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# **CHARACTERIZATION OF PARTICULATE MATTER IN URBAN AIR**

## **Instrumentation development and experimental results**

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## Abstract

The general aim of the project is the assessment of the effect of emissions of traffic on the air quality in urban agglomerations (and on climate) and the determination of the cost and benefits of various possible local measures. In this report the results of the first part of the project are described.

Traffic emissions contribute to a large extent to the health effects of air pollution. It is still uncertain in which way these effects are related to aerosol mass, chemical composition or number density. Accurate measurements are highly desirable but relatively scarce due to technical difficulties. The need for technical refinements of the current sampling and analyses techniques of particulate matter is motivated. The temperature dependence of the accuracy of the TEOM measurement technique, the installation for the weighing of aerosol material under temperature controlled conditions, the technical improvements of the particulate carbon monitor for soot measurements, and the further improvement of the Steam-Jet Aerosol Collector (SJAC) are highlighted in this report. The improved techniques were implemented in a number of field campaigns yielding data on the influence of traffic emissions on PM concentration levels. The report here includes: 1) direct measurement of particulate matter in exhaust gases of passenger cars, 2) measurements of aerosol number and mass concentrations in a traffic tunnel, and 3) measurements in an urban environment at a fixed location or by means of a moving unit.

The evaporation of ammonium nitrate as a function of the temperature of the heated filter in a TEOM demonstrates the need for temperature-controlled measurements and raises questions about the accuracy of TEOM during measurements of the (semi-)volatile aerosol. The development of the humidity and temperature-controlled installation in combination with a designed weighing protocol improved the accuracy of weighing of collected aerosol samples. Tests on the SJAC have been performed in order to study its operation when measuring the heavy metals and organic compounds. The results indicate that the SJAC can be used for sampling in an urban environment as its collection efficiency is virtually 100% at high number concentrations and does not depend on the water-solubility of the aerosol. The limit of detection of the SJAC can be reduced by insulation and applying higher flow rates.

The emissions of road traffic in a tunnel have a significantly larger proportion of nanometer-sized particles than when directly measured at the outlet. This suggests the production of new particles in ambient air by homogeneous nucleation. The experiment with the moving van demonstrates that the variation in particulate matter in and near streets can be attributed to prevailing traffic densities; for example, higher number concentrations are measured at streets with densely packed through traffic as compared to the numbers found in quiet residential areas. The aerosol number concentration is mostly due to the urban traffic; this is especially apparent when air has first traversed over a city when low background levels occur. These experiments, performed in the Drecht tunnel, Nijmegen, Amsterdam and Petten, substantiate that aerosol number concentration may be a better indicator than mass concentration for adverse effects on health observed in cities. More knowledge on the emissions of the ultrafine particles is necessary to describe the dynamics in the aerosol concentrations (number and composition). If this knowledge is acquired, relations with health indicators can be assessed more accurately and the design of an effective abatement strategy becomes within reach.

### Keywords

Particulate matter, urban air quality, vehicle emissions, health effects, number, mass, chemical composition, sampling, analysis, TEOM, steam-jet aerosol collector, SJAC.

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## CONTENTS

1.	INTRODUCTION	7
2.	INSTRUMENTATION DEVELOPMENT	9
2.1	Introduction	9
2.2	Temperature dependence of the accuracy of the TEOM when sampling ammonium nitrate aerosol	9
2.2.1	Introduction	9
2.2.2	Experimental set-up	10
2.2.3	Results	10
2.2.4	Conclusions	12
2.3	Controlled temperature and relative humidity installation for weighing	12
2.4	Improvement of RP5400 Particulate Carbon Monitor for soot measurements	12
2.4.1	Description	13
2.4.2	Results	13
2.5	Steam-Jet Aerosol Collector improvements / characterization	15
2.5.1	Introduction	15
2.5.2	Sampling efficiency at high aerosol number concentrations	15
2.5.3	Sampling efficiency for water-insoluble aerosol	15
2.5.4	Adaptation of SJAC to measurements of heavy metals in airborne particulate matter	16
2.5.5	Improvement of the Limit of Detection (LOD) by thermal insulation and higher sampling flow rates	17
2.5.6	Modeling	18
2.5.7	Conclusions	18
3.	FIELD EXPERIMENTS	20
3.1	Introduction	20
3.2	Dynamometer measurements	20
3.3	Drecht-tunnel measurements	22
3.3.1	Introduction	22
3.3.2	Measurement set-up	22
3.3.3	Results and discussion	24
3.3.4	Conclusions	28
3.4	Pilot measurements with a moving system of the spatial variation of PM in Nijmegen	28
3.4.1	Introduction	28
3.4.2	Experimental set-up	28
3.4.3	Results	29
3.5	Ultra-fine particle monitoring in Amsterdam and Petten	33
3.5.1	Introduction	33
3.5.2	Methods	34
3.5.3	Results	35
3.5.4	Conclusions	42
4.	DISCUSSION AND CONCLUSIONS	43
	REFERENCES	46



## 1. INTRODUCTION

There is a growing concern about the role of airborne particulate matter (PM) in the adverse environmental effects of air pollution, especially in urban agglomerations. This is reflected by a number of governmental measures, planned or carried out, around the world to curb the particulate air pollution. In 1997, the U.S. Environmental Protection Agency (EPA) revised the National Ambient Air Quality Standards (NAAQS) for concentrations of particulate matter (PM) with an aerodynamic diameter of 2.5 micrometers ( $10^{-6}$  m) or less (PM<sub>2.5</sub>). The European Commission is planning to introduce new guidelines for particles smaller than 10 micrometers in an aerodynamic diameter (PM<sub>10</sub>). Based on the limited existing data of ambient PM concentrations, it appears very likely that the new standards will be exceeded and it will be very hard to reach the targets.

The concern for the elevated concentrations of PM is mainly derived from the evidence of human health effects associated with atmospheric particles. The epidemiological literature has more than 100 published papers, which, for the most part, support association of PM with increases in morbidity and/or mortality. There is also substantial evidence from toxicological studies that airborne particulate matter or some of its chemical constituents may cause the health effects. However, there is no epidemiological evidence identifying the PM chemical constituents as potential causative agents. A number of aerosol characteristics have been proposed as the potential causes of observed health effects, such as particle number, surface and mass, TSP (total suspended particles), PM<sub>10</sub>, and PM<sub>2.5</sub>. Also a number of chemicals found in ambient PM were linked with the adverse effects, like soot (elemental carbon), heavy metals, aerosol acidity, etc.

Large gaps exist in our understanding of the nature of, effects of, and control of ambient PM. These are due to the fact that PM is a complex mixture of multi-component particles whose size distribution, composition, and morphology can vary significantly in space and time. Atmospheric aerosol particles have diameters ranging from a few nanometers ( $10^{-9}$  m) to tens of micrometers. Major components include sulfate, nitrate, ammonium, organic material; elemental carbon (or soot), trace elements (including toxic and transition metals) and crustal components. PM is emitted directly from sources such as diesel and gasoline engines and is also formed in the atmosphere from gaseous precursors.

Development of effective control strategies requires a better understanding of the properties of PM. It is important to notice that serious doubt exists on the appropriateness of the PM<sub>10</sub> guideline proposed by the EU. Various indications can be found in literature for this supposition: first, the PM<sub>10</sub> concentrations hardly show any spatial variation over the Netherlands. Secondly, measurements indicate that the fraction between PM<sub>10</sub> and PM<sub>2.5</sub> mainly consists of soil dust, sea salt, etc. But perhaps most important in this respect is the revelation in German and American research that (statistical) relationships exist between the chemical composition and/or the number of the ultrafine particles (smaller than 100 nm in diameter) and the frequency of health effects (in cities). Local industries and traffic are the main sources of high concentrations of this ultrafine matter. If proven correct this will lead to the introduction of a guideline for PM<sub>2.5</sub>, PM<sub>1</sub> or ultrafines and will imply a substantially different abatement strategy e.g. focussed on traffic emissions.

Identifying the PM characteristics and/or sources causing the negative health effects requires the understanding of sound data sets of PM measurements. Such data sets do not exist at the moment. Standard techniques such as filters do not measure most of the aforementioned characteristics and often suffer from sampling artifacts. The difficulty and cost of the PM measurements have impaired our ability to characterize the temporal and spatial variability, to

understand the processes that control the formation and removal, and to quantify the exposure of populations to PM. Overcoming these difficulties requires an evaluation of existing PM measurement methodologies and the development of new technologies allowing accurate measurement of PM characteristics and assessment of causal relationships necessary to develop cost-effective abatement measures.

One of the major sources of PM in the urban environment is vehicular traffic. These mobile sources are known to emit large quantities of primary particles, composed mostly of soot and organic material, as well as gases that act as precursors for new (secondary) particle formation or attribute to the growth of existing particles. The emitted PM has a larger proportion of ultra-fine particles and contains a number of other possible causative agents, such as soot, polycyclic aromatic hydrocarbons (PAH) and toxic metals. There are, however, very few data on the emission factors for these PM characteristics. Again, this lack of data is explained by the difficulties associated with PM measurements.

In this context, the work presented here consists of two major parts: at first, refinements of (existing) measuring techniques that were designed to overcome (to a certain extent) the impediment of lack of accurate data are described. To this purpose, the new installation for the weighing of aerosol material, the further developments of the particulate carbon monitor for soot measurements, and the Steam-Jet Aerosol Collector (SJAC), and a critical testing of the capabilities of the (widely used) TEOM will be highlighted in more detail.

Secondly, the improved equipment was employed in the experimental measuring campaigns performed in 1999. These campaigns yielded data on the emissions from vehicular traffic in three different experimental settings: 1) direct measurement of particulate matter in exhaust gases of driving cars, 2) measurements of aerosol number and mass concentrations in a traffic tunnel (Drecht tunnel), and 3) measurements in an urban environment at fixed locations (Amsterdam) or by means of a moving unit (Nijmegen). Emission factors for vehicular traffic are estimated and quality, (dis-)agreement as well as implications for future research are discussed in the second part of this report.

## 2. INSTRUMENTATION DEVELOPMENT

### 2.1 Introduction

Several measuring techniques require weighing of collected aerosol mass. Such techniques are standard filter measurements and cascade impactors. These instruments are widely used to measure total and size segregated mass concentration of PM. Collected mass is usually very low, which requires the weighing to be accurate within a few micrograms. The weighing of the collected aerosol material is also complicated by other factors. For instance, the substrate on which PM is collected is often static, which disturbs the weighing. The collected aerosol material usually contains a substantial fraction of water-soluble material that absorbs water vapor. If the relative humidity around the balance is not controlled, the weighing becomes highly erroneous due to the absorption of water. The temperature around the balance should be controlled too, because it not only influences the performance of the high precision balance, but also can lead to loss of volatile substances from the collected aerosol particles. Maintaining temperature and relative humidity constant during one weighing but also from day to day helps to avoid the above problems and insures reproducible conditions. The work presented in the next sections explains the refinements of (existing) measuring techniques that were designed. The new installation for the weighing of aerosol material, the further developments of the particulate carbon monitor for soot measurements, and the Steam-Jet Aerosol Collector are highlighted. As a start, the results of a critical testing of the capabilities of the (widely used) TEOM are given more detail.

### 2.2 Temperature dependence of the accuracy of the TEOM when sampling ammonium nitrate aerosol

#### 2.2.1 Introduction

The increased health effects of ambient particulate mass (PM) has focussed attention on the evaluation of existing mass measurement methodologies. One of them is the Rupprecht and Patashnick Tapered Element Oscillating MicroBalance (TEOM). The TEOM is frequently used and as cost-effective method for measurement of PM when daily or hourly concentrations are needed for regulatory purposes, atmospheric studies or epidemiological studies of human health effects.

In its standard operation, the TEOM collects particles on an oscillating filter heated to 50 °C. This is done in order to eliminate interference from particle bound water (PBW). Removal of the particle bound water is critical to the operation of the TEOM which is based on the measure of incremental mass. If the collected PM is not heated sufficiently to remove all of the water, any change in the ambient water vapor concentration will produce a change in particle bound water which will in turn change the outcome of the measurement.

Semi-volatile organic and inorganic compounds can represent a substantial fraction of ambient PM. Heating of the air sample to a temperature 20-30 °C above ambient is expected to introduce the loss of the semi-volatile constituents from the TEOM filter. These losses depend on particle composition which varies with location and time. Thus, it is not possible to determine the true concentration by using empirical correction factors. This underestimation of the true mass is most likely to occur in urban areas, where nitrates and (semi-volatile) organics may comprise a substantial fraction of the PM mass.

In literature (e.g. Allen et al, 1997), results are indeed described that the TEOM does underestimate in case of the presence of semi-volatile compounds. The purpose of this study was to evaluate the performance of the TEOM method with laboratory aerosol (pure ammonium nitrate) when the filter is kept at different temperatures in order to test the above findings. The TEOM used in this experiment has kindly been placed at our disposal by TNO-MEP.

### 2.2.2 Experimental set-up

Pure ammonium nitrate was tested. The test aerosol was produced by spraying the water solution of the salt with a modified Wiesbadener nebulizer. The aerosol laden air was mixed with a ten-fold excess of dry pressurized air (RH<10%). The dry aerosol was then introduced into the test tunnel where it was mixed with a flow of 500 l/min of particle-free ambient air. The stability of the aerosol concentration in the tunnel was monitored with an integrated nephelometer (MRI1560). The nephelometer provides the total light scattering by aerosol particles, which can be used to estimate the aerosol mass concentration. Though such estimation is not as accurate as gravimetric methods, it is very useful for monitoring stability of the aerosol generation or for comparison of aerosol concentrations during several experiments. Relative comparability of the TEOM and the nephelometer was assessed during measurements of ammonium sulfate aerosol. This aerosol compound is stable and thus no artifacts are expected in TEOM measurements. The instruments were found to be comparable within 15%.

The TEOM sampled from the tunnel through 50 cm of ½" copper tubing. The TEOM was operated at two temperature settings: at 50 °C (nominal operation) and at 30 °C (to test whether the reduction of the compartment temperature results in better performance). To test how the TEOM reacts to sharp changes in ammonium nitrate aerosol concentration, the instrumental response was monitored when aerosol concentration was switched on or off.

### 2.2.3 Results

Two tests have been carried out with the TEOM:

1) *ammonium nitrate, operation temperature TEOM is 50 °C*

Running 10 min averages (logged every minute, no smoothing) produced by the TEOM are shown in Figure 2.1. At t=0:00 the collection of ammonium nitrate on the TEOM filter has started. After t=40 min the spraying of the nebulizer has been turned off.

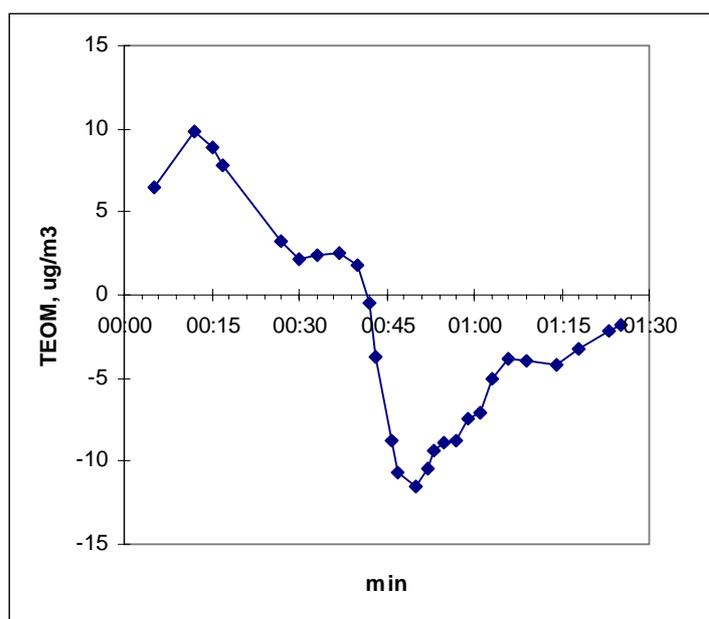


Figure 2.1 *TEOM readings during the first experiment*

Clearly, the (incremental) measurement of mass at the TEOM filter does not reflect a constant collection of ammonium nitrate at the filter. According to the TEOM the concentration attains its maximum after 12 min and is about  $10 \mu\text{g}/\text{m}^3$ . Apparently, the evaporation is larger than the input. After about 25 min the measured concentration has been stabilized around  $2.5 \mu\text{g}/\text{m}^3$ , below the detection limit of the TEOM ( $5 \mu\text{g}/\text{m}^3$ ). The evaporation of ammonium nitrate at the filter is now about the same as the input to the filter.

After 40 min the generator has been switched off. The (incremental) 'concentration' according to the TEOM rapidly becomes negative indicating a continuous loss of accumulated ammonium nitrate from the filter surface. The lowest value (which means a maximum loss of ammonium nitrate per unit time from the filter) is found 10 min after the spray of ammonium nitrate has stopped. After this point the evaporation rate gradually becomes less and slowly stabilizes as the amount of ammonium nitrate on the filter apparently diminishes to zero.

## 2) ammonium nitrate, operation temperature TEOM 30 °C

After the first experiment the operation temperature has been lowered to 30 °C in order to find out if the loss rate of ammonium nitrate changes. Results can be found in Figure 2.2.

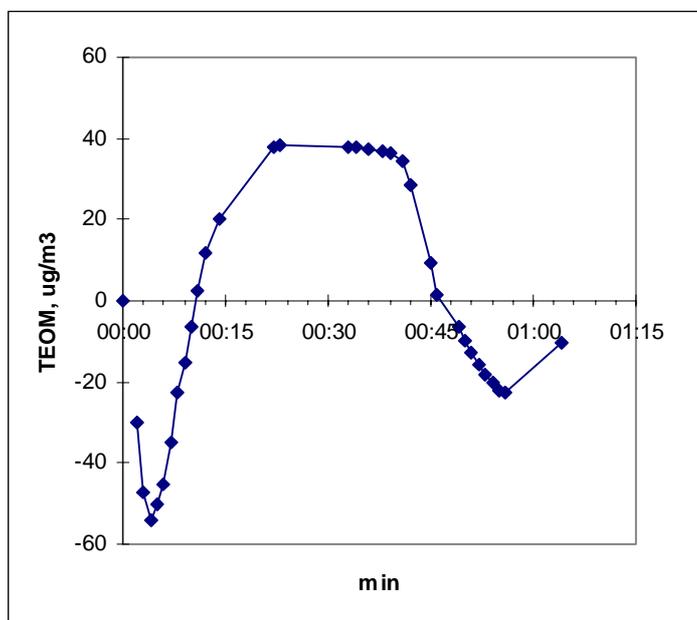


Figure 2.2 *TEOM reading during the second experiment*

After sufficient cooling of the TEOM, the generation was started at  $t=0:00$ . Surprisingly, in this test a negative concentration value is attained at first; the sudden increase in aerosol concentration may have destabilized the oscillating TEOM filter. However, an additional experiment performed with a more stable mixture of nitrate and sulfate under further similar circumstances did not show similar behavior. This remains to be investigated further.

After about 10 min the same pattern as in the previous Figure 2.1 is followed. Stabilization occurs after 22 min. At this time, however, the "steady-state" concentration is higher than the lower detection limit, being  $40 \mu\text{g}/\text{m}^3$ . Although this is still twice as low as what is measured with the nephelometer, it is an improvement in comparison with the first test performed at 50 °C. At  $t=0:40$  the generator is turned off again causing a sharp decline. The minimum "concentration" is  $32.5 \mu\text{g}/\text{m}^3$ .

## 2.2.4 Conclusions

Clearly, loss of ammonium nitrate from the heated filter is demonstrated. Although lowering of the operational temperature to 35 °C improves the operation of the TEOM, the concentration still does not represent the actual concentration, as it is about 2 times lower than the concentration indicated by the nephelometer.

The TEOM instruments often are widely used in monitoring networks. Ammonium nitrate constitutes an important fraction of PM. These measurements show that one ought to be careful and anticipate underestimation of the true values. It remains still to be investigated what the negative effect will be in the ordinary application of a TEOM producing (at least) one-hour averages. Already in 1993, the US Protection Agency has conditionally approved a low temperature operation (at 30 °C) during certain periods in winter to decrease the temperature difference. Also interesting is the question to what extent the on-line response of the TEOM is comparable with the actual behavior (e.g. the nebulizer concentration).

## 2.3 Controlled temperature and relative humidity installation for weighing

A temperature and humidity controlled installation has been built in order to assure accurate weighing of collected aerosol material. The installation consists of a Plexiglas “clean”-box, which is hermetically isolated. The relative humidity and temperature of the air inside the box is controlled with PT100 element and a dew-point probe. The temperature is kept at  $20 \pm 1$  °C and the relative humidity between 40 and 45%. The temperature is kept constant by controlling the temperature in the room where the installation is placed with an air-conditioner. The relative humidity inside the box is controlled by pumping dry air through the box when the relative humidity exceeds 45%. The pumps are switched off during the weighing in order to avoid the negative effects of trilling caused by the pumps. The precision balance is modified by placing a grounded metal cage around it to reduce the negative effects of static electricity. The pincet is also grounded for the same reasons.

An operation protocol has been developed to insure the quality control. The balance is internally calibrated before each of the weighing. In addition, a standard blank impactor foil is weighed before and after each weighing. This is done to control zero and span drift of the balance during the weighing. If the drift is not substantial, the measurements can be corrected for it, otherwise the weighing should be repeated.

The humidity and temperature controlled installation in combination with the designed weighing protocol improved the accuracy of weighing by a factor of 5 to be  $\pm 2$  µg. The accuracy of aerosol concentration measurements depends on the load of the foils, being lower at higher loads. The foil load is proportional to the aerosol concentration and the duration of sampling. When sampling ambient aerosol at a concentration of  $50 \mu\text{g}/\text{m}^3$  during 8 hours with a 8-stage Berner impactor, the accuracy of measured aerosol concentration will be about 2% per stage and 6% total.

## 2.4 Improvement of RP5400 Particulate Carbon Monitor for soot measurements

The RP5400 Particulate Carbon Monitor (Rupprecht and Potaschnik Co.), also called ACPM, provides automated measurements of organic and elemental carbon (soot) mass concentration in PM with the time resolution of 1 hour or longer. The instrument operates by collecting the particulate matter on an impactor with the cut-off size of  $0.15 \mu\text{m}$  (diameter) and thermally converting the collected organic and soot carbon into  $\text{CO}_2$  following the collection phase. The concentration of the evolved  $\text{CO}_2$ , which is measured with an FTIR sensor, is translated into the organic or soot mass concentration in PM.

This instrument is fully automated and provides very promising means for monitoring of the carbonaceous aerosol. The instrument was approved by VDI as the standard measurement instrument of soot in Germany. There are numerous indications, however, that the monitor misses a substantial part of the soot particles due to a rather high cut-off size of the impactor. The ACPM was found to underestimate the BC concentration by 40% relatively to a conventional filter technique (Mückler, 1997 and Fischer, 1997). The soot particles emitted by internal combustion engines have their mass median diameters at around 0.1 - 0.2  $\mu\text{m}$  in diameter. Consequently, an impactor with the cut-off size of 0.15  $\mu\text{m}$ , as the one in the ACPM, would miss about 50% of the soot mass, which is a plausible explanation for the observed underestimation relatively to the filter techniques.

#### 2.4.1 Description

To improve the collection of soot aerosol, the instrument was modified by replacing the impactor with a filter. The filter and the filter holder were adopted from another RP soot monitor (RP5100). To test the hypothesis that replacing the impactor with a filter will improve the collection efficiency of the ACPM (RP5400), the tests were done by replacing the impactor in one of the two sampling lines of the ACPM. The other line was left unchanged with the impactor. Comparison of the line with the filter with the line with impactor will provide the information on whether the filter will sample more soot particles than the impactor. For testing the instrument was installed at an urban background location in Amsterdam. In addition, the modified monitor is compared with black smoke measurements to check the accuracy of the ACPM. Black smoke is measured using an optical method. It is a surrogate for black carbon measurements and correlates well with it (Erdmann, 1993). Samples for black smoke measurements were collected on a filter behind a  $\text{PM}_{2.5}$  inlet. Measurements with both monitors were performed during a 4-month campaign at an urban background site in Amsterdam, the Netherlands.

#### 2.4.2 Results

The black carbon concentration sampled in the impactor line is on average 60% of that of the concentration collected in the filter line (see Figure 2.3a). Thus it seems likely that on average 40% of the black carbon mass is associated with particles smaller than 0.14  $\mu\text{m}$  in diameter at the measuring site. The comparison of successive measurements could be biased by a possible daily pattern in the BC concentrations. This was not the case as the comparability of the results for sample times of 1 and 3 hour shows.

Sampling with a filter may introduce gaseous absorption artifacts for OC that are larger than those for the original impactor. Therefore, though we focus on the BC measurements, the consequences of sampling OC on a filter are presented. The organic carbon concentrations were measured simultaneously with black carbon in both lines of the instrument. Comparison of organic carbon measured in both lines suggests an underestimation of the organic carbon concentration when sampled with the impactor (Figure 2.3b). However, this result may be influenced by the increase of the gaseous adsorption artifact in the filter-line when compared to the impactor-line. To avoid the adsorption artifact on the filter, a denuder must be used so that the modified instrument can also be used for organic carbon.

The BC concentrations from the adapted ACPM (filter) were compared with black smoke measurements. The results are plotted in Figure 2.4. Though no conclusions can be drawn on the absolute accuracy of the BC measurements with the ACPM, it is worthwhile to mention that the correlation between both methods, 0.92, is good.

In summary, the black carbon measurements with the ACPM are improved when a quartz filter is used instead of the impactor, so that black carbon is sampled quantitatively. The modified ACPM correlates well with black smoke measurements.

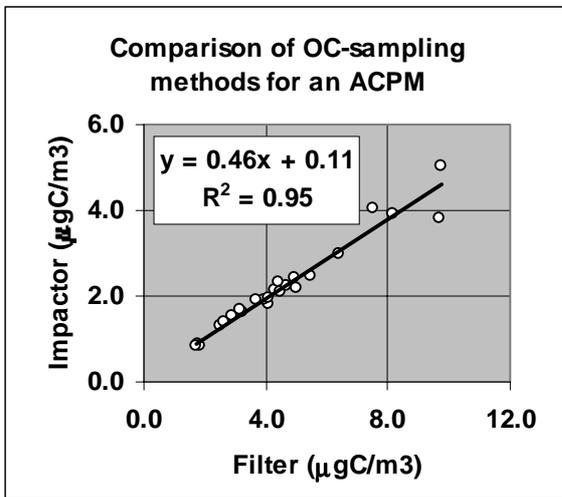
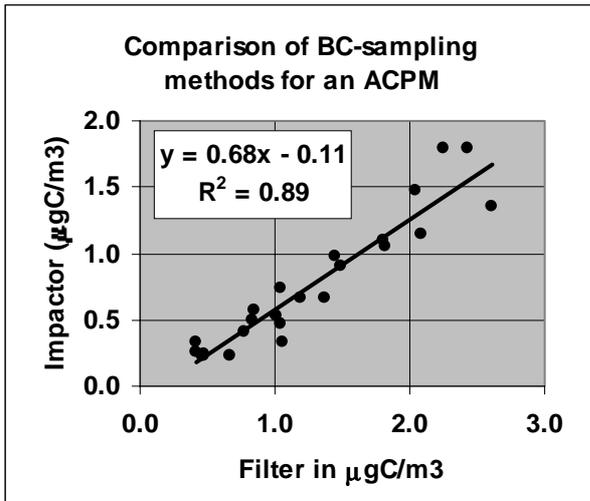


Figure 2.3a,b ACPM sampling alternately on a filter and impactor, 24 h average

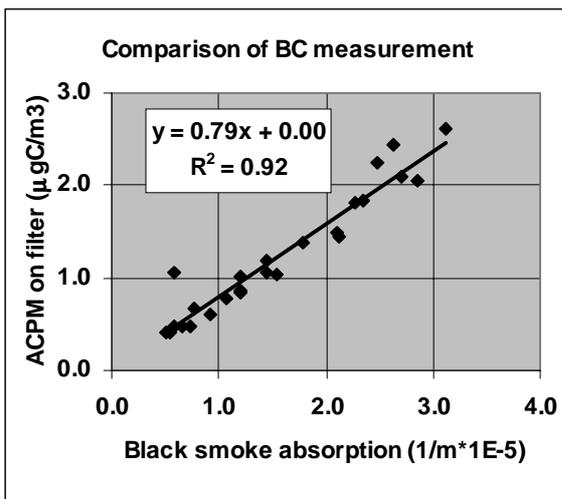


Figure 2.4 ACPM sampling compared with Black Smoke Absorption

## 2.5 Steam-Jet Aerosol Collector improvements / characterization

### 2.5.1 Introduction

The conventional techniques such as filter-packs and impactors are very labor intensive and suffer from sampling artifacts. The Steam-Jet Aerosol Collector (SJAC) was developed for artifact-free, automated, high time resolution measurements of water-soluble inorganic aerosol fraction (Khlystov et al., 1995). Performance of the SJAC at the concentration ranges and chemical composition relevant for aerosol climate forcing has been extensively characterized (Mikuska et al., 1997; Khlystov et al., 1998; Slanina et al., 2000). The characteristics of SJAC make it very attractive for application in urban environment in relation to the health effects studies. In this project we have assessed the feasibility of such an application. Both the performance of the SJAC at high aerosol concentrations and its applicability for sampling insoluble aerosol components (such as heavy metals) was tested. Feasibility of lowering the detection limit by thermal insulation and increasing the sample flow were investigated. Also a basic modeling of the SJAC was made in order to gain insight into its performance.

### 2.5.2 Sampling efficiency at high aerosol number concentrations

The SJAC operates by growing water droplets on existing aerosol particles under conditions of high supersaturation (Khlystov et al., 1995). Due to the water condensation the aerosol particles are easy to collect and analyze automatically. A possibility exists, however, that when the aerosol number is very high, the amount of available water vapor would not be sufficient for each particle to grow sufficiently large, which would lead to poor collection efficiency. The previous tests were done at number concentrations of  $60,000 \text{ cm}^{-3}$ . The tests indicated that particles down to 10 nm in diameter were collected with the efficiency of 99% (Khlystov et al., 1995).

In this study we have tested the performance at even higher aerosol number concentration,  $300,000 \text{ cm}^{-3}$ . The tests were performed using a procedure described in Khlystov et al. (1995). Ammonium sulfate aerosol was produced by nebulizing water solution of the salt with a TSI constant-output atomizer. The aerosol number median size was between 20 and 30 nm. The collection efficiency of the SJAC was assessed by measuring the number concentration behind the SJAC with a CPC3010 (TSI Inc.). The total number concentration of the aerosol before the SJAC was measured with a TSI CPC3022. It was found that the collection efficiency of the SJAC even at such high number concentrations ( $300,000 \text{ cm}^{-3}$ ) is virtually 100%.

### 2.5.3 Sampling efficiency for water-insoluble aerosol

Urban aerosol contain a large proportion of water-insoluble aerosol mass, such as soot and some organic compounds. It is known that it is difficult to initiate water droplet growth on water-insoluble (hydrophobic). This may have negative effects for sampling efficiency of the SJAC which uses water droplet growth in order to collect the particles. To test this we have measured the collection efficiency of the SJAC using a hydrophobic sebacate aerosol. Aerosol was generated in a similar way to that described above, with the difference that sebacate was dissolved not in water but in alcohol. The total number concentration of the aerosol was  $30,000 \text{ cm}^{-3}$ . The collection efficiency was measured in the same way as described in the previous section. Again, the collection efficiency of the SJAC was found to be virtually 100%.

After collection, insoluble aerosol can be lost on the walls of the sampler before reaching the analytical instrument. The extent of wall-losses was tested. Black carbon particles of a few tenths of micrometer in size (a size common of BC in ambient aerosol) were suspended in water at a concentration relevant for that during sampling ambient aerosols. This suspension passed the SJAC, floating along its walls, as the collected sample does. The amount of black carbon in the suspension before and after passing the SJAC was determined a DOC/TOC analyzer (Shimadzu). It was found that virtually 100% of the insoluble material passed the SJAC,

indicating negligible wall losses. It thus concluded that the SJAC is suitable for sampling insoluble aerosol particles as its collection efficiency is virtually 100% and the wall losses are minimal. It should be noted though, that the losses in the tubing leading the sample to the analytical instrument were still substantial. It is therefore necessary to avoid contact with tubings other than glass or metal.

#### 2.5.4 Adaptation of SJAC to measurements of heavy metals in airborne particulate matter

Heavy metals are considered to be one of the causes of the adverse effects of PM. Measurements of these metals are however complicated due to the low concentrations of these metals in air. The usual techniques like filters require long sampling times and suffer from contamination artifacts during the handling of the samples. The SJAC sampler offers a solution to this problem. Sampling of metals with the SJAC is in some respect simpler than sampling of gases, because there is no denuder required to strip the gases. The collected sample can be also pretreated to increase the concentration of the species (for example by evaporation) in the sample. There are also difficulties, however. The major problem that can occur when sampling metals with the SJAC is that the water-insoluble metal compounds can be lost on the walls of the system. Though the tests with water insoluble compounds have shown that such losses are negligible on the walls of the sampler itself, there is still a substantial loss of insoluble particles in the tubing, leading the sample to the analytical instrument as explained in the previous section.

To avoid the losses in the SJAC (both on the walls and in the tubing) when sampling metals, a small adjustment was made to the construction of the sampler. The sampler was modified in such a way that a flow (10 ml/min) of 1 M analytical grade HNO<sub>3</sub> was introduced into the sampler at the top of the mixing reservoir. The nitric acid mixes with water condensing on the walls and in this way acidifies the sample. All the water-insoluble metal compounds should be dissolved by the nitric acid, such that the wall losses are avoided. The samples obtained with the modified SJAC were collected each 15 min and were off-line analyzed using ICP / AAS.

The modified sampler was tested using laboratory generated water-insoluble copper oxide aerosol. A special effort was undertaken to produce water insoluble aerosol with sizes representative for the metal-containing ambient particles. Metals are expected in ultra-fine particles (smaller than 100 nm). Laboratory generation of metal particles in this size range is very problematic and there is no commercial instrument available for this purpose.

The copper oxide aerosol was produced by thermal decomposition of copper acetate aerosol. The copper acetate aerosol was produced by spraying a water solution of the salt with the TSI constant output atomizer. The aerosol was mixed with the dry pressurized air for drying and then introduced into a quartz flow-through oven. The oven consisted of annular quartz tube surrounded by a heating wire. The oven was operated at 250 °C. At such temperature copper acetate decomposes into copper oxide and CO<sub>2</sub>. In this way no water-soluble components are left in the particles.

To achieve a sufficient aerosol loading on the reference filters (see below) the generation was run for several hours, over night. The size distribution of the aerosol was observed with the SMPS. If decomposition of the acetate occurs, the aerosol spectrum should shift to smaller sizes as particles loose CO<sub>2</sub>, which was indeed observed. After passage through the oven, the aerosol became substantially smaller due to decomposition and loss of CO<sub>2</sub>. We can conclude that the aerosol was converted to copper oxide. The resulting spectrum has number mean diameter around 50 nm, which is similar to the sizes of particles found in urban air.

The total mass concentration of metal was measured with a filter. The aerosol was collected using a Teflon filter (Millipore) at a flow of 10 l/min. After collection the filter was analyzed for

metal content using ICP / AAS. The solution containing dissolved CuO was collected after the SJAC in tubes every hour and analyzed by ICP / AAS.

The time series of metal concentration measured with the SJAC is shown in Figure 2.5. At around 18:00 a transition has occurred such that the Cu concentration has decreased while that of Zn increased. Though it is not clear what exactly has caused this transition (because it occurred at night when no one was present in the laboratory), the most probable reason for that is a substitution of Cu by Zn in the solution of copper acetate in the nebulizer. The nebulizer contains metal parts immersed into the solution that is being sprayed. If these metal parts are covered with Zn, it would react with the solution of copper acetate to release Zn ions into the solution.

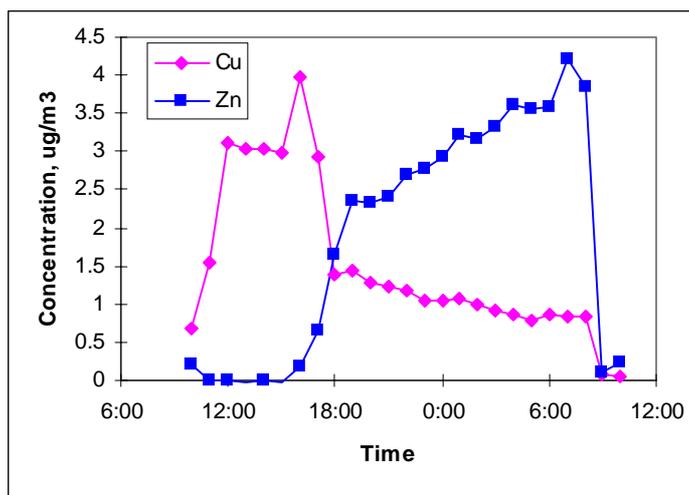


Figure 2.5 Batch measurements of CuO with the SJAC

The Teflon filter that was sampling in parallel to the SJAC also contained Zn, consequently the observed Zn concentration in the SJAC is not a result of an artifact in the SJAC. Comparison of the concentrations measured with the SJAC and the filter, however, do not agree well. The average concentration of Cu and Zn measured with the SJAC were 1.5 and 2.4  $\mu\text{g}/\text{m}^3$ , respectively. The concentrations measured with the filter were, respectively, 0.19 and 0.30  $\mu\text{g}/\text{m}^3$ . The SJAC gave a higher concentration than the filter (a factor of 8, for both Cu and Zn), and thus it cannot be attributed to losses of insoluble particles in the SJAC. The most probable reason for the lower concentrations found with the filter is a leak in the filter, such that a part of aerosol has escaped without being collected on the filter.

It is concluded that the results of the tests indicate that the SJAC is suitable for sampling of heavy metals, however, further tests need to be done in order to verify this.

### 2.5.5 Improvement of the Limit of Detection (LOD) by thermal insulation and higher sampling flow rates

During preliminary tests with organic compounds (Even, personal communication) and during measurements of heavy metals in ambient air close to a high-way (Vermeulen et al., 1999) it was found that the current configuration of the SJAC in combination with the available analytical systems does not allow for a sufficiently low detection limit (during the highway measurements, at the time resolution of 1 hour, practically all metals were below LOD). For this reason the tests were carried out in order to assess the feasibility of increasing the sampling flow rate and decreasing the amount of condensed water in the SJAC by thermally insulating it. Both of these two options will lead to a better LOD, provided that the sampling efficiency is not compromised.

To reduce the amount of the sample, and thus increasing its concentration by reducing the amount of condensed water, the SJAC (in its total, both the mixing reservoir and the cyclone) was thermally insulated using a 2 cm-thick polyethylene foam. The sampling efficiency was measured using a procedure described in section 2.5.2 using a TSI CPC3761. It was found that insulation does not have any negative effects on the sampling efficiency (virtually 100%) and reduces the amount of collected condensate (sample) by 10 to 40%. An additional advantage of insulation is that the performance of the SJAC (collection efficiency, sample output) becomes more stable.

The effect of higher sampling flow rates on the sampling efficiency was investigated by placing critical orifices for different flow rates. It was found that a maximum of about 50 l/min can be sampled with the SJAC. Higher flow rates are not possible because of the restriction introduced by the cyclone of the SJAC. At flows from 30 l/min and higher care must be taken to avoid the absorbing solution from the wet denuder being blown into the SJAC. This was resolved by tilting the wet denuder. The collection efficiency at high flow rates was determined using ion chromatography (IC). It was not possible to use the CPC because of too high a pressure drop behind the SJAC at high flow rates. The results of sampling efficiency experiments were inconclusive because of apparent presence of ambient aerosol in the test circuit. Because the ambient aerosol concentration is unstable it did not allow for a clear comparison at different flow rates. The tests therefore should be repeated.

#### 2.5.6 Modeling

For a better understanding of the SJAC performance a numerical modeling of the basic processes in the SJAC was made. The supersaturation as a function of steam injection rate was modeled to find the optimum injection rate. The effect of ambient temperature on the supersaturation was also modeled. The growth of droplets in the SJAC was also investigated. The results of the modeling are summarized below:

- a) There is an optimum steam injection rate (or the ratio of mass of sample air to the mass of the injected steam) at which the supersaturation at an instantaneous mixing is maximum. In the real SJAC the mixing is fast due to its turbulent nature. At the current sample flow of about 20 l/min a steam injection rate of 2 to 3 g/min is optimal. At lower or higher flow rates proportionally lower or higher injection rates should be applied.
- b) Below the optimum injection rate, the supersaturation is decreasing fast with decreasing injection rate, conclusion: one should be careful with decreasing the steam injection.
- c) At the optimum and at higher injection rates the supersaturation is in the order of 150-200% (at sample air  $T=20\text{ }^{\circ}\text{C}$ ), high enough to allow activation of the smallest particles (few nanometers in diameter) and a rapid growth of the droplets.
- d) The supersaturation depends on temperature of the sample air, being higher at lower temperatures. Supersaturation at  $20\text{ }^{\circ}\text{C}$  is about 2 times higher than that at  $30\text{ }^{\circ}\text{C}$ . Consequently, high ambient temperature can cause problems if the steam injection is low.

#### 2.5.7 Conclusions

- The SJAC can be used for sampling in background areas, remote areas and even in urban environment as its collection efficiency is virtually 100% at high number concentrations and does not depend on the water-solubility of the aerosol.
- In principle, the SJAC can be used to measure heavy metals in aerosol. Further tests are needed, however, to verify its performance and to study losses in the system behind the cyclone.
- The limit of detection of the SJAC can be reduced by insulation and applying higher flow rates. Further tests are needed, however, to verify its performance at high flow rates.

- The modeling indicates that the optimal steam injection rate for the sampling flow of 20 l/min is 2 to 3 g/min. It is therefore advised to use this injection rate, especially at high ambient temperatures (30 °C and higher). At lower or higher flow rates proportionally lower or higher injection rates should be applied.

## 3. FIELD EXPERIMENTS

### 3.1 Introduction

The abatement strategies to curb particulate matter air pollution require knowledge on the emission factors from different sources. Motor vehicles and in particular the diesel powered ones are known to be one of the major sources of particulate matter. For this reason accurate measurements of emission factors from mobile sources are required. In general, vehicular emissions are determined by testing a vehicle (or an engine) on a dynamometer installation or by direct measurements of road traffic emissions near roads and in road tunnels:

- *vehicle emissions*; The dynamometer tests provide emission measurements of vehicles under standardized conditions. This concerns various driving cycles such as urban and highway cycles. Dynamometer tests are mostly applied to test engine specifications and to measure exhaust emissions of regulated compounds such as NO<sub>x</sub>, CO and PM. Most of our present knowledge on size distribution of PM derives from experiments on dynamometer installations (Maricq et al., 1999; Greenwood et al. 1996; Hall et al., 1998). From these limited number of experiments, it is learned that the number size distributions are usually lognormal with a mode size diameter from about 50 -100 nm. Extrapolation of dynamometer results to actual road traffic emissions is hampered by the following problems. Firstly, it is costly to test a sufficient number of vehicles statistically representative for the whole motor fleet. Secondly, dynamometer tests only constitute exhaust pipe emissions, while PM emitted by road traffic also contains tire wear and re-suspension of road dust. Thirdly, conditions such as dilution rate, air temperature and relative humidity in the dynamometer test may be different from emissions in ambient air. For example, it was observed recently that conditions of strong dilution and high relative humidity favor formation of ultra-fine particles in dynamometer tests.
- *road traffic emissions*; Measurements near roads or in road tunnels involve a more representative sample of traffic related to actual speed, vehicle maintenance and composition of light- and heavy-duty vehicles. Road tunnels provide several advantages relatively to up- and down-wind road measurements, such as higher aerosol concentrations and better-defined dilution rates. Several measurements of aerosol emissions have been carried out in road tunnels (Weingartner et al., 1997; Miguel et al., 1998; Fraser et al., 1998). However, only in few of these studies aerosol size distributions were measured (Weingartner et al., 1997; Kirchstetter et al., 1999).

Results of our measurements at the dynamometer test site at TNO in Delft (the Netherlands) are reported as well as of two campaigns in which the aerosol size distribution was measured in a road tunnel. First, effects of car speed and petrol used on the number of particles emitted are described. Thereafter, the dynamometer test results are compared to road measurements.

### 3.2 Dynamometer measurements

The dynamometer test facility at TNO-WT provides an experimental facility to test the impact of various engine types, fuel types, and driving cycles on particle emissions. In a preliminary investigation size distribution and number of particles emitted were studied as function of car speed and type of petrol used. The exhaust emissions from the tail-pipe of a vehicle on the dynamometer installation is diluted a factor 10 by ambient air. The temperature of this gas mixture is about 35 °C and a relative humidity of 70%. From this gas mixture, the exhaust emissions (size and number) were measured by the SMPS (which was also applied in the Drecht tunnel experiment.) Three types of vehicles were tested: diesel, gasoline and LPG powered

cars. One drove with two different speeds (50 and 100 km/h) in order to compare the effect of different loadings on the emission.

In Figure 3.1 the size distribution of the emitted particles is given. Here, it is seen that the majority of particles emitted by diesel lies around 0.1  $\mu\text{m}$  while most of the particles emitted by LPG cars have diameters below 0.1  $\mu\text{m}$ . Whether the high emissions of the LPG vehicle at 100 km/h is not a result of homogeneous condensation of the emitted hydrocarbons remains to be investigated.

In the next figure (Figure 3.2) the total number of particles emitted is displayed as function of velocity and fuel used. Emission factors for number of particles are expressed in billion per kilometer traveled. First conclusion is that the number of particles emitted by diesel-driven cars is much larger than emitted by petrol-driven cars (both at 50 km/h and at 100 km/h). Even higher is the number emitted by LPG cars at 100 km/h.

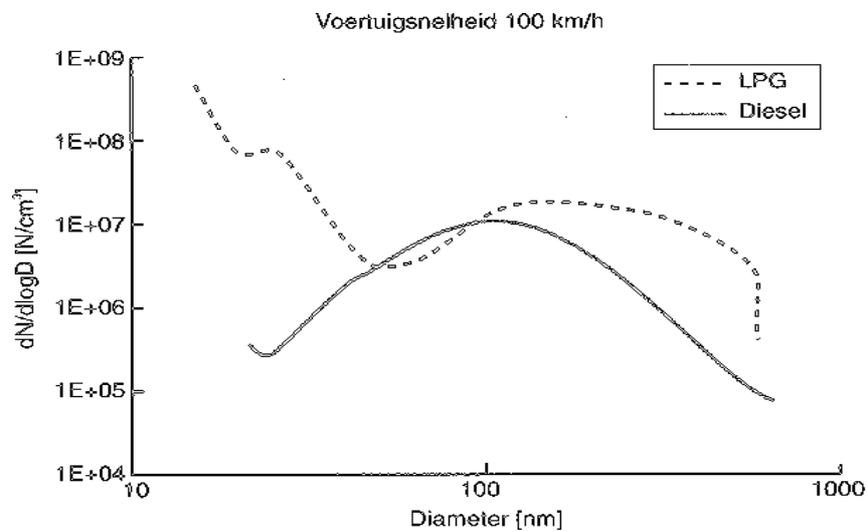


Figure 3.1 Size number distribution at 100 km/h for diesel and LPG vehicles

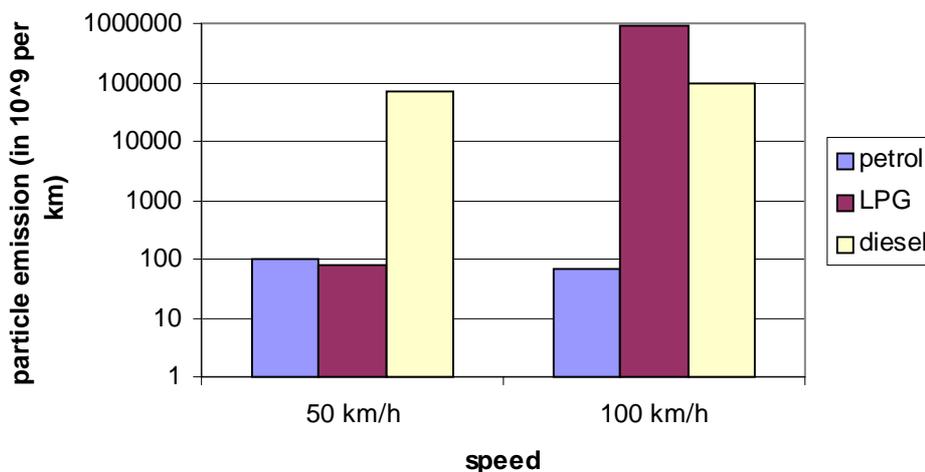


Figure 3.2 Number of particles emitted per kilometer travelled as function of car speed and fuel type

The preliminary conclusions of this experiment are:

- in-situ measurements at dynamometer facilities are well feasible
- the number concentration when driven at LPG is huge at high speed
- representativity of these and similar experiments described in literature should be compared with the emissions at roads and in tunnels. This is done in the next section.

### 3.3 Drecht-tunnel measurements

#### 3.3.1 Introduction

Here, results of two campaigns are reported in which the aerosol size distribution from about 10 nm to 10  $\mu\text{m}$  were measured in a road tunnel. Emission rates of the total number concentration,  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  as well as elemental carbon were determined for light- and heavy-duty vehicles. The results are compared to data measured on a dynamometer test facility. From the findings, it is concluded that dynamometer tests and road measurements are complementary for research to better understand PM and ultra-fine emissions by road traffic.

#### 3.3.2 Measurement set-up

##### 3.3.2.1 Sampling site

The measurements were performed in the Drecht tunnel, which is on the A16 highway, south of Rotterdam in the Netherlands. It is comprised of 4 traffic bores (2 in each direction), which are about 570 m long, 9 m wide and 5 m high. Both light- (LDV) and heavy-duty vehicles (HDV) use the right bore, while only LDV use the left bore. The ventilation in the tunnel is passive, i.e. caused by vehicles driving through the bores.

Two 2-day measurement campaigns were carried out in 1997 and 1998. In a pilot study the size distribution inside the light-duty and heavy-duty bores was measured on two separate days (16/7/97 and 15/7/97, respectively). The sampling was made between 16:30 and 18:30 local time. Dilution rate in the tunnel was not determined during that study and no measurements of the background aerosol were made. During the second campaign sampling was conducted both outside (background) and in the tunnel. The measurements were also made on two days. On the first day (27/5/98) sampling was performed in the right bore with both LDV and HDV, on the second day (28/5/98) the measurements were made in the left bore with only LDV. The sampling was performed between 13:00 and 16:00 on the first day and between 12:00 and 17:00 on the second.

The instruments were installed in a service corridor that lies between the left and right traffic bores of the tunnel. The instruments were sampling through a rectangular opening in one of the doors, which was about 340 m away from the entrance into the tunnel. The distance between the sample inlets and the traffic lane was about 0.5 m. In the second campaign, parallel to the measurements in the tunnel, measurements of background aerosol were carried out outside the tunnel. On the first day the measurements were performed on an upwind side of the highway, 10 m from the road shoulder. On the second day outside air was sampled about 10m above the tunnel entrance.

The volumetric flow rate of air through the tunnel, the so-called "ventilation factor" was determined in the second campaign by using the tracer gas  $\text{SF}_6$ . A known amount of  $\text{SF}_6$  was released 50 m from the entrance in the tunnel and the concentration measured at the sampling point 340 m in the tunnel.  $\text{SF}_6$  was emitted at a rate of 100 ml/min. To facilitate mixing in the tunnel,  $\text{SF}_6$  was mixed with pressurised air and released at a speed of 5 m/sec. The amount of released  $\text{SF}_6$  was determined by weighing the gas cylinder before and after the experiment. The hourly concentration of  $\text{SF}_6$  at the measurement point was determined by sampling the air into Teflon bags and analysing the  $\text{SF}_6$  content in the laboratory by gas-chromatography. The average ventilation factor during the measurements in the right traffic bore (LDV and HDV)

was  $2.1 \pm 0.6 \cdot 10^6 \text{ m}^3/\text{hour}$ . During the 4<sup>th</sup> hour of measurements, the ventilation factor in the left traffic bore (LDV) was  $1.5 \pm 0.4 \cdot 10^6 \text{ m}^3/\text{hour}$ . The average ventilation factor during the whole measurement period in the left traffic bore was  $5.1 \pm 0.2 \cdot 10^5 \text{ m}^3/\text{hour}$ .

Turbulent mixing of air in the tunnel is a prerequisite to measure correctly the emission factors. If the ventilated airflow along the tunnel wall is laminar, there is insufficient mixing of air pollution in the direction perpendicular to the traffic flow. Consequently, sampling near the wall of the tunnel results in erroneous emission factors. Adequate mixing of air pollution in the Drecht tunnel was assessed by measuring CO concentrations in the tunnel at different distances from the wall. From the results, it was learned that there is no significant gradient of CO concentration from 0.1 to 1 m distance from the wall into the tunnel and thus no laminar layer was present. The sampling inlets of the instruments were more than 0.1 m from the wall. Consequently, the measured aerosol concentrations are representative for the whole cross-section of the tunnel and can be used to estimate emission factors.

### 3.3.2.2 Number size distribution

During the first campaign in 1997, the number size distributions in the tunnel were measured using a Scanning Mobility Particle Sizer - SMPS (Model 3934, TSI Inc.) and Electric Aerosol Analyser - EAA (Model 3030, TSI Inc.). The SMPS consisted of an electrostatic classifier (EC3071, TSI Inc.) connected to a particle counter (CPC3022, TSI Inc.). The SMPS measured the size distribution in the range of 14 – 800 nm in diameter. The majority of traffic-emitted particles have sizes smaller than 100 nm and therefore, the integrated number concentration measured with the SMPS provides also a good estimate of the *total* aerosol number concentration. The EAA size range was 20 – 1000 nm in diameter

In the second campaign in 1998, two SMPS systems were used with a size range of 7 - 300 nm in diameter. These systems consisted of a DMA (EC3761, TSI Inc) in combination with a CPC (3025, TSI Inc.) inside the tunnel and a CPC (3010, TSI Inc.) outside the tunnel. The air flow of the systems were controlled by digital mass flow-controllers (5850S, Brooks Instrument BV). It is known that the accuracy of the measurements with the SMPS is sensitive to the precision of its flow settings. The precision of the flow controllers used in this study was better than 1%. The scan rates of the SMPS were 300 sec per scan and the software version 2.4 was used to invert the data. Air was sampled through a 1 m of 0.65 mm i.d. copper tubing.

Prior to the measurements, the SMPS systems were calibrated in laboratory with monodisperse PSL (latex) aerosol. In addition, both systems were inter-compared by measuring laboratory-generated ammonium sulfate aerosol with an average diameter around 50 nm. The integrated number concentrations measured with the two SMPS did not differ by more than 5% during the 8-hour experiment. The accuracy of one of the SMPS systems was also tested during several experiments in which it was inter-compared with the condensation particle counters and other aerosol spectrometers.

### 3.3.2.3 Mass size distribution

During the second campaign in 1998, Berner low-pressure cascade impactors (BLI) were used to measure the mass size distribution of aerosol in and outside the tunnel. The BLI used in the tunnel had 10 stages with cut-off sizes ranging from 15 nm to 8  $\mu\text{m}$  in aerodynamic diameter. The BLI used outside the tunnel had 8 stages, ranging from 60 nm to 8  $\mu\text{m}$  in aerodynamic diameter. In both impactors the stages were arranged in such way that the cut-off size of each stage was about 2 times larger than the cut-off of the proceeding stage. The sampling flow of the 10-stage impactor was 25 l/min, and of the 8-stage impactor 28 l/min. No inlet tubing was used to collect particles. In both impactors, aerosol was collected on aluminium foils. Before and after collection the foils were weighed at controlled relative humidity (40-45%) and temperature ( $20 \pm 1^\circ\text{C}$ ). The accuracy of weighing is 2  $\mu\text{g}$  per each impactor stage. On each day of the measurements one 4-hour sample was collected both in- and outside the tunnel.

### 3.3.2.4 Elemental carbon

Concentration of elemental carbon in aerosol both inside and outside the tunnel was measured using quartz filters (QM-A). Prior to the measurements the filters were pre-fired at 750 °C for 2 hours in order to remove any possible carbonaceous contamination. The blank of the filters was determined by analyzing 2 non-handled and 4 handled blank filters. Handling consisted of loading and unloading the blank filters into the filter holder without performing actual sampling. The average blank concentration for EC (in mg of carbon per cm<sup>2</sup> of the filter surface) was found to be 0.1 ± 0.2 mg/cm<sup>2</sup>. The variation of the blank concentrations between individual filters was within the error of the analysis. No observable effect of the handling on the value of the blank was found. All measurements reported here were corrected for blank values.

Sampling was performed by placing the filters into a stainless steel filter holder. The sampling flow rate was 10 l/min. No inlet tubing was used. On each day of the measurements one sample was taken in the tunnel and one sample was taken outside the tunnel. After the sampling, the filters were separately transported in hermetically closed Petri dishes. The filters were analyzed at Sunset Laboratory (Oregon, USA) by thermal method with a correction for charring artifact.

### 3.3.2.5 Calculation of emission factors

Emission rates can be determined per vehicle-kilometer-traveled (Chang et al., 1981) or per kg of used fuel (Fraser et al., 1998; Kirchstetter et al., 1999). In this study emission rates were determined per vehicle-kilometer. Emission rates were determined by comparing the concentrations measured inside and outside the tunnel. The emission rate of a light duty vehicle in mg/km is determined using the following formula:

$$F_1 = \frac{\Delta C_1 * W_1}{N_1 * L} \quad (1)$$

in which  $\Delta C_1$  is the increase of concentration in the LDV-traffic bore of the tunnel relative to the outside air;  $W_1$  is the volumetric flow rate through the bore;  $N_1$  is the number of vehicles passing through the bore per unit time and  $L$  is the distance between the entrance to the tunnel and the point of measurements (340 m).

After the emission rates of LDV have been determined, emission rates from HDV are determined, using the following formula:

$$F_2 = \frac{\Delta C_2 * W_2}{N_2 * L} - \frac{F_1 * N_1}{N_2} \quad (2)$$

in which  $\Delta C_2$  is the increase of concentration in the HDV-traffic bore of the tunnel relative to the outside air;  $W_2$  is the volumetric flow rate through the bore;  $N_2$  is the number of HDV passing through the bore per unit time,  $N_1$  is the number of LDV and  $L$  is the distance between the entrance to the tunnel and the point of measurements.

## 3.3.3 Results and discussion

### 3.3.3.1 Number size distribution

The size distributions measured during both campaigns are shown in Figures 3.3 and 3.4. The shape of the distributions is similar on both campaigns in 1997 and 1998. The remarkable feature of the size distributions measured in the tunnel is that they are characterized by a continuous increasing number of particles towards the smaller sizes. It is noted that both SMPS and EAA indicate such spectral shape, which excludes the possibility of instrumental artifact. This spectral feature differs the measured distributions on dynamometer installations. These size distributions are usually fairly log-normal in shape with the mode size between 30 and 100 nm in diameter (Maricq et al., 1999; Greenwood et al. 1996; Hall et al., 1998).

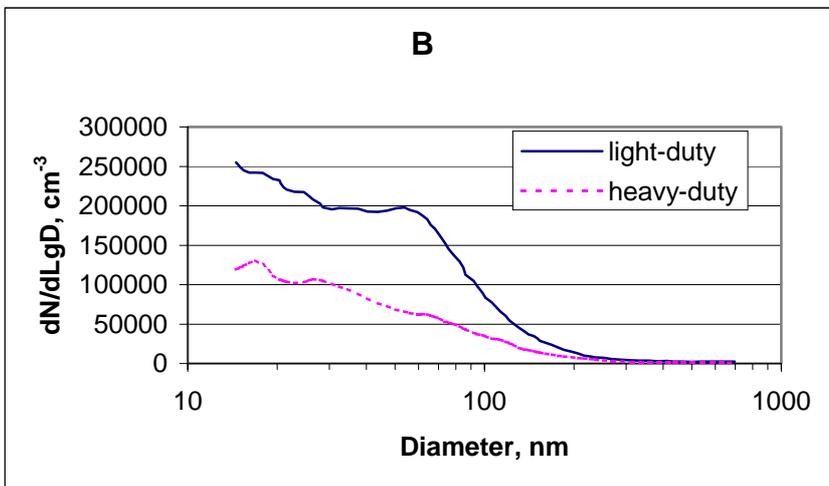
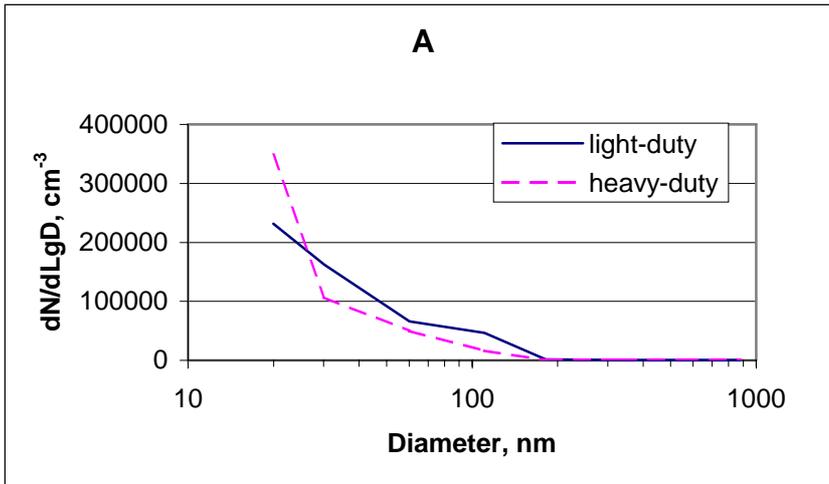


Figure 3.3 Average number size distributions measured in the tunnel during the first campaign. (A: distributions measured with the SMPS, B: distributions measured with the EAA).

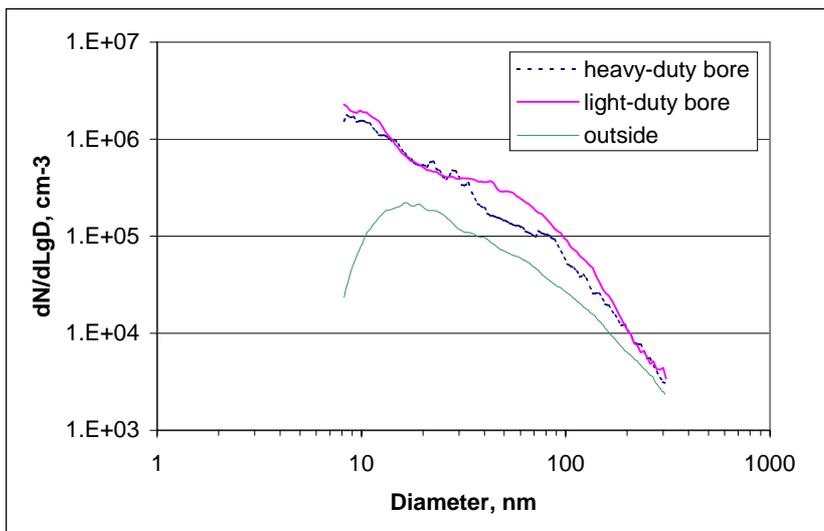


Figure 3.4 Average number size distributions measured in and outside the tunnel during the second campaign.

These reports are confirmed by our measurements at the dynamometer test site at TNO-WT at Delft. Two mechanisms are proposed to explain the observed differences between the measured size distributions in the tunnel and those measured on the dynamometer installations. One mechanism may be the loss of the smallest particles due to coagulation or diffusion in the (confined) test-bank installations. The other mechanism may be the production of new ultra-fine particles in the road tunnel due to homogeneous nucleation of gases (like organic vapors, sulfuric acid, ammonia and water) in ambient air. Nucleation of ultra-fine particles may also occur during conditions of a high dilution ratio and high relative humidity. These possible mechanisms are tested in the second campaign.

During this campaign the integrated (total) number concentration in the right and the left traffic bores were compared with ambient air concentrations. In both bores the number concentrations were increased relatively to ambient air by  $5 \cdot 10^5 \text{ cm}^{-3}$ . As shown in Figure 3.3 and 3.4 the increase in number concentration is mostly due to the smallest particles. This is the size range where the deviation with dynamometer results is observed. This suggests that the results from the dynamometer tests underestimate the number of ultra-fine particles emitted by road traffic.

### 3.3.3.2 Mass size distributions

Figure 3.5 shows a comparison of the mass size distributions measured with the BLI in and outside the tunnel. The mass size distributions show that the traffic has contributed not only to the smallest, ultra-fine particles, but also to the particles larger than 100 nm in diameter. The mass size distributions measured with the BLI are used to estimate  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  concentrations. The  $\text{PM}_{2.5}$  mass concentrations in the HDV/LDV and LDV traffic bores were increased relatively to the outside air by 28.8 and 18.3  $\mu\text{g}/\text{m}^3$ , respectively. The increase in  $\text{PM}_{10}$  was, respectively, 39.2 and 25.9  $\mu\text{g}/\text{m}^3$ .

### 3.3.3.3 Elemental carbon aerosol

Elemental carbon (EC) concentration in the HDV/LDV traffic bore was  $15.0 \pm 1.7 \mu\text{g}/\text{m}^3$ , while the concentration outside the tunnel was  $0 \pm 3.2 \mu\text{g}/\text{m}^3$ . During measurements in the LDV traffic bore, the concentrations of EC in and outside the tunnel were  $25.8 \pm 3.1 \mu\text{g}/\text{m}^3$  and  $2.0 \pm 1.7 \mu\text{g}/\text{m}^3$ , respectively. The EC concentrations in the tunnel were increased several orders of magnitude relatively to the outside air. A comparison with the  $\text{PM}_{10}$  concentrations shows that the elemental carbon fraction of the emitted particles in the HDV/LDV bore is  $0.4 \pm 0.1$ , while in the LDV bore its fraction is  $0.9 \pm 0.1$ .

### 3.3.3.4 Emission factors

Emission factors were calculated using the results from the second campaign and Eqs. 1 and 2. The emission rates of the LDV estimated in Eq. 1 are applied in Eq. 2. However, during 3 hours the average speed of LDV in the left bore was about 30 km/h lower than the speed of LDV in the right bore. Therefore, the emission rate of LDV for the total number concentration is estimated from the 4<sup>th</sup> hour measurements in the left bore when LDV traffic conditions were equal to the right bore LDV. It is not possible to apply this procedure for  $\text{PM}_{2.5}$ ,  $\text{PM}_{10}$  and EC, as these measurements are based upon 4-hour sampling. Due to the average lower speed of LDV in the left bore as compared to LDV in the right bore, emission factors of LDV are underestimated and therefore, it is expected that emission factors of HDV are over-estimated in our study. Based upon emission factors derived from dynamometer tests in the range from 70 to 100 km/h (HBEFA: Handbuch Emissionsfaktoren des Strassenverkehrs 1999), it is expected that the LDV emission factors in the right bore are underestimated with 10-20% and hence the HDV overestimation is in the same order.

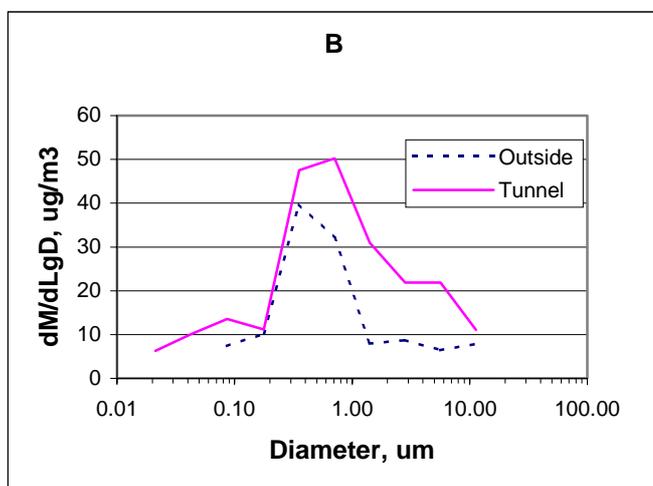
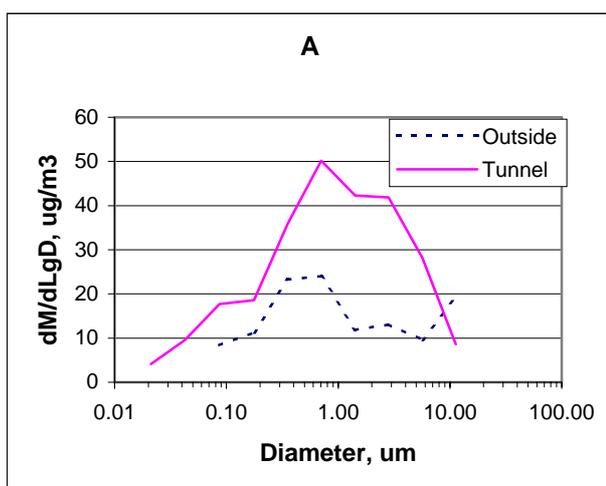


Figure 3.5 Comparison of average mass size distribution measured in the traffic bores and outside the tunnel on 27/5/98 (A) and 28/5/98 (B).

Taking into account these aforementioned aspects, the emission factors for total number concentration,  $PM_{2.5}$ ,  $PM_{10}$  and elemental carbon were calculated using Equations 1 and 2. It is concluded that the total number and elemental carbon emission rates for HDV are 36 times higher than the emission rates for LDV. HDV emit per kilometer about 20 times more  $PM_{2.5}$  and  $PM_{10}$  than the LDV. These latter emission factors are consistent with  $PM_{2.5}$  and  $PM_{10}$  derived from dynamometer testing results.

Emission factors for number of particles emitted by motor vehicles measured on dynamometer installations vary greatly between different studies and for different vehicles. Greenwood et al. (1996) reported emission factors at 120 km/h of  $1.1 \cdot 10^{11}$  to  $7.4 \cdot 10^{13}$   $km^{-1}$  for gasoline powered passenger cars, and  $2.4 \cdot 10^{13}$  to  $1.1 \cdot 10^{14}$   $km^{-1}$  for diesel powered cars. Hall et al. (1998) reported emission factors of  $3.6 \cdot 10^{13}$  -  $6.4 \cdot 10^{13}$   $km^{-1}$  for gasoline cars and  $1.1 \cdot 10^{14}$  to  $1.9 \cdot 10^{14}$   $km^{-1}$  for diesel passenger cars. These factors are about a factor of 10 lower than the factors found in this study for light-duty vehicles ( $7 \cdot 10^{14}$   $km^{-1}$ ). The higher emission rates in our study are at least partly explained by the presence of a substantial number of particles at around 10 nm in diameter, which were not observed in the above mentioned dynamometer tests.

Kirchstetter et al. (1999) determined emission rates of aerosol number measured in a road tunnel in California. The emissions were reported per kilogram of fuel used. Using the average fuel

consumption and fuel properties, given in Kirchstetter et al. (1999), the emissions per kg fuel were recalculated to emission per km travelled. The emission factors for light- and heavy-duty vehicles found in that study were, respectively,  $4.0 \cdot 10^9$  and  $2.5 \cdot 10^{12} \text{ km}^{-1}$ . These factors are substantially lower than those found in our study and dynamometer tests. The emission rates for  $\text{PM}_{2.5}$  found by Kirchstetter et al. are, in contrary, comparable to our measurements: 1 g/km for HDV and 0.01 g/km for LDV. The differences in emission rates of aerosol number may be explained by different emission characteristics of vehicles at our site and in California. The other reason may be the poorer sensitivity of the CPC3670 used by Kirchstetter et al. and/or particle losses in 46m long sample-line tubing used in their study.

### 3.3.4 Conclusions

Emission rates of health-related aerosol characteristics as the total number concentration,  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$ , as well as elemental carbon were determined for both LDV and HDV. The HDV emit 36 times more particles (in number) per kilometer-travelled than the LDV. Emission rates from HDV for  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  are about 20 times higher than those from LDV. The HDV emit about 10 more elemental carbon than the LDV. The data for  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  are consistent with emissions factors derived from dynamometer testing for “high-way” traffic.

The number of particles emitted in the road tunnel and on a dynamometer installation were measured in the diameter range from 8 nm to 10  $\mu\text{m}$ . From the experimental data it was concluded that size spectra emitted by actual road traffic have a significant larger proportion of nanometer-sized particles. This finding suggests production of new particles in ambient air by homogeneous nucleation. Hence, dynamometer testing seems to underestimate the emission factors of the total number of particles emitted by road traffic. It is concluded that monitoring actual road traffic emissions and dynamometer testing are complementary to gain more insight on ultra-fine particles emissions by traffic. The latter provides an experimental facility to test the impact of various engine types, fuel types, driving cycles on particle emissions, while the former provides information on the impact of actual emissions in ambient air.

## 3.4 Pilot measurements with a moving system of the spatial variation of PM in Nijmegen

### 3.4.1 Introduction

Traffic emits large quantities of ultrafine particles and contribute substantially to the PM mass and number (Earnshaw and Booker, 1998). Because of the large spatial variability of traffic intensity within a city, the traffic contribution to the number and mass concentration is expected to be spatially inhomogeneous.

The direct daily exposure of city inhabitants to PM originating from traffic prevailing in their living area is difficult to assess. Urban networks are usually built up by stationary equipment measuring over prolonged periods. This yields a quantitative impression of the prevailing average air concentrations in a city. However, local troublesome situations, the so-called “hot spots”, will not be discovered in the network’s data. A pilot study is described here in which PM measurements have been performed using a set of instruments installed on a moving vehicle in the city of Nijmegen located in the eastern part of the Netherlands. In this area a small network of 8 stations measuring  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  was operated by ECN (Vermeulen et al., 1999). Results show small spatial variation.

### 3.4.2 Experimental set-up

The measurements were performed with an ultra-fine condensation particle counter, CPC 3025 (TSI Inc.) and an optical particle spectrometer, LAS-X (PMS Inc. Modified with new electronics package from DMT Inc.). The CPC measures number concentration of particles with diameters larger than approximately 3 nm. The LAS-X measures concentration of particles with

diameters between 0.1 and 10  $\mu\text{m}$  in 15 size bins. The difference between the number concentration measured with the CPC and the integrated number concentration measured with the LAS provides the measure of the number concentration of ultra-fine aerosol, particles smaller than 100 nm in diameter. The LAS-X provides number size distributions, which can be converted, using the average size of each size bin, to volume size distribution. The volume distribution, in turn, can be converted to the mass size distribution using the density of the particles, which usually has to be assumed. In other words, the LAS measurements provide information about the size range where most of the particulate mass resides, which can not be deduced from conventional filter measurements.

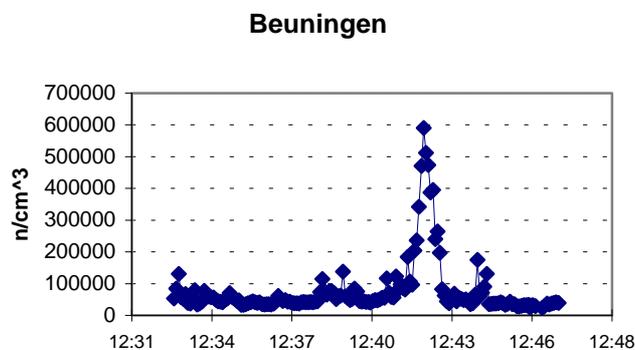
To study the spatial variability of the aerosol number and volume concentrations in urban atmosphere, the CPC and the LAS-X were installed into a van. The instruments were placed inside the van's cabin, with the sampling inlets being at the roof of the cabin, facing the front of the vehicle (about 2.5 m above the ground). No influence of the van's exhaust on the measurements was observed under normal driving conditions. The instruments were sampling through approximately 1.5 meters of 1/4" copper tubing. The sampling flow of the CPC was 1.5 l/min, while that of the LAS was 0.3 l/min. To allow for better spatial resolution of the measurements, the time resolution of the instruments was set to 5 seconds. The position of the vehicle was recorded with a GPS. Also notes were taken of the situation on the road to help interpretation of the measurements.

Several (overlapping) tracts were made through the city. Neighborhoods like industrial terrain, busy roads, quiet residential areas, downtown, quiet streets were traversed. For analysis of the data the principle of ensemble averaging has been applied. This gives the possibility to estimate number and mass distribution of PM on location frequently found in a town (like crossings or residential areas). To this purpose each measuring point in the data set has been classified according to its local property: (busy) streets with through traffic, streets with relatively little traffic, crossings and residential areas. The distinction between busy and quiet street was based on mean daily traffic intensity data provided by the City of Nijmegen. Heavy traffic streets are characterized by  $14.4 \cdot 10^3$  cars per day (at the highest), quiet streets less than  $6.6 \cdot 10^3$  cars per day while residential areas a maximum of  $3.3 \cdot 10^3$  cars per day are passing through.

### 3.4.3 Results

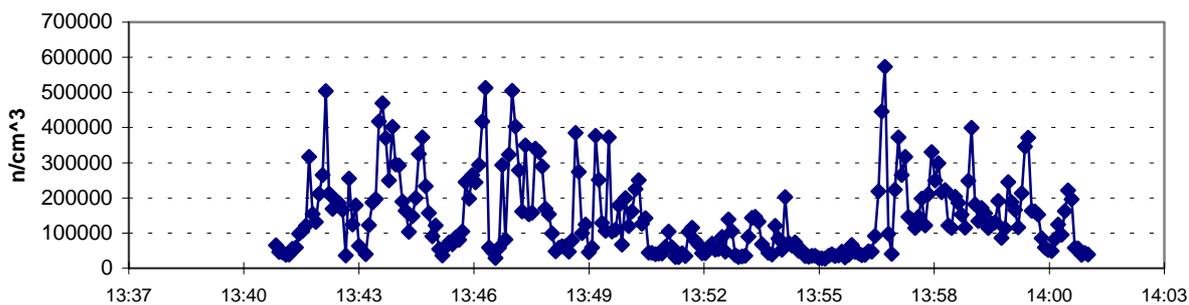
#### 3.4.3.1 General considerations

To obtain a first impression of the number variability due to the nearby traffic the on-line measurements at four representative sections are shown in Figures 3.6. Only the measurements of the CPC are given here because the number concentration is largely determined by particles with a diameter of less than 100 nm (lower detection limit LAS is 0.1  $\mu\text{m}$ ). In table 1 the statistics for these sections are summarized.



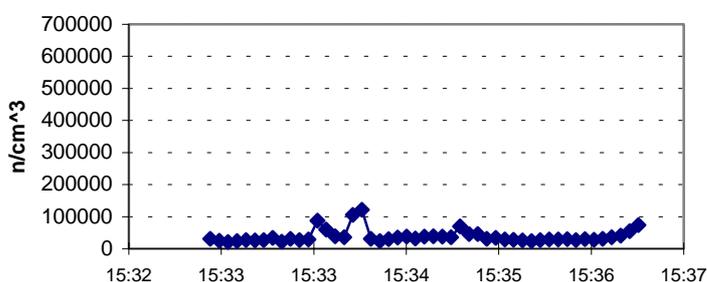
(a)

roundabout/Berg en Dalseweg/Tooropstraat



(b)

residential area



(c)

Figure 3.6 On-line measurement results at three sections: (a) Beuningen (includes the period behind the bus); (b) roundabout and traffic jam (up to 13:50), Tooropstraat (fairly quiet driving lane, up to 13:57); (c) quiet residential area

Table 3.1 Average, standard deviation, extreme values and difference of number ( $\cdot 10^3/\text{cm}^3$ ) for selected tracts

Number of Particles ( $10^3 \text{ cm}^{-3}$ )	average	standard deviation	max	min	max-min
Beuningen	76	90	590	28	463
Beuningen (without bus)	59	51	395	23	372
Berg en Dalseweg	185	127	513	29	484
Tooropstraat	84	57	250	31	219
Residential area	38	20	121	21	90

Figure 3.6a displays a high maximum value but a moderate average in the neighboring municipality of Beuningen. The reason is that for a period of about 50 s the measurement van drove at the rear end of a transportation bus. The maximum concentration is near  $600 \cdot 10^3 \text{ cm}^{-3}$ . Discarding this period the average number becomes around  $59 \cdot 10^3 \text{ cm}^{-3}$ , comparable with another neighboring municipality (Weurt). Figure 3.6b shows the influence of the slow traffic on a roundabout characterized by the second maximum at 12:42. The acceleration and slowing down of cars in a traffic jam can be seen in the period from 13:44 up to 13:50. Number concentrations may reach levels as high as  $500 \cdot 10^3$  probably due to measurements within undiluted plumes. However, while driving in the same street levels may also drop down to  $40\text{--}50 \cdot 10^3 \text{ cm}^{-3}$ . The average level for the Berg and Dalseweg is  $100 \cdot 10^3 \text{ cm}^{-3}$ . The moment (at 13:50) that the van takes the corner into the Tooropstraat (a relatively quiet street) is clearly marked: the number concentration drops almost immediately to an average of  $50 \cdot 10^3 \text{ cm}^{-3}$ . The

same effect is noted at 13:57 in the same figure; turning back into the Berg en Dalseweg concentrations and variability rise again remarkably. In Figure 3.6c the ride in a residential area in Nijmegen is shown; clearly the absence of traffic is reflected: maximum numbers hardly rise above  $100 \cdot 10^3 \text{ cm}^{-3}$  with an average level of  $38 \cdot 10^3 \text{ cm}^{-3}$ .

From the figures and table it is suggested that the sections with high numbers of PM can be attributed to streets or situations where many vehicles are passing. Standard deviation and the differences between maximum and minimum level as measured in the same street/section indicate that streets/section with heavy (often slowly riding) cars can be distinguished from streets/section in quiet neighborhoods with less traffic. This feature will be used in the next paragraph in order to estimate average number and mass concentrations characteristic for specific situations.

### 3.4.3.2 Number and volume variability

In this paragraph the result is discussed of the averaging for the different areas that were traversed. In Figure 3.7 the number concentrations are given for the different classes.

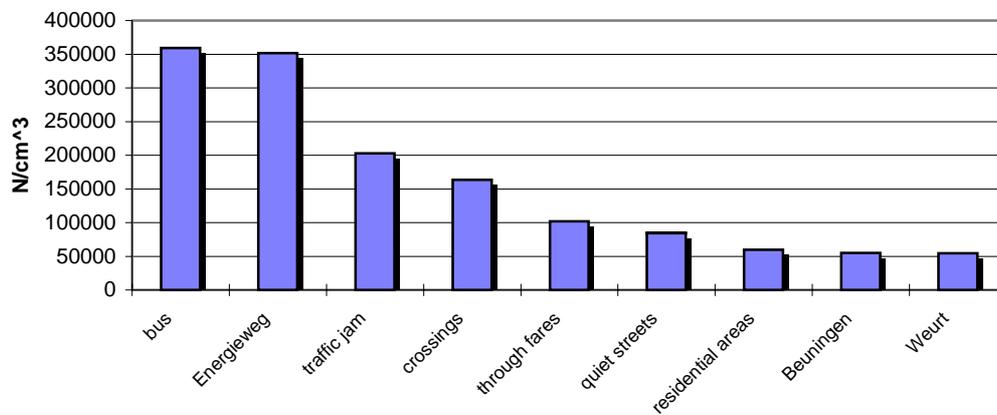


Figure 3.7 Numbers of particulate matter after partitioning into the different classes

As expected, the numbers of PM are lowest in the quiet municipalities of Beuningen and Weurt and in the residential areas with less traffic circulation: average particle numbers are around  $50 \cdot 10^3 \text{ cm}^{-3}$ . Increasing numbers are found on roads with relatively little traffic ( $80 \cdot 10^3 \text{ cm}^{-3}$ ), through fares ( $100 \cdot 10^3 \text{ cm}^{-3}$ ) and on crossings ( $160 \cdot 10^3 \text{ cm}^{-3}$ ). The Energieweg and driving behind the transportation bus are characterized by the highest numbers: from  $200 \cdot 10^3 \text{ cm}^{-3}$  (downtown traffic jam) up to  $350 \cdot 10^3 \text{ cm}^{-3}$  (at the Energieweg and behind the transportation bus).

Figure 3.8 displays the average number as measured by the CPC versus volume (LAS-X) for the different classes.

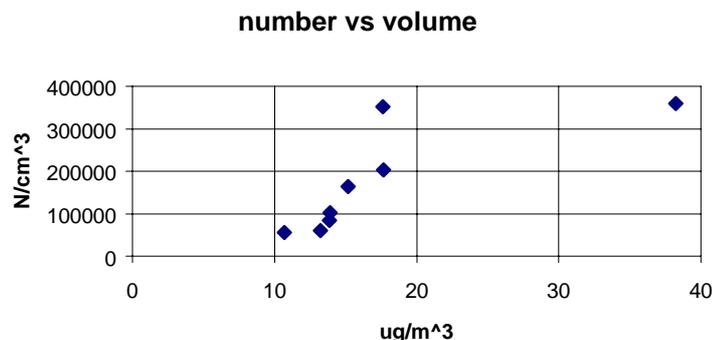


Figure 3.8 Number concentrations vs. volume for the different classes

Clearly, the sharp rise in number concentration, from  $50 \cdot 10^3$  up to  $200 \cdot 10^3 \text{ cm}^{-3}$  (starting with the residential areas, then quiet streets, through fares, crossing up to the class of the traffic jam) is not accompanied by a proportional increase in volume (and hence mass). Apparently, the rise in numbers is largely due to the ultrafine particles ( $0.1 \mu\text{m}$ , not measured by the LAS-X). Also, it can be seen that the average background contribution to the city levels of PM lies between  $10$  and  $20 \mu\text{g}/\text{m}^3$ , which are comparable to the values measured in the network (Vermeulen et al., 1999). It is notable that the LAS-X measurements show that most of the aerosol volume (and thus mass) is below  $2.5 \mu\text{m}$ . The measurements behind the transportation bus, however, indicates that the bus emitted a substantial fraction of mass between  $2.5$  and  $10 \mu\text{m}$ . This indicates that the traffic contributes mostly to  $\text{PM}_{2.5}$ , though some of (heavy) vehicles may also contribute to the large size fraction.

Considering the volume size distribution as measured by the LAS-X it appears that the volume in the size range  $100\text{-}200 \text{ nm}$  is  $34\%$  higher on through fares with intense traffic than in the residential areas with little traffic. The difference in the size ranges  $200 - 500 \text{ nm}$  and  $500 - 1000 \text{ nm}$  is less than  $7\%$ . This indicates that the traffic contributes mostly to the smallest particles (even in volume terms), while the lower differences at larger sizes are explained by the large contribution of the background aerosol (not from the city / traffic). Most of the volume (and consequently mass) is in the large particles, i.e. the traffic contribution is masked by the background and would be difficult to find using integrated measuring techniques such as filters. Most particles are found by the LAS-X in the range  $100\text{-}200 \text{ nm}$ . The event of the transportation bus shows that the emitted particles can be between  $2.5$  and  $10 \mu\text{m}$ , i.e. depends on the type of engine used.

### 3.4.3.3 Gradient

In Figure 3.9 an illustrative change in number of PM is shown when driving from a residential area into a busy street (Berg en Dalseweg).

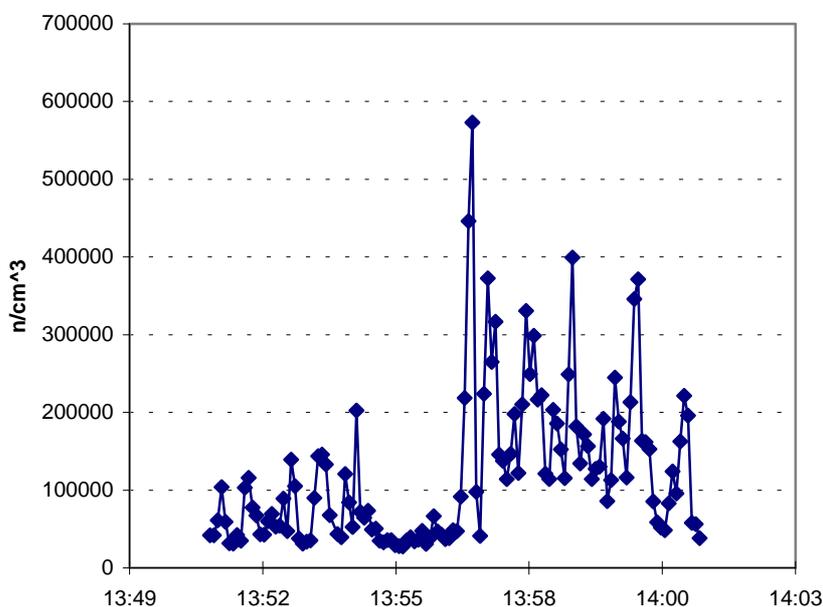


Figure 3.9 *Number concentration change when driving from a residential area into a street with heavy traffic*

Taking the average number concentration and volume within the residential area and at the busy street in this example it was calculated that the number concentrations increase by a factor of 3

while the volume (mass) increases by a factor of 2 (within a distance of some 10-30 m) when going from the residential area into a street with heavy traffic.

#### 3.4.3.4 Conclusions

Several studies show a definite connection between daily variations in the volume or number of breathable particles in the air and effects on the respiratory system and even mortality. In this study high-resolution intraurban particles measurements (CPC, LAS-X) were performed by driving through the city of Nijmegen with a moving van. The aim was to measure the spatial variations of aerosol concentration in urban air on an ordinary working day yielding an estimate of the actual direct exposure of city inhabitants 'in the street' to particulate matter.

The maximum number concentrations observed in the data set are measured behind a transportation bus or when lining up in a traffic jam. Diesel-driven vehicles especially emit large amounts of particles - the emissions of diesel cars being 10-30 times greater than those from petrol-driven. As expected, (in decreasing order) high numbers are observed during the (slow) passage of crossings and roundabouts, at roads with heavy traffic, low intensity roads. The lowest numbers are measured in residential areas with limited vehicular traffic. In cases of high intensity of traffic (jam, crossings, through traffic roads) high number of relatively smaller particles are found; large particles are emitted by the transportation bus and measured, to a lesser extent, in residential areas.

A clear gradient going from a residential area into a busy road is observed: for one example the number concentrations increase by a factor 3 over 30 meters. The strong gradient observed indicates that the traffic contribution to the  $PM_{2.5}/PM_{10}$  mass would be clearly observable only within some 30 m from the street. At greater distances from the source the contribution becomes less substantial in comparison to the background concentrations. If PM samplers employed in a monitoring network are placed more than 50 m away from the "hot spots", this means that they would not observe/indicate the presence of such hot spots. This may be an explanation that the  $PM_{2.5}$  monitoring network in Nijmegen indicated no or little spatial variation of PM mass within the city (Vermeulen et al., 1999)

These preliminary measurements were done only once and results should therefore be considered with care. Nevertheless, the tendency of the findings observed here can be rather well accounted for. Naturally, by repeating the experiment, on various times of the day and under different meteorological conditions, data robustness and representativity improves. In this way it may even provide a methodology to discover problematic 'hot spots' within a city more accurately.

### 3.5 Ultra-fine particle monitoring in Amsterdam and Petten

#### 3.5.1 Introduction

Within the framework of a EU-funded project ULTRA-2 total aerosol number concentration and aerosol number size distribution in the size range of 8 nm to 10  $\mu$ m have been monitored at an "urban-background" site in Amsterdam during a period of 7.5 months (1.11.98 till 18.6.99). The monitoring was made in connection with an epidemiological study aimed to assess the health effects of urban air pollution, especially the effects of aerosol number and size. The results of this epidemiological study are currently being interpreted by LUW (Wageningen Agricultural University, WAU).

In parallel to the ULTRA-2 monitoring, during a shorter period of time (23.12.98 till 31.3.99), measurements of total aerosol number concentration and aerosol size distribution in the size range 8 nm to 0.3  $\mu$ m have been made at Petten, on the territory of ECN. ECN is located in a rural agricultural area near the coast distant from large cities and busy roads. Measurements at ECN, thus, provide characteristics of the "background" aerosol, unaffected by urban sources.

Here, the major aerosol characteristics observed during this study both at the urban Amsterdam site and the rural background site at ECN are discussed. The differences in the observed characteristics provide insight into the contribution of traffic to urban aerosol.

### 3.5.2 Methods

#### 3.5.2.1 Sampling sites

The sampling site in Amsterdam was located in the southeastern border of the city (Figure 3.10). The instruments were placed in a ventilation compartment on the roof of a 2-story building (retirement home). The site was chosen such that it was not directly affected by local sources and was at least 300 m away from major streets. The second set of instruments was installed at ECN, Petten. Petten is located about 50 km to the north-northwest from Amsterdam. The instruments were sampling through a window in a laboratory, located on the second floor of a 2-story building.

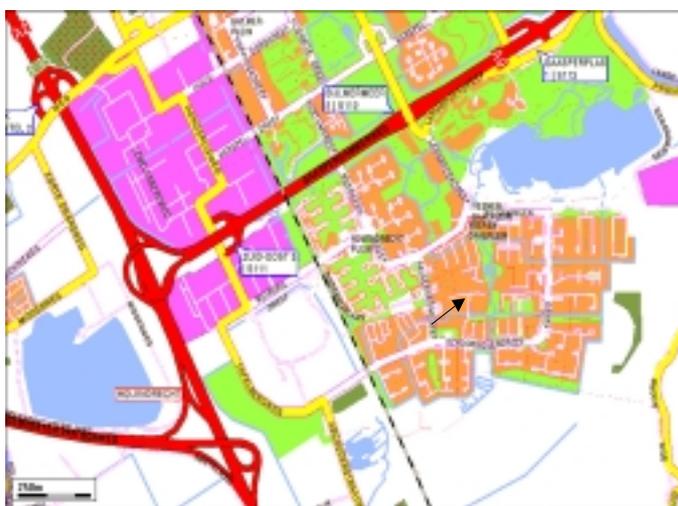


Figure 3.10 *The sampling site location (see arrow) in the Southeast of Amsterdam*

#### 3.5.2.2 Instrumentation

##### *Amsterdam*

An SMPS, CPC3022 (TSI Inc.) and a LAS-X (PMS inc.) were used in Amsterdam. The CPC measured the integrated (total) aerosol number concentration of particles larger than about 8 nm in diameter. The sampling flow of the CPC was 0.3 l/min. The SMPS consisted of a DMA (EC3071, TSI Inc) and a CPC3010 (TSI Inc.). The SMPS was measuring aerosol number size distribution in the size range 8 – 265 nm. The sampling flow of the SMPS was 1 l/min, the sheath flow rate was 10 l/min. The LAS-X was measuring particles in the diameter range 265 nm – 10  $\mu$ m. The sampling flow of the LAS-X was 0.3 l/min.

The flows of the SMPS and the CPC were controlled with digital mass flow controllers (Brooks BV) such that the accuracy of the flows was constantly within 1%. The use of flow controllers improved the accuracy of concentration measurements by about a factor of 3. The flows were logged every minute by a PC. The flow of the LAS-X was monitored with a flow meter and logged with a PC. The logging of the flows allowed remote control (see below) of the integrity of the flows such that a fast action could be taken in case of malfunction which drastically reduced data loss.

The instruments were sampling through a small hole in the wall at a height of 1 m from the roof, 10 m above ground level. The sampling line consisted of about 30 cm  $\frac{1}{4}$ " copper tubing. The tubing was then split into three lines, all of which were made of  $\frac{1}{4}$ " copper tubing. A 10 cm line

lead to the CPC, a 20 cm line lead to the LAS-X and a 60 cm line was lead to the SMPS. The data were corrected for diffusion losses in the tubing.

The instruments were operated and the data were logged using homemade text-window based software. Unlike commercially available software the homemade software was more stable and allowed remote control of the operation. The SMPS were sampling at a rate of 1 sample per 6 min. The CPC and the LAS-X were sampling at a rate of 1 sample per minute. The operation of the instruments was checked on daily basis using a remote control (see below).

The collected data were then hourly averaged. One hourly average was made only if at least 66% of valid data were available within that hour, i.e. the instruments were normally functioning during at least 40 min of the hour. In total 4800 to 5100 of valid hourly averages were collected during the campaign. Only about 10% of the data were lost.

#### *Petten*

In Petten the CPC3025 (TSI Inc.) was used to measure the integrated number concentration of particles larger than 5 nm in diameter during 23.12.98 – 5.1.99 and 8.3.99 – 31.3.99. The SMPS, consisted of DMA (EC3071, TSI Inc.) and CPC3025 (TSI Inc.). The SMPS measured aerosol size distribution in diameter range 8 to 300 nm during 5.1.99 – 4.3.99. The instruments were sampling through 1m of 1/4" copper tubing. The sampling flows were 1.5 l/min. The sheath flow of the SMPS was 10 l/min. All flows were controlled and logged using digital flow controllers (Brooks BV).

The SMPS were measuring at a rate of 1 sample per 6 min, and the CPC at a rate of 1 sample per minute. The data were then hourly averaged according to the criteria used for the Amsterdam data set. Because the instruments were used on basis of their availability, the percentage of the available data is about 60% (1350 hours in total).

#### 3.5.2.3 Sampling protocol

The instruments were operated under quality control protocol developed within the ULTRA-2 project. The operation of the instruments in Amsterdam was remotely controlled on daily basis by logging onto the remote computer using a modem connection. The flows were checked to be within 1% of the set values. The reading of the three instruments should not differ from each other by more than 30% during 3 consecutive hours. If these criteria were not met, an experienced operator inspected the instruments at the site within a short time after the deviations were observed. In addition to the daily control, weekly maintenance of the instruments was made, during which the instruments were calibrated with monodisperse PSL aerosol, the flows were checked and sampling lines was checked for leaks.

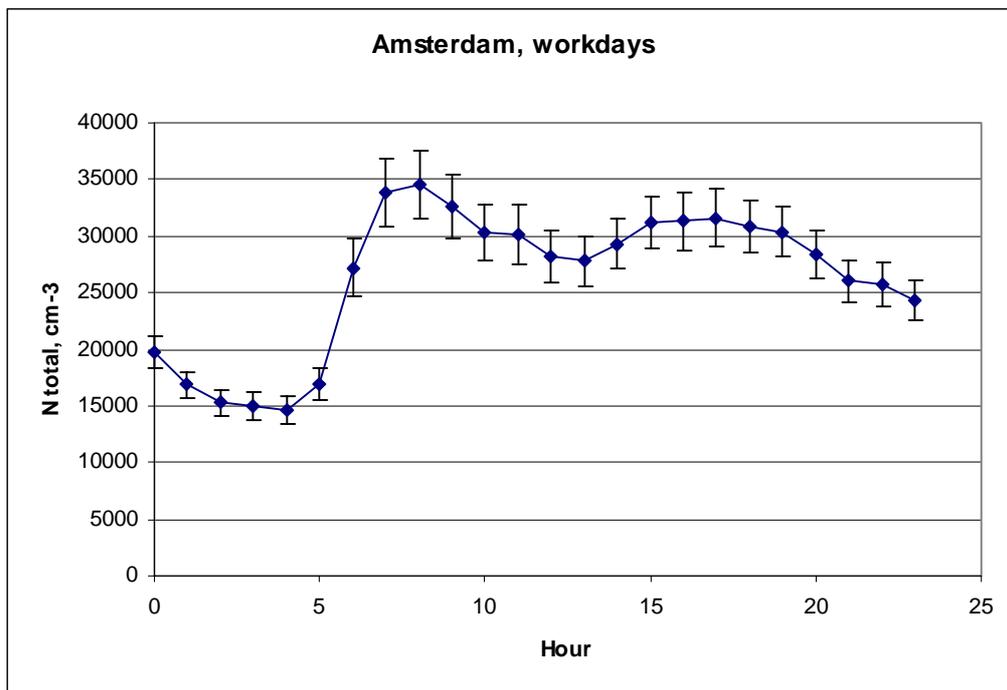
A similar protocol was used in Petten. However, instead of remote control, the operation of the instruments was visually observed directly at the site.

### 3.5.3 Results

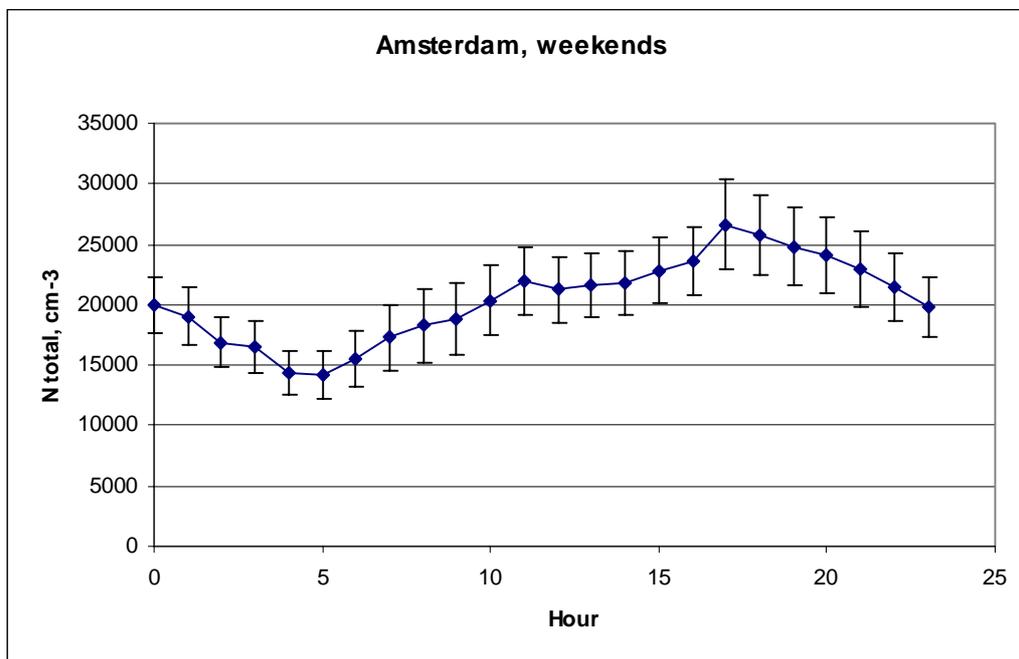
#### 3.5.3.1 Diurnal variability of aerosol concentration

The average daily variability of the aerosol number concentration in Amsterdam (for particles larger than 8 nm in diameter, as measured with the SMPS) is shown in Figure 3.11. The error bars indicate the 95% confidence limits. Both on workdays and on weekends the number concentration shows a clear diurnal variability. On workdays (i.e. Monday till Friday) the number concentration shows its lowest values between 3 and 4 a.m., after which it sharply rises from 15000 to 35000 cm<sup>-3</sup>. The daily pattern shows two maximum values at about 8 a.m. and 5 p.m., apparently corresponding to the traffic rush hours. The daily pattern on weekends exhibits a different pattern. Similarly to the workdays, the lowest concentrations are found at 4 – 5 a.m. and are, similarly around 15000 cm<sup>-3</sup>. After that time the concentration slowly rises until it reaches the single maximum (about 25000 cm<sup>-3</sup>) at 5 p.m. The difference in daily pattern of the

number concentration between workdays and weekends is most probably explained by different traffic intensity: on weekends people tend to have different preferences for travelling, such that no morning peak is observed.



(a)

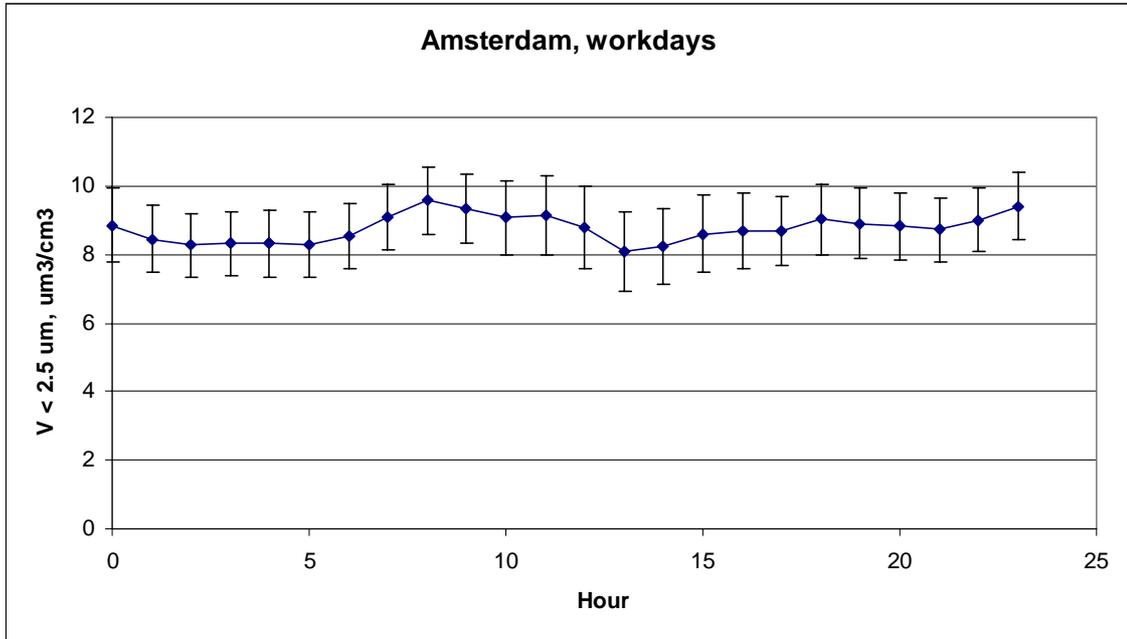


(b)

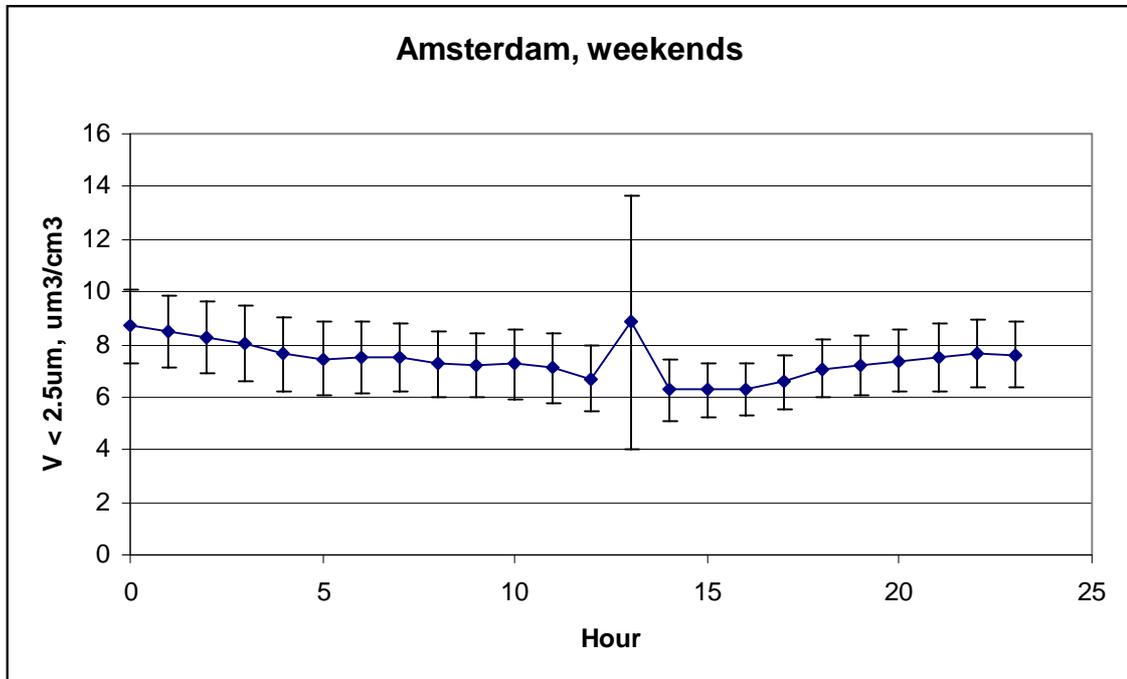
Figure 3.11 Diurnal variability of the aerosol number concentration in Amsterdam on workdays (a) and in weekends (b). The error bars indicate the 95% confidence limit

The average daily variability of aerosol volume (and thus approximately mass) of particles smaller than 2.5  $\mu\text{m}$  in diameter is shown in Figure 3.12 for the city of Amsterdam. Unlike the number concentration, the volume concentration shows no or a very weak diurnal variability on

both workdays and weekends. Obviously, the number concentration correlates better with diurnal pattern of traffic intensity than the volume concentration does. The weak diurnal pattern of aerosol volume is explained by the small contribution of the urban sources to the aerosol volume relatively to the background aerosol concentration. This is in line with  $PM_{10}$  and  $PM_{2.5}$  mass measurements at different sites (e.g. Vermeulen et al., 1999) which are more or less correlated with volume concentrations. It is thus concluded that the number, not the mass of particles is a better indicator of the PM sources in a city.



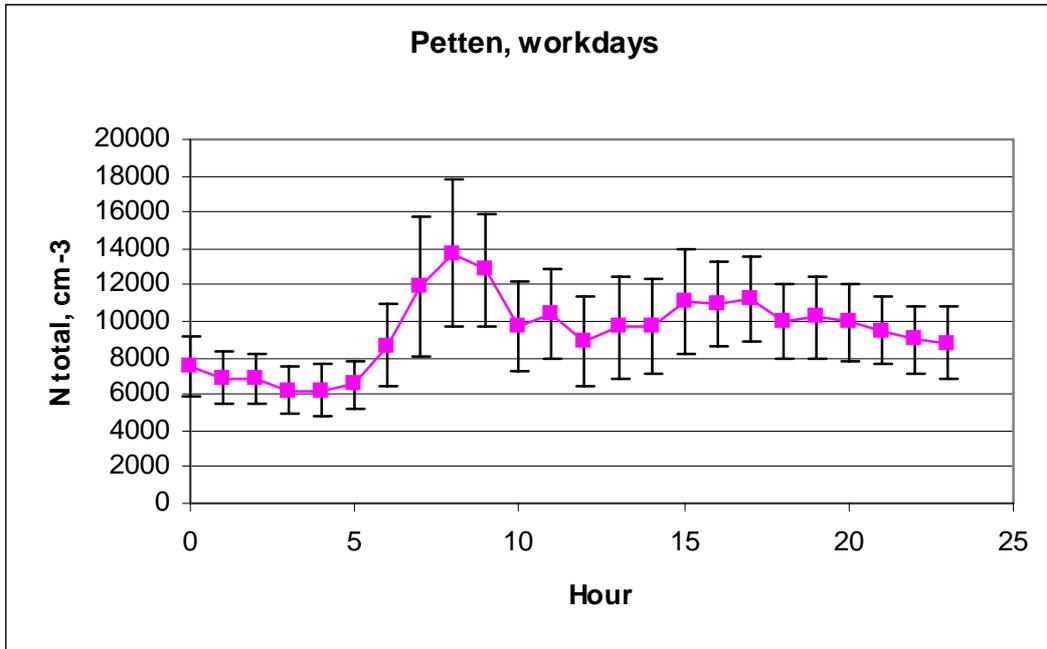
(a)



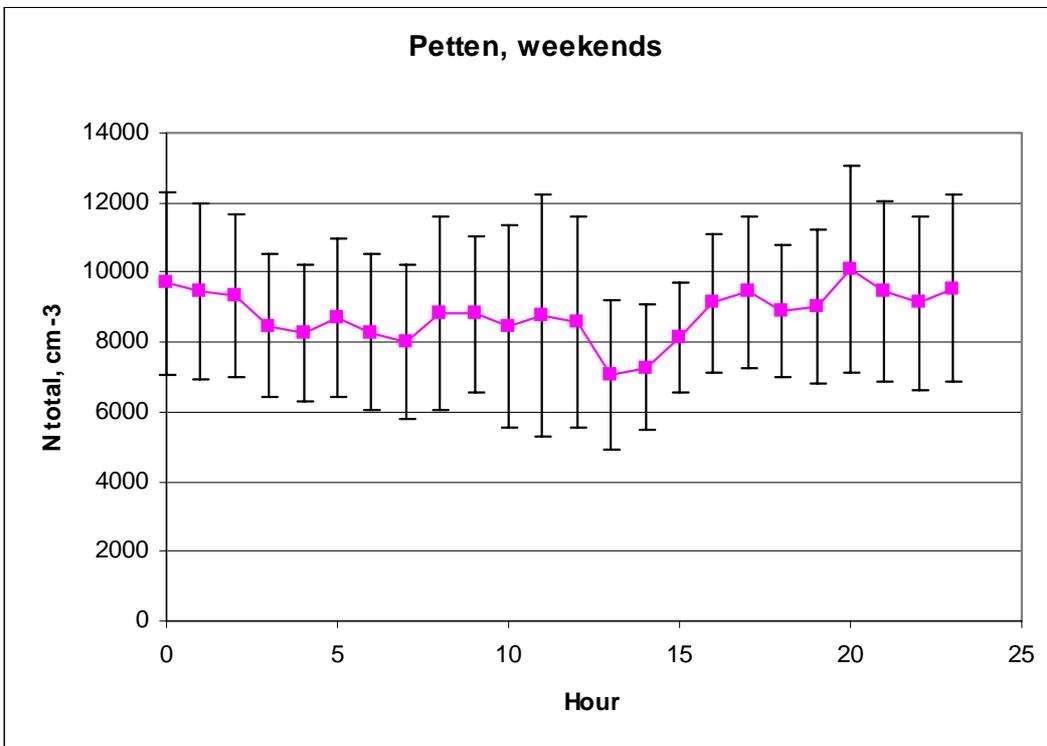
(b)

Figure 3.12 Diurnal variability of the volume of particles smaller than 2.5  $\mu\text{m}$  in diameter (a surrogate for the  $PM_{2.5}$  mass) during workdays (a) and weekends (b) in Amsterdam. The error bars indicate the 95% confidence limit

The average daily variability of the aerosol number concentration in Petten is shown in Figure 3.13. Workdays show a pattern similar to that in Amsterdam, though the absolute concentrations are lower. There is no pattern observed, however, on weekends. It suggests that the diurnal variability in Petten may be in part due to the traffic activity on the territory of ECN and on the adjacent roads. Because the aerosol distribution data in Petten are available only up to 300 nm in diameter, no analysis of aerosol volume is done here.



(a)



(b)

Figure 3.13 Diurnal variability of the aerosol number concentration during workdays (a) and weekends (b) in Petten. The error bars indicate the 95% confidence limit

### 3.5.3.2 Wind direction dependency of aerosol concentration

Figure 3.14 shows the wind dependence of aerosol number and volume ( $PM_{2.5}$ ) in Amsterdam. The wind-direction dependence for the aerosol number and mass is obviously different. The number concentration is the highest when the wind comes from the city and the surrounding highways, the western wind sector. The volume on the other hand is highest when the wind comes from the eastern sector, where practically no nearby roads or highways are present. This shows that the aerosol number and volume or mass have different sources: the number concentration is more influenced by the city and the surrounding highways, while the volume (and thus mass) is mostly due to the background aerosol coming from the continent. This also confirms our observations of diurnal variability of the aerosol number and volume concentrations in Amsterdam (see above).

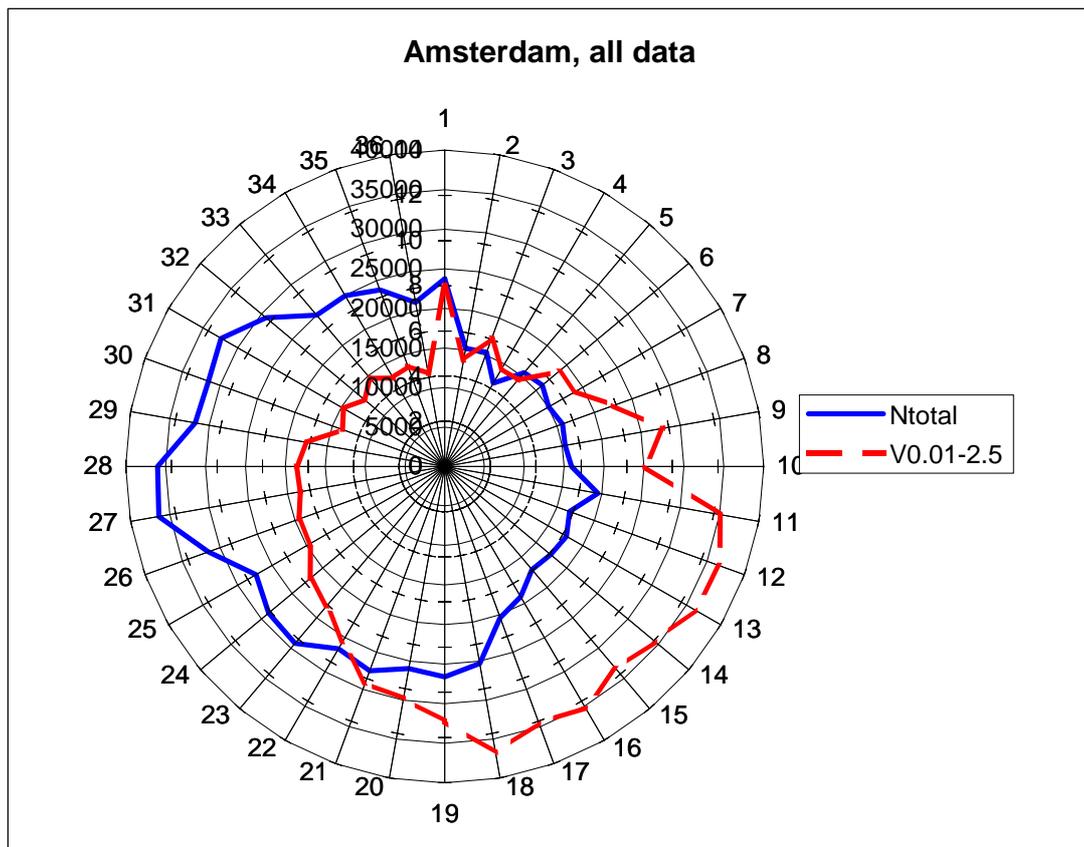


Figure 3.14 *The wind direction dependence of the aerosol number and volume concentrations in Amsterdam*

The wind-direction dependence of the aerosol number concentration in Petten is shown in Figure 3.15. The wind dependence in Petten is different from that in Amsterdam. Higher aerosol number concentrations are observed in the eastern wind sector. This is explained by the fact that Petten lies on the shore of the North Sea. The westerly winds bring relatively clean marine air, such that aerosol concentrations in westerly airflow are low. The easterly airflow brings polluted continental aerosol associated with higher aerosol loading. About 10 years of aerosol measurements in Petten using denuder – filter pack technique show a wind direction dependence of aerosol concentration which is very similar to that for aerosol volume in Amsterdam (report on ECN project 7.2723, in preparation). This again suggests that most of the aerosol volume (and thus mass) in Amsterdam is due to the background aerosol.

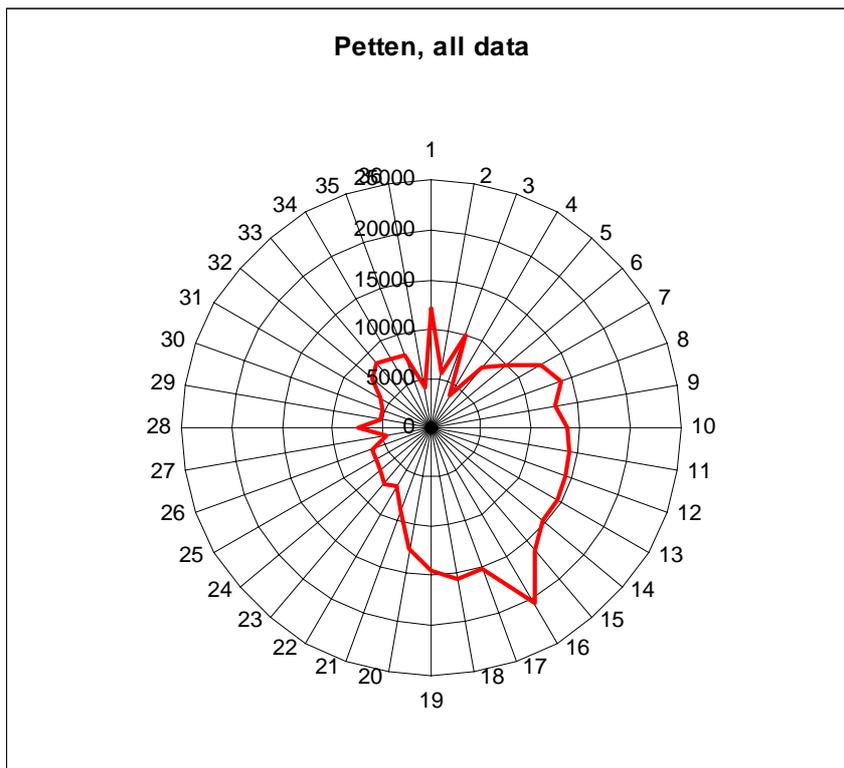


Figure 3.15 *The wind direction dependence of the aerosol number concentration in Petten*

The difference in wind-direction dependence of aerosol number concentration in Petten and Amsterdam suggests a higher contribution of background aerosol to the number concentration in Amsterdam during easterly winds. Indeed the wind direction dependence of the increase in the number concentration in Amsterdam relatively to Petten (Figure 3.16) shows a relatively little increase in the eastern wind sector. The highest increase is observed during westerly winds, when the wind is coming from the city and when the background concentrations are low.

The average number concentration in Amsterdam during easterly winds ( $0^{\circ}$  to  $180^{\circ}$ ) is about  $18000 \text{ cm}^{-3}$ . During the westerly winds the concentration is about  $29000 \text{ cm}^{-3}$ . The concentration during westerly winds, when the air comes from the city, is about 40% higher than the concentration in the easterly winds with little influence of the city. In westerly flows the contribution of the city to the total number concentration is high: 80%. However, during easterly winds only 50% of the aerosol is due to the city sources and the other half is due to the aerosol background. The background aerosol can thus substantially contribute to the aerosol number concentration in the city.

It should be also noted that the background aerosol and the aerosol from the city sources most probably have different chemical composition. We have shown that a substantial part of particles in number can be due to the background origin and thus have different chemical properties. If both absolute number of particles and their chemical composition is of importance for the health effects of PM, then both these parameters should be measured simultaneously to obtain adequate information.

### 3.5.3.3 Size distributions

The average size distributions of aerosol in Amsterdam and Petten are shown in Figure 3.17. The size distribution in Amsterdam shows that the difference in number concentration is mostly due to the smallest particles, 10 to 30 nm in diameter. The size distribution in Amsterdam is similar to that observed in the Drecht tunnel (section 3.3.3.1). During the Drecht tunnel measurements the increase in number concentration in the tunnel relatively to the background air was also mostly due to the smallest particles. Interestingly, the size distribution measured in

Amsterdam is also similar to that measured during the ULTRA-1 project in Alkmaar (Figure 3.18; measurement location only 300 m away from the roundabout at the A9-motorway), suggesting that such size distributions are common in the Netherlands.

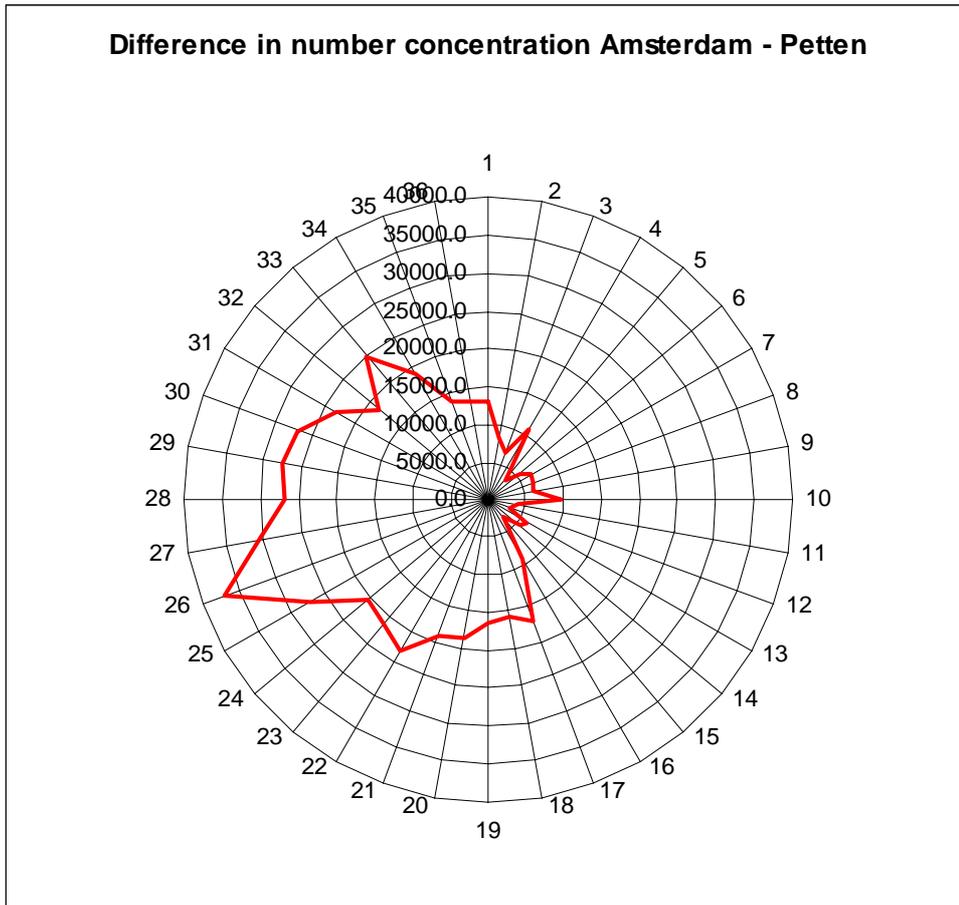


Figure 3.16 The wind direction dependence of the difference in aerosol number concentration between Amsterdam and Petten.

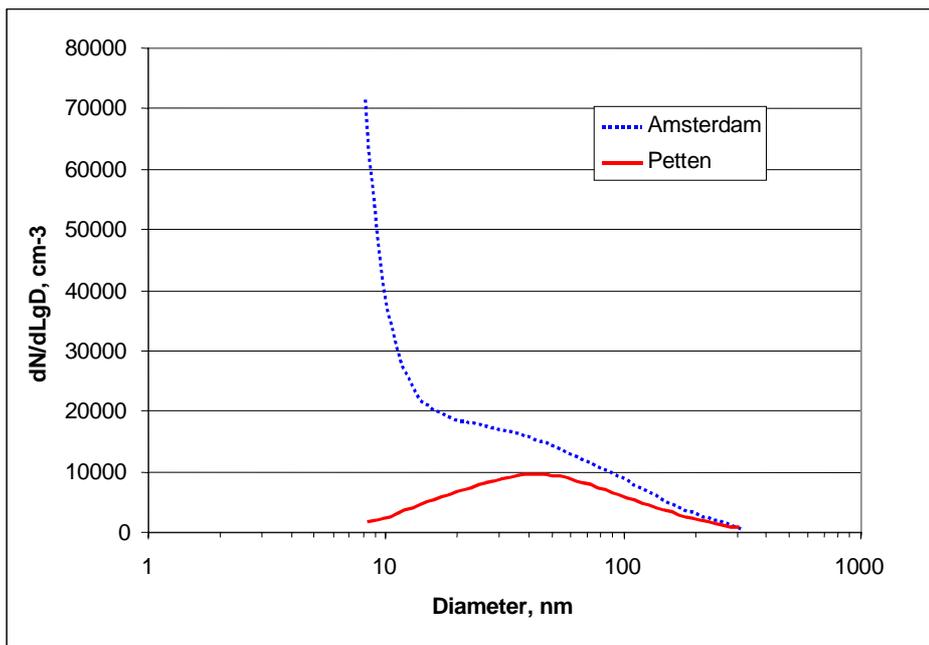


Figure 3.17 Average size distributions of aerosol in Amsterdam (urban background) and in Petten (rural)

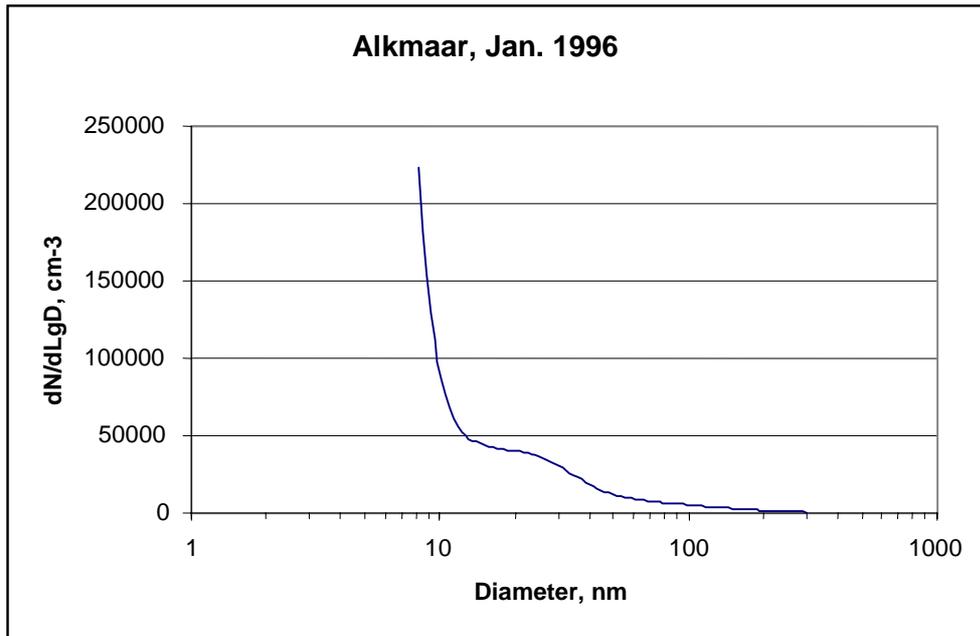


Figure 3.18 Average size distribution during January 1996 of aerosol in Alkmaar measured during ULTRA-1 project

#### 3.5.4 Conclusions

- The aerosol number concentration is a better indicator for the traffic pollution than the aerosol volume or mass is.
- At the monitoring site in Amsterdam the volume (and thus the mass) of particles smaller than  $2.5 \mu m$  in diameter is mostly determined by the background aerosol. Sources from the city have a relatively small contribution to the aerosol mass.
- The aerosol number concentration is mostly due to the dominant source in the city (traffic), especially when the air traverses a long distance over the city and when the background concentration is low. In easterly flows, however, the background aerosol contributes of up to 50% to the total aerosol number concentration.
- Because the background aerosol number concentration has a strong contribution in certain wind directions, measurements of the total number concentration should be supplemented with measurements of aerosol chemical composition.
- The aerosol size distribution in Amsterdam shows that most of the increase in number concentration relatively to the background site is due to the smallest particles, 10 to 30 nm in diameter. This observation is similar to the observation in Alkmaar and in the Drecht tunnel.

## 4. DISCUSSION AND CONCLUSIONS

In this report results are described over the first year of the ENGINE project 'Stedelijke Luchtkwaliteit' ('Urban Air Quality'). Several activities have been started such as the (further) development of instrumentation, measurement campaigns of PM in laboratory and in the field. It is believed that the proposed EU guideline on PM<sub>10</sub> may not be correct as an indicator for the adverse health effects discovered in several cities. This supposition is mainly based on two observations: i) PM<sub>10</sub> concentrations hardly show any variation over the Netherlands, and ii) the fraction between PM<sub>10</sub> and PM<sub>2.5</sub> is mainly determined by dust, sea salt etc. Results from German and American research indicate that the small fraction of particulate matter, with respect to composition or number, may be responsible for the effects. However, there is no epidemiological evidence identifying the PM chemical constituents or the number density as potential causative agents. This has still to be investigated and the work described in this report can be seen as a contribution to this research. Traffic (and local industry) are mainly responsible for the large number of these ultrafine particles in urban agglomeration. A directive on the ultrafine particles would probably be more effective in improving the urban air quality and reduction of health effects. An abatement strategy on PM<sub>2.5</sub> would introduce measures of a different nature, e.g. the application of alternative (electrically driven) transportation.

In this respect the work presented here consists of two major parts: at first, refinements of (existing) measuring techniques that were designed to overcome (to a certain extent) the impediment of lack of accurate data are described. The new installation for the weighing of aerosol material, the further developments of the particulate carbon monitor for soot measurements, and the Steam-Jet Aerosol Collector (SJAC), and a critical testing of the capabilities of the TEOM are important here. The measurement campaigns yielded data on the emissions from vehicular traffic in three different experimental settings: 1) direct measurement of particulate matter in exhaust gases of driving cars, 2) measurements of number and mass concentrations in a traffic tunnel, and 3) measurements in an urban environment at a fixed location or by means of a moving unit.

Several measuring techniques require weighing of collected aerosol mass to be accurate within a few micrograms. The weighing of the collected aerosol material is also complicated by certain factors. The temperature around the balance should be controlled because it not only influences the performance of the high precision balance, but may lead to the loss of volatile substances from the collected aerosol particles. In the experiment with the TEOM the evaporation of ammonium nitrate as a function of the temperature of the heated filter has been shown. These measurements give a clear example that one should anticipate an underestimation of the true values in the weighing procedure when the temperature variable is not controlled.

Maintaining temperature (but also the relative humidity) constant during one weighing but also from day to day helps to avoid the above problems and insures reproducible conditions. To this purpose, a temperature and humidity controlled installation has been built in order to assure accurate weighing of collected aerosol material. The temperature is kept at  $20 \pm 1$  °C and the relative humidity between 40 and 45%. An operation protocol has been developed to insure the quality control. The humidity and temperature controlled installation in combination with the designed weighing protocol improved the accuracy of weighing from about 10 µg to 2 µg.

The RP5400 Particulate Carbon Monitor (Rupprecht and Potaschnik Co.) provides automated measurements of organic and elemental carbon (soot) mass concentration in PM with the time resolution of 1 hour or longer. This instrument is fully automated and provides very promising means for monitoring of the carbonaceous aerosol. However, the monitor misses a substantial part of the soot particles due to a rather high cut-off size of the impactor. To improve the

collection of soot aerosol, the instrument was modified by replacing the impactor with a filter. The tests show that this modification has improved the collection efficiency for soot by almost a factor of 2, such that the soot is sampled quantitatively.

In the determination of the factors (number or composition) responsible for the adverse effects it is necessary to measure the chemical composition toxicity of particulate matter as function of its size. Important are the acidifying components, the (insoluble) organic fraction, heavy metals and basic cations. The Steam Jet Aerosol Collector (SJAC) has been developed in order to measure all air aerosols. Particles can be discerned according to their size. Tests have been performed to study its operation when measuring the heavy metals and organic compounds. Results of these tests indicate that the SJAC can be used for sampling in urban environment as its collection efficiency is virtually 100% at high number concentrations and does not depend on the water-solubility of the aerosol. The collector can be used to measure heavy metals in aerosol but further tests are needed for verification. The limit of detection of the SJAC can be reduced by insulation and applying higher flow rates. Modeling indicates that the optimal steam injection rate for the sampling flow of 20 l/min will be 2 to 3 g/min, especially advisory at high ambient temperatures (30 °C and higher). In future, the instrument will be further developed to perform on line measurements.

The abatement strategies to curb particulate matter air pollution require knowledge on the emission factors from different sources. Motor vehicles and in particular the diesel powered ones are known to be one of the major sources of particulate matter. In the experimental part of this study, emissions of particulate matter have been measured at the outlets of cars (at TNO-WT). Under these typical experimental conditions the number of (ultrafine) particles emitted by diesel driven cars was much larger than the number emitted by gasoline driven cars (at both low and high speeds). Even larger was the number of particles emitted by LPG driven cars at high speed (100 km/h).

Also, measurements in air have been performed in the Drecht tunnel to investigate the emissions in outer air circumstances. From the experimental data it was concluded that size spectra emitted by actual road traffic have a significant larger proportion of nanometer-sized particles. This finding suggests production of new particles in ambient air by homogeneous nucleation. Hence, dynamometer testing seems to underestimate the emission factors of the total number of particles emitted by road traffic. It is concluded that monitoring actual road traffic emissions and dynamometer testing are complementary. The latter provides an experimental facility to test the impact of various engine types, fuel types, driving cycles on particle emissions, while the former provides information on the impact of actual emissions in ambient air.

With a moving van an experiment has been performed to measure the variability of PM in the city of Nijmegen. From the findings it can be concluded that the variation in PM in a city can be attributed to the traffic under the influence of prevailing local infrastructure, i.e. clearly higher actual concentration levels are measured in though fares with heavily packed traffic compared to (relatively) quiet residential areas. Another important conclusion here is the observation that the traffic contribution is only measurable within some 30 m from the street. At a greater distance from the source the contribution is less substantial compared to the background concentration. Such a strong gradient means that measuring equipment must be positioned relatively close to its source in order to measure its impact and may explain why monitoring networks show little spatial variations of PM mass in a city.

Within the European project ULTRA-II, the particles size has been measured in Amsterdam during the winter season and compared with similar measurement done in Petten unaffected by urban sources. The difference provides insight in the contribution of traffic to urban aerosol. The monitoring was made in combination with an epidemiological study to assess the health effects in an urban environment (currently being worked out at LUW). The findings of this study are in agreement with those in Nijmegen and in the Drecht tunnel. It is concluded that the

aerosol number concentration appears to be a better indicator than the aerosol volume or mass. Volume (and mass) of particles smaller than 2.5  $\mu\text{m}$  is mostly determined by the background aerosol. The aerosol number concentration is mostly due to the urban traffic. This is especially apparent when the air has traversed over the city and when background concentrations are low. The increase is due to the smallest particles (10-30 nm) which is similar to observations in the Drecht tunnel. In future research, the measurements of number concentrations should be accompanied with measurements of the chemical composition to identify the chemical differences with background aerosol.

The main incentive for these experiments was to show if any correspondence between the different results could be derived from their results. Although differences exist, the agreement in results is obvious. The experiments in the Drecht tunnel, Nijmegen, Amsterdam and Petten clearly substantiate that number concentration are a better indicator for adverse effects on health due to the vehicular traffic in a city. In the abatement of PM, therefore, it is believed that further measurements with respect to vehicular traffic will be most important. It will be necessary to show that the ultrafine fraction and/or the chemical composition is responsible for the health effects. The technical improvements of the SJAC make it possible to carry out epidemiological studies in order to find which property of the PM is responsible for the effects on human health. More knowledge on the emissions of the ultrafine particles is also necessary to describe the dynamics in the concentrations (number and composition). If such knowledge is available, relations with health indicators can be assessed and it becomes possible to develop an effective abatement strategy.

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