coarse	0.8 ± 0.1	1.5 ± 0.2	1.3 ± 0.1	-	1.0 ± 0.1	2.0 ± 0.2
VAPS fine	0.3 ± 0.1	0.3 ± 0.1	0.3 ± 0.1	0.4 ± 0.1	0.2 ± 0.1	0.6 ± 0.1
VAPS coarse	1.7 ± 0.2	2.2 ± 0.3	1.5 ± 0.2	2.9 ± 0.3	1.0 ± 0.2	2.0 ± 0.3

Table 10B gives the concentration of Na^+ in the fine and coarse fractions. The table shows the ratio [Na^+ in $PM_{2.5}$ / Na^+ in PM_{10}] to vary between 0.42 and 0.52 (average 0.47).

Table 10B Annual average Na^+ concentrations in the fine and coarse fractions of PM_{10} with two instruments at six sampling sites. Error bounds represent 68% confidence limits.

Annual average Na^+ concentrations	**1 Nijmegen N=57 (µg/m^3)**	**2 Rotterdam Overschie N=51 (µg/m^3)**	**3 Amsterdam Overtoom N=62 (µg/m^3)**	**4 Amsterdam Stadh. kade N=57 (µg/m^3)**	**5 Vredepeel N=54 (µg/m^3)**	**6 De Zilk N=64 (µg/m^3)**
Dichote fine	0.8 ± 0.1	1.0 ± 0.1	1.2 ± 0.1	-	0.9 ± 0.2	1.1 ± 0.1
Dichote coarse	0.8 ± 0.1	1.4 ± 0.1	1.1 ± 0.1	-	1.0 ± 0.1	1.3 ± 0.1

If we assume that both Dichote-Cl^- and Dichote-Na^+ are indicators for sea salt, the ratios [sea salt in $PM_{2.5}$ / sea salt in PM_{10}] are consistent: 0.46 and 0.47, respectively.

3.4 Carbonaceous aerosol

Spatial variation
We measured organic carbon (OC) and elemental carbon (EC) at all sites. Total carbonaceous aerosol (OC + EC) will be denoted as 'OCEC'. The spatial coherence of OCEC is good for all sites (see **Figure 9)**. The same good coherence is found for OC and OC individually. Correlations for OCEC range from R = 0.84 (sites Amsterdam Stadhouderskade and Vredepeel) to R = 0.98 (sites Rotterdam Overschie and Amsterdam Stadhouderskade).

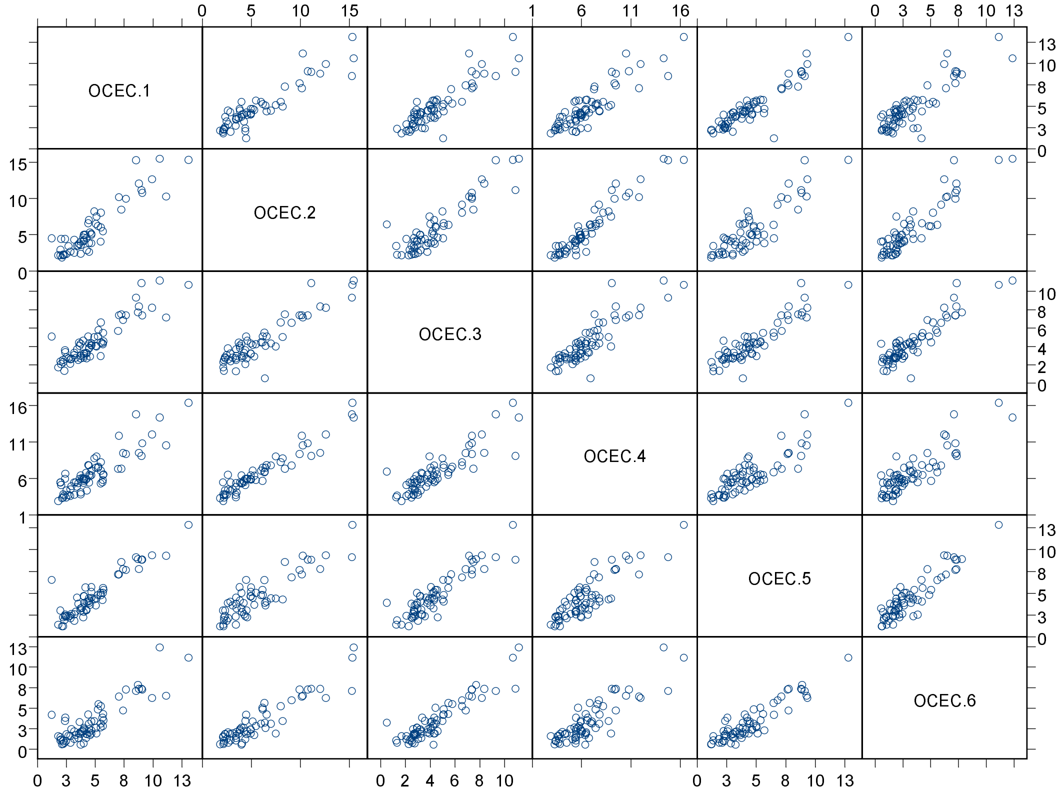


Figure 9 Daily totals of carbonaceous aerosol (OCEC), expressed in µg/m³, in a scatter-plot matrix for six sampling sites (1= Nijmegen, 2= Rotterdam Overschie, 3= Amsterdam Overtoom, 4= Amsterdam Stadhouderskade, 5= Vredepeel and 6= De Zilk).

Annual averages

The annual averages of OC, EC and total carbonaceous are given in **Table 11**. The table shows the ratio [OC / (OC + EC)] to vary between 0.71 (Amsterdam Stadhouderskade) and 0.85 (Vredepeel and De Zilk). The average ratio is 0.79.

Table 11 Annual average VAPS concentrations of carbonaceous aerosol at the six sampling sites. Error bounds represent 68% confidence limits.

Annual average concentrations by VAPS	**1 Nijmegen N=71 (µg/m^3)**	**2 Rotterdam Overschie N=62 (µg/m^3)**	**3 Amsterdam Overtoom N=71 (µg/m^3)**	**4 Amsterdam Stadh. kade N=73 (µg/m^3)**	**5 Vredepeel N=70 (µg/m^3)**	**6 De Zilk N=73 (µg/m^3)**
Organic carbon (OC)	4.0 ± 0.2	4.2 ± 0.3	3.6 ± 0.2	4.7 ± 0.3	3.9 ± 0.2	2.8 ± 0.2
Elemental carbon (EC)	0.83 ± 0.05	1.60 ± 0.13	0.87 ± 0.05	1.92 ± 0.09	0.71 ± 0.06	0.48 ± 0.06
Total carbonaceous aerosol (OC+EC)	4.8 ± 0.3	5.8 ± 0.4	4.5 ± 0.3	6.6 ± 0.3	4.6 ± 0.3	3.3 ± 0.3

3.5 Elemental composition

We measured such elements as Na, Cl and S, along with the following elements on a daily basis: K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Pb, Al and Si. For some elements only a small percentage of daily concentrations is found above the detection limit.

Spatial variation

The spatial coherence for individual elements between sites is reasonably good. As an example, **Figure 10** shows the spatial coherence between sites for Si in PM_{10}. Correlation R varies from 0.40 to 0.80. For the element Ca, the correlation R varies from 0.16 to 0.80, for K from 0.56 to 0.86, for Fe from 0.48 to 0.69, and for Al from 0.32 to 0.77. For all elements the highest correlations are between Nijmegen (site 1) and Rotterdam Overschie (site 2). The lowest correlations are found between Amsterdam Stadhouderskade (site 4) and De Zilk (site 6). Generally, De Zilk has the lowest correlations with respect to the other sites.

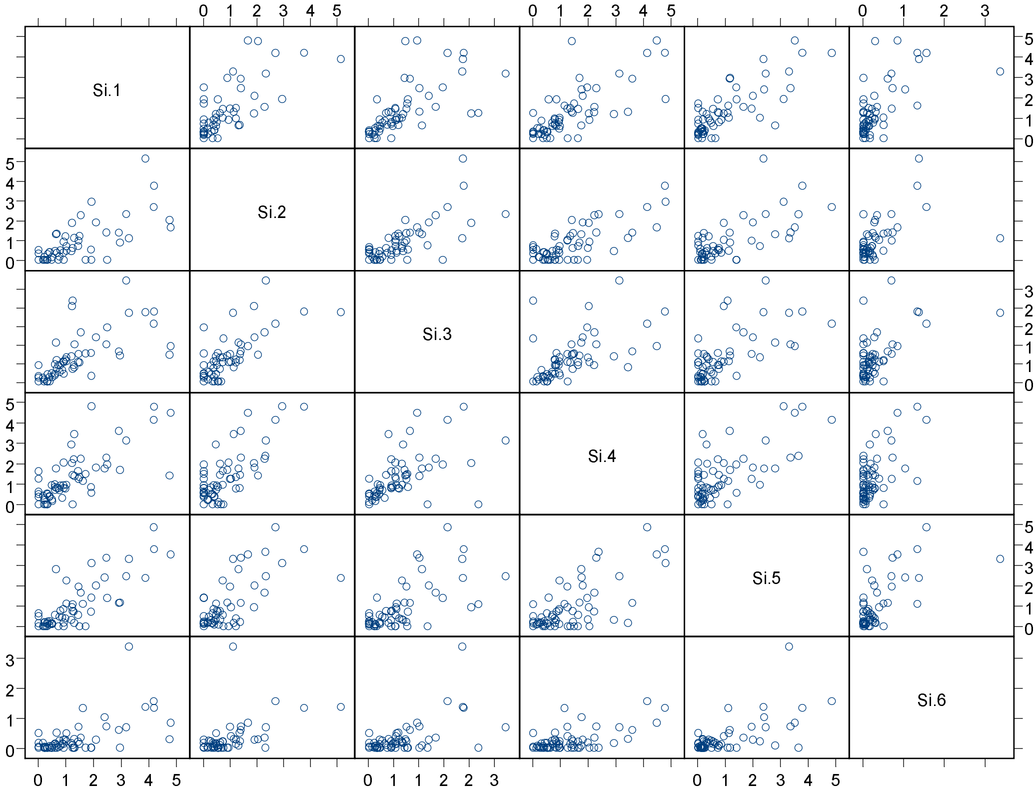


Figure 10 Daily concentration of Si in PM_{10}, expressed in µg/m^3, in a scatter-plot matrix for six sampling sites (1= Nijmegen, 2= Rotterdam Overschie, 3= Amsterdam Overtoom, 4= Amsterdam Stadhouderskade, 5= Vredepeel and 6= De Zilk).

Annual averages
We recalculated all elemental concentrations to their respective oxide concentrations, the most probable form in PM_{10}. Oxide weights are obtained from the elements K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Pb, Al and Si with the respective correction factors of 1.20 1.40, 1.51, 1.15, 1.41, 1.29, 1.43, 1.14, 1.13, 1.23, 1.00, 1.04, 1.14, 1.00, 1.89 and 2.14.

Annual average oxide weights, split up for the fine and coarse fractions, are given in **Table 12A**. The table shows the largest weights for K, Ca, Fe, Al and Si. These elements were also used in the calculation of crustal material (compare Equation 1).

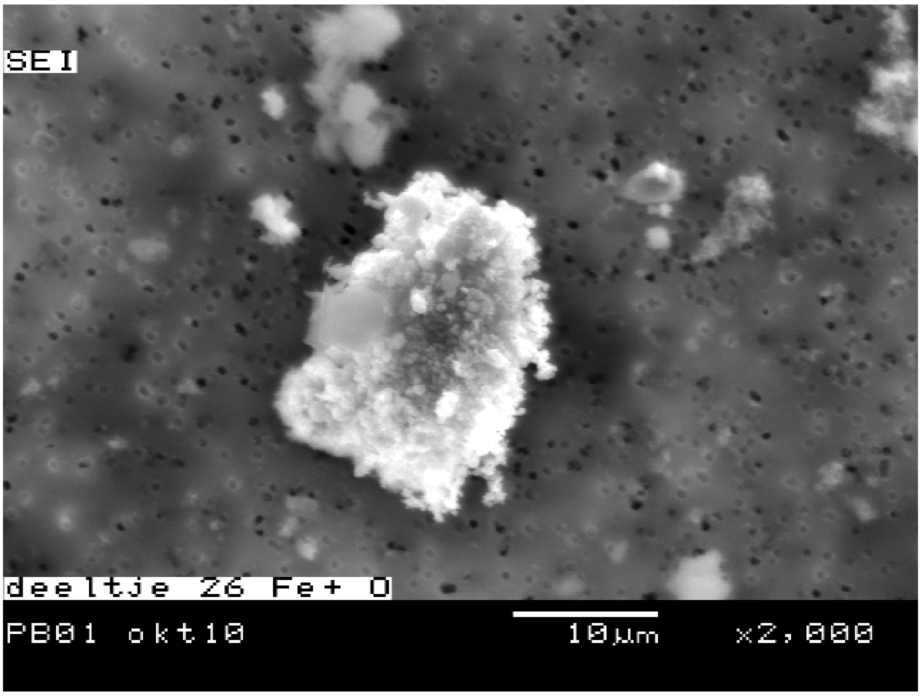


Figure 11 A SEM projection of a Fe-oxide particle. One cannot deduce which oxide is present from a Rőntgen spectrum. We can only detect the elements, Fe and O. in the red-brown Fe_2O_3 or the red-black Fe_3O_4. Less likely to show up is the black-coloured oxide FeO. Source: Timmner (2000^b).

Table 12A Contribution of oxidised elements in PM_{fine} and PM_{coarse} (ng/m^3).

	1 Nijmegen (ng/m^3)		**2 Rotterdam Overschie (ng/m^3)**		**3 Amsterdam Overtoom (ng/m^3)**	
PM fraction	Fine N=72	Coarse N=69	Fine N=72	Coarse N=66	Fine N=74	Coarse N=70
K_2O	116	232	115	165	101	110
CaO	75	954	88	750	76	465
Ti_2O_3	3	25	8	35	2	11
VO	4	2	12	3	6	1
Cr_2O_3	2	4	3	7	1	2
MnO	8	19	8	17	5	9
Fe_2O_3	162	948	207	744	139	429
NiO	2	2	6	3	3	1
Cu_2O	4	11	7	14	3	7
ZnO	41	44	42	30	29	12
Br	3	3	4	3	5	2
Rb_2O	0	0	0	0	0	0
SrO	0	1	0	2	0	2
Pb	17	7	20	6	13	2
Al_2O_3	73	473	58	382	52	157
SiO_2	156	2489	140	1667	138	1153
Sum	**666**	**5214**	**718**	**3828**	**573**	**2363**

	4 Amsterdam Stadh. kade (ng/m^3)		**5 Vredepeel (ng/m^3)**		**6 De Zilk (ng/m^3)**	
PM fraction	fine N=74	coarse N=73	fine N=70	coarse N=69	Fine N=76	coarse N=74
K_2O	108	205	132	206	110	91
CaO	96	1057	104	658	102	347
Ti_2O_3	3	26	4	22	2	6
VO	6	2	3	1	6	1
Cr_2O_3	1	6	2	2	1	1
MnO	6	6	6	13	4	5
Fe_2O_3	202	1447	172	525	106	192
NiO	3	3	1	1	3	1
Cu_2O	7	34	4	6	3	2
ZnO	32	37	46	30	25	7
Br	4	5	5	1	4	4
Rb_2O	0	0	0	0	0	0
SrO	0	3	0	1	0	1
Pb	17	15	18	4	14	2
Al_2O_3	56	432	103	435	58	142
SiO_2	161	2489	353	1787	128	505
Sum	**702**	**5767**	**953**	**3692**	**566**	**1307**

The total mass of all oxides, fine fraction plus coarse fraction, are given in **Table 12B**. The table shows the weight of all oxides to be highest on the industrial site, Nijmegen and the street station, Amsterdam Stadhouderskade. The lowest estimates are found at the coastal station De Zilk.

We also calculated the ratio [total oxidised elements in $PM_{2.5}$ / total oxidised elements in PM_{10}]. Table 12A shows a ratio varying from 0.11 (Nijmegen) to 0.30 (De Zilk).

Table 12B Annual average mass of oxidised elements in PM_{10} at the six sampling sites.

Annual average concentrations	**1 Nijmegen (µg/m³)**	**2 Rotterdam Overschie (µg/m³)**	**3 Amsterdam Overtoom (µg/m³)**	**4 Amsterdam Stadh. kade (µg/m³)**	**5 Vredepeel (µg/m³)**	**6 De Zilk (µg/m³)**
Total mass	5.9	4.5	2.9	6.4	4.6	1.9

3.6 Total mass

3.6.1 Mass recovery for PM_{10}

In the preceding sections PM_{10} has been 'split up' into a number of compounds:

- NO_3, SO_4 and NH_4, summed as total inorganic aerosol
- sea salt
- organic and elemental carbonaceous aerosol, summed as total carbonaceous aerosol
- elemental aerosol, calculated as oxides.

Now, it is considered an important check on our data to see if the weights of these individual components sum up to the VAPS-PM_{10} estimate.

The result of this exercise is given in **Table 13**, where the ratio [Total mass / VAPS-PM_{10}] is given in the last row. The table shows the ratio to vary between 0.75 (De Zilk) and 1.07 (Nijmegen). If we test the hypothesis that a specific ratio equals 1.0, using $\alpha = 0.05$, it appears that the sites 1, 2, 4 and 5 do not differ significantly from 1.0. The ratios of site 3 and 6 are too low. Given the complexity of the measurements, we conclude this result to be very good.

Table 13 *Mass recovery for PM_{10} measurements at the six sampling sites. Error bounds represent 68% confidence limits. Data on secondary aerosol, sea salt, carbonaceous aerosol and VAPS-PM_{10} within each column are based on the same measurement days. Therefore the averages differ slightly from those shown in Tables 7, 9A, 11 and 3A, respectively. The same holds for Total mass and the Ratio Total mass to PM_{10}. We note that the annual ratio [Total mass/PM_{10}] in the last row is not equal to the annual average Total mass divided by the annual average PM_{10} concentration (taking the relationship $y_t = x_t / z_t$, the expectation of y_t, $E[y_t]$, is not equal to $E[x_t]/E[y_t]$).*

Annual average concentrations in PM_{10} aerosol	**1 Nijmegen N=56 (µg/m^3)**	**2 Rotterdam Overschie N=50 (µg/m^3)**	**3 Amsterdam Overtoom N=60 (µg/m^3)**	**4 Amsterdam Stadh. kade N=58 (µg/m^3)**	**5 Vredepeel N=55 (µg/m^3)**	**6 De Zilk N=64 (µg/m^3)**
Total secondary aerosol (Dichote)	11.9 ± 1.4	10.1 ±1.2	10.3 ± 1.0	10.3 ± 1.0 *	11.3 ± 1.0	6.3 ± 0.6
Sea salt (VAPS)	3.3 ± 0.5	4.1 ± 0.5	3.0 ± 0.5	5.3 ± 0.6	2.0 ± 0.3	4.3 ± 0.5
Total carbonaceous aerosol (VAPS)	4.9 ± 0.3	5.5 ± 0.5	4.5 ± 0.3	6.7 ± 0.4	4.7 ± 0.3	3.2 ± 0.3
Total elemental aerosol (VAPS)	5.9	4.5	2.9	6.4	4.6	1.9
Total mass	26.0 ± 1.6	24.2 ± 1.4	20.7 ± 1.1	28.7 ± 1.2	22.6 ± 1.2	15.7 ± 0.8
PM_{10} (VAPS)	25.5 ± 1.7	27.5 ± 1.9	25.1 ± 1.5	30.1 ± 1.7	26.0 ± 1.7	22.3 ± 1.3
Ratio total Mass / PM_{10}	1.07 ± 0.04	0.95 ± 0.04	0.86 ± 0.03	0.99 ± 0.03	0.92 ± 0.04	0.75 ± 0.02

* Taken from the Amsterdam Overtoom station

3.6.2 Mass recovery for fine and coarse fractions

In **Table 14** we split our results from Table 13 into fine (upper panel) and coarse fractions (lower panel). The table shows the fine fraction ratio [Total mass / $PM_{2.5}$] to be slight to low. The ratio varies from 0.76 (De Zilk) to 0.96 (Amsterdam Overtoom), with an average of 0.86.

For the coarse fraction we found four ratios much larger than 1.00 (sites 1, 2, 4 and 5), and two much lower than 1.00 (sites 3 and 6). The average of the above ‘1.00’ sites is 1.35, the average of the below ‘1.00’ sites is 0.78.

The ratios for the fine fraction are slightly below 1.00. Given the fact that we did not measure all contributing compounds, this result is reasonably good. However, it is difficult to explain why the ratios for the *coarse* fraction are so variable.

Table 14 *Mass recovery for the fine fraction (upper panel) and the coarse fraction (lower panel), at the six sampling sites. Error bounds represent 68% confidence limits. Data on secondary aerosol, sea salt, carbonaceous aerosol and VAPS-$PM_{2.5}$ within each column are based on the same measurement days. Therefore averages differ slightly from those shown in Tables 8A, 10A, 11 and 6A. The same holds for Total mass and the Ratio total mass to $PM_{2.5}$.*

Annual average concentrations in $PM_{2.5}$ aerosol	**1 Nijmegen N=56 ($\mu g/m^3$)**	**2 Rotterdam Overschie N=50 ($\mu g/m^3$)**	**3 Amsterdam Overtoom N=60 ($\mu g/m^3$)**	**4 Amsterdam Stadh. kade N=58 ($\mu g/m^3$)**	**5 Vredepeel N=55 ($\mu g/m^3$)**	**6 De Zilk N=64 ($\mu g/m^3$)**
Total secondary aerosol (Dichote)	10.9 ± 1.3	8.7 ±1.1	9.3 ± 1.0	9.3 ± 1.0 *	9.7 ± 0.9	5.5 ± 0.7
Sea salt (VAPS)	0.5 ± 0.1	0.5 ± 0.1	0.5 ± 0.1	0.6 ± 0.1	0.3 ± 0.1	1.0 ± 0.2
Total carbonaceous aerosol (VAPS)	4.9 ± 0.3	5.5 ± 0.5	4.5 ± 0.3	6.7 ± 0.4	4.7 ± 0.3	3.2 ± 0.3
Total elemental aerosol (VAPS)	0.7	0.7	0.6	0.7	1.0	0.6
Total mass	**17.0 ± 1.6**	**15.4 ± 1.5**	**14.9 ± 1.1**	**17.3 ± 1.3**	**15.7 ± 1.2**	**10.3 ± 0.9**
$PM_{2.5}$ (VAPS)	18.3 ± 1.5	19.3 ± 1.8	17.5 ± 1.4	20.2 ± 1.6	19.3 ± 1.5	14.2 ± 1.2
Ratio total Mass / $PM_{2.5}$	**0.91 ± 0.03**	**0.86 ± 0.05**	**0.96 ± 0.07**	**0.92 ± 0.03**	**0.83 ± 0.03**	**0.76 ± 0.03**

Annual average concentrations in coarse aerosol	**1 Nijmegen N=54 ($\mu g/m^3$)**	**2 Rotterdam Overschie N=50 ($\mu g/m^3$)**	**3 Amsterdam Overtoom N=60 ($\mu g/m^3$)**	**4 Amsterdam Stadh. kade N=56 ($\mu g/m^3$)**	**5 Vredepeel N=54 ($\mu g/m^3$)**	**6 De Zilk N=64 ($\mu g/m^3$)**
Total secondary aerosol (Dichote)	1.1 ± 0.2	1.5 ±0.1	1.0 ± 0.1	1.0 ± 0.1 *	1.6 ± 0.1	2.0 ± 0.3
Sea salt (VAPS)	3.0 ± 0.5	3.5 ± 0.3	2.5 ± 0.3	4.6 ± 0.5	1.7 ± 0.3	1.0 ± 0.2
Total carbonaceous aerosol (VAPS)	-	-	-	-	-	-
Total elemental aerosol (VAPS)	5.2	3.8	2.4	5.8	3.7	1.3
Total mass	**9.3 ± 0.3**	**8.8 ± 0.3**	**5.9 ± 0.2**	**11.4 ± 0.4**	**7.0 ± 0.2**	**4.3 ± 0.3**
PM_{coarse} (VAPS)	7.2 ± 0.4	8.3 ± 0.4	7.7 ± 0.4	9.8 ± 0.6	6.7 ± 0.4	8.1 ± 0.5
Ratio total Mass / PM_{coarse}	**1.50 ± 0.09**	**1.21 ± 0.07**	**0.85 ± 0.05**	**1.30 ± 0.07**	**1.40 ± 0.17**	**0.70 ± 0.12**

* Taken from Amsterdam Overtoom station

3.7 Contribution of crustal material and traffic

3.7.1 Crustal material

Spatial variation

We calculated the weight of crustal material using Equations (1a) and (1b). The spatial coherence is given for Crustal2 (Equation (1b)) in **Figure 12**. The scatter-plot matrix shows that the crustal-material estimates to be reasonably coherent, except for site 6, De Zilk. Correlations range from R = 0.36 (sites 4 Amsterdam Stadhouderskade and 6 De Zilk) to R = 0.81 (sites 1 Nijmegen and 2 Rotterdam Overschie).

It is not clear why estimates for coastal site De Zilk deviate. Perhaps higher wind speeds along the coast generate deviating patterns of crustal-material concentrations.

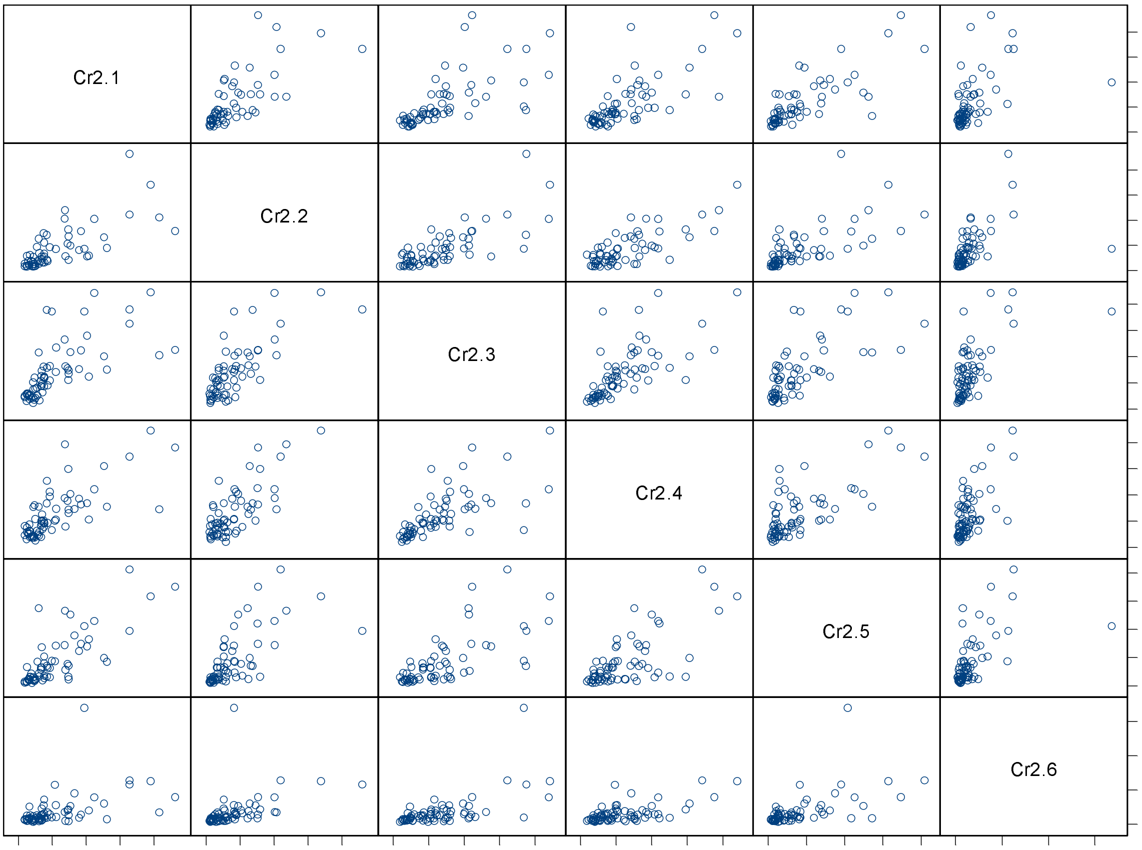


Figure 12 Daily Crustal2 concentrations, expressed in µg/m^3, in a scatter-plot matrix for six sampling sites (1= Nijmegen, 2= Rotterdam Overschie, 3= Amsterdam Overtoom, 4= Amsterdam Stadhouderskade, 5= Vredepeel and 6= De Zilk).

Annual and seasonal concentrations

In **Table 15A** we give the annual average crustal-material estimates, following Equations (1a) and (1b). The table shows Crustal1 estimates to be, on average, 45% lower than Crustal2 estimates. In the following we will apply Crustal2 estimates because they are based on five elements in stead of two.

Highest crustal concentrations are found for the industrial site Nijmegen and street station Amsterdam Stadhouderskade. Lowest values are found for the coastal site, De Zilk and the urban background site, Amsterdam Overtoom.

Table 15A Contribution of crustal material using two approaches. Crustal1 was calculated using Equation (1a), and Crustal2, Equation (1b). Error bounds represent 68% confidence limits.

Annual average crustal concentrations in PM$_{10}$ aerosol	**1 Nijmegen N=69 (µg/m^3)**	**2 Rotterdam Overschie N=66 (µg/m^3)**	**3 Amsterdam Overtoom N=70 (µg/m^3)**	**4 Amsterdam Stadh. kade N=73 (µg/m^3)**	**5 Vredepeel N=69 (µg/m^3)**	**6 De Zilk N=74 (µg/m^3)**
Crustal1 (Equation (1a))	4.0 ± 0.5	3.0 ± 0.5	1.8 ± 0.2	3.8 ± 0.5	3.5 ± 0.5	1.2 ± 0.2
Crustal2 (Equation (1b))	5.7 ± 0.6	4.3 ± 0.5	2.8 ± 0.2	6.3 ± 0.5	4.4 ± 0.5	1.7 ± 0.3
Ratio Crustal1/Crustal2	0.58 ± 0.03	0.53 ± 0.04	0.52 ± 0.03	0.49 ± 0.03	0.65 ± 0.04	0.52±0.03

In **Table 15B** we calculated crustal concentrations for summer and winter months. For Crustal2, summer concentrations were found, on average, to be 50% higher than winter concentrations.

We noted a small overlap between estimates for sea salt and crustal material: the elements K and Ca originate partly from sea salt spray. This contribution should not be attributed to crustal material using Equation (1b). Giving the fact that the sea-salt contribution of K is 1.2% of the sea-salt weight and that the sea-salt weight is, on average, 6 µg/m^3, we estimate K from sea salt at ~0.06 µg/m^3. If we apply the weighing factor 1.2 from Equation (1b), we find the contribution of sea-salt K to the estimate Crustal2 to be ~0.07 µg/m^3. In the same way we find the contribution of sea-salt Ca to Crustal2 to be ~0.08 µg/m^3. Both estimates are small, and we have neglected these overlaps in our analyses.

Table 15B *Contribution of crustal material in the 5 summer months (May through September) and 5 winter months (November through March). Crustal1 was calculated using Equation (1a), and Crustal2 using Equation (1b). Error bounds represent 68% confidence limits. The number of days varies per instrument, period and site. We have not added these numbers to the table. The number of days varies from 26 to 33.*

Annual average crustal concentrations in PM_{10} aerosol	**1 Nijmegen ($\mu g/m^3$)**	**2 Rotterdam Overschie ($\mu g/m^3$)**	**3 Amsterdam Overtoom ($\mu g/m^3$)**	**4 Amsterdam Stadh. kade ($\mu g/m^3$)**	**5 Vredepeel ($\mu g/m^3$)**	**6 De Zilk ($\mu g/m^3$)**
Crustal1 summer	4.8 ± 0.7	4.2 ± 1.0	2.5 ± 0.4	4.2 ± 0.8	4.7 ± 0.9	1.8 ± 0.5
Crustal1 winter	3.6 ± 1.0	2.1 ± 0.6	1.1 ± 0.3	3.3 ± 0.8	2.4 ± 0.7	0.7 ± 0.2
Crustal2 summer	6.6 ± 0.7	5.6 ± 0.9	3.7 ± 0.4	6.6 ± 0.8	5.7 ± 0.9	2.4 ± 0.6
Crustal2 winter	5.3 ± 1.1	3.3 ± 0.6	2.1 ± 0.3	5.8 ± 0.9	3.1 ± 0.7	1.3 ± 0.2

3.7.2 Traffic

Source profile

The source profile of traffic emissions, as obtained from three samples collected in the IJ-tunnel shows an OC/EC ratio of 1.24 (see **Figure 13)**. We can use this factor as the parameter α in Equation (2a): $\alpha = 1.24$.

The parameter β in Equation (2b) can be estimated using Dutch estimates for primary particulate matter emissions for various industrial sectors as given in the Environmental Balance (2000) in Dutch only. Traffic emissions for the year 1998 are estimated to be 18.1 kTon, emissions of industry and refineries sum to 13.3 kTon (consumers and other sources sum to an additional 9.3 kTon). These figures can be used to estimate the factor β in Equation (2b). Using traffic relative to traffic plus industrial emissions, we find $\beta_1 = 0.58$.

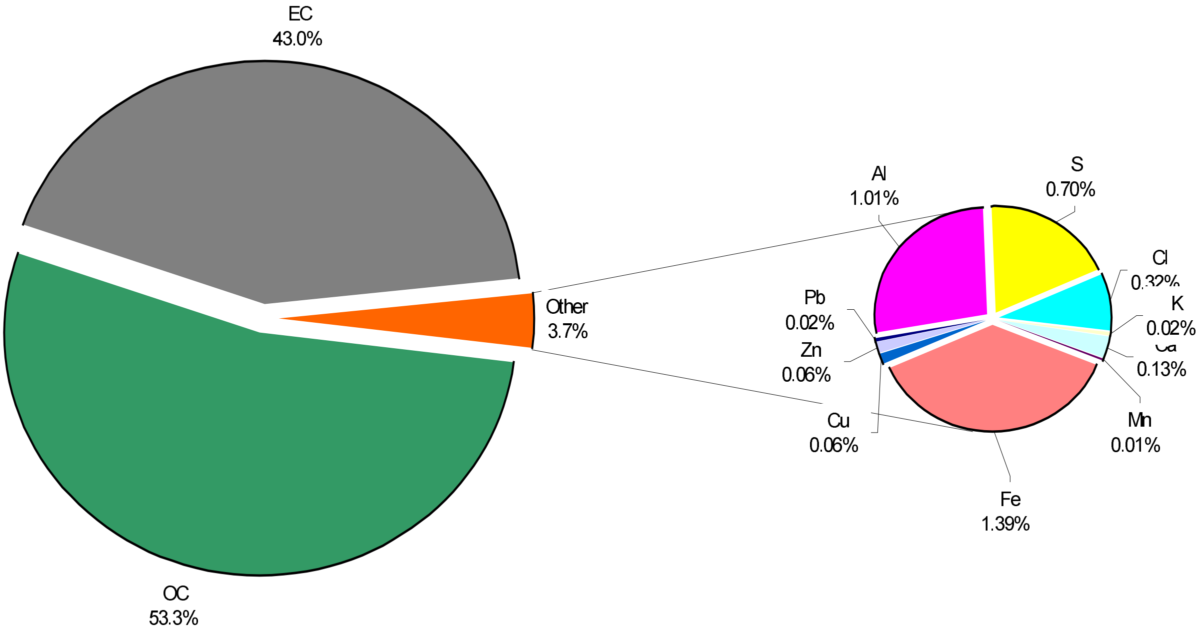


Figure 13 *Composition of $PM_{2.5}$ collected in the IJ tunnel. Figures represent averages of three samples.*

Spatial variation

We calculated the traffic contribution to PM_{10} by Equations (2a) and (2b), leading to a high and a low estimate, respectively. The spatial coherence of the high traffic estimates is shown in **Figure 14**. The highest scattering is found for station De Zilk (last row of the scatter matrix). The coherence between sites 1 and 5 is good.

Correlations range from R = 0.49 (sites Amsterdam Stadhouderskade and De Zilk) to R = 0.95 (sites Nijmegen and Rotterdam Overschie).

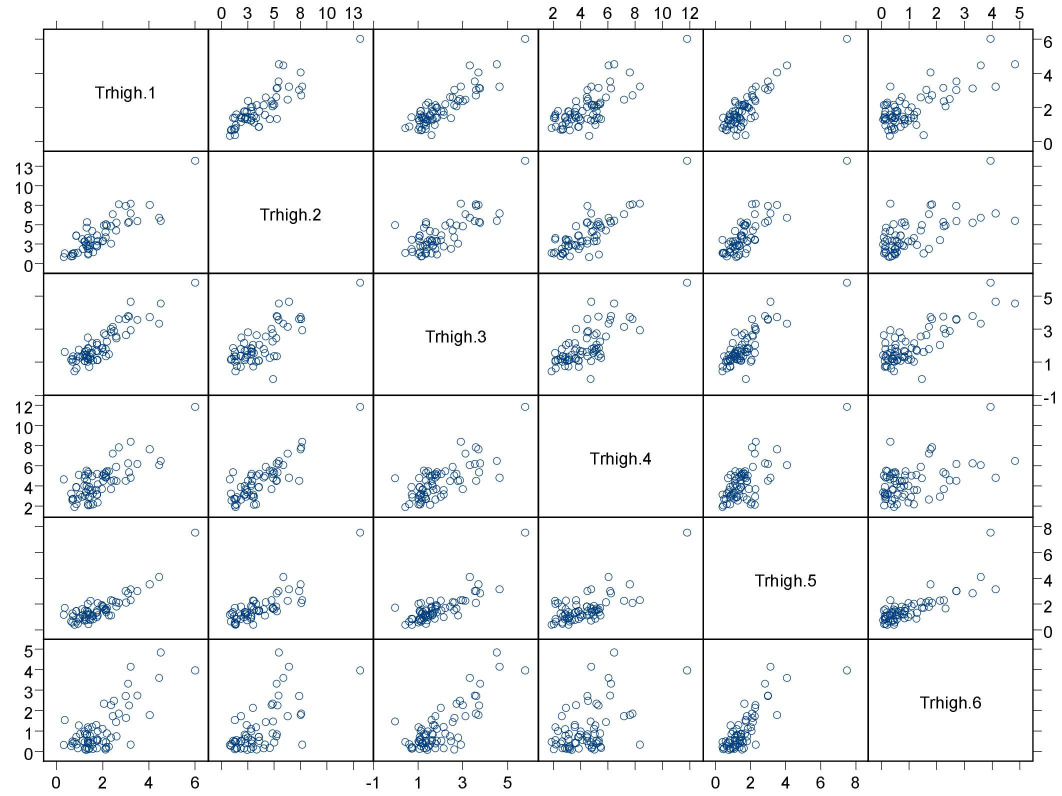


Figure 14 *Traffic-related concentrations on a daily averaged basis expressed in µg/m^3, in a scatter-plot matrix for six sampling sites (1= Nijmegen, 2= Rotterdam Overschie, 3= Amsterdam Overtoom, 4= Amsterdam Stadhouderskade, 5= Vredepeel and 6= De Zilk).*

Annual averages

Annual averages of both traffic estimates are given in **Table 16**. The table shows the high estimate to be, on average, 70% higher than the low estimate. Furthermore, urban street sites 2 and 4 show the highest traffic contribution, as was to be expected. The lowest traffic influence is found at the background stations of Vredepeel and De Zilk, again as expected.

Table 16 Contribution of traffic emissions using two approaches. Traffic1 was calculated using Equation (2a), and Traffic2 using Equation (2b). Error bounds represent 68% confidence limits.

	1	**2**	**3**	**4**	**5**	**6**
Annual average concentrations in PM_{10} aerosol	**Nijmegen N=72 (µg/m^3)**	**Rotterdam Overschie N=62 (µg/m^3)**	**Amsterdam Overtoom N=72 (µg/m^3)**	**Amsterdam Stadh. kade N=73 (µg/m^3)**	**Vredepeel N=70 (µg/m^3)**	**De Zilk N=73 (µg/m^3)**
Traffic1 (Equation (2a))	1.5 ± 0.1	3.6 ±0.3	1.9 ± 0.1	4.3 ± 0.2	1.6 ± 0.1	1.0 ± 0.1
Traffic2 (Equation (2b))	1.1 ± 0.1	2.1 ± 0.2	1.1 ± 0.1	2.5 ± 0.1	0.9 ± 0.1	0.6 ± 0.1

4. Modelling PM_{10} concentrations

4.1 The OPS model

The OPS model is a long-term Lagrangian transport and deposition model that describes relationships between individual sources or source areas, and individual receptors. Local transport and dispersion is described with a Gaussian plume model. The model is statistical in the sense that concentration and deposition values are calculated for a number of typical meteorological situations and the long-term value is obtained by summing these values, weighted with their relative frequencies. All relationships governing the transport and deposition processes are solved analytically, allowing the use of non-gridded receptors and sources, and variable grid sizes. Transport from a source to a receptor is assumed to take place in straight, well-mixed sectors of height and horizontal angles of 30º. Corrections are applied close to the sources to account for height of emission and vertical dispersion; a correction for the curved nature of real transport paths is applied to larger distances.

The OPS model consists of two main parts:

- A special meteorology pre-processor calculates hourly transport trajectories arriving at a receptor on the basis of wind observations. Secondary parameters, like stability and mixing height classification, which define the atmospheric state along the trajectories, are also derived from the observed data. Together, they provide the necessary frequency distribution statistics for the period of interest. These statistics are then stored in a climatological database for use in the main part of the model.
- The model itself carries out the actual calculations. The mathematical formulation of the model is based on the change of mass for a pollutant due to chemical conversion and deposition. These processes are based on variables, like dry deposition velocities, wet scavenging coefficients, pseudo first-order chemical reaction constants for inorganic secondary aerosol precursors (formation of organic secondary aerosol is not included), chemical inertness of primary emitted particles (no nucleation and agglomeration included) and the mixing-layer height. The roughness length is based on a 5 x 5 km grid map of the Netherlands on land use.

The model can be applied for time resolutions for seasons, months or years. The receptor spatial resolution is determined by the spatial resolution of the emission inventories (typically 5 x 5 km or 1x1 km). Emissions are to be located in a 2000 x 2000 km area (Europe). Contributions from beyond this area are not calculated and have to be added to the outcome of the model calculation, as we will point out in Chapter 6.

4.2 The SIGMA post-processor

The SIGMA model is a so-called post-processor, which uses the relationships as once-only established with OPS between emissions and concentrations or depositions for a 5 x 5 km grid. On a detailed level, emission scenarios of target groups in the Netherlands can be processed fast by SIGMA to calculate the consequences for the expected concentrations or depositions.

SIGMA enables the summing the concentration fields ($Conc_{c,br,ld,jr}$) of each of the PM constituents (index 'c'), for each source category (index 'br'), each country or cluster of countries (index 'ld') and year (index 'jr'). Computations for the base year (1995) are obtained from the very time consuming TREND/OPS model. Weight factors ($PSF_{c,br,ld}$) for the particle size distribution of primary emissions and update factors ($UDF_{c,br,ld,jr}$) for changes in emission fluxes compared to the base year are applied as follows:

$$PM_{x\,Rgr,br,ld,jr} = \sum_c \left\{ UDF_{c,br,ld,jr} \cdot PSF_{c,br,ld} \cdot Conc_{c,Rgr,br,ld} \right\} \tag{3}$$

The particle size class weight factor ($PSF_{c,br,ld}$) is used to weight the percentages of the total particle mass. Such an approach is especially useful for modelling primary-emitted particles because they cover a broad range of particle sizes. The factors are:

1. <0.95 µm: 0.70
2. 0.95 – 4 µm: 0.20
3. 4 – 10 µm: 0.055
4. 10 – 20 µm: 0.025
5. >20 µm: 0.02.

The update factors are based both on changes of the emissions due to abatement measures and on new insights and retrospectively improved data. The concentration values, which are calculated for the grid of the monitoring sites, are extracted from the concentration fields obtained.[2]

4.3 Uncertainties in the model

The emission-dispersion system as used in this study incorporates a number of uncertainties.[3] These can be distinguished as:

a. uncertainties in the dispersion model. Shortcomings in the description of the different processes (emission, dispersion, transport, conversion and deposition), uncertainties in meteorological data used as model input, and uncertainties in parameters that are specific for the substance(s) in question. Examples of the latter are dry and wet deposition parameters and chemical conversion rates.

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[2] The SIGMA model will be described in an RIVM report, *SIGMA – A post processor for air quality assessments*, to be published by Vissenberg H.A., Bloemen H.J.Th.M., Eerens H.C., Smeets W.L.M. and Brandes L.J.

[3] This work is partly based on unpublished work of J..A. van Jaarsveld.

b. uncertainties in emissions. Aspects such as incomplete recognition of particle producing processes and uncertainties in emission factors can be mentioned, as well as uncertainties in a number of process parameters such as location of the sources, release height, initial size distribution, and diurnal and seasonal variations.

Model uncertainties
On the basis of comparisons with measurements, the average concentrations and depositions on regional and national scales can be calculated with the OPS model in the case of properly chosen loss parameters and a correct emission file. Errors will be smaller than found in Van Jaarsveld (1989) [4] (and can be interpreted as 1-σ or 68% confidence limits) as recorded below:

Period of time	Concentration	Deposition
Long term	Ca. 10%	Ca.15%
Specific year	Ca. 15%	Ca. 20%
Specific summer or winter	Ca. 20%	Ca. 30%
Specific month	Ca. 30%	Ca. 40%

Emission uncertainties
The spatial resolution of concentration and deposition estimates can be no better than the spatial resolution of the emission description. The accuracy of emissions is, however, apparently not known. Tentative guesses for systematic errors in national total SO_2 en NO_x emissions are 15% and 20%, respectively. Some support for the latter is given by the scatter in emission totals for the Netherlands, as reported by different authors. More detailed information on emission uncertainties can be found in Van Jaarsveld (1995). We note that only anthropogenic emissions are used in the model, as biogenic emissions are unknown.

Total uncertainty
In this above report, total uncertainties in annual modelled PM_{10} concentrations in Tables 29, 30, 32 and 33 are estimated at 25% (1-σ or 68% confidence limits). The uncertainty (15%) of the estimates in Table 31, where the contribution of traffic emissions is shown, is equal to the model uncertainty for a specific year (traffic emissions are reasonably well documented).

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[4] Jaarsveld, J.A. van, 1989. *An operational atmospheric transport model for priority substances; specifications and instructions for use*. Report 228603008, National Institute of Public Health and the Environment (RIVM), Bilthoven, The Netherlands.

4.4 PM_{10} and secondary aerosol concentrations

Primary PM_{10} (concentration of PM emitted as aerosol) and secondary PM_{10} (the aerosol concentration formed from its precursors NH_3, SO_2 and NO_x) are calculated separately in our model. We recall that only *anthropogenic* emissions were used as input in the model.

The emissions are summarised in **Table 17**. The target groups 'Industry' and 'Traffic' contribute 80% to the primary PM_{10} concentration and 87% to the emission of the precursor SO_2. 'Agriculture' contributes 94% to NH_3 emissions, and 'Traffic' 65% to the NO_x emissions.

Table 17 Emissions of primary particulate matter and the secondary aerosol precursors NH_3, NO_x and SO_2 based on national (upper panel) and European inventories (lower panel). Calculations for 1997 were done with SIGMA.

Origin and source category for the Netherlands	**$PM_{10\ primary}$** 10^6 kg/year	**NH_3** 10^6 kg/year	**NO_x** 10^6 kg/year	**SO_2** 10^6 kg/year
Industry	14.9	4.1	75.8	79.6
Energy	5.2	0.0	65.0	13.0
Traffic	17.4	0.0	292.7	22.6
Agriculture	0.1	176.5	0.0	0.2
Other	2.4	6.8	10.7	2.3

Origin and source category for Europe	**$PM_{10\ primary}$ 10^6 kg/year**	**NH_3 10^6 kg/year**	**NO_x 10^6 kg/year**	**SO_2 10^6 kg/year**
Netherlands	40.0	187.4	453.1	117.7
Germany	446.2	649.0	1803.1	1466.9
France	343.0	668.0	1641.0	1031.0
Belgium and Luxembourg	70.4	104.0	256.1	248.3
United Kingdom and Ireland	230.6	447.0	1949.6	1804.7
Italy, Switzerland, Austria, Norway, Sweden, Finland, Denmark	399.0	760.9	3530.6	1926.2
Greece, Spain and Portugal	207.3	514.5	1855.0	2876.0
Bulgaria, Czech Republic, Slovakia, Hungary, former Yugoslavia	732.6	731.1	1478.6	3771.6
Russia, Poland, Turkey, other European states from the former Russia Federation	5129.6	1593.2	4670.4	7488.1
Total	**7639**	**5666**	**18082**	**20848**

The contribution of different source categories of PM_{10} with SIGMA to the annual averages in the Netherlands can be found in **Table 18,** and **Figures 15** (total PM_{10}) and **16** (contribution of traffic). According to the SIGMA model, particulate matter concentrations consist for roughly 40% of primary particles. The remainder consists of NH_x, SO_y and NO_x secondary aerosol particles. The NO_x contribution is roughly equal to the summed NH_x and SO_y contribution. NO_x and NH_x aerosol concentrations are mainly emitted by the target groups ‘Traffic’ and ‘Agriculture’, respectively. The contribution of SO_x aerosol concentrations from Dutch emissions is small (~ 4%) and comes mainly from the group 'Industry', while from the emissions abroad the SO_x aerosol contribution is larger (~20%), mainly from the target groups ‘Energy’, ‘Industry’ and ‘Other’. The spatial distribution of secondary aerosol over the Netherlands is given in **Figure 17 a and b**.

Table 18 Contribution of source categories from the Netherlands (upper panel), abroad (middle panel) and the total of Netherlands plus abroad (lower panel) to primary and secondary aerosol concentrations. Calculations for 1997 were done with SIGMA.

The Netherlands	**Industry ($\mu g/m^3$)**	**Energy ($\mu g/m^3$)**	**Traffic ($\mu g/m^3$)**	**Agriculture ($\mu g/m^3$)**	**Other ($\mu g/m^3$)**	**Total ($\mu g/m^3$)**
Primary	0.3	0.2	0.9	0.0	0.2	**1.7**
NH_x	0.0	-	-	1.3	0.1	**1.3**
NO_y	0.1	0.1	1.1	0.0	0.1	**1.5**
SO_x	0.1	0.0	0.0	0.0	0.0	**0.2**
PM_{10} Total	**0.6**	**0.4**	**2.1**	**1.3**	**0.4**	**4.7**

Abroad	**Industry**	**Energy**	**Traffic**	**Agriculture**	**Other**	**Total**
Primary	1.6	0.3	1.1	0.0	2.2	**5.2**
NH_x	0.0	0.0	0.0	1.2	0.0	**1.2**
NO_y	0.2	1.1	2.2	0.0	0.3	**3.7**
SO_x	0.3	1.9	0.1	0.0	0.3	**2.6**
PM_{10} Total	**2.1**	**3.3**	**3.3**	**1.2**	**2.8**	**12.7**

NL + Abroad	**Industry**	**Energy**	**Traffic**	**Agriculture**	**Other**	**Total**
Primary	1.9	0.5	2.0	0.0	2.4	**6.9**
NH_x	0.0	0.0	0.0	2.5	0.1	**2.5**
NO_y	0.3	1.2	3.3	0.0	0.4	**5.2**
SO_x	0.4	1.9	0.1	0.0	0.3	**2.8**
PM_{10} Total	**2.7**	**3.7**	**5.4**	**2.5**	**3.2**	**17.4**

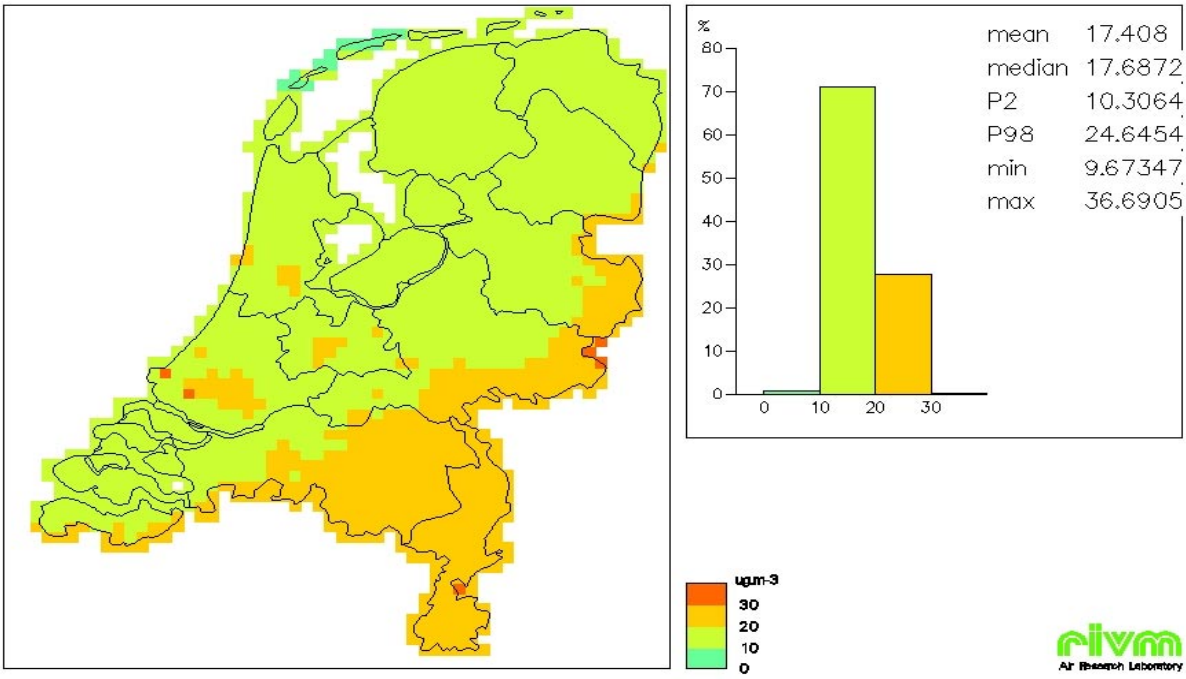


Figure 15 *Annual PM_{10} concentrations (primary plus secondary, expressed in $\mu g/m^3$) in the Netherlands due to domestic and foreign sources. Calculations for 1997 are done with SIGMA.*

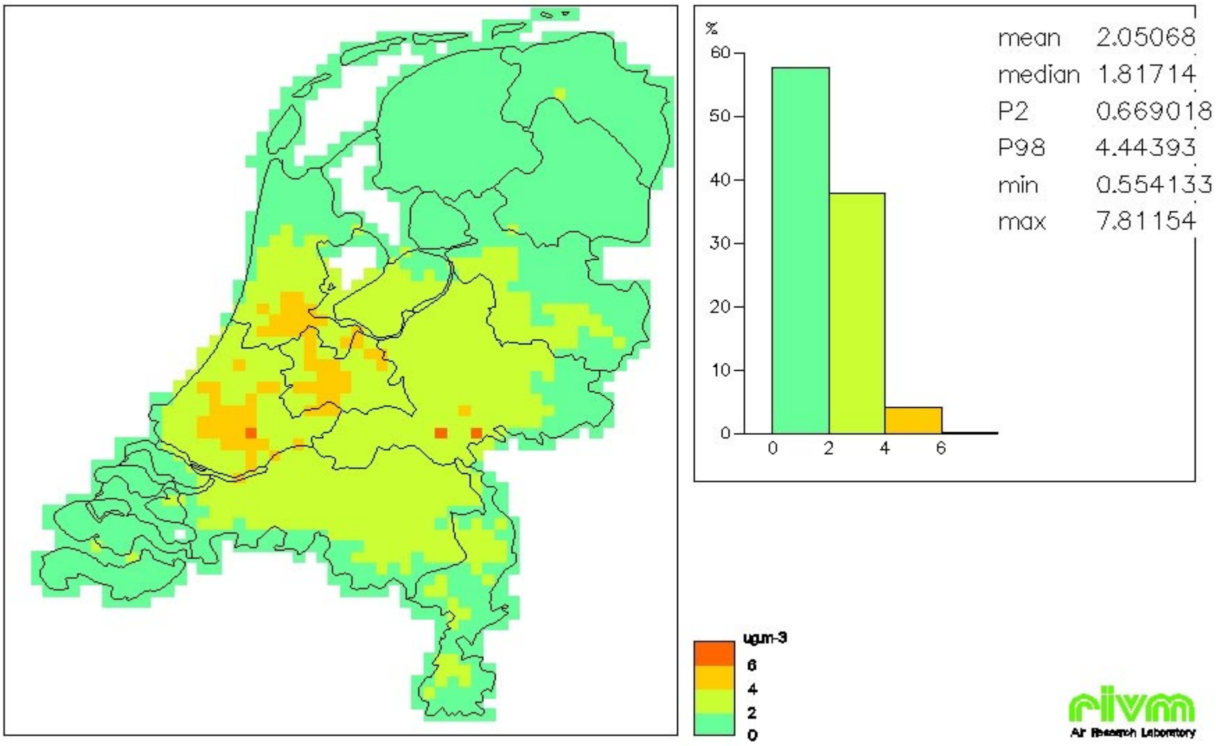


Figure 16 *Contribution of domestic traffic sources to annual total PM_{10} (primary plus secondary, expressed in $\mu g/m^3$) in the Netherlands. Calculations for 1997 are done with SIGMA.*

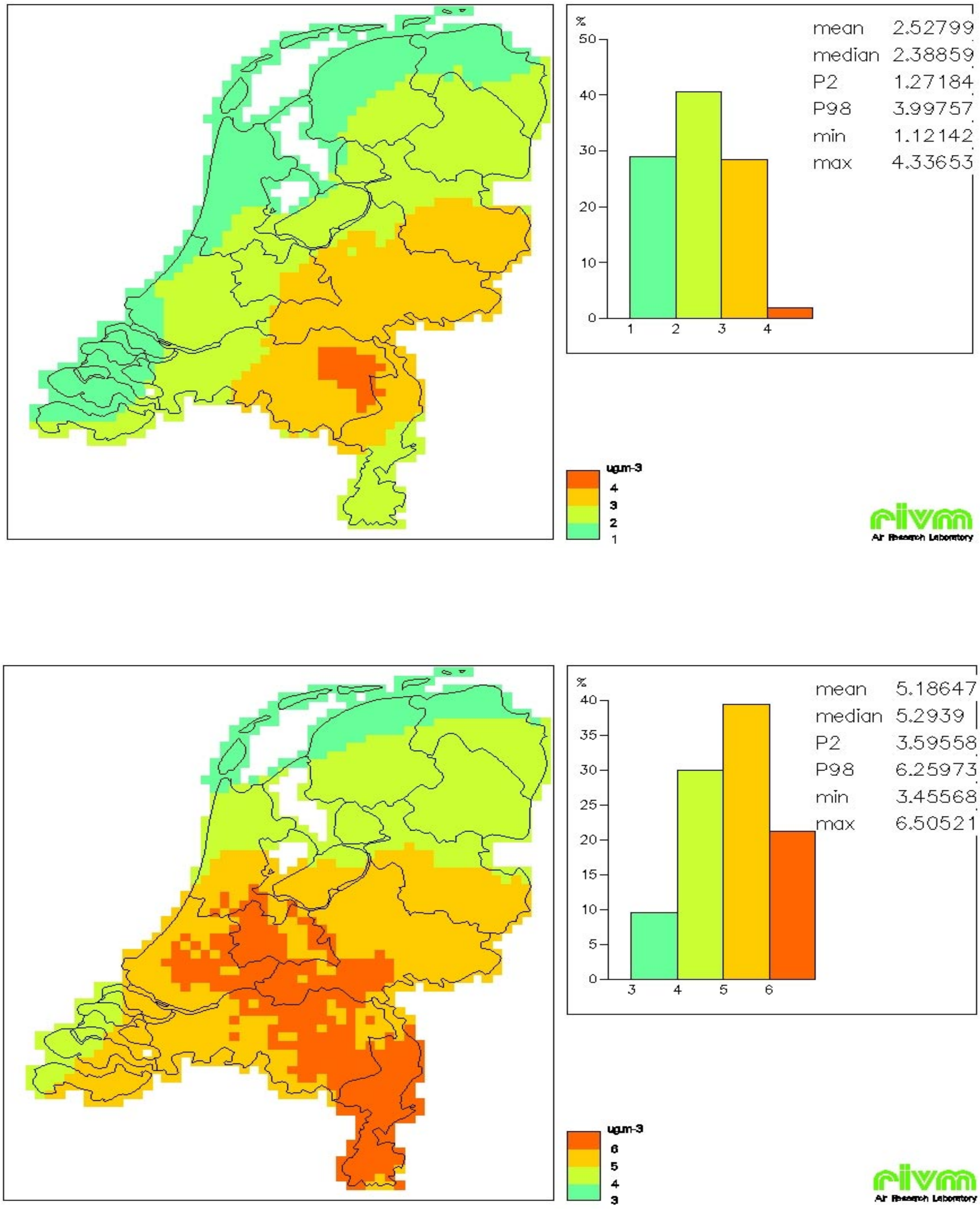


Figure 17a *Annual NH_x (higher panel) and SO_y (lower panel) secondary aerosol concentrations in the Netherlands due to domestic and foreign sources. Calculations for 1997 are done with SIGMA.*

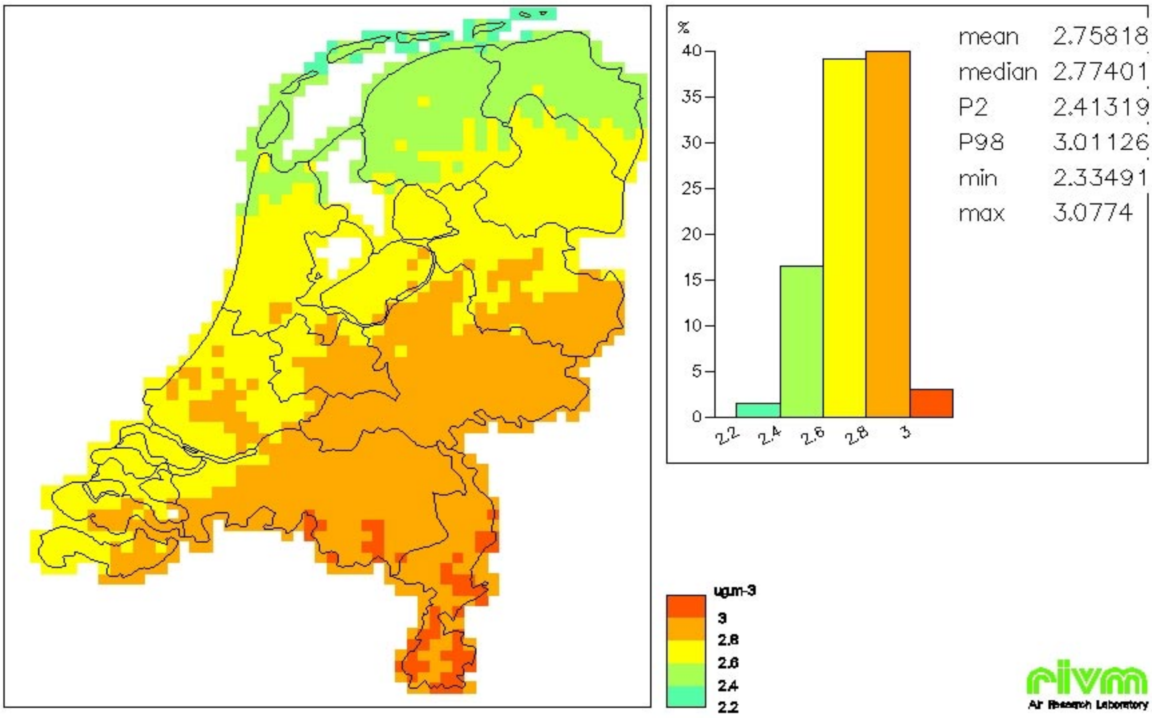


Figure 17b *Concentrations for* NO_x *secondary aerosol concentrations in the Netherlands, due to domestic and foreign sources. Calculations for 1997 are done with SIGMA.*

Table 19 shows calculated primary and secondary particulate matter concentrations on specific monitoring sites, as calculated for 1997 with SIGMA. For the sites, Rotterdam and Amsterdam, Dutch emissions are calculated to contribute mainly to total PM_{10} concentrations, while for the sites, Nijmegen, De Zilk and Vredepeel emissions from abroad make the largest contribution.

For the Dutch emissions, the proportion of primary particulate matter to total PM_{10} is significantly larger for the locations in Amsterdam and Rotterdam (the Rijnmond area) than for the other locations. This can be explained by the relatively high and local emissions of primary particles by the target groups ‘Traffic’ and ‘Industry’ (compare **Figure 18**).

Table 19 *Concentrations of primary and secondary Particulate Matter. Calculations for 1997 are done with SIGMA on specific monitoring sites. The 68% confidence limits are obtained by assuming a relative error of ± 25%.*

Netherlands	**1** **Nijmegen** **(µg/m³)**	**2** **Rotterdam** **(µg/m³)**	**3 & 4** **Amsterdam** **(µg/m³)**	**5** **Vredepeel** **(µg/m³)**	**6** **De Zilk** **(µg/m³)**
Primary	2.8	8.3	9.2	1.3	2.7
NH_x	2.3	1.3	1.3	2.7	1.0
NO_y	2.2	2.5	2.6	1.6	1.9
SO_x	0.2	0.2	0.2	0.2	0.2
PM_{10} Total	7.5	12.3	13.2	5.7	5.8
Primary/Total PM_{10}	**0.37**	**0.67**	**0.70**	**0.23**	**0.46**

Abroad	**1** **Nijmegen**	**2** **Rotterdam**	**3 & 4** **Amsterdam**	**5** **Vredepeel**	**6** **De Zilk**
Primary	5.4	4.2	3.5	6.5	3.4
NHx	1.2	1.1	0.9	1.4	0.9
NOy	4.0	3.6	3.4	4.4	3.4
SOx	2.7	2.7	2.6	2.8	2.6
PM_{10} Total	13.3	11.5	10.3	15.1	10.2
Primary/Total PM_{10}	**0.41**	**0.37**	**0.34**	**0.43**	**0.33**

NL+Abroad	**1** **Nijmegen**	**2** **Rotterdam**	**3 & 4** **Amsterdam**	**5** **Vredepeel**	**6** **De Zilk**
Primary	8.2	12.5	12.6	7.7	6.1
NH_x	3.5	2.3	2.2	4.1	1.9
NO_y	6.2	6.1	6.0	6.0	5.3
SO_x	2.9	2.9	2.8	2.9	2.7
PM_{10} Total	20.8	23.8	23.5	20.8	16.0
Primary/Total PM_{10}	**0.39**	**0.53**	**0.54**	**0.37**	**0.38**

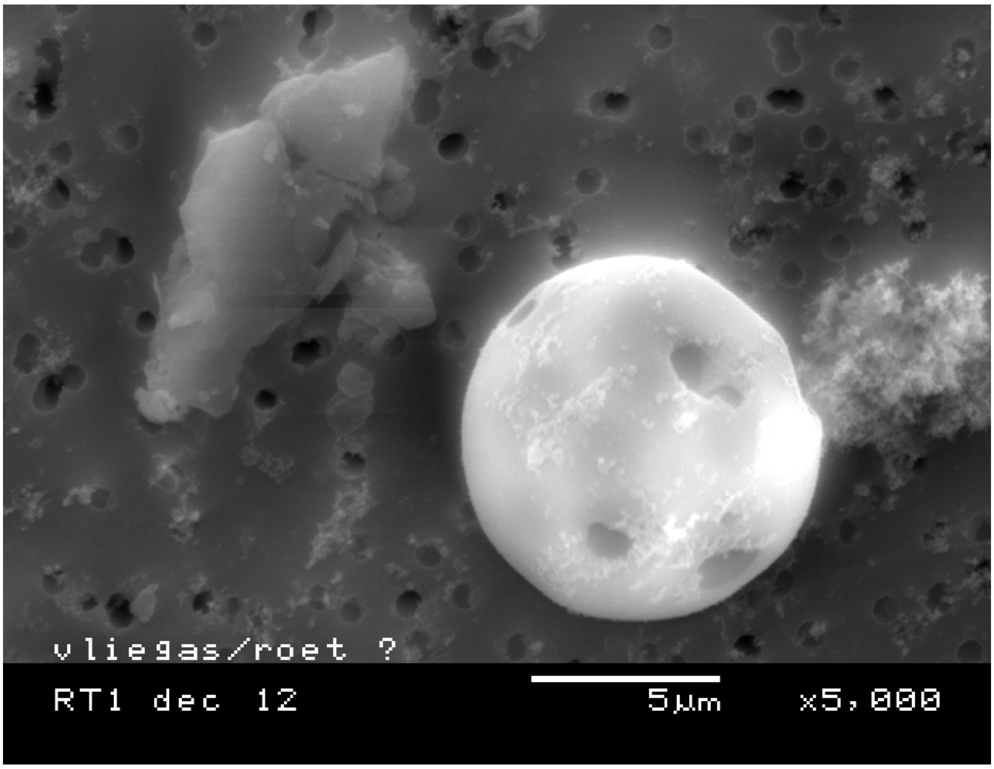


Figure 18 *SEM projection of a fly-ash particle. The sample was taken at the site, Rotterdam Overschie. These particles are typical of emissions by coal-fired power plants. Source: Timmner (2000*^{b}*).*

5. Discussion

5.1 Instrumental differences

5.1.1 PM_{10} and $PM_{2.5}$

Table 3A presents annual average PM_{10} concentrations based on three instruments: the TEOM, the VAPS and the FAG. But what is the 'true value'? And how can we explain the instrumental differences in this table?

The 'true' concentrations of PM_{10} have their origins in a reference instrument, e.g. the WRAC (Wide Range Aerosol Classifier) and the KFG (German: Klein Filter Gerät). For the Netherlands a number of recent comparisons of daily average concentrations of PM_{10} measured by FAG and TEOM have been made with those of KFG, and reported by Arkel et al. (2001[a,b]) and Van Putten et al. (2001[a,b]).

From the literature it is known that both the TEOM and the FAG underestimate the 'true' PM_{10} concentrations when ammonium nitrate and OC are present, making a correction factor necessary (Williams and Bruchmann, 2001). Such a correction factor has to be found experimentally and depends, amongst other aspects, on the chemical composition of the aerosol. Since 1993 a standard correction factor of 1.3 has been used for FAG in the Netherlands. All reported FAG results have since then been automatically corrected with this factor. Data of FAG in this report is corrected even when this is not mentioned explicitly.

Recent results of Arkel et al. (2001[a,b]) and Van Putten et al. (2001[a,b]), confirming the currently used numerical value of the existing relationship for the FAG, have revealed a slightly larger correction factor for the TEOM for urban situations (in $\mu g/m^3$):

$$\text{'True' } PM_{10}\text{ (KFG)} = 1.6 * [\text{ TEOM }] - 4.0 \qquad (4a)$$

$$\text{'True' } PM_{10}\text{ (KFG)} = 1.3 * [\text{ FAG }] \qquad (4b)$$

Although deduced from comparison experiments these relations have to be considered as tentative. This holds in particular for 4a. The calculations using the equations above will be used for the instrumental comparisons with the 'true' concentrations. Unfortunately, no comparison with a reference instrument was available for the VAPS. The results are presented in Table 20.

The values in Equations (4a) and (4b) are based on the 'Klein Filter Gerat' as a reference instrument. Depending on the filter material, this instrument may miss some ammonium nitrate, indicating that the 'true' numerical values may be even higher.

Table 20 shows that for all the six concentrations of VAPS-$PM_{10,}$ each of them differs significantly from the 'true' FAG- and/or TEOM- PM_{10} values. Comparing the results of TEOM and FAG. We find that at two of the measurement sites the 'true' values of PM_{10} with TEOM and FAG match, while at two others, they are significantly different from each other.

Table 20 'True' annual average PM_{10} concentrations, measurements with various instruments at six sampling sites and error bounds representing 68% confidence limits.

	1	2	3	4	5	6
Annual average PM_{10} concentrations	**Nijmegen ($\mu g/m^3$)**	**Rotterdam Overschie ($\mu g/m^3$)**	**Amsterdam Overtoom ($\mu g/m^3$)**	**Amsterdam Stadh. Kade ($\mu g/m^3$)**	**Vredepeel ($\mu g/m^3$)**	**De Zilk ($\mu g/m^3$)**
Corrected TEOM (Equation 4a)	29.8 ± 1.8	34.2 ± 1.6	30.6 ± 1.4	35.5 ± 1.4	-	-
VAPS	25.0 ± 1.4	28.1 ± 1.7	24.5 ± 1.3	29.3 ± 1.4	25.3 ± 1.4	22.4 ± 1.2
Corrected FAG (Equation 4b)	31.1 ± 1.9	38.7 ± 2.0	34.3 ± 1.9	33.9 ± 1.9	34.5 ± 1.8	31.1 ± 1.6
Ratio VAPS/TEOM	0.76 ± 0.02	0.73 ± 0.03	0.70 ± 0.02	0.74 ± 0.02	-	-
Ratio VAPS/FAG	0.84 ± 0.03	0.71 ± 0.02	0.74 ± 0.02	0.90 ± 0.03	0.74 ± 0.01	0.72± 0.01

The average differences between 'true' PM_{10} levels of VAPS and TEOM are 5.5 $\mu g/m^3$, and for VAPS and FAG, 8.1 $\mu g/m^3$. One should realise that the average differences between FAG and VAPS are probably underestimated, as the FAG measurements are not from a similar street station but from an urban background station, which has, on average, lower PM_{10} concentrations than a street station. The average difference between 'true' PM_{10} levels from FAG and TEOM is 2.1 $\mu g/m^3$.

Conclusion 1: The VAPS (uncorrected) underestimates, on average, the 'true' PM_{10} levels (corrected FAG or TEOM) by 10% to 30%, depending on the location of the comparison (ratios in Table 20).

Unfortunately, compliance of VAPS with the US Federal reference method (FRM) for PM_{10} and $PM_{2.5}$, or with the European reference method EN 12341, has not yet been demonstrated. For VAPS, only a comparison with different monitors is available in the scientific literature. Such a comparison was carried out by Williams et al. (2000). These measurements showed good agreement for VAPS and $PM_{2.5}$. However, for PM_{10} (with a diameter larger than 2.5 µm, the coarse fraction of PM_{10}) the situation was different. In this situation the VAPS measured 5.2 $\mu g/m^3$ coarse PM_{10}, while an FRM corrected TEOM found 9.3 $\mu g/m^3$, indicating that the VAPS in the coarse region only measured 56% if a corrected TEOM was taken to represent a method that has been found equivalent with FRM.

A comparison with the other instrument used by Williams, the PEM, gives a similar, but slightly smaller underestimation of the coarse PM_{10} by VAPS. The PEM measured 8.0 $\mu g/m^3$

of coarse PM_{10}, indicating that VAPS measured approximately 65% of this part of the PM_{10} spectrum.

In a similar manner to the TEOM and the FAG, it may be concluded that a VAPS is not giving a precise, but only a relative, result for the measurement of PM_{10} and needs also to be corrected. Such a conclusion can be corroborated by the day-to-day correlation of FAG and VAPS. This correlation, $R^2 = 0.83 - 0.89$, is very good, indicating that a VAPS may be used as a relative measure of PM_{10}, which is capable of finding consistent day-to-day differences in relative concentrations (compare Figure 5B).

Conclusion 2: It seems that the VAPS needs some correction factor but for now it can be used as a relative measure of 'true' PM_{10} levels.

The summary, the report on the quality of PM measurements in the Netherlands by Van Putten et al. (2001[b]) concludes that the correction factor for the FAG, due to volatilisation losses and water, is approximately 1.3 in the Netherlands. Van Putten et al. (2001[b]) present the following equations for the relationship between the 'true' concentrations of PM_{10} and the FAG for regional (5a) and urban (5b) situations.

$$\text{'True' } PM_{10}\ (\text{KFG}) = 1.15 * [\ \text{FAG}\ ] \quad \text{regional} \tag{5a}$$

$$\text{'True' } PM_{10}\ (\text{KFG}) = 1.45 * [\ \text{FAG}\ ] \quad \text{urban} \tag{5b}$$

If the correction factor had been location-dependent (1.15 in the regional situation and 1.45 in the urban situation), the resulting differentiation would lead to a closer match between VAPS and FAG in the regional background, but would, on the contrary, lead to an even larger mismatch between VAPS and FAG in urban situations. This is illustrated in **Table 21**.

Table 21 'True' annual average PM_{10} concentrations, VAPS and FAG measurements with location-specific correction factors (Equation (5a)) and (Equation (5b)) at six sampling sites, where error bounds represent 68% confidence limits.

Annual average PM_{10} concentrations	**1 Nijmegen ($\mu g/m^3$)**	**2 Rotterdam Overschie ($\mu g/m^3$)**	**3 Amsterdam Overtoom ($\mu g/m^3$)**	**4 Amsterdam Stadh. kade ($\mu g/m^3$)**	**5 Vredepeel ($\mu g/m^3$)**	**6 De Zilk ($\mu g/m^3$)**
VAPS	25.0 ± 1.4	28.1 ± 1.7	24.5 ± 1.3	29.3 ± 1.4	25.3 ± 1.4	22.4 ± 1.2
Corrected FAG (Equation 5a)	-	-	-	-	30.5 ± 1.6	27.5 ± 1.4
Corrected FAG (Equation 5b)	34.7 ± 2.1	43.2 ± 2.2	38.3 ± 2.1	37.8 ± 2.1	-	-
Ratio VAPS/corr. FAG	0.75 ± 0.03	0.64 ± 0.02	0.66 ± 0.02	0.81 ± 0.03	0.84 ± 0.01	0.81 ± 0.01

Conclusion 3: VAPS measurements during this project did not support a site-specific correction factor of 1.15 – 1.45 for the FAG.

A discussion on the measured $PM_{2.5}$ levels with the different instruments is not really possible, as the ‘true’ values of $PM_{2.5}$ are currently unknown in the Netherlands. From the measurements done by Williams et al. (2000) it is clear that the relative correction of the TEOM is larger for $PM_{2.5}$ than for PM_{10} as, fractionally, a larger part of $PM_{2.5}$ volatises than of PM_{10}.

5.1.2 Inorganic secondary aerosol concentrations

Measurements of inorganic secondary aerosol concentrations with the LVS and, in the project, with a Dichote are compared in **Table 22**. The effects of the results on the modelling of inorganic secondary aerosol concentrations and measurements are compared in Section 6.1.2

Table 22 Annual average secondary aerosol concentrations of two instruments at the six sampling sites, where error bounds represent 68% confidence limits.

Annual average concentrations	**1 Nijmegen (µg/m^3)**	**2 Rotterdam Overschie (µg/m^3)**	**3 Amsterdam Overtoom (µg/m^3)**	**4 Amsterdam Stadh. kade (µg/m^3)**	**5 Vredepeel (µg/m^3)**	**6 De Zilk (µg/m^3)**
Total Dichote	11.9 ± 1.3	9.4 ± 0.9	9.6 ± 0.8	-	11.0 ± 0.9	6.5 ± 0.6
Total LVS	-	-	-	-	9.6 ± 0.6	6.6 ± 0.6

At two regional stations, Vredepeel and De Zilk (**Figure 19**), a comparison of both instruments is possible, despite the lower sampling efficiency for coarse aerosol of the LVS relative tot the Dichote. The total secondary aerosol with Dichote and LVS compare fairly well, and no significant differences between the instruments are found.

A further comparison of Amsterdam Overtoom (site 3) with the secondary aerosol concentrations measured in Bilthoven (LVS) also shows much similarity. The annual average of total secondary aerosol as measured by LVS in Bilthoven was 10.0 µg/m^3. Although the locations of Amsterdam and Bilthoven differ (the distance is 50 km), the concentrations may be compared because, generally speaking, the annual average secondary aerosol concentrations are quite uniformly distributed over the Netherlands.

Conclusion 4: The annual average levels of total inorganic secondary aerosol measured with a Dichote and LVS match.

It would be of use to see if this match with Dichote and LVS still holds if the three chemical components of the inorganic secondary aerosol are compared. There are two locations with an LVS secondary aerosol measurement and a Dichote, the latter of which can be used for a more detailed comparison (see **Table 23)**.

Figure 19 Vredepeel (upper photo) and De Zilk (lower photo) sites.

Table 23 shows that the Dichote and LVS, on average, seem to measure both ammonium and nitrate quite well, as the results are within ± 30% of those of each other. The concentrations measured with Dichote and LVS do not differ significantly. Such a result is quite remarkable as the volatilisation losses are concentrated in the ammonium and nitrate and not in the sulphate. Losses in the order of 15% to 35% ammonium and nitrate with a Dichote

have been reported in the past (Diederen et al., 1983). It would seem reasonable to conclude that for losses they seem quite similar. In Section 6.1.2 it will be shown that both instruments measure less of the annual average values of ammonium and nitrate than those modelled.

However, for sulphate there seems to be an overestimation of approximately 40-50% for the Dichote, or a similar underestimate for LVS. The annual average sulphate concentrations of Dichote and LVS differ significantly. In Section 6.1.2 it will be shown later that the results of the LVS match those of models better than those of the Dichote.

It could be argued that a Dichote sampler should measure more aerosol than the LVS because a Dichote has its 50% cut-off point at 10 µm, in contrast to an LVS, which has a non-determined cut-off point between 2.5 µm and 10 µm. Therefore, higher results for sulphate with the Dichote could be seen to be given more credence than those with LVS.

A second complicating factor with the measurements of inorganic secondary aerosol is that the results of the VAPS had been analysed separately for sulphur, and that these results did not match with those of either the Dichote or NAQMN. At the Zilk the results for the Dichote come to 1.2 µg/m^3 of S, while VAPS results are 1.8 µg/m^3 and NAQMN would result in 0.9 µg/m^3 of recalculated S. The results for Vredepeel give a similar picture: Dichote 1.5 µg/m^3 and VAPS 2.0 µg/m^3, while NAQMN would result in 1.0 µg/m^3 of S.

A possible explanation for the differences between VAPS and LVS/Dichote is the chemical speciation of sulphur. The VAPS analysed for total sulphur, including the sulphur that is chemically bound in organic or inorganic compounds, while for LVS and Dichote only sulphate is analysed. It needs additional experiments to study the possible explanations for the differences in sulphur levels.

Conclusion 5: VAPS and Dichote seem to measure higher levels of sulphur/ if compared to LVS.

Table 23 *Annual average secondary aerosol concentrations of two instruments at two sampling sites, where error bounds represent 68% confidence limits.*

Annual average concentrations	**5 Vredepeel Dichote (µg/m^3)**	**5 Vredepeel LVS (µg/m^3)**	**5 Vredepeel Dich/LVS ratio**	**6 De Zilk Dichote (µg/m^3)**	**6 De Zilk LVS (µg/m^3)**	**6 De Zilk Dich/LVS ratio**
NH_4	2.2 ± 0.2	2.2 ± 0.2	1.0	1.1 ± 0.2	1.4 ± 0.2	0.8
SO_4	4.6 ± 0.4	3.0 ± 0.2	1.5	3.4 ± 0.4	2.4 ± 0.2	1.4
NO_3	4.2 ± 0.4	4.4 ± 0.3	1.0	2.0 ± 0.4	2.7 ± 0.3	0.7
Total	**11.0 ± 0.9**	**9.6 ± 0.6**	**1.2**	**6.5 ± 0.6**	**6.6 ± 0.6**	**1.0**

5.1.3 Sea salt

Sea-salt aerosol is generated in sea water by spray processes on the coast, as well as in the open sea, and is transported over short (large particles) to long distances (fine particles). Fine sea-salt aerosol is found at large distances from the shore, up to hundreds of kilometres. The particle composition reflects that of sea water. These compositions of 10.82, 0.41, 1.30, 0.39, 19.46 and 2.72 g/l holds for the elements, Na, Ca Mg, K, Cl, SO_4, respectively. The total of these elements comes to 35.09 g/l.

For sea salt two common tracers, Na^+ and Cl^-, are available. Both will be discussed in this section. There is a number of arguments supporting both in their outcomes. Here, they will be presented as an upper and a lower bound for sea salt.

The use of Na^+ has the advantage that there are no known losses due to chemical reactions. Furthermore, it can be reliably measured. The drawback of the Na^+ measurement is that it has only been measured with a Dichote. For the sea salt with Na^+ as tracer, see below:

$$\text{Sea salt} = 3.24 * [Na^+] \quad (6)$$

The factor of 3.24 follows from the composition of sea water, as described above.

The use of Cl^- as a tracer has the drawback that it reacts in the atmosphere with available sulphuric and nitric acid, resulting in the depletion of Cl^-. These depletion reactions follow:

$$H_2SO_{4\,(g)} + NaCl_{(s)} \rightarrow NaSO_{4(s)} + HCl_{(g)}\uparrow \quad (7a)$$

$$HNO_{3\,(g)} + NaCl_{(s)} \rightarrow NaNO_{3\,(s)} + HCl_{(g)}\uparrow \quad (7b)$$

The strong point of using Cl^- as tracer is that it has been measured with three different instruments: Dichote, VAPS and LVS.

Of these instruments, the LVS has the drawback that it does not have a very determined cut-off point. Especially at the coastal site at De Zilk, this may be considered a serious drawback as coarse fresh sea spray with sea salt will be underestimated by the LVS. For the inland situation in Vredepeel, this is, however, different.

Sea salt with Cl^- as a tracer comes to:

$$\text{Sea salt} = 1.80 * [Cl^-] \quad (8)$$

Both the tracers Na^+ and Cl^- have the drawback that during the winter months, common salt (NaCl) is used lavishly in the Netherlands for the de-icing of roads. Passing traffic re-suspends this salt, which can be measured as part of PM_{10}. As this last source can not be easily isolated from the sea spray (which is more important in magnitude), all the Na^+ and Cl^- will be assumed to originate from sea salt. If de-icing as a source of PM10 is not negligible, using the estimates for sea salt of Equations (6) and (8) could be overestimates.

It may be argued that generally speaking an estimate based on the concentrations of Na^+, will be an upper bound for the sea-salt contribution. As Cl^- will be depleted during transport from sea to more inland locations. The estimates based on Cl^- can be seen as a lower bound of the sea-salt contribution. This section will present both approaches and the upper and the lower bounds.

When the Na^+ concentration is taken as the tracer of sea salt, the following picture appears. The Na^+ measurements with the Dichote are presented in this section and in **Table 24**.

Table 24 Annual average Na^+ concentrations in PM_{10} measured with Dichote at six sampling sites and the derived sea salt, where error bounds represent 68% confidence limits.

Annual average Na^+ concentrations	**1 Nijmegen (µg/m³)**	**2 Rotterdam Overschie (µg/m³)**	**3 Amsterdam Overtoom (µg/m³)**	**4 Amsterdam Stadh. kade (µg/m³)**	**5 Vredepeel (µg/m³)**	**6 De Zilk (µg/m³)**
Dichote	1.6 ± 0.1	2.3 ± 0.2	2.2 ± 0.2	-	1.9 ± 0.3	2.4 ± 0.2
Sea salt	5.2 ± 0.3	7.5 ± 0.6	7.1 ± 0.6	-	6.2 ± 1.0	7.8 ± 0.6

The sea-salt values obtained in Table 24 indicate that an annual average value of 8 µg/m³ is to be expected at coastal sites, while at 125 km from the coast, Vredepeel, the annual average concentration of sea salt will have decreased to 6.2 µg/m³, indicating a transport loss of 26%.

However low, such a transport loss should still lead to a relative enrichment of the fine Na^+ at 125 km from the coast. The coarse fraction of Na^+ was 54% on the coast in De Zilk and 53% inland in Vredepeel (Table 10B) not supporting this possible enrichment.

When, on the other hand, the concentration of Cl^- is be used as a tracer for sea salt, the following picture appears. This section and **Table 25** present a comparison between Cl^- measurements of Dichote, VAPS and LVS. Table 25 shows that the absolute levels of VAPS-Cl^- and Dichote-Cl^- are not significantly different. However, there is a significant difference between the LVS-Cl^- measurements and measurements from the other two instruments.

The general picture of the annual average chloride depletion and transport losses on a coastal versus inland site in the Netherlands (De Zilk compared to Vredepeel) is about 50% (for all methods) These very similar losses indicate a match in the pictures emerging of the different instruments. Like Na^+ also Cl^- measurements do not support enrichment of the fine fraction over 125 km. The difference, however, is in the absolute values of chloride measured by each of the instruments.

Table 25 *Annual average Cl^- concentrations in PM_{10} measured with three instruments at six sampling sites and derived sea salt, where error bounds represent 68% confidence limits.*

Annual average Cl^- concentrations	**1 Nijmegen ($\mu g/m^3$)**	**2 Rotterdam Overschie ($\mu g/m^3$)**	**3 Amsterdam Overtoom ($\mu g/m^3$)**	**4 Amsterdam Stadh. kade ($\mu g/m^3$)**	**5 Vredepeel ($\mu g/m^3$)**	**6 De Zilk ($\mu g/m^3$)**
Dichote	1.8 ± 0.2	2.3 ± 0.3	2.4 ± 0.2	-	1.6 ± 0.1	3.0 ± 0.3
VAPS	2.0 ± 0.3	2.5 ± 0.3	1.8 ± 0.3	3.3 ± 0.4	1.2 ± 0.2	2.6 ± 0.3
LVS	-	-	-	-	0.7 ± 0.1	1.5 ± 0.2
Sea salt Dichote	3.2 ± 0.3	4.1 ± 0.5	4.3 ± 0.3	-	2.9 ± 0.2	5.4 ± 0.5
Sea salt VAPS	3.6 ± 0.5	4.5 ± 0.5	3.2 ± 0.3	5.9 ± 0.7	2.2 ± 0.3	4.6 ± 0.5
Sea salt LVS					1.3 ± 0.2	2.7 ± 0.3

The annual average Cl^- in de Zilk for our 1998-1999 sampling period using LVS is 1.5 $\mu g/m^3$. This does not compare very well with the 2.6 $\mu g/m^3$ measured with VAPS. VAPS sampled 0.6 $\mu g/m^3$ Cl^- in the fine fraction and 2.0 $\mu g/m^3$ in the coarse fraction. Thus, Cl^- concentrations at a coastal station can be found more in the coarse than in the fine PM. For the Vredepeel station, LVS found an annual average Cl^- of 0.7 $\mu g/m^3$ while for VAPS fine this was 0.2 $\mu g/m^3$ and for VAPS coarse, 1.0 $\mu g/m^3$.

Similar to the discussion on inorganic secondary aerosols, it can be argued that a Dichote and VAPS sampler should measure more coarse aerosol particles than the LVS. A Dichote/VAPS has its 50% cut-off point at 10 μm, in contrast to an LVS, which has a non-determined cut-off point between 2.5 μm and 10 μm. Therefore the Dichote/VAPS results of the Cl^- fraction of PM_{10} should be given more credence than those of the LVS.

Also in neighbouring countries with a possible large influence from the sea, as in the UK, the annual average Cl^- values appear to be lower than the levels indicated by VAPS. QUARG (1996) presents 1.5 $\mu g/m^3$ Cl^- as an annual average in 1982 in Leeds and 1.1 $\mu g/m^3$ Cl^- as a.a. at a rural station in Haverah Park. Concerning de-icing in winter, QUARG (1996) states on page 127 that : '.., it is clear that samples taken during the winter period contained up to three times the chloride found during late summer and autumn.' Harrison et al. (2000) found only 2% of PM_{10} to be Cl^-, as sampled in PM_{10} in Birmingham UK. For more inland parts of Europe: Berlin and Waldhof in Germany, Israel et al., (1992) presented an annual average Cl^- level of 0.7 $\mu g/m^3$, measured as a part of PM_{10}.

Conclusion 6: The Na^+ concentrations determined with a Dichote lead possibly to an upper bound of the annual average sea-salt contributions of 8 μg/m^3 on the coast and 5 to 7 μg/m^3 inland in the Netherlands.

The Cl^- concentrations determined with the measurement from Dichote and VAPS are higher compared with LVS. When the results of Cl^- measurements from LVS are used for the calculation of the sea-salt contribution to the annual average aerosol levels, a lower bound of 2.7 μg/m^3 on the coast and around 1.3 μg/m^3 inland was found.

The results for the sea salt contributions to PM_{10} seem high compared to some foreign results.

5.2 Traffic

Annual average Traffic$_t$ contribution (tailpipe)
In Section 2.6 two algorithms have been presented to calculate the contribution of tailpipe emissions to traffic. The calculated results were presented in Section 3.7.2. Table 16 presents the annual average traffic tailpipe contributions that were calculated with the two methods described in Section 2.6. As one of the methods is an overestimation and the other clearly an underestimation, it is assumed that the true values of the traffic contribution will probably lie somewhere in between.

These values can be compared with those that were modelled with OPS for these specific locations on the basis of the average emissions for traffic included in the emission database. These contributions are presented in Table 31.

Comparison of the values in Tables 16 and 31 shows that the calculated tailpipe traffic contribution for the Netherlands with Equations (2a) and (2b) seems to be quite low. For instance, in the urban background situation of Amsterdam Overtoom (site 3), the high and low estimates of the annual average tailpipe contribution by traffic are 1.9 and 1.1 μg/m^3, respectively.

The VAPS-EC values are somewhat low in comparison with EC values abroad. In the BRD recent results show that annual average EC values are 14-18% of PM_{10} in Germany, compared to the 2-6% of VAPS-PM_{10} in the Netherlands. Recent results in the USA in the ARIES project for an urban background situation in Atlanta (Van Loy et al., 2000) show 11-13% of $PM_{2.5}$ as EC and 23-26% of $PM_{2.5}$ as OC. QUARG (1996) in the UK presents a value of approximately 10% PM_{10} as EC, and 15% as OC. Harrison et al. (2000) present an average value of 18% PM_{10} (25.7 μg/m^3) as EC and 20% as OC in Birmingham, UK. The extent to which this is caused by differences in the composition of the total motor fuels is not known.

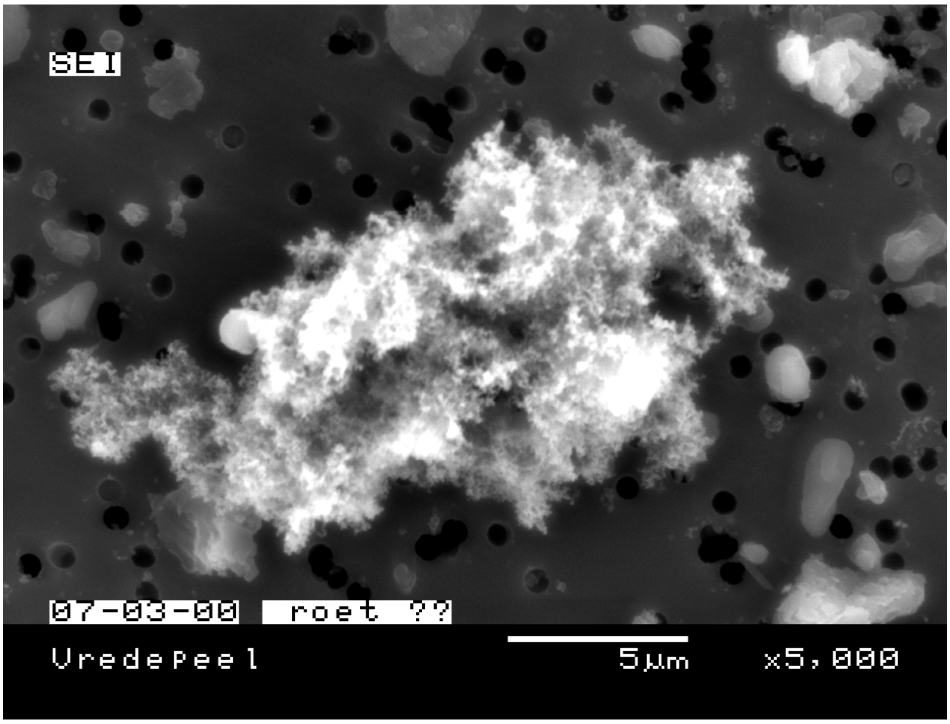


Figure 20 SEM projection of soot conglomerate. The sample was taken at the Vredepeel site. Source: Timmner (2000[c]).

Other Dutch measurements for the airways ii ('Luchtweg II') project (Janssen et al., 1999[a]), which are not annual average results but only valid for the period of measurement, produced an average "soot" content of 5.7 $\mu g/m^3$ in the most densely populated area of the western Netherlands to 4.5 $\mu g/m^3$ in the least populated area. Allowing for some non-descript factors, this "soot" content should be more or less similar to EC.

A second complicating factor with these comparisons is, of course, differences in analysis methods for EC and OC, and the correction factors used to calculate OC from the C content. A factor of 1.4 for the ratio of the non-C to C content has been used in this project, but 1.2 is generally used in Germany and 1.4 in the USA. In the USA this factor of 1.4 is corroborated by the high content of secondary organic fraction in the OC. Such secondary OC in the USA usually has a higher ratio of non-C to C than the higher alkanes and carboxy acids that are generally found in OC in Germany (Israel et al., 1992) and Belgium (Van Vaeck et al., 1978), for instance.

A third complicating factor is that part of the EC and OC in PM has a larger diameter than 2.5 µm; however, this coarse fraction has not been measured in this project. For a street station (174) in Berlin approximately 9% of EC is larger than 2.5 µm and 24% of OC is larger than 2.5 µm. For the urban background in Berlin these percentages are 7% and 27%, respectively.

These numbers signify that the contribution of carbonaceous to PM_{10} is certainly not restrained to the fine part of the aerosol.

A source for the coarse OC fraction of PM_{10} might also be found in plant material. Which fraction of OC can be considered material of biogenic origin remains unknown.

The fraction of EC and OC from PM_{10} seems to be higher in the UK and in Germany than in the Netherlands, while sources of EC and OC are quite similar in the EU. Because coarse EC and OC were not measured during this project, it may therefore be deduced that such a fraction would also have been found in the Netherlands if it had been measured. To estimate this missed fraction quantitatively, a fraction of 8% of fine EC is taken for coarse EC and a fraction of 25% of fine OC is taken for OC. Both values are based on the results of similar German measurements of fine and coarse EC and OC.

With the CAR-model estimates for traffic contributions in streets are made on the basis of emission factors for traffic. In a street with heavy traffic a contribution of 10-15 $\mu g/m^3$ to the annual average PM_{10} concentrations is calculated. Such values should be added to the modelled urban background concentrations as presented in Table 31 if the street concentration is to be found. Such values may be compared with measurements that have been done elsewhere. The *total* street contribution in Berlin was approximately 15 $\mu g/m^3$, as described by Abraham (2000).

Conclusion 7: Tailpipe traffic contribution in an urban background situation would probably be at least 1-2 $\mu g/m^3$ on an annual average basis. In a busy street this could be augmented by another 2 $\mu g/m^3$. At a regional background site the annual average tailpipe traffic contribution would come to approximately 1 $\mu g/m^3$. Compared to foreign estimates and model results with OPS/SIGMA, the calculated traffic contributions with measured values of EC/OC seem rather low. The highest estimates are found using the CAR-model.

Annual average Traffic$_r$ contribution (re-suspension)

The traffic contribution to ambient PM_{10} is not solely a tailpipe contribution; however, also a re-suspension of for instance crustal material will lead to a contribution to PM_{10} that is generated by traffic. Such air pollution would not have occurred if the traffic had not been there. Traffic contributions by re-suspension of dust are indicated with the subscript 'r' for re-suspension: traffic$_r$.

As such, re-suspended material was not measured directly during the project, but may be inferred from a number of observations. The average vehicular contribution of crustal material in a busy street may be derived from the difference in the crustal contribution in the urban background and street station in Amsterdam (Tables 15 and 16; sites 3 and 4, sites 3 and 2). In the Netherlands this difference is approximately 2-4 $\mu g/m^3$ on an annual average basis. The difference between an urban background station and a regional station is approximately 1 $\mu g/m^3$ (sites 3 and 6).

How do these estimates of the traffic contribution compare to measurements that have been taken elsewhere? Abraham (2000) describes a similar situation to that measured in Amsterdam of a busy street in Berlin (Frankfurter Allee) in which the crustal contribution by traffic at the curb site was 7 $\mu g/m^3$ on an annual average basis (EC was augmented with on average 4.2 $\mu g/m^3$, while OC was 3.6 $\mu g/m^3$ higher).

The German ratio of 3.6/4.2 (46%-54%) for the ratio OC/EC is not completely similar - 43% EC and 53% OC with 4% other elements (compare Figure 12) – to what is found in a traffic tunnel (IJ tunnel) in the Netherlands.

Conclusion 8: The average Traffic$_r$ contribution of primary PM$_{10}$ by re-suspension is estimated to be 1 $\mu g/m^3$ in an urban background situation and 2-4 $\mu g/m^3$ extra in a busy street.

5.3 Crustal material

From Tables 15 and 16 it can be seen that both methods of estimating the crustal material correlate fairly well. A location with heavy traffic like the Stadhouderskade in Amsterdam has a higher level of crustal material than an urban background station like Amsterdam Overtoom. Because of the larger number of elements involved in the estimation of the crustal contribution, we give preference to the Crustal2 estimates. The measurement errors are smaller with a larger number of elements than with a fewer number.

Vrins and Schulze (2000) estimated the Aeolic component of PM$_{10}$ at de Zilk to be approximately 3.5 $\mu g/m^3$ based on short-term fluctuations in wind speed, wind direction and concentration differences. Such a completely different method of estimation leads to results that are somewhat higher than the estimates in Tables 15 and 16 (1.7 $\mu g/m^3$ for De Zilk). In an urban background station in Rotterdam Vrins and Schulze (2000) estimated the crustal fraction to be approximately 1.5 $\mu g/m^3$. Here, our estimate is higher: 4.3 $\mu g/m^3$, albeit for an urban street station. Our estimate for an urban background site, 2.8 $\mu g/m^3$ (Amsterdam Overtoom) is an only somewhat higher value.

As the contribution of crustal material may be estimated from the average Si and Al concentrations, an extra check on both components can be done by comparing the Si/Al ratios for different locations (**Table 26**). Within a certain range these ratios are more-or-less constant for aerosols and crustal material. Israel et al. (1992) presented the average Si/Al ratios for an urban station in Berlin and the rural background station of Waldhof in Germany. For Berlin this was 2.9 and 2.6 for < or > 2.5 µm (average 2.7); for the rural background this was 5.7 and 3.4 for < and > 2.5 µm (average 4.1). The authors indicate an average value of this ratio of 2.7 ± 0.7 for atmospheric aerosols, and state that clay mineral may have ratios of 1.0 up to 2.1.

Harrison et al. (2000) presented Si/Al ratios for various places in the USA which vary between 2.0 and 2.8. The ratio presented in the Handbook of Chemistry and Physics for the earth's crust is 3.4. The latter value more or less agrees with our ratios in PM$_{10}$ of 2.8 to 5.5, with an average ratio of 4.1.

Table 26 Average Si/Al ratios for the six stations.

Annual average ratios	**1 Nijmegen N=16 (µg/m^3)**	**2 Rotterdam Overschie N=15 (µg/m^3)**	**3 Amsterdam Overtoom N=8 (µg/m^3)**	**4 Amsterdam Stadh. kade N=13 (µg/m^3)**	**5 Vredepeel N=21 (µg/m^3)**	**6 De Zilk N=8 (µg/m^3)**
Si/Al < 2.5 µm (fine fraction)	1.9	2.1	2.4	2.5	3.0	1.9
Si/Al > 2.5 µm (coarse fraction)	4.7	3.9	6.5	5.1	3.6	3.1
Si/Al PM$_{10}$	**4.3**	**3.6**	**5.5**	**4.8**	**3.5**	**2.8**

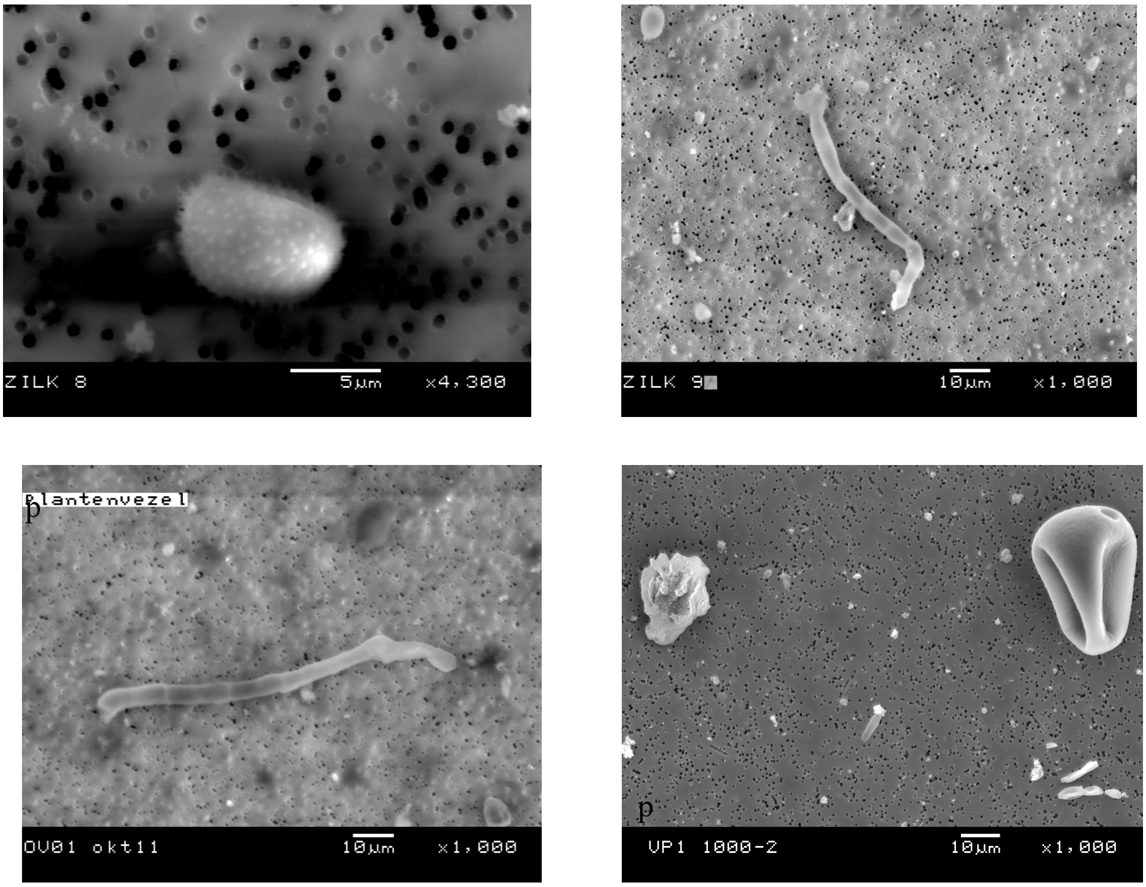


Figure 21 SEM projections of organic particles. Photo on upper left shows pollen (sample taken at site De Zilk), while photos on upper right and lower left show plant fibres (samples taken at De Zilk and Amsterdam Overtoom, respectively); photo lower right shows plant material (sample taken at site Vredepeel) Source: Timmner (2000^b).

In the Netherlands the measurements for the ‘airways ii’ project (Janssen et al., 1999[a]), which are not annual average results but only valid for the period of measurement, produced an Si/Al ratio of 1.7 to 1.9 for $PM_{2.5}$, which seems a little more in agreement with the German results. The ratios of Table 26 seem to be different from those in the BRD.

Sources of crustal material can be found in nature, in the re-suspension by wind- or traffic-generated turbulence of road silt, in agricultural activities, and in building and demolition activities. Remarkably, Table 16 shows a considerably higher crustal contribution in summer (approximately 60%) than in winter, notwithstanding the fact that dispersion is considerably higher (± 40 %) in summer than in winter due to the higher mixing height in summer. This indicates that the regional agricultural and/or natural contribution to the primary PM_{10} levels is probably considerably higher than anticipated previously.

Finally, we looked for data on element concentrations within the Netherlands (Equation (1a) is based on world estimates). Unfortunately, no concentrations are available for the Netherlands as a whole. Duijvenbooden et al. (1995) report element concentrations for 10 selected combinations of soil exploitation and soil type. However, their study was not aimed at giving concentrations representative for the Netherlands. Despite this drawback we have indicated their estimates here and discuss the implication of using their estimates in preference to world estimates.

Duijvenbooden et al. (1995) found Si concentrations varying between 200,000 and 500,000 ppm, with an average estimate of 400,000 ppm (compare their Figure 4.2d). The world average value is 330,000 ppm, which is 18% lower. We note that the Si concentrations in their Tables, 4.2, 4.4 and 4.5, are erroneous: a factor 10 too low. Duijvenbooden et al. (1995) reported Al concentrations varying between 8000 and 47,000 ppm, with an average estimate of 20,000 ppm (compare their Figure 4.2a). The world average estimate is 81,300 ppm, which is 400% higher.

If we were to use the concentration estimates for Si (400,000 ppmv) and Al (20,000 ppmv) from Duijvenbooden et al. (1995) as tracer for crustal material, an inconsistent result would be obtained: estimates for crustal material are a factor 5 higher if based on Al as a tracer instead of Si. We would expect estimates in the same order of magnitude, as in the application of Equation (1a) to the six locations in this study. The large discrepancy is difficult to explain and needs further investigation. Because of the conflict with the aerosol measurements we have decided not to use the estimates of Duijvenbooden et al. (1995) in this report.

Conclusion 9: The estimated crustal contribution in the Netherlands is approximately 4-5 $\mu g/m^3$ in a rural background situation and 2-3 $\mu g/m^3$ in an urban background. In a busy street it may be approximately 3-4 $\mu g/m^3$ higher due to re-suspension of road dust by passing traffic.

5.4 Other elements in PM_{10}

Harrison et al. (2000) present an overview of the average urban concentrations for trace metals at different locations in Europe, Asia and the USA. **Tables 27** and **28,** taken from Harrison et al. have been supplemented by the average concentrations in Berlin and Waldhof in 1990, presented by Israel et al. (1992). For the Netherlands the average elemental concentrations from this project have been presented for four different typical situations: an urban background situation (Amsterdam Overtoom, site 3), an urban street situation (Amsterdam Stadhouderskade, site 4), an inland regional situation (Vredepeel, site 6) and a coastal situation (De Zilk, site 5).

A comparison of the elements presented in Table 27 and 28 and those that are measured in this project, indicate that the concentrations found are generally within the ranges found elsewhere. For the Netherlands as a whole all elements seem to lie in the ranges that are also found outside the Netherlands. There is one exception to this statement though: Na^+. The concentrations of Na^+ estimated with the VAPS are in the same range as those seen in Lahore (Pakistan), were the PM concentrations were an order of magnitude higher than those currently found in the Netherlands.

A number of elements and components have not been analysed in this project. This will lead to some underestimation of the PM concentrations based on these elements in the Netherlands. Such an omission could have some consequences for the 'gap closure' when sources which are currently not in the emission database will not have been considered. Missing elements, **P** and **Mg,** can be mentioned and also the compound, **CO_3-** with a non-negligible contribution to PM_{10}, should be mentioned. According to Williams and Bruchmann (2001), the average CO_3^- concentration is 1.5* [Ca] + 2.5* [Mg]. This would probably lead to a measurable carbonate contribution to the Dutch PM_{10}.

Conclusion 10: Except for Na^+, the elemental concentrations in the Netherlands are quite comparable to those in neighbouring countries such as Germany and the UK, and even with some countries on a different continent such as the USA.

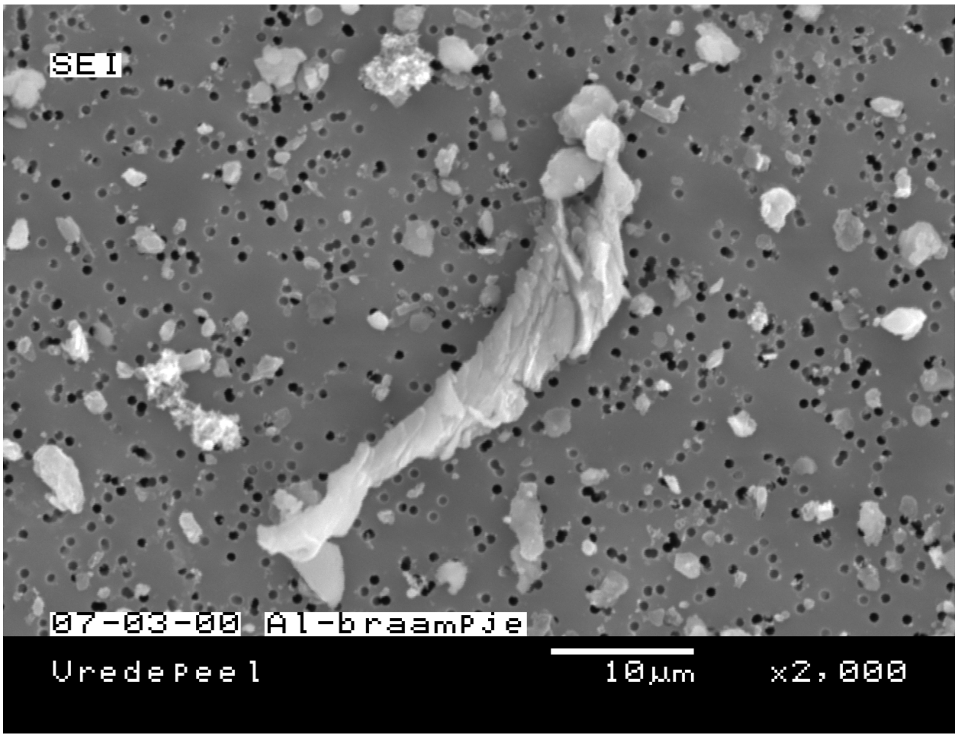


Figure 22 SEM projection of an Al wire edge. Source: Timmner (2000^c^).

Table 27 *Average urban concentrations in ng/m^3 in PM$_{10}$ and regional concentrations in Waldhof (BRD) for trace metals at different locations in Europe, Asia and USA. Sources: Israel et al. (1992) for Germany and Harrison et al. (2000) for all other countries.*

Species	**Birmingham UK**	**Coimbra Port.**	**Lahore TSP Pakist.**	**Wageningen NL**	**Arnhem NL**	**Anaheim USA**	**Azusa USA**	**Edison USA**	**Berlin 1990 BRD**	**Waldhof 1990 BRD**
Na	1050	1490	2740	201	327	1660	1542		700	700
K	199	510	3300	367	269	279	618	1378	500	300
Ca	208	1760	4060			491	1305	1204	1700	500
Mg		130	490			349	605		200	100
Sc	13									
Be		.3	9							
Cd		2	43					3	1	1
Sb		1						9		
Al		1340	37400			701	2271	2684	700	300
Ti	17					60	251	173		
V	7	16	127	10	6	5	8	3	6	2
Cr	13	25	113			20	20	1		
Mn	16	22	350	13	25	24	79	36		
Fe	301	530	9930	426	1169	599	1841	2140	1200	800
Ni	5	6	80			5	5	4	7	5
Cu	39	40	420	22	140	10	14	11	1	1
Zn	353	70	27700	148	185	25	168	28	81	54
As	6	2	29			7	7	2	7	3
Se	3	1				8	9	1	1	1
Sr						19	18	13		
Pb	91	310	3920			50	81	10	134	35
Si				650	1140	1923	5721	6708	1900	1100
Ba						42	138	68		
Hg						20	21			
Rb								5		
Zr								3		
Pd								5		
Ag								8		
In								6		
Sn								9		
La								23		
PM$_{10}$ in µg/m^3	**47**	**52.1**	**607**	**35.7**	**68.2**	**51.3**	**92.1**	**52.5**	**57.6**	**26.9**

Table 28 *Average urban concentrations in ng/m^3 in PM$_{10}$ for trace metals at different locations in the USA and the Netherlands. Sources: Harrison et al. (2000) for the USA and this report for the Netherlands.*

Species	**Boston USA**	**Phoenix USA**	**Los Angeles USA**	**Chicago USA**	**Houston USA**	**St. Louis USA**	**Adam Stadh. NL site 4**	**Adam Overt. NL site 3**	**De Zilk NL site 6**	**Vredepeel NL site 5**
Na			518	22	<1490		-	2350	2440	1970
K	629	880	460	161	289	653	259	176	160	282
Ca	1139	2100	1190	761	2935	2949	801	388	309	549
Mg			287	118						
Sc										
Be										
Cd				<41	<12	5				
Sb				<59	6	7				
Al	3458	2670	847	269	1216	1412	258	111	106	232
Ti	154	140	165	19	36	587	41	23	19	41
V	28		9	<13	<45	6	9	8	8	7
Cr	8	10	42	<7	7	15	11	6	6	10
Mn	30	50	63	13	35	71	23	12	11	17
Fe	1733	1470	2192	423	766	1493	1148	403	206	493
Ni	34	10	5	<2	8	9	7	5	6	5
Cu	58	40	178	17	46	43	37	10	8	11
Zn	100	90	293	90	142	175	56	43	28	61
As	3		19	<4	<15	3				
Se	1		10	<2	<3	5				
Sr		14	24			9	7	5	5	6
Pb	462	60	251	32	589	877	36	24	24	29
Si	6904	7440	2162	831	3200	4928	1238	603	296	1000
Ba		10	127	<130	139	54				
Hg										
Rb					<6	2	4	3	3	4
Zr										
Pd										
Ag										
In										
Sn				<70		10				
La										
PM$_{10}$ in µg/m^3	**104.4**	**62.5**	**67.4**	**28.5**	**63.4**	**62.0**	**34.0**	**34.0**	**31.5**	**34.4**

5.5 Foreign levels of PM_{10} and $PM_{2.5}$

Foreign levels of PM_{10}

Currently, a more or less kaleidoscopic comparison of various measurements is carried out in neighbouring countries with similar climates and similar or lower emission densities as the Netherlands. Of course the specific local conditions at the various locations may differ considerably. The recent annual average levels of PM_{10} in densely populated areas of Germany are quite comparable to those in the Netherlands. In Berlin the measured urban background in 1999 was between 29 and 33 $\mu g/m^3$. At street stations annual averages were 37. 39 and 41 $\mu g/m^3$ (Lenschow and Pesch, 2000). In 1997 averages in the centre of Stuttgart were 58 $\mu g/m^3$ for a traffic station and 30 $\mu g/m^3$ for an urban background site at Karlsruhe (Rodt, 2000). Rural background stations seem to be somewhat lower in Germany than in the Netherlands, 18 $\mu g/m^3$ for a rural background station in Erpfingen in Baden-Würtemberg.

A similar picture appears for annual average PM_{10} in the province of North-Rhine Westphalia in Germany for the year 1999: 48 $\mu g/m^3$ in a traffic station in Düsseldorf, and 30 and 31 $\mu g/m^3$ in an urban background station in Cologne and Essen, respectively. A rural background station in the Eiffel had a concentration of 20 $\mu g/m^3$ (Englert et al., 2000).

The PM_{10} levels currently presented in the UK have no correction whatsoever and are measured with a TEOM. Therefore the Dutch PM data of the same instrument without correction should be used for a comparison. In Rotterdam Overschie, a heavy traffic point near a highway in Rotterdam, the uncorrected annual average TEOM PM_{10} was 24.1 $\mu g/m^3$, which compares fairly well with a kerbside point along the A3 in London in 1997: 24 $\mu g/m^3$. For the Nijmegen site, the annual average uncorrected TEOM-PM_{10} was 21 $\mu g/m^3$, which can be compared to the 21 $\mu g/m^3$ found in London North Kensington. The data for the UK have been retrieved from the UK National Air Quality Information Archive, which can be reached online. The UK data for 1998 and 1999 had not yet been analysed for annual average statistics.

Conclusion 11: Annual average PM_{10} levels in the Netherlands measured during this project compare well with those found in BRD and UK, at least if the differences of various measurement methods are taken into account.

Foreign $PM_{2.5}$ / PM_{10} ratio

In Berlin the $PM_{2.5}$ concentrations for three months in 2000 have only been determined recently. For a traffic station (174), the $PM_{2.5}$ / PM_{10} ratio was 0.82 relative to 28.9 $\mu g/m^3$ and for an urban background station (42), 0.84 relative to 23.2 $\mu g/m^3$. The $PM_{2.5}$ fraction of 0.67 for 1989-1990, previously found by Israel et al. (1992), has probably been altered by the recent changes in the emission patterns in Germany .

In 1997 in the centre of Stuttgart the ratio was 0.72 for a traffic station, and 0.77 for an urban background site at Karlsruhe (Rodt, 2000). In a rural background station in Erpfingen in Baden-Würtemberg this ratio was 0.82 of annual average PM_{10}. In North-Rhine Westphalia the ratio of $PM_{2.5}$ in 1999 was 0.68 of PM_{10} for an industrial station in Duisburg, 0.78 for an urban background station in Essen and 0.78 for a rural background station in the Eiffel (Englert et al., 2000).

Williams et al. (2000) indicated that they used two different correction factors for the TEOM. They found a higher factor (1.5) for the fine fraction of $PM_{2.5}$ than for PM_{10} (1.2). This has the consequence that when only one correction factor for PM_{10} is available, as for TEOM measurements in this study, the fine fraction, with diameters smaller than 2.5 µm, will automatically be underestimated. This also leads to a lower $PM_{2.5}/PM_{10}$ ratio in this report than found elsewhere with a more precise measuring method.

Conclusion 12: For the ratio of $PM_{2.5}/ PM_{10}$, the recently found fractions in Germany (0.70 - 0.85) are slightly higher than those currently found in this project (0.60 - 0.75).

6. Closing the 'gap'

6.1 Measurements versus model estimates

6.1.1 Total PM_{10}

PM_{10} levels calculated with OPS/SIGMA for 1997 are compared in **Table 29** with the 1998-1999 measurements with TEOM, VAPS and FAG.

Table 29 Measured and modelled annual average PM_{10} concentrations; measurements with various instruments at six sampling sites, where error bounds represent 68% confidence limits.

Annual average PM_{10} concentrations	**1** **Nijmegen** **(µg/m³)**	**2** **Rotterdam Overschie** **(µg/m³)**	**3** **Amsterdam Overtoom** **(µg/m³)**	**4** **Amsterdam Stadh. Kade** **(µg/m³)**	**5** **Vredepeel** **(µg/m³)**	**6** **De Zilk** **(µg/m³)**
Modelled OPS/SIGMA	20.8 ± 5.2	23.8 ± 6.0	23.5 ± 5.9	23.5 ± 5.9	20.8 ± 5.2	16.0 ± 4.0
Corrected TEOM (Equation (4a))	29.8 ± 1.8	34.2 ± 1.6	30.6 ± 1.4	35.5 ± 1.4	-	-
VAPS	25.0 ± 1.4	28.1 ± 1.7	24.5 ± 1.3	29.3 ± 1.4	25.3 ± 1.4	22.4 ± 1.2
Corrected FAG (Equation (4b))	31.1 ± 1.9	38.7 ± 2.0	34.3 ± 1.9	33.9 ± 1.9	34.5 ± 1.8	31.1 ± 1.6

* = Modelled for an urban background, no street contribution.

The results in Table 29 indicate that, on average, the model-PM_{10} concentrations are 63% to 71% of the TEOM and FAG concentrations (corrected for the KFG). The modelled results are, on average, 83% of those measured with the VAPS. This last result is probably an overestimate, as the measurements of the VAPS have not been related to those of a KFG or other reference instruments.

Conclusion 13:In this study slightly lower values of PM_{10} have been measured in 1998-1999 (34-35 µg/m³) compared to the national annual averages of 1993 (40 µg/m³) and 1995 (39 µg/m³). Emissions have also decreased during this period. Part of this better fit between modelled and measured PM_{10} levels is caused by these lower measurements.

6.1.2 Secondary inorganic aerosol

Table 30 shows a comparison for inorganic secondary aerosol between the measured values in 1998-1999 and modelled values with the emissions of precursor gases in 1997. For SO_4 the figures from Table 7 have been reduced for the weight of SO_4 originating from sea salt. This part is from a natural source and is not included in the OPS/SIGMA calculations.

From the composition of seawater, mentioned in Section 5.1.3, it can be deduced that 7.7% of the weight of sea salt at a certain site originates from sea salt. The corrections vary from 0.1 µg/m^3 for LVS at Vredepeel to 0.5 µg/m^3 for Dichote at De Zilk.

Table 30 Annual average measured and modelled secondary aerosol concentrations of two sampling sites, where error bounds represent 68% confidence limits.

Annual average concentrations	**5 Vredepeel Dichote (µg/m^3)**	**5 Vredepeel LVS (µg/m^3)**	**5 Vredepeel Modelled (µg/m^3)**	**6 De Zilk Dichote (µg/m^3)**	**6 De Zilk LVS (µg/m^3)**	**6 De Zilk Modelled (µg/m^3)**
NH_4	2.2 ± 0.2	2.2 ± 0.2	4.1± 0.5	1.1 ± 0.2	1.4 ± 0.2	1.9± 0.2
SO_4	4.2 ± 0.4	2.9 ± 0.2	2.9± 0.4	2.9 ± 0.4	2.2 ± 0.2	2.7± 0.3
NO_3	4.2 ± 0.4	4.4 ± 0.3	6.0± 0.8	2.0 ± 0.4	2.7 ± 0.3	5.3± 0.7
Total	**10.6 ± 0.9**	**9.5 ± 0.6**	**13.0± 1.6**	**6.0 ± 0.6**	**6.4 ± 0.6**	**9.9± 1.2**

LVS sulphate and model sulphate show the best agreement in this table.

Remarkable is that for both components, ammonium and nitrate, for which we know that filter measurements lead to an underestimate due to volatilisation, such good agreement is found between different measuring methods (Dichote and LVS). Nevertheless both methods, in combination with the filters used, could have some losses. The modelled concentrations of ammonium and nitrate are considerably higher.

When the molecular equivalents of positive and negative ions of the inorganic secondary aerosol are calculated for the measurements presented in Table 30, the results of the Dichote lead to a deficit of a factor of 4 higher for positive ions than those of the LVS did.

6.1.3 Traffic

Table 31 compares the calculated and modelled primary traffic contributions. These contributions are due to emissions in the Netherlands and abroad.

Table 31 Contribution of primary traffic emissions following two approaches. Traffic1 has been calculated using Equation (2a), and Traffic2 using Equation (2b). Error bounds represent 68% confidence limits. The modelled estimates are from OPS/SIGMA

Annual average concentrations in PM_{10} aerosol	**1 Nijmegen N=72 (µg/m^3)**	**2 Rotterdam Overschie N=62 (µg/m^3)**	**3 Amsterdam Overtoom N=72 (µg/m^3)**	**4 Amsterdam Stadh. Kade N=73 (µg/m^3)**	**5 Vredepeel N=70 (µg/m^3)**	**6 De Zilk N=73 (µg/m^3)**
Traffic1 (Equation (2a))	1.5 ± 0.1	3.6 ±0.3	1.9 ± 0.1	4.3 ± 0.2	1.6 ± 0.1	1.0 ± 0.1
Traffic2 (Equation (2b))	1.1 ± 0.1	2.1 ± 0.2	1.1 ± 0.1	2.5 ± 0.1	0.9 ± 0.1	0.6 ± 0.1
Traffic by OPS/SIGMA	1.8 ± 0.3	3.5 ± 0.5*	3.4 ± 0.5	3.4 ± 0.5*	0.8 ± 0.1	1.2 ± 0.2

* = Modelled for an urban background situation; there is no street contribution.

The correlation between the modelled (OPS/SIGMA) and calculated tailpipe traffic contribution is fairly good. The absolute values of the various contributions, calculated by Equations (2a) and (2b), are probably somewhat low compared to foreign estimates. This has been treated in more depth in Section 5.2.

For the conclusions we refer you to Section 5.2.

6.2 What progress has been made?

In this section the modelled and measured sources are brought together to find an answer to the question on what progress has been made in explaining modelled and measured levels of PM_{10} during the whole of the project. As a basis the modelled values of the PM_{10} levels with OPS/SIGMA will be taken as a basis. These model estimates will be complemented by the annual average contribution to the PM_{10} levels of sources that have been measured during the project but have *not* been modelled.

Three sources are relevant in this respect:
- sea salt,
- the crustal contribution
- and in addition to them the background PM and sulphate of the Northern Hemisphere.

For both sea salt and crustal material the estimates have been presented in Section 3 and discussed in Section 5. These estimates will be taken over for this exercise of ‘gap closure’; both the high and low estimates for sea salt will be used.

The coarse fraction of EC and OC, which was not measured during the project, but could eventually be estimated from foreign studies, has not been taken into account in this 'gap closure'. This contribution has, in principle, been included in the modelled traffic emissions.

For background PM and sulphate, the report of Weijers et al. (2000) was used as it contains an estimate of the contribution to the background concentration of PM_{10} and sulphate on the Northern Hemisphere. This estimate concerns PM and its precursors from outside the 2000 x 2000 km area that has been the basis for the calculations by OPS/SIGMA. Weijers et al. (2000) indicated that the annual average PM_{10} contribution from North America may be estimated at 0.6 - 0.9 $\mu g/m^3$, and the contribution from sulphate at an extra 3% from North America and 1.3% from Asia and Europe outside the 2000 x 2000 km source area. This leads, on average, to an extra contribution of 0.9 $\mu g/m^3$ from the Northern Hemisphere.

The exercise of ‘gap closure’ is done for two different ‘scenarios’ for the FAG correction factors. The first scenario is a uniform correction factor of 1.3 over the whole of the Netherlands (Equation (4b)). This is covered in Section 6.2.1. The second scenario is a location-specific correction factor (Equations (5a) and (5b)), which differs for the regional (1.15) and the urban situation (1.45). This is covered in Section 6.2.2.

6.2.1 Uniform correction factors

Table 32 presents measured contributions and modelled annual average PM_{10} concentrations; the correction of the FAG is given by Equation (4b). The Table shows that the average ratio [modelled / measured], more popularly known as the ‘gap’, is closed to a large extent. Generally speaking, the average gap, averaged over all six different sites, is now **0.98 ± 0.20**, with a high estimate of sea salt, and **0.90 ± 0.20** with a low estimate for sea salt (error bounds are 1-σ).

Table 32 Measured and modelled annual average PM$_{10}$ concentrations, measurements with various instruments at six sampling sites. Error bounds represent 68% confidence limits. The upper panel is for the high estimate of sea salt (based on Dichote-Na$^+$ estimates) and the lower panel for the low estimate of sea salt (based on Dichote-Cl$^-$ estimates).

Annual average PM$_{10}$ concentrations	**1 Nijmegen (μg/m^3)**	**2 Rotterdam Overschie (μg/m^3)**	**3 Amsterdam Overtoom (μg/m^3)**	**4 Amsterdam Stadh. Kade (μg/m^3)**	**5 Vredepeel (μg/m^3)**	**6 De Zilk (μg/m^3)**
Modelled OPS/SIGMA	20.8 ± 5.2	23.8 ± 6.0*	23.5 ± 5.9	23.5 ± 5.9*	20.8 ± 5.2	16.0 ± 4.0
Sea salt high (Dichote Na$^+$)	5.2 ± 0.3	7.5 ± 0.6	7.1 ± 0.6	7.1 ± 0.6	6.2 ± 1.0	7.8 ± 0.6
Northern Hem. Background	0.9	0.9	0.9	0.9	0.9	0.9
Crustal estimate	5.7 ± 0.6	4.3 ± 0.5	2.8 ± 0.2	6.3 ± 0.5	4.4 ± 0.5	1.7 ± 0.3
Summed total high	**32.4 ± 5.3**	**36.5 ± 6.1***	**34.3 ± 6.0**	**37.8 ± 6.0***	**32.2 ± 5.3**	**26.4 ± 4.0**
Corrected FAG (Equation (4b))	31.1 ± 1.9	38.7 ± 2.0	34.3 ± 1.9	33.9 ± 1.9	34.5 ± 1.8	31.1 ± 1.6
Fraction modelled/measured	**1.04 ± 0.23**	**0.94 ± 0.21**	**1.00 ± 0.23**	**1.12 ± 0.25**	**0.94 ± 0.20**	**0.85 ± 0.17**

Annual average PM$_{10}$ concentrations	**1 Nijmegen (μg/m^3)**	**2 Rotterdam Overschie (μg/m^3)**	**3 Amsterdam Overtoom (μg/m^3)**	**4 Amsterdam Stadh. Kade (μg/m^3)**	**5 Vredepeel (μg/m^3)**	**6 De Zilk (μg/m^3)**
Modelled OPS/SIGMA	20.8 ± 5.2	23.8 ± 6.0*	23.5 ± 5.9	23.5 ± 5.9*	20.8 ± 5.2	16.0 ± 4.0
Sea salt low (LVS CL$^-$)	3.2 ± 0.3	4.1 ± 0.5	4.3 ± 0.3	4.3 ± 0.3	2.9 ± 0.2	5.4 ± 0.5
Northern Hem. Background	0.9	0.9	0.9	0.9	0.9	0.9
Crustal estimate	5.7 ± 0.6	4.3 ± 0.5	2.8 ± 0.2	6.3 ± 0.5	4.4 ± 0.5	1.7 ± 0.3
Summed total low	**30.6 ± 5.3**	**33.1 ± 6.2***	**31.5 ± 6.0**	**35.0 ± 6.0***	**29.0 ± 5.3**	**24.5 ± 4.1**
Corrected FAG (Equation (4b))	31.1 ± 1.9	38.7 ± 2.0	34.3 ± 1.9	33.9 ± 1.9	34.5 ± 1.8	31.1 ± 1.6
Fraction modelled/measured	**0.98 ± 0.23**	**0.86 ± 0.21**	**0.92 ± 0.23**	**1.03 ± 0.24**	**0.84 ± 0.20**	**0.79 ± 0.17**

* = Modelled for an urban background situation; there is no street contribution.

However, if the uncertainty bands are taken into account, there is no significant gap. This holds for both high and low estimates. A test for the ratio of [model/measured] to be equal 1.00 would require 2-σ bounds around the estimated ratio (assuming $\alpha = 0.05$). If such bounds are applied to the ratios in Table 33, we accept the null hypothesis of ratios being equal to 1.00 in all cases.

This result may almost be called an adequate gap closure when account is taken of a number of elements and components not being measured during the project. For instance, the influence of biogenic carbonaceous material has not been included (compare Figure 21). A possible water content of measured PM mass has also been left out of this analysis as well as organic secondary aerosols. If the uncertainty ranges are taken into account, the corrected model values do not differ from the measurements, if tested with an $\alpha = 0.05$.

The model estimates for comparison with the observations at the street sites Rotterdam Overschie and Amsterdam Stadhouderskade (sites 2 and 4) are taken for an urban background situation and not for 'street'. From Table 15 it could be seen that the crustal contribution by traffic in a street situation could be seen to be approximately 3-4 $\mu g/m^3$. If a street situation had been modelled with the CAR-model (annual average ± 10 $\mu g/m^3$ higher than the urban background) the average 'gap' would be even closer to 1.0.

It should be remembered that the modelled inorganic secondary aerosol concentrations are on average somewhat higher (40%) than those measured by LVS or Dichote. Possible losses have, of course, been accounted for in the correction factor of 1.3 (or 1.15-1.45) for the FAG. Therefore this does not point to a higher 'gap' for primary aerosol.

Finally, we note a small overlap in the crustal estimate and the sea salt estimates in Table 32. The elements, K and Ca, are used in the estimate for 'crustal'. However, these elements are also part of sea-salt aerosol. We calculated this contribution of sea-salt K and sea-salt Ca from the composition of these elements in seawater, as described in Section 5.1.3. For both elements the contribution to the crustal estimate (Equation 1b) appears to be small: ~0.07 $\mu g/m^3$. Therefore we have did not correct the figures in Table 32 for this overlap.

Conclusion 14: Comparison of measurements in 1998-1999 and modelled concentrations of PM_{10} (emissions 1997) show nearly no gap. If uncertainty estimates are taken into account, the gap is closed adequately. If models and measurements are to be brought into a closer agreement in the future, inclusion of sources of crustal and biogenic material should be considered for the emission inventories as this fraction seems to play an important role for the 'gap' closure.

6.2.2 Location-specific correction factors

For the correction of the FAG there also are location-specific correction factors that have been established for the Netherlands. These factors are presented in Equations (5a) and (5b). When these factors are used, a slightly different picture arises from the previous one in Table 32. This is presented in **Table 33**.

Table 33 Measured and modelled annual average PM_{10} concentrations, measurements with various instruments at six sampling sites. Error bounds represent 68% confidence limits.

Annual average PM_{10} concentrations	**1 Nijmegen ($\mu g/m^3$)**	**2 Rotterdam Overschie ($\mu g/m^3$)**	**3 Amsterdam Overtoom ($\mu g/m^3$)**	**4 Amsterdam Stadh. Kade ($\mu g/m^3$)**	**5 Vredepeel ($\mu g/m^3$)**	**6 De Zilk ($\mu g/m^3$)**
Summed total high	32.4 ± 5.3	36.5 ± 6.1*	34.3 ± 6.0	37.8 ± 6.0*	32.3 ± 5.3	26.4 ± 4.0
Corr. FAG (5a, b)	34.8 ± 2.0	42.3 ± 2.2	37.9 ± 2.2	37.9 ± 2.2	30.4 ± 1.6	27.9 ± 1.4
Fraction modelled/measured	**0.93 ± 0.21**	**0.86 ± 0.19**	**0.91 ± 0.21**	**1.00 ± 0.22**	**1.06 ± 0.22**	**0.95 ± 0.19**

Annual average PM_{10} concentrations	**1 Nijmegen ($\mu g/m^3$)**	**2 Rotterdam Overschie ($\mu g/m^3$)**	**3 Amsterdam Overtoom ($\mu g/m^3$)**	**4 Amsterdam Stadh. Kade ($\mu g/m^3$)**	**5 Vredepeel ($\mu g/m^3$)**	**6 De Zilk ($\mu g/m^3$)**
Summed total low	30.6 ± 5.3	33.1 ± 6.2*	31.5 ± 6.0	35.0 ± 6.0*	29.0 ± 5.3	24.5 ± 4.0
Corr. FAG (5a, b)	34.8 ± 2.0	42.3 ± 2.2	37.9 ± 2.2	37.9 ± 2.2	30.4 ± 1.6	27.9 ± 1.4
Fraction modelled/measured	**0.88 ± 0.21**	**0.78 ± 0.18**	**0.83 ± 0.21**	**0.92 ± 0.21**	**0.95 ± 0.22**	**0.88 ± 0.18**

* = Modelled for an urban background situation; there is no street contribution.

In Table 33 the differences between modelled and measured values is closed to a large extent. Generally speaking, the average ratio over all six different sites is now **0.95 ± 0.20** with the high sea-salt estimate, and **0.87 ± 0.20** with the low sea-salt estimate. As in the preceding section, this result may almost be called a gap closure. Of course, similar remarks to those for the previous table can be made about modelling the ‘street’. If the uncertainty bands are taken into account, also in this case the gap is closed adequately.

The total picture in Table 33, however, seems to be slightly preferable to that of Table 32, as the average differences between the modelled and measured values are somewhat less extreme and a better agreement is found for rural locations. In Table 32 the difference between the highest and lowest values is 31-33%, while it is only 18-19% in Table 33. It also seems prudent to make maximal use of relevant information by including the location-specific correction factors in the calculations as this information is based on recent measurements that have been specifically validated for the Dutch situation. Therefore, a slight preference is given to the situation presented in Table 33. We note that such a preference was not found in Table 21.

Conclusion 15: The 'gap' between models and measurements has almost been closed. A preference is given to the location-specific correction factors for the FAG.

6.3 Potential effect of abatement

Now, what is the importance of closing the gap between measurements and model estimates? The importance is that model estimates by OPS/SIGMA have a much more solid basis: i.e. model estimates are in line with our measurements. This result is true, even if we apply different corrections to PM_{10} measurements due to volatile losses and influence of moisture. In other words, the OPS/SIGMA model output has been *validated* in the first approximation (a full validation would require a more detailed study based on a correct prediction of temporal and spatial patterns).

As a consequence, we can use our model estimates to answer questions which are not obvious from measurements alone. As an example we will use the results from Tables 19 and 32 to give a quantitative estimate of the question: what part of PM_{10} concentrations could be influenced by abatement measures? And how does the influence of what we do in the Netherlands relate to what we could reach with measures on an EU-wide scale?

In the upper panel of **Table 34A** we have summarised the anthropogenic contribution of emissions sources for our six sites in the Netherlands (taken from the upper panel of Table 19). In the second row, the influence of anthropogenic crustal material has been added (we took the crustal value of De Zilk as a natural background value. Values larger than this background are regarded as anthropogenic).

The sum of both contributions leads to an estimate of what we could *maximally* reach with measures in the Netherlands. Interesting is that the influence of abatement is highly variable over our six sites. The lowest value, ~6 $\mu g/m^3$, is found for the coastal site, De Zilk. The highest values, ~14 $\mu g/m^3$ and ~18 $\mu g/m^3$, respectively, are found for the Amsterdam sites Overtoom and Stadhouderskade.

The second panel of Table 34A shows the estimate for that part of anthropogenic PM_{10} which comes from *abroad*. The panel shows that highest values, ~15 $\mu g/m^3$, are to be expected along the eastern border of the Netherlands. The lowest values, ~10 $\mu g/m^3$, are found for the west coast.

Finally, the natural part of PM_{10} concentrations is given in **Table 34B**. This part of PM_{10}, 5 to 7 µg/m^3, does not vary much over the Netherlands.

Please note that the figures in Table 34 are indicative: they will vary from year to year due to varying meteorological conditions.

Table 34A Maximum PM_{10} that can be influenced by abatement in the Netherlands (upper panel) and by abatement abroad (lower panel).

Maximal part of PM_{10} which can be reduced by NL abatement	**1 Nijmegen (µg/m^3)**	**2 Rotterdam Overschie (µg/m^3)**	**3 Amsterdam Overtoom (µg/m^3)**	**4 Amsterdam Stadh. Kade (µg/m^3)**	**5 Vredepeel (µg/m^3)**	**6 De Zilk (µg/m^3)**
Anthropogenic NL	7.5	12.3	13.2	13.2	5.7	5.8
Anthropogenic crustal	4.0	2.6	1.1	4.6	2.7	0.0
Total anthropogenic NL	**12**	**15**	**14**	**18**	**8**	**6**

Maximal part of PM_{10} which can be reduced by abatement abroad	**1 Nijmegen (µg/m^3)**	**2 Rotterdam Overschie (µg/m^3)**	**3 Amsterdam Overtoom (µg/m^3)**	**4 Amsterdam Stadh. Kade (µg/m^3)**	**5 Vredepeel (µg/m^3)**	**6 De Zilk (µg/m^3)**
Anthropogenic abroad	**13**	**12**	**10**	**10**	**15**	**10**

Table 34B Natural part of PM_{10}.

Part of PM_{10} which can be not be reduced by abatement	**1 Nijmegen (µg/m^3)**	**2 Rotterdam Overschie (µg/m^3)**	**3 Amsterdam Overtoom (µg/m^3)**	**4 Amsterdam Stadh. Kade (µg/m^3)**	**5 Vredepeel (µg/m^3)**	**6 De Zilk (µg/m^3)**
Natural crustal	1.7	1.7	1.7	1.7	1.7	1.7
Sea salt	4.2	5.8	5.7	5.7	4.6	6.6
Hemispheric background	0.9	0.9	0.9	0.9	0.9	0.9
Total natural	**7**	**8**	**8**	**8**	**7**	**9**

In conclusion we have summarised the estimates from Tables 34A and 34B in **Figure 23**.

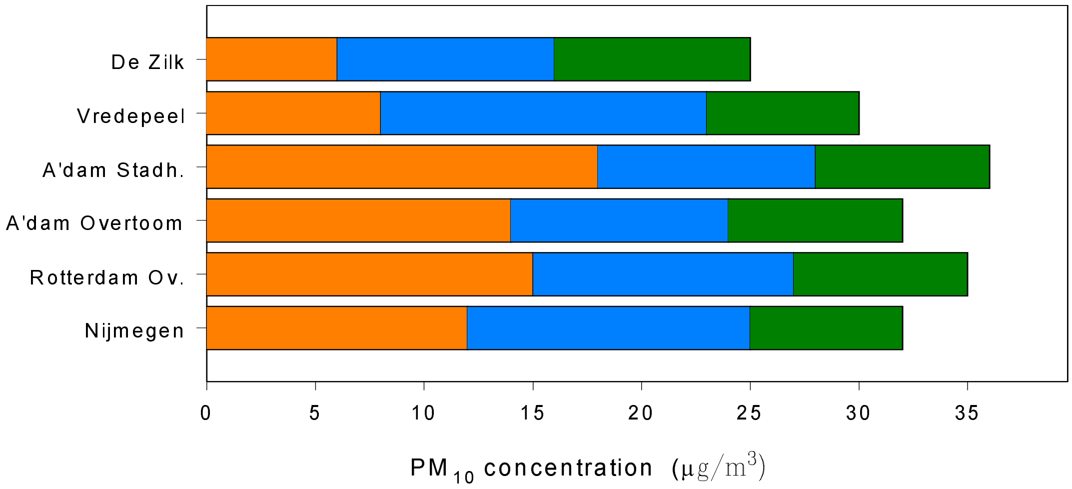


Figure 23 *PM$_{10}$ concentrations at six sampling sites, divided into (i) the maximal part which can be influenced by measures within the Netherlands (orange), (ii) the maximal part which can be influenced by measures outside the Netherlands (blue), and (iii) the contribution of natural sources (green). Data are taken from Tables 34A and 34B.*

Conclusion 16: The maximum PM$_{10}$ that can be influenced by abatement within the Netherlands varies from 6 to 18 $\mu g/m^3$. The maximum PM$_{10}$ that can be influenced by abatement abroad varies from 10 to 15 $\mu g/m^3$. The natural part of PM$_{10}$ in the Netherlands is estimated to be 7 - 9 $\mu g/m^3$. These figures are indicative due to year-to-year variations in meteorological conditions.

7. Conclusions

An important conclusion of this study is that the average 'gap' between modelled and measured PM_{10} has been almost closed. The average ratio between model estimates and measured concentrations is 0.94 (uniform correction factors for the FAG instruments) or 0.91 (location-specific correction factors for the FAG instruments). In earlier studies, in which not all sources were taken into account, a 'gap' of approximately 50% was found.

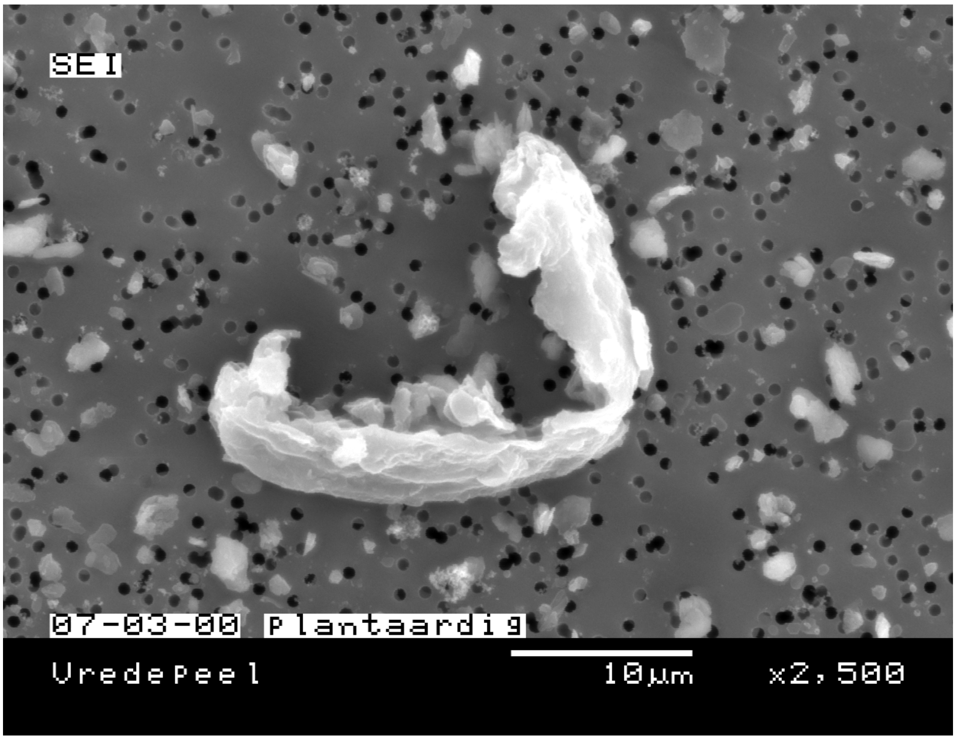
The first part of the gap closure occurred due to the lower values of PM_{10}, recorded in 1998/1999 (34 $\mu g/m^3$), in comparison to the national annual averages of 1993 (40 $\mu g/m^3$) and 1995 (39 $\mu g/m^3$). Emissions also decreased during this period, however, at a lower rate than the decrease in measured PM concentrations. As a consequence, a slightly larger fraction of PM_{10} has been modelled now compared to previous modelling.

The second part of the gap closure occurred by adding the contribution of (i) crustal material, (ii) sea salt and (iii) the background concentration of the Northern Hemisphere to the model calculations. The contribution of crustal material varies from 2 $\mu g/m^3$ at coastal sites to 6 $\mu g/m^3$ at urban street sites or industrial sites. The estimate of sea salt varies from 7 $\mu g/m^3$ at coastal sites to 4 - 6 $\mu g/m^3$ at more inland sites. The hemispheric background is estimated at 0.9 $\mu g/m^3$.

Taking the uncertainty in the various estimates into account, we found that the 1-σ confidence limits in the ratio [modelled/ measured] to be 0.20. Hence we can conclude that the gap between measurements and model estimates has been adequately closed.

As an example we combined OPS/SIGMA calculations and results from this study to get an impression of what abatement could do. We found that the maximum PM_{10} that can be influenced by abatement within the Netherlands to be is highly variable: from 6 to 18 $\mu g/m^3$. The maximum PM_{10} that can be influenced by abatement abroad (EU) varies from 10 to 15 $\mu g/m^3$. The part of PM_{10} in the Netherlands with a natural origin is estimated at between 7 and 9 $\mu g/m^3$.

If models and measurements are to be brought into a closer agreement in the future, inclusion of sources of crustal material should be considered for the emission inventories as this fraction seems to play a pivotal role for the 'gap' closure (compare **Figure 24**). Furthermore, we prefer the location-specific correction factors for the FAG.



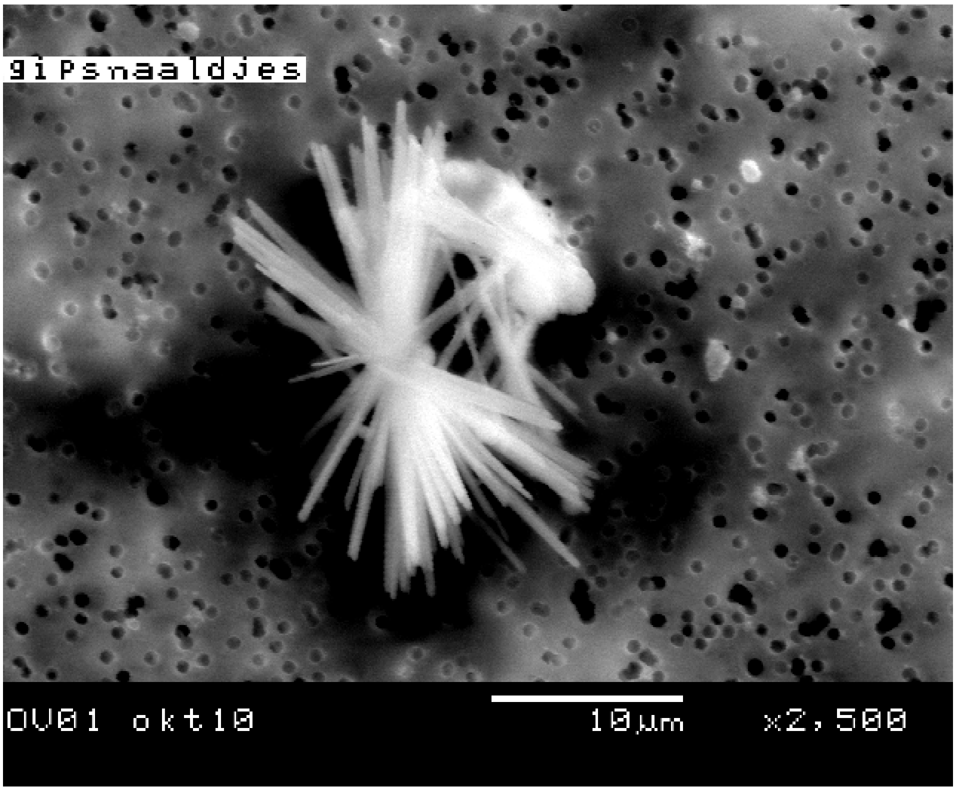


Figure 24 *SEM projections of plant material, possibly from agricultural activities (upper photo from the Vredepeel site) and gypsum needles, originating from building activities (lower photo from the Amsterdam Overtoom site). Both types of sources have not been taken into account in our gap closure approach (Source: Timmner (2000b,c)).*

The results of the project show a large number of minor conclusions, including:

- the (uncorrected) VAPS instrument underestimates the 'true' PM_{10} levels (corrected FAG or TEOM), on average, by 21% to 31%, depending on the location of the comparison. However, the VAPS can be used as a relative measure of 'true' PM_{10} levels.

- the annual average levels of total inorganic secondary aerosol measured by a Dichote and LVS match. The VAPS and Dichote seem to measure higher levels of sulphur/sulphate when compared to LVS. On an annual average basis there seem to be considerable sources of non-sulphur in the Netherlands. This needs further investigation.

- Na^+ and Cl^- have been used as tracers for sea salt, presenting an upper and a lower bound for sea-salt contribution. Na^+ will possibly lead to estimates, which are too high. As the Cl^- depletion will not have been taken into account, Cl^- will lead to a lower estimate. We found the annual average sea-salt concentrations inland in the Netherlands to be approximately 1 $\mu g/m^3$ and in coastal regions of the country approximately 3 $\mu g/m^3$ in a low estimate based on Cl^-. This same annual average sea-salt contribution is estimated at 5-7 $\mu g/m^3$ inland and 8 $\mu g/m^3$ on the coast in a high estimate based on Na^+. To some extent these estimates are too high, as a possible role of road de-icing has not been taken into account.

- the tailpipe traffic contributions have been estimated with the measured values of EC and OC. In an urban background situation this contribution would probably be at least 1-2 $\mu g/m^3$ on an annual average basis, while in a busy street this could increase by another 2 $\mu g/m^3$. At a regional background point the annual average tailpipe traffic contribution would come to approximately 1 $\mu g/m^3$. Compared to foreign estimates and modelling with OPS/SIGMA the calculated traffic contributions with EC/OC seem rather low. Considerably higher values result from estimates with the CAR-model.

- the average traffic contribution of primary PM_{10} by re-suspension is estimated at 1 $\mu g/m^3$ in an urban background situation and 2 - 4 $\mu g/m^3$ extra in a busy street.

- except for Na^+, the elemental concentrations in the Netherlands are quite comparable to those in neighbouring countries like Germany and the UK, and even to some countries that are on a different continent, like the USA.

- annual average PM_{10} levels in the Netherlands measured during this project are comparable with those found in Germany and the UK, at least if the differences of various measurement methods are taken into account. For the ratios of [$PM_{2.5}$ / PM_{10}] the conclusion seems to be that the fractions recently found in Germany (0.70 - 0.85) are slightly higher than those currently found in this project (0.60-0.75).

- due to the higher fractions of OC and of ammonium nitrate in $PM_{2.5}$ than in PM_{10}, the correction factors in Equations (4a) and (4b) would have been even higher if $PM_{2.5}$ had been observed instead of PM_{10}. It is advisable to quantify these factors specifically for $PM_{2.5}$ so that this conjecture can be substantiated.

The conclusions drawn above have been based on an extensive measurement exercise. Nevertheless, they are based on only one year of observations (79 sampling days, in total).

Although we have tested the representativeness of the sampling days in relation to averages based on all days of the year, results should be handled with some care.

We can therefore make the following remarks, which should lead to more support for some of our findings:

- as traffic seems to play a pivotal role in the PM health effects, a better characterisation of this source in chemical EC/OC, including the speciation of OC, crustal and biogenic contribution by re-suspension, and in physical terms (particle size distribution, UF) would seem necessary.

- to obtain a full mass balance of PM, supplementary measurements of specific fractions are warranted: carbonate, Mg, P, biogenic aerosols > 2.5 µm, coarse EC, and secondary organic aerosols.

- more insight in the agricultural, and building/demolition, contribution to the crustal material, and a quantitative source contribution of these emissions categories will give the necessary instruments to estimate the effectiveness of abatement measures and their costs.

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