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# ULTRAFINE PARTICLES AND CARBON FROM ROAD TRAFFIC EMISSIONS

## A literature study

H.M. ten Brink (ECN)
M.P. Keuken (TNO-MEP)

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| Made by:<br><br>H.M. ten Brink | Approved:<br><br>J. Slanina | ECN-Clean Fossils<br>Environmental Analysis and Technology |
| Checked by: | Issued:<br><br>C.A.M. van der Klein | |

## Abstract

Dit rapport beschrijft een studie uitgevoerd voor het Ministerie van Volkshuisvesting, Ruimtelijke Ordening en Milieubeheer (VROM), onder begeleiding van VROM en RIVM (Rijksinstituut voor Volksgezondheid en Milieu).

Het doel van de studie was het lot aan te geven dat deeltjes ondergaan vanaf het punt van uitstoot door wegverkeer tot het punt van blootstelling in de bebouwde omgeving. Achtergrond van de vraagstelling naar het lot van die deeltjes vormt het nog onbegrepen verband tussen respiratoire aandoeningen en het niveau aan fijn-stof. Een mogelijkheid is dat de effecten samenhangen met puur het aantal (zeer kleine) deeltjes of de samenstelling. Grote aantallen deeltjes worden met name door het verkeer in de lucht gebracht. Over de echte aantallen emissie en de verspreiding van deze zgn. ultrafines is zeer weinig bekend. ECN/TNO werd daarom gevraagd in kaart te brengen wat er in de literatuur hierover bekend is. Spoedig bleek dat er weinig informatie is. Er is meer bekend over de hoeveelheid koolstof,, "roet", dat door wegverkeer wordt uitgestoten en over de concentraties daarvan. Daarom is geprobeerd na te gaan of er een relatie bestaat tussen de aantallen deeltjes die worden uitgestoten en de hoeveelheid koolstof. Als dit het geval zou zijn kan koolstof als surrogaat kunnen dienen voor de aantallen. Het lijkt op het eerste gericht dat een dergelijk direct verband zou moeten bestaan zijn tussen de hoeveelheid materiaal en de aantallen deeltjes in een auto-uitlaat. In het rapport wordt aangetoond dat dit niet (noodzakelijkerwijs) het geval is.
Uit een literatuurstudie waarbij bestaande gegevens over zwarte-rook in Nederland werden geanalyseerd werd afgeleid dat de bijdrage van koolstof aan PM10 in steden in Nederland een factor twee hoger kan zijn dan nu wordt aangenomen. Gepleit wordt daarom voor verder onderzoek naar de echte hoeveelheid koolstof in stedelijk gebied. Voor bepalen van aantal en het lot het aangeven van de ultrafijne deeltjes langs wegen zijn separate metingen nodig.

# CONTENTS

# SUMMARY

ECN and TNO made a literature search on the relation between ultrafine particles/carbon emitted by road traffic and their off-road concentrations after dispersion. Background of the study is the correlation of respiratory health effects with the levels of particulate matter in urban environments. This association may be caused by various characteristics of the particulates: the number of ultrafine particles, the mass concentration of $PM_{2.5}$ and $PM_{10}$ or the chemical composition. In this report, an attempt is made to quantify the contribution of road traffic to the number of ultrafine particles and the amount of carbon. "Black-smoke", for which a large national data set is available, was used as a proxy for carbon. A search was made for information on a relation between the number of ultrafine particles and levels of black smoke. Therefore the study was initiated along two lines, separately described in parts A and B: Part A is devoted to a description of the knowledge on ultrafine particles, while Part B is focused on a more quantitative assessment of carbon levels and emissions.
The study was funded by the Ministry of Housing, Physical Planning and Environment and performed in the period November 1999 - February 2000.

*Part A "ultrafines":* Based upon own expertise, gained in recent years in concerted European measuring campaigns, the rather limited literature on fine particles was critically evaluated. It was found that Europe is ahead of the US in measuring ultrafines in urban areas and that also in Australia more studies have been made. Most of the data come from short-term campaigns and only the exposure research group of GSF-Munich has experience in long-term monitoring. An overview of data available, with critical notes on the quality is provided. Data on particle emissions come from test-laboratory set-ups (dynamometer/rollenbank) and from road tunnels. The number of data is as scarce as that of outside measurements. We merely used own data for evaluation here.
It was concluded in our evaluation of the sections in the published papers on the experimental approach that the quality of many of the data is questionable. Problem is that the absolute calibration of the instruments for aerosol particle number are only made by four institutes. The critical overview of measuring techniques in the appendix gives more detailed examples of the complications associated with some of the methods used.
Also a more theoretical description of the possible fate (dynamics) of ultrafine particles after emission is given. It indicates that the number quite rapidly decreases because of coagulation. This is the process by which small particles come into contact with each other. Particles can be composed of semi-volatile components and they may evaporate inside measuring instruments. All of these complications make it currently difficult to provide more than an overall picture on ultrafine particles as presented here.

*Part B "carbon":* Monitoring methods for black smoke were evaluated as a proxy for concentrations of elemental carbon, EC, (and organic carbon, OC). Both for the more comprehensive "aethalometer" and the standard "black smoke monitor" a very significant correlation between instrument readings and EC/OC concentrations was established. The ratio of black smoke (measured by the black smoke monitor) and EC concentrations for urban areas in the Netherlands is as follows: EC ($\mu g/m^3$)= 0.15*BS ($\mu g/m^3$) + 3 $\mu g/m^3$. The ratio for concentrations of EC:OC is expected to be 1:1.5 in urban areas. At more remote areas the ratio may increase to 1:2 due to the contribution of so-called secondary (photochemically formed) OC.

Black smoke concentrations estimated by the CAR-model in urban areas have been compared with actual measurements. It was concluded that black smoke emission factors of heavy-duty traffic (mainly buses) are underestimated. In addition, annual average concentrations of EC and

OC were computed with emission factors of EC/OC for urban traffic. These modelled values compare well with the EC/OC concentrations estimated from black smoke monitoring data (using the established relation between black smoke and EC/OC). This suggests that black smoke monitoring data may be used as a proxy for EC/OC concentrations.

It is estimated that trucks contribute 30% of EC and OC ("soot") emissions by highway traffic, while buses and vans in urban traffic contribute respectively, 20% and 30% to soot emissions in urban areas. Using average urban black smoke data in 1995 of 18 $\mu g/m^3$, it is estimated that the sum of EC and OC is in the order of 14 $\mu g/m^3$. This is a factor 2 higher than estimated for urban areas in the Netherlands in 1995. Therefore, EC and OC concentrations are identified as parameters to fill the $PM_{10}$ gap in the Netherlands.

It is noted that experimental data on black smoke and EC/OC are limited and therefore, the data and conclusions in this study may contain large uncertainties. However, the outcome of Part B of the study illustrates that there is a need for further research on EC/OC emissions by road traffic and dispersion to built-up areas.

**Concluding remarks: relation between the number of ultrafine particles and carbon mass**

At first sight a good correlation would be expected between the number of particles and the amount of carbon emitted by traffic. In that case carbon or black-smoke measurements could serve as a proxy to assess emission and dispersion of ultrafine particles from roads. However, this report shows that there is insufficient experimental proof for such a relation. Moreover test-bank studies show that such a relation is absent for LPG-vehicles. Even when a relation between number of particles emitted and the amount of carbon exists in the exhaust, the number of particles decreases more rapidly during dispersion in the atmosphere than the amount of (elemental) carbon, which is a conservative quantity. Therefore separate measurements have to be performed when the exposure of ultrafines and carbon are to be studied.

# 1. INTRODUCTION

A literature search was made for information on the relation between ultrafine particles/carbon emitted by road traffic and their off-road concentrations. Background of the study is the correlation of respiratory health effects with the levels of particulate matter in urban environments. This association may be caused by various characteristics of the particulates: the number of ultrafine particles, the mass concentration of $PM_{2.5}$ and $PM_{10}$ or the chemical composition. In this report, an attempt is made to quantify the contribution of road traffic to the number of ultrafine particles and the amount of carbon. "Black-smoke", for which a large national data set is available, was used as a proxy for carbon.
Current interest in ultrafine particles stems from findings of a stronger association of health effects with the number of particles than with mass [e.g. [1]Peters et al., 1997]. Most particles in the atmosphere are smaller than 100 nm and particles of this size are called "ultrafines". In addition to the mentioned epidemiological studies, toxicological studies showed that a high number of ultrafine particles can caused serious health effects in rats. The PM-mass concentration in those tests was low. The foregoing explains the special interest for the "ultrafine" fraction of the atmospheric aerosol.

Very early in the study it became clear that no textbook or review papers are available from which a first assessment of the dynamics of particles after emission could be taken. Even an overview of the contribution of traffic to the measured number of particles in an urban environment could not be found. Since the material emitted by traffic is carbon it was thought that this carbon could be a proxy for the number of particles tracer for particle. Therefore a search was made for data on carbon emissions, concentrations and gradients and specifically for combined data on carbon and particle number.

[1] Peters A., Wichmann, H.E., Tuch, Th., Heinrich, J., Heyder, J. (1997) Respiratory Effects are Associated with the Number of Ultrafine Particles. *Am.J.Resp. and Critical Care Med.*, **155**, 1376-1383.

# 2. OBJECTIVE

The objective of the study is to provide the state-of-the-art knowledge with respect to emission and spatial and temporal variation of the number of ultrafine and carbon mass emitted by road traffic and a possible interrelation.

# 3. APPROACH

The tasks in the study were split. ECN was to provide an overview of the knowledge on data on particle number, TNO would be involved in a search for information of mass. Most, or virtually all, of the mass emitted is carbon and therefore the study was limited to data on this compound. Because of the complexity of the carbonaceous species this is a very difficult task in itself. It should be borne in mind that the more specific question raised in the progress meeting of the project by the sponsor (VROM) was to indicate whether a simple relation exists between particle number and the amount of "carbon/soot" at sites where humans are exposed to pollution from nearby road traffic.

The research consists of a combined literature review and data analysis:

1. A review of open literature provides information on the "state-of-the-art" of international research on
 i.) ultrafine particles; with a critical evaluation of the measuring methods
ii.) carbon mass from traffic
2. Analysis of the concentrations and gradients of carbon in the Netherlands, using data from the National Air Quality Network. The "CAR" model was used to compute the contribution of traffic

In the report we separately present our findings on "ultrafines" and "carbon" and conclude with a short chapter on a possible relation between the two.

# Part A. ULTRAFINES

Before we turn to the results of our literature search we first briefly discuss the origin/ formation of small particles.

*A.1. Formation of ultrafines*

The smallest and most numerous particles in an urban atmosphere derive from incomplete combustion in vehicles or from processes in the atmosphere in which condensable material is formed from gases. In diesel engines pyrolysis of species produces the typical "soot" particles with their core of graphitic/elemental carbon and species which condense onto these nuclei when the air cools in the exhaust. In petrol-type engines the particles are less graphitic. We will not go into further detail here with respect to the nature of the particles and take the exhaust as the starting point in the discussion. The most typical characteristic of the particle-emission is the high number concentration and the small size of the particles, which we will address now in the framework of measurements in the urban atmosphere.

## A.2. URBAN MEASUREMENTS AND SITES

No textbook or review papers were found from which a first assessment of the dynamics of particles after emission could be taken. Even an overview of the contribution of traffic to the measured number of particles in an urban environment is absent.

Whereas PM-related studies are predominantly performed in the US, with a large scale effort to assess in detail cause effect relations of PM, monitoring of particle number and size has only occasionally be performed in short measuring campaigns [1]. In contrast, in Europe already in the early nineties the exposure research group of GSF had initiated a long-term program in Frankfort and Erfurt, as described below.

Germany

GSF-Munich started both to monitor particle number and to perform epidemiological studies in the town/city of Erfurt [2]. (This is an interesting site because the air pollution mix has obviously rapidly changed after the "Anschluss" of the former DDR in which the city was situated from classical industrial to modern traffic dominated pollution).

Most of the study was performed with a large grant from the US (!) National Health Institute, indicating the great interest of the epi community there. Quality control was mandatory as was a very high data coverage. This required very serious quality assurance of the research instrumentation used at the site a permanent presence of technical staff, daily cleaning of the spectrometer used and at least a weekly calibration of the size classification of the in turn provides the best information record base both on instrument performance and data. Unfortunately some of this information on exposure is in classified reports, however, because of our co-operation with the research group in a concerted European project we had and have a direct contact and are thus able to profit from of the experience gained there as reflected in common intercomparison of the spectrometers used.

In Leipzig, a city not to far from Erfurt, also the full size spectrum of the aerosol is being monitored [3]. This is at on a campus of the institute at a larger distance from the road than the site in Erfurt (own estimation from site visits). The data have only been presented at meetings in a generalized way. It was explained in a private discussion that assessment of the traffic contribution to the aerosol particle number is severely hampered by an obvious atmospheric formation of particles in the morning hours [Wiedensohler private comm.].

Australia

A second country in which ultrafine particles have been quite high on the agenda is Australia. Here the gradient/decrease in the number of particles from the road-side both horizontally and in

the vertical was determined [,4,5,6]; however this was done only campaigns of a very limited duration.

UK
In the UK longer term measuring campaigns has been started after some initial measuring campaigns. The responsible scientist, Harrison, indicated in a private communication the problem of having the sites not being regularly checked by own staff: it lead to periods with missing data or unreliable data because of (simple) clogging of the entrance. At a workshop in November 1999 Harrison presented a poster on gradient measurements in London, in which the full size spectrum at a road-site and a city-background were compared.

Finland
In Finland also the gradient was studied but for the number of particles only. The number concentration was measured at several sites in the city 7]. Part of this effort was performed within the mentioned EU-program in which ECN participates. Site-visits make the results more meaningful.

Denmark
Unpublished results were received of measurements of particle spectra in a street canyon, which should be treated as confidential information until (possible) publication later this year in Atmospheric Environment [Palmgren-Jensen, private communication].

Netherlands
There are as yet only unpublished measurements.
A comprehensive set of data was obtained in own work in Alkmaar (December 1997–March 1998) and Amsterdam (November 1998- June 1999) in the context of two Europan projects " ULTRA I" and "ULTA II". The instrument was twice intercalibrated with the instrument used in Erfurt, see above, and the one in Helsinki. Differences between the instruments with respect to total particle number and spectral distribution were within 20%, on an hourly basis [8,9].

RIVM [10] has measured size distributions using an SMPS system; details of the measurements are not yet available.

The GG&GD-Amsterdam started continuous measurement of total particle number at three sites in Amsterdam in early 1999; data are not yet available [11].

## A.3. CRITICAL REMARKS

From the reports and publications and from direct contact with the responsible scientists it became clear that the central weak point in the monitoring of ultrafine particle concentrations is the quality of the measurements and especially the long-term consistency of the data. The problem is an absence of a possibility for in-situ calibration at the site of the number of particles. Only when more instruments are present, for instance for gradient measurements, they can be intercompared for a relative quality check. This also means that gradients given should be more reliable. In the mentioned concerted EU-project, comparability has been checked in several campaigns and it was quite satisfactory [8,9]. Checking of the size classification is much easier because of the existence of particles of a reference size.

Absolute calibration of the instruments measuring aerosol particles number is possible. However, this is very tedious and costly and done only by the institutes in Leipzig and Helsinki. They even do it on quite a regular basis. ECN has an own, even more tedious procedure [12], which is only occasionally applied. This means that utter caution should be taken with respect to

numbers stated in literature and comparison of data on particle number from different sites does not seem warranted unless the calibration or intercomparison procedure is stated.

Apart from total number also the number of particles as a function of size is measured. Those spectral data are more reliable, because they only imply a relative measurement. A rather common factor in all data seen so far is the maximum number of particles at a size of around 25 nm. In the Netherlands quite persistently, and occasionally elsewhere, there is not such a definite peak in the distribution and particles of 10 nm seem to be more abundant. It should be realised in this respect that the spectrometers measure in the size range between 10 and 100 nm in diameter. Thus there might even be a substantial number of smaller (ultra-ultrafine) particles (diameter < 10 nm) present.

## A.4. DYNAMICS OF PARTICLES AFTER EMISSION

### A.4.1. Theory

From a theoretical point of view the number of particles should quite rapidly decrease because of coagulation This is the process by which a small particle comes into contact with another mostly larger particle. Such a small particle remains attached, because of the strong attraction forces exerted by small particles. The reason that specifically small particles attach to other particles is their high diffusivity. The characteristic time for the decrease in particle number depends also on the number and can be very small. The most obvious example is the coagulation of the small primary soot particles together to form a characteristic large aggregate. This already occurs in motor and exhaust within a fraction of a second.
Note: in the coagulation process the number of particles decrease but the volume/mass of the aerosol is remains the same (is conserved).

Coagulation is the basis for the dynamics in the population of the smallest aerosol particles after emission. However, also new particles are being formed in the atmosphere which complicate the assessment of the dynamics of the directly emitted particles. Another complication can be volatility of the particles. Because the particles represent very little mass a small change in vapor pressure induces rapid volatilization. This can even occur inside measuring instruments. That this can be a serious problem has been demonstrated by us for ultrafine ammonium nitrate particles which evaporated inside the spectrometer used.

### A.4.2. Relevant measurements

Particle emissions from vehicles is determined in a test-laboratory set-up (dynamometer/rollenbank in Dutch [TNO private data]). The numbers observed there are then compared with those measured along-side a road. A better approach for such a comparison seems to be to take concentrations measured in a road tunnel. In such a system atmospheric dispersion of the emission is limited, rather the dilution factor is well-known. On the other hand the emissions are produced under more realistic conditions. As a reference the concentration of a conservative tracer from auto-exhaust can be used (CO, NOx) and a tracer can also be released inside the tunnel to assess the dilution factor even more directly. Exactly such experiments were also performed by us and results have been summarized in table 1.

The main conclusion of the tests in the road tunnel was that the number of particles was much higher than that on the dynamometer. It also appears that the large discrepancy stems from the particles with a size between 10 and 20 nm. Soot particles from diesel seem to mostly have a size larger than 20 nm so that particles which are significantly smaller presumably derive from

vehicles not using diesel. It is thus also to be assumed that there is little correlation between number and mass when the traffic is dominated by non-diesel traction.

NB: For black carbon mass the emission figures seems to compare well between the lab tests and tunnel. It should be considered though that the tunnel is in a highway and that data may not be representative of emissions and concentrations at the lower traffic speeds in cities.

Summarizing: the main difference in character of particle number and mass is the conservative nature of the mass, especially that of the inert elemental carbon.

## A.5. CONCLUDING REMARKS

There are some data available in Europe on the number of ultrafine particles near roads, but certainly over half of these are of unknown quality. A first task should therefore not be to obtain more data, but data which are quality assured. More effort should also be given in Europe to assess the gradient in particle size and number away from busy roads. This could only be done in large co-operative studies of several institutes at a central site, instead of spending time and resources in various small local investigations.

## A.6. LITERATURE


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10. RIVM; SMPS data, unpublished data.

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12. A. Khlystov, G.P.A. Kos and H.M. ten Brink (1996) A high-flow turbulent cloud chamber. Aerosol Science Technol. V24, 59-68.

# Appendix A1 Measuring techniques for ultrafines with critical evaluation

There are spectrometers which measure both the size and the number of particles at that size. (Optical sizers, which are used for measuring larger particles [2], can not detect ultrafines). The current instruments all use the deflection of electrically charged particles in an electric field as the method to separate the particles by size.
Almost all of the research mentioned in the main text has been done with a DMPS (incidentally a method established by ECN) in which the transmitted particles are counted in commercial Condensation Particle Counter, see below. The instruments are research tools and are adapted for long-term monitoring [8,9]. They require very regular maintenance, see main text.
The oldest way of assessing the number of particles in a size class is by measuring the current induced by particles collected in an electrometer. Examples of such instruments are the commercial EAA (TSI03030) and the home-built EAS [8]. Unfortunately both instruments suffer from rather poor sensitivity and size resolution and need complex inversion calculations to assess the particle size spectrum.

The CPC is an instrument in which butanol is being condensed unto the particles so that they grow to such a size so that they are optically detectable. The instruments are also used to measure total particle number.

The problem with all instruments is the calibration of the actual numbers measured, see main text. For amore detailed description the reader is referred to textbooks.

A recent development is the which seems an interesting instrument: it uses inertia in a so-called impactor for classification and the current induced by the charged particles to deduce the number. By using inertia as the separation mechanism it classifies particles according to another parameter than in the other spectrometers. Problems of the ELPI are the low size resolution and the absence of a means of direct calibration. Its added value is the possibility to weigh the deposited material to obtain a mass distribution as function of size.

# Part B: Black smoke, EC and OC.

## B.1. INTRODUCTION

### B.1.1. Background

Carbonaceous particles are an important fraction of $PM_{10}$ in ambient air. The interest in carbonaceous particles over the last two decades is related to potential health impact, soiling of surfaces and radiative effects. In urban areas in the Netherlands, the main source of emissions of carbonaceous particles is *traffic*. This encompasses for the larger part exhaust pipe emissions and to a smaller extent tire wear.

Traffic emissions of carbonaceous particles (also known as “soot” or “black smoke” or “black carbon”) consist of elemental carbon (EC) “mixed” with organic compounds (OC). In addition to these primary emissions, OC is also formed by photochemically reactions in the atmosphere from gaseous precursors, both emitted by biogenic and anthropogenic sources. This so-called secondary OC is not part of this study, though it is acknowledged that data on OC are a combination of primary and secondary OC. The sum of EC and OC is regarded the $PM_{carbonaceous}$ ($PM_{carb}$) fraction of particulate matter in ambient air. $PM_{carb}$ also includes mineral carbon, such as calciumcarbonate, but in general this fraction is not significant, as compared to EC and OC. Presently, there is only limited knowledge on i.) the primary emissions of EC/OC by traffic (and other combustion sources), ii.) the temporal and spatial variation, and iii.) the impact on the air quality in built-up areas.

### B.1.2. Set up of Part B

In Section B2. the issue of EC and OC is further detailed and definitions are provided. In Section B3., the measurements of black smoke , EC and OC in ambient air are discussed. The outcome of a literature review on EC and OC are presented in Section B4. In Section B5 EC and OC concentrations are estimated from black smoke measurements and models. Section B6 provides conclusions and recommendations and a list of cited literature is given in Section B7.

Annex B1, presents an overview of balck smoke monitoring methods. In Annexes B2a and B2b, emission factors of EC and OC for highway and urban traffic are included.

## B.2. WHAT IS THE PROBLEM?

Carbonaceous particles in ambient air are distinguished in organic carbon (OC), elemental carbon (EC) and mineral carbon (e.g. carbon containing minerals, such as $Ca/MgCO_3$) [2]. This distinction is important, as the origin and atmospheric behaviour (and probably health effects) are different. Carbonate minerals originate from re-suspension processes of soil and road dust. In particles smaller than 2.5 μm, the fraction of mineral carbon is in general less than 5% of

total carbon [3]. This research is mainly directed to exhaust pipe emissions and therefore, carbonate minerals are not further discussed in this report.

The definitions of EC and OC are operational and reflect the method of measurement. *Thermochemical* methods for the determination of EC and OC are based upon oxidation at various temperatures, while o*ptical* methods are related to the light-absorbing properties of (black) elemental carbon. The following definitions are applied [2]:

- *elemental carbon* (EC) is defined by its *thermal* behaviour: EC does not volatilise in an inert atmosphere at temperatures as high as 650 $^{o}$C; it can only be gasified by oxidation which starts at temperatures above 340 $^{o}$C. EC is emitted by incomplete combustion. In the summer, diesel engine exhaust is the main source for EC, while in the winter, emissions by fossil-fuel burning (e.g. fly ash) are also important;
- *organic carbon* (OC) is defined as carbonaceous material gasified by low temperature oxidation or the organic compounds measured after solvent extraction. OC is emitted directly in the atmosphere after combustion processes (e.g. particles of polycyclic aromatic hydrocarbons; condensation of un-burnt diesel; lubrication oil) - *primary* OC or is formed by photochemical reactions from gaseous precursors - *secondary* OC. Hence, OC in ambient air consist of a *primary* and *secondary* fraction. In this study the focus is on primary OC;
- *diesel soot* is defined as the sum of EC and OC emitted by diesel engine exhaust; and
- *black smoke* (BS) refers to methods based on the light-absorbing properties of the sum of EC and "tarry" OC compounds;

Various studies in USA and Europe indicate that $PM_{carb}$ in urban $PM_{2.5}$ is of the order of 10-40 % with a ratio of 2/1 for OC/EC [3-4]. It is concluded that the carbonaceous fraction of $PM_{10}$ may be relevant to understand the cause-effect relation of health effects due to $PM_{10}$ [5-8]. In addition, $PM_{carb}$ may be a important tracer for particulate matter emitted by (diesel) traffic [9-10]. Till date most monitoring data of $PM_{carb}$ is based upon the semi-quantitative measurement of "black smoke". Hence, there is a need to further address the issue of $PM_{carb}$. In this research assignment, this pertains to the following questions:

- What is the relation between traffic emissions and ambient concentrations of "black smoke", EC and OC?
- What is the relation between "black smoke" measurements and EC/OC concentrations?
- What is the need for specific measurements of EC/OC complementary to "black smoke" monitoring?

**The situation in the Netherlands is examined taking into account these questions. First, in the next section some background is provided on the formation and measurement of "back smoke" and EC/OC.**

# B.3. MEASUREMENT OF EC AND OC

Methods to measure EC and OC in ambient air are distinguished in optical, thermographic and miscellaneous techniques. They are described in detail in Annex B1. Here we give a summary of the most significant aspects of the methods which are in use for monitoring.

## B.3.1 Optical techniques as a proxy for EC

EC has a graphitic microstructure and is strongly light-absorbing. *Due to the strong light absorption of EC (as compared to "tarry" OC), optical methods are regarded a proxy for EC.* The following optical techniques are distinguished: aethalometer and black smoke monitor.

### B.3.1.1 Aethalometer

The aethalometer samples particulate matter on a filter and the attenuation of light *transmitted* through the filter is measured [11]. It is a low-cost method, which may provide hourly measurements of BS concentrations. In order to calculate the mass concentration of BS from the measured attenuation, a site-specific calibration is required [2; 12-14].

Due to interest in EC, various studies examined the relation between EC *(mass of elemental carbon)* and *optical* BS readings of the aethalometer:

- Allen et. al. [4] in 1990 measured both by an aethalometer and a thermograph respectively BS and EC. The following relation was established for a background location: EC = BS;
- Niessner [2] in 1995 established a relation for EC and BS measurements at an urban background location in Munich and near a heavy traffic location. These measurements were performed by an aethalometer, a black smoke monitor and a thermograph over a period of five months. The aethalometer readings (BS) and EC correlated as follows: EC = 2.2 * BS (urban background) and EC = 1.4 * BS (heavy traffic);
- RIVM [15] in Bilthoven in 1995 established a relation of EC = 2 * BS;
- Lavanchy et. al. [14] in 1997 measured BS and EC at an alpine background location (the Jungfraujoch) in Switserland. The following relation was found: EC = 2 * BS;
- Hitzenberger et. al. [13] in 1999 established the following relation with test aerosol of black carbon particles: EC = 2 * BS.

*It is concluded that the aethalometer can be used as a proxy for EC in ambient air. For the Netherlands a similar relation for EC and BS as in Germany seems appropriate:*

*Aethalometer: EC = 2 * BS (urban background) and EC = 1.4 * BS (heavy traffic*)

### B.3.1.2 Black smoke monitor

The second optical technique to measure black carbon is the so-called "black smoke monitor". This instrument (EEL 43 Smoke Stain Reflectometer) measures the attenuation of light *reflected* by a filter. Samples of particulate matter are collected on a Whatman No. 1 filter.

Blackening of the filter results in decreasing reflectance, which is a measure of the BS concentration [16]. The sampling period is 24 hour for a detection limit of 1 $\mu g/m^3$.

Similar to the aethalometer method, one can not directly correlate the black smoke readings to *mass* concentrations. To estimate the mass of BS, an OESO standardised calibration curve is applied. The calibration curve of 1964 is based upon experiments in the period 1959-63, when carbonaceous particles were mainly emitted by coal-fired power plants. Similar to the aethalometer, *a site-specific calibration is required* to estimate mass concentrations from the black smoke monitor.

Analogous to the aethalometer, the relation between EC and BS-readings of the "black smoke" monitor has been established in various studies:

- The number of EC measurements in the Netherlands are limited. TNO measured from 1979 to 1981 EC concentrations in ambient air near Delft [20]. The annual value of EC was 5.8 $\mu g/m^3$, while BS in this area was 25 $\mu g/m^3$. Hence, for an urban area in the Netherlands in 1981, EC = 0.23 * BS;

- In Düsseldorf in 1991 a relation of EC = 0.2 * BS + 4.2 $\mu g/m^3$ was established near a traffic location;

- Penner in 1993 [15] established a relation of EC = 0.2 * BS based upon a global inventory for background locations;

- Erdmann et. al. [19] in 1993 compared black smoke monitoring and thermograph measurements at an urban background location in Berlin. The following relation was established: EC = 0.22 * BS + 0.6 $\mu g/m^3$;

- In Düsseldorf - Germany in 1993, the black smoke monitor has been compared with measurements by a thermographic technique [19]. In the range of 5 - 120 $\mu g/m^3$ EC, the black smoke monitor measured five times *higher* black smoke concentrations than EC. Hence, EC = 0.2 * BS;

- RIVM compared at a background and urban location EC measurements and BS concentrations measured by an aethalometer and the black smoke monitor [15]. The following relation for the black smoke monitor was found during a pilot study of 10 days in 1995 in Amsterdam: EC = 0.3 * BS + 3 $\mu g/m^3$;

- Niessner in 1995 [2] found the following relations for : EC = 0.2 * BS + 2 $\mu g/m^3$ (urban background) and EC = 0.15 * BS + 3.8 $\mu g/m^3$ (heavy traffic);

*It is concluded that similar to the aethalometer, the black smoke monitor can be used as a proxy for EC in ambient air. For the Netherlands similar relations for EC and BS as in Germany seems appropriate:*

*Black smoke monitor: EC = 0.2 * BS + 1.5 μg/m$^3$ (background) and EC = 0.15 * BS + 3 μg/m$^3$ (urban and heavy traffic)*[2].

### B.3.2. Thermographic techniques for EC and OC

Thermographic methods are based on volatilization and oxidation of OC and EC at different temperatures and different atmospheres (100% nitrogen or mixed with oxygen) [3]. The resulting $CO_2$ is measured.

### B.3.3. Conclusions

From the aforementioned description and application of techniques to measure EC and OC in ambient air, it is concluded that till the 1990's routine measurements of carbonaceous particles were limited to "black smoke - BS" by the aethalometer and the "black smoke" monitor. In the Netherlands, measurements of black smoke in the National Air Quality Monitoring Network are performed by the black smoke monitor. The following relations for EC and "Black Smoke" monitoring readings in the Netherlands are proposed:

*EC = 0.2 * BS + 1.5 μg/m$^3$ (background) and EC = 0.15 * BS + 3 μg/m$^3$ (urban and traffic locations).*

[2] The relation between EC concentrations and BS readings by the black smoke monitor implies that at "zero" readings of the black smoke monitor, there is a EC "treshold" of 1.5 and 3 μg/m$^3$ of EC at background and urban locations. With other words, the black smoke monitor can not detect EC concentrations below these values.

# B.4. LITERATURE REVIEW ON TRENDS AND CONCENTRATIONS OF EC AND OC

Especially, in the USA and Germany in the 1980-90's, studies were dedicated to carbonaceous aerosols in urban and industrial areas with emphasis on the $PM_{2.5}$ fraction:

- From an extensive study in Los Angeles in the 1980's, it was concluded that 40% of the annual $PM_{2.5}$ consisted of EC and OC in a ratio of 1:2. The remaining mass was attributed for 40% to the sum of ammonium sulfate and nitrate, and for 20% to "others" [21];

- In the Netherlands a trend analysis of back smoke was performed [17] on data collected in various monitoring networks using the black smoke monitor. The trend in the period 1965 - 1995 was as follows:

  * 1965 - 1980: a decreasing trend of 1 $\mu g/m^3$ per year from an annual average for BS of 30 (1965) to 15 (1980) $\mu g/m^3$;
  * 1980 - 1995: a decreasing trend of 0.2 $\mu g/m^3$ per year from an annual average for BS of 15 (1980) to 12 (1995) $\mu g/m^3$.

  The decreasing trend in the period 1965-1980 is related to increasing use of gas/oil-fired power plants and introduction of electrostatic precipitators to remove fly-ash from remaining coal-fired power plants. The stagnation of the decline in BS concentrations after 1980 is attributed to increasing traffic emissions with emphasis on diesel-soot. At the end of the 1980's, it was estimated that traffic contributes to 90% of EC emissions in Europe [22];

- TNO measured EC concentrations in ambient air near Delft from 1979 to 1981 [20]. The annual value of EC was 5.8 $\mu g/m^3$, while "black smoke" concentrations in this area were 25 $\mu g/m^3$;

- Hamilton [22] concluded that urban background concentrations of EC in the period 1985-1990 in European cities (Hamburg, Paris, Strasbourg, Leeds and Athens) was 2 - 6 $\mu g/m^3$. In the USA a similar value of 4 $\mu g/m^3$ for the annual average EC in urban areas was established, while the rural background amounted to 0.5 - 1 $\mu g/m^3$ in the USA;

- In Düsseldorf in 1990 and 1991 near heavy traffic, EC concentrations of respectively 14 and 12 $\mu g/m^3$ were measured [23]. At working days the annual average was 13.2 $\mu g/m^3$, while during weekend days the annual average was 9.8 $\mu g/m^3$ in 1991. This illustrates the impact of traffic on EC concentrations;

- In a more recent study in Berlin in 1995, an urban background of 3 $\mu g/m^3$ EC was measured, while EC concentrations at a location near heavy traffic were 7 $\mu g/m^3$ [24]. In this study, the contribution to EC by the fractions $PM_{2.5}$ and $PM_{2.5-10}$ was distinguished. In the urban background less than 5% of EC was attributed to $PM_{2.5-10}$, while near traffic locations 20% of EC contained $PM_{2.5-10}$ particles. These particles relate to emissions of EC by tire wear: tires are produced from material containing 25% black carbon;

- Allen et. al. [4] measured EC and OC concentrations in Philadelphia in the summer of 1992. A range was found of 0.4 - 4 $\mu g/m^3$ for EC and 0.8 - 8 $\mu g/m^3$ for OC;

- In Berlin in 1993 [19] an annual average for EC of 6 $\mu g/m^3$ was measured with a winter average of 8.2 $\mu g/m^3$ and a summer average of 3.8 $\mu g/m^3$;

- In the Netherlands from February till May 1995 [15] EC concentrations were determined: Amsterdam: 0.5 - 6 $\mu g/m^3$, Biddinghuizen: 0.5 - 7 $\mu g/m^3$ and Bilthoven: 0.5 - 4 $\mu g/m^3$;

- In a research programme in Switzerland at an Alpine background location, EC was measured from July 1995 to June 1997 [14]. A range of 0.1 - 0.6 $\mu g/m^3$ EC was established at this remote background location. The ratio of OC/EC was 1.2;

- Petzold and Niessner [13] reported on EC/OC measurements at various locations in Germany from 1993 - 1997. At a rural background location (the Hohenpeissenberg) in July 1997 EC was 0.4 - 2.7 $\mu g/m^3$, while OC was 0.8 - 4.6 $\mu g/m^3$. The average of several urban locations in 1993 - 1995 resulted in an EC of 3 - 20 $\mu g/m^3$ and OC of 5 - 25 $\mu g/m^3$. Near an urban high way in 1994, the range for EC was 3 - 24 $\mu g/m^3$ and for OC 5 - 32 $\mu g/m^3$;

- In an extensive study on the chemical composition of urban aerosols, a ratio for OC/EC of 1.5 was established in the USA [21].

*From these international studies with emphasis on Germany, it expected that the rural background in Netherlands for EC is 4 $\mu g/m^3$ and OC 6 $\mu g/m^3$. The annual average for the urban background is estimated 5 $\mu g/m^3$ for EC and 7 $\mu g/m^3$ for OC. The average ratio for OC/EC is in the range of 1.5 - 2. Near heavy traffic locations, especially with heavy duty trucks, OC/EC ratio's in the range of 1 - 1.5 may be expected.It is noted that the uncertainty in these estimates may be considerable, as the EC/OC data result from studies during the last decade and in various countries.*

# B.5. EMISSION FACTORS FOR ROAD TRAFFIC IN THE NETHERLANDS

In order to further examine the impact of traffic on black smoke and thus EC/OC concentrations, a dispersion model is applied. This implies the use of emission factors. Emission factors for traffic are established by the National Bureau of Statistics (CBS). Van den Brink performed recently an extensive literature review on traffic emission factors of particulate matter [1]. Also, EC/OC emission factors were estimated. Based upon this review, road traffic emission factors of EC/OC are presented.

## B.5.1. EC and OC emissions by highway traffic

In Annexe B 2a, the emission factors for *highway* traffic are presented for different types of vehicles. In addition, also the percentage of Vehicle Kilometer Transport (VKT) for various types of vehicles on highways in the Netherlands are provided. From the data in Annex B 2a, emission factors of EC and OC for an "average highway vehicle" have been estimated. These factors are computed by multiplying the percentage of a type of vehicle (e.g. petrol car with and without catalysts, heavy duty truck) with its corresponding emission factor in Annex B 2a. Subsequently, these factors are added up to the sum for light, medium and heavy duty vehicles. The results are presented in Table 1a.

*Table 1a: Emission factor of EC/OC per kilometer transport (VKT) of an "average highway vehicle" and distinguished in contributions by light, medium and heavy duty vehicles.*

| type of vehicle | % of highway traffic | exhaust EC/OC (mg VKT) | tire wear EC/OC (mg VKT) | road dust EC/OC (mg VKT) | ***total EC (mg VKT)*** | ***total OC (mg VKT)*** |
|---|---|---|---|---|---|---|
| light | 84 | 11/10 | 0.8/1.6 | 0.8/1.6 | *13* | *13* |
| medium | 12 | 9/6 | 0.2/0.3 | 0.2/0.3 | *9* | *7* |
| heavy | 4 | 12/8 | 0.3/0.6 | 0.3/0.6 | *13* | *9* |
| *total* | *100* | *32/24* | *1.3/2.5* | *1.3/2.5* | ***35*** | ***29*** |

From Table 1a, it is concluded that average highway traffic in the Netherlands emits 35 mg EC and 29 mg OC per kilometer transport. More than 90% of the EC/OC emission result from the exhaust pipe (and thus consists of $PM_{2.5}$). The ratio for highway emissions of EC/OC is 1, which is according to the estimated value in the former section. From Annex B 2a and Table 1a, it is concluded that heavy duty trucks which represents 4% of total transport kilometers contribute 30% of the EC and OC emissions (e.g. diesel-soot) by highway traffic. *Hence, sootfilters on trucks may reduce 30% of EC/OC emissions by highway traffic.*

## B.5.2. EC and OC emissions by urban traffic

Similar to highway traffic also for urban traffic, emission factors may be calculated. In addition, break lining emissions are added. Also, the composition of urban traffic is different from highways. The results are presented in Annex B2b and Table 6b. From Annex B2b, the emission factors of EC and OC for urban traffic are estimated. These factors are computed by

multiplying the percentage of a type of vehicle with its corresponding emission factor (Annex 1b). Subsequently, these factors are added up to the sum for light, medium and heavy duty vehicles. The results for an "average urban traffic" are presented in Table 1b.

*Table 1b: Emission factor of EC/OC per kilometer transport (VKT) for "average urban traffic" and distinguished in contributions by light, medium and heavy duty vehicles.*

| type of vehicle | % of urban traffic | exhaust EC/OC (mgVKT) | tire wear EC/OC (mgVKT) | brk lining EC/OC (mgVKT) | road dust EC/OC (mgVKT) | ***total EC (mg/VKT)*** | ***total OC (mg/VKT)*** |
|---|---|---|---|---|---|---|---|
| light | 77 | 17/15 | 0.8/1.6 | 2.4/2.8 | 0.8/1.6 | *21* | *21* |
| medium | 20 | 23/15 | 0.4/0.6 | 0.6/1.2 | 0.4/0.6 | *24* | *17* |
| buses | 1 | 11/7 | 0.1/0.2 | 0.1/0.2 | 0.1/0.2 | *11* | *8* |
| heavy | 2 | 4/10 | 0.2/0.3 | 0.1/0.2 | 0.2/0.3 | *5* | *11* |
| *total* | *100* | *55/47* | *1.5/2.7* | *3.2/4.4* | *1.5/2.7* | ***61*** | ***57*** |

From Table 1b, it is concluded that average urban traffic in the Netherlands emits 61 mg EC and 57 mg OC per VKT. More than 80% of the EC/OC emission result from the exhaust pipe and thus consist of $PM_{2.5}$ particles. The ratio of EC/OC is 1, which is in line with experimental research in Germany. From Annex B2b and Table 1b, it is concluded that buses which constitute 1% of the total urban road transport kilometers contribute 20% of the EC and OC emissions by urban traffic. Transport of goods by medium duty vehicles (e.g. vans) representing 10% of urban transport kilometers contribute 35% of dieselsoot emissions by urban traffic. *Hence, soot filters on buses and vans may reduce urban EC/OC emissions by 50%.*

# B.6. RESULTS OF EXPERIMENTAL RESEARCH ON EC EMISSIONS IN THE NETHERLANDS

In this last section on black smoke and EC, black smoke monitoring data from the National Air Quality Monitoring Network are analysed.

## B.6.1. Utrecht - black smoke

Black smoke data have been collected at a background location ("University Library" - UB) and two traffic locations in Utrecht ("K. de Jongweg" and "Wittevrouwen"). At K. de Jongweg the traffic intensity was 24000 vehicles/24 h with 4% heavy duty (trucks and buses), while at Wittevrouwen the intensity was 7100 vehicles/24 h with 4% heavy duty (mainly buses). Using the CAR model, the annual average concentrations for BS are estimated. The results are presented in Table 2.

*Table 2: The BS concentrations derived from black smoke monitoring in 1998 in Utrecht and estimates by the CAR model.*

| Monitoring location | BS ($\mu g/m^3$) measured annual | BS ($\mu g/m^3$) CAR-model annual |
|---|---|---|
| UB (background) | 10 | - |
| DeJongweg (traffic) | 19 | 14* |
| Wittevrouw (traffic) | 38 | 17* |

*: including a background value of 10 $\mu g/m^3$.

Increased BS concentrations measured at the heavy traffic locations, as compared to the background, reflect the impact of local traffic on black smoke concentrations. The high values in Wittevrouwen are related to a narrow streetcanyon with mainly buses, while K. de Jongweg is a wide street with a both trucks and buses.

Comparison of the measured (*19*: de Jongweg and *38*: Wittevrouwen) and computed (*14*: de Jongweg and *17*: Wittevrouwen) black smoke concentrations suggests that the CAR model underestimates black smoke concentrations. The same emission factors for trucks and buses have been used in the CAR model, which are mainly derived from exhaust pipe tests. The high measured values in Wittevrouwen indicates that buses actual have higher emission factors than based upon test values. *This indicates that maintenance of (some) buses is not optimal and therefore, black smoke emissions are higher than expected.*

The seasonal variation of black carbon concentrations is presented in Table 3 for background and heavy traffic locations.

*Table 3: The BS concentrations derived from black smoke monitoring in four seasons 1998 in Utrecht during working days.*

| Monitoring location | BS (μg/m$^3$) (measured) | | | |
|---|---|---|---|---|
| | winter | spring | summer | autumn |
| UB (background) | 16 | 10 | 8 | 13 |
| DeJongweg (traffic) | 25 | 20 | 20 | 24 |
| Wittevrouw (traffic) | 42 | 42 | 37 | 51 |

From Table 3, it is concluded that especially in summer with favourable atmospheric dispersion the lowest BS concentrations are encountered. In traffic locations the winter values are about 20% higher than in the summer, while the background location is twice as high. This indicates that in the winter an additional regional factor may increase background concentrations, for example more eastern winds with higher BS from Germany.

### B.6.2 Utrecht – EC

In this section, EC concentrations in Utrecht are examined. The black smoke data collected at the background location and the two heavy traffic locations as distinguished in the foregoing section are applied. Using the relations between EC and black smoke (section B 3.1.2), EC concentrations are calculated from the BS monitoring data . The results for Utrecht are presented in Table 4a.

*Table 4a: The EC concentrations derived from black smoke monitoring in 1998 in Utrecht and the relation: EC = 0.15 * BS + 3 μg/m$^3$.*

| Monitoring location | BS (μg/m$^3$) measured annual | EC (μg/m$^3$) calculated from BS annual |
|---|---|---|
| UB (background) | 10 | 4.5 |
| DeJongweg (traffic) | 19 | 6 |
| Wittevrouwen (traffic) | 38 | 9 |

Using the CAR model, the average annual concentrations for EC have been calculated. The following EC emission factors are applied: 23 mg EC per VKT (light and medium duty vehicles; see Table 1b), 375 mg EC per VKT (buses - Wittevrouwen; see Annex B2b) and 472 mg EC per VKT (buses/trucks - deJongweg; see Annex B2b). The results are presented in Table 4b.

*Table 4b: The EC concentrations derived from the CAR model with data of traffic in 1998 in Utrecht for K. de Jongweg and Wittevrouwenstraat.*

| | EC (μg/m$^3$) |
|---|---|
| | annual |
| UB (background) | 4.5 |
| DeJongweg (traffic) | 7 |
| Wittevrouwen (traffic) | 6 |

It is concluded that in the EC concentrations derived from the BS measurements in Table 4a match quite well with the computed EC concentrations in Table 4b. This suggests that the relation derived for EC and BS in section B3.1.2, as well as EC emission factors are quite adequate. Though, the low EC values in Wittevrouwen in Table 4b suggest that the EC emission factor for buses in Annex 1b is too low.

### B.6.3. Consequences for the so-called $PM_{10}$ gap in the Netherlands

RIVM concluded from measurements and modelling of $PM_{10,}$ that there is a "gap" in $PM_{10}$ concentrations in the Netherlands. This was attributed mainly to the $PM_{2.5-10}$ fraction (e.g. road dust, agricultural dust, sea-spray). However, it was concluded from recent research that the gap may result from the $PM_{2.5}$ fraction. Especially, $PM_{carb}$ is a likely candidate.

RIVM estimated the annual urban background of $PM_{carb}$ in 1995 at 7 $\mu g/m^3$ [25]. RIVM monitored a background of BS in urban areas of 18 $\mu g/m^3$. In accordance to our estimates this results in an EC concentration of: 0.15 * 18 + 3 = 5.7 $\mu g/m^3$ and an OC concentration of 1.5 * 5.7 = 8.5 $\mu g/m^3$. This results in a $PM_{carb}$ of 14 $\mu g/m^3$. This is a factor 2 higher than the $PM_{carb}$ concentration estimated by
RIVM for that year. As aforementioned, there are a number of uncertainties in our study, which complicates interpreatation of our data. However, this example illustrates that more research on $PM_{carb}$ is required to examine the contribution of EC and OC emissions by road traffic to $PM_{10}$ in the Netherlands.

# B.7. CONCLUSIONS AND RECOMMENDATIONS

The conclusions of the research are as follows:

- the review of international research indicates, that the black smoke measurements are a proxy for elemental carbon (EC) concentrations. This relation is quite consistent and especially research in Germany is relevant for the relation of EC and BS in the Netherlands. For the rural background the following relation is proposed for black smoke (BS) - measured by a black smoke monitor - and EC: EC = 0.2 * BS + 1.5 $\mu g/m^3$ and for urban/heavy traffic locations: EC = 0.15 * BS + 3 $\mu g/m^3$;

- the ratio of EC to OC in the Netherlands is estimated 1.5 - 2 (background) and 1 - 1.5 (urban/heavy traffic);

- it is estimated that trucks contribute 30% of EC and OC ("soot") emissions by highway traffic, while buses and vans in urban traffic contribute respectively, 20% and 30% to soot emissions in urban areas;

- $PM_{carb}$ is an important candidate to fill the so-called $PM_{10}$ gap in the Netherlands. In 1996, RIVM estimates a $PM_{carb}$ of 7 $\mu g/m^3$, which (in accordance to this study) may have been a concentration of 14 $\mu g/m^3$. More research on EC/OC (e.g. emission inventories; exhaust pipe emissions and concentrations in ambient air near roads) is recommended to further examine $PM_{carb}$.

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# Annex B1 Overview of methods in use for measuring carbon

## Optical methods

*Aethalometer*. This instrument samples particulate matter on a filter and the attenuation of light *transmitted* through the filter is measured [11]. It is a low-cost method, which may provide hourly measurements of BS concentrations. At a constant airflow, the deposition of black carbon on the filter is proportional to its mass concentration (BS), as measured by the increase of light absorption (A). This is given by the equation:

$$A = \sigma * BS \qquad (B1)$$

with sigma ($\sigma$) the specific attenuation coefficient of black carbon. The aethalometer is calibrated with a default $\sigma$ of 19 $m^2.g^{-1}$. However, experimental data shows that $\sigma$ ranges from 2 $m^2.g^{-1}$ for remote areas to 25 $m^2.g^{-1}$ for urban areas [12]. This variation mainly depends on i.) the type of combustion process (e.g. coal-fired power plant or diesel exhaust) and ii.) ageing of carbonaceous aerosol during atmospheric transport, including internal and external mixing with non-light-absorbing material. Hence, in order to calculate the mass concentration of BS from the measured attenuation, a site-specific calibration is required [2; 12-14].

*Black smoke monitor*. The second optical technique to measure black smoke is the so-called "black smoke monitor". This instrument (EEL 43 Smoke Stain Reflectometer) measures the attenuation of light *reflected* by a filter. Samples of particulate matter are collected on a Whatman No. 1 filter. Blackening of the filter results in decreasing reflectance, which is a measure of the BS concentration [16]. The sampling period is 24 hour for a detection limit of 1 $\mu g/m^3$.

Similar to the aethalometer method, one can not directly correlate the black smoke readings to *mass* concentrations. To estimate the mass of BS, an OESO standardised calibration curve is applied. The calibration curve of 1964 is based upon experiments in the period 1959-63, when carbonaceous particles were mainly emitted by coal-fired power plants. Experiments in the UK in the period 1963-78, indicated that values of "black smoke" (estimated with the original calibration curve) should be multiplied with a factor 2.5 [17]. Hence, carbonaceous particles have become lighter in colour and thus, represent a higher mass per "black absorption unit" in this method. A new calibration curve, based upon absorption coefficients of various particles has been established in 1995 [18]. The calibration curve agreed with a curve prepared in 1982. However, similar to the aethalometer, a site-specific calibration is required to estimate mass concentrations from the black smoke monitor.

## Thermographic techniques for EC and OC

Thermographic methods are based on volatilization and oxidation of OC and EC at different temperatures and different atmospheres (100% nitrogen or mixed with oxygen) [3]. The resulting $CO_2$ is measured. This method has been developed over the last 25 years. This has recently, resulted in commercial available instruments, such as the Rupprecht & Patashnick 5400 monitor in 1996. This instrument allows for hourly EC and OC measurements at a flow rate of 1 $m^3/h$ and sampling inlets for $PM_{10}$, $PM_{2.5}$ and $PM_1$. Due to costs and hardware, this technique is not appropriate for a monitoring network with a large number of sampling stations. The thermograph is used to measure temporal variation of EC and OC at a location.

Subsequently, a site-specific calibration of an aethalometer or black smoke monitor may be established. The latter two can than be applied for routine, monitoring purposes of EC, as a thermograph is relatively costly

## Miscellaneous techniques

In addition to the aforementioned methods, other techniques have been developed to measure carbonaceous particles. These techniques have been mainly applied for experimental work at a limited number of locations. This relates to solvent extraction of sampled carbonaceous particles and subsequently, analysis of OC [2] or identification of a large number of organic compounds with gaschromatography [21]. Also, carbonaceous samples have been collected by denuder/filter pack combinations followed by thermographic analysis [4]. Recently, a so-called "integrating sphere" technique has been developed which is based on dissolving sampled filters in chloroform and subsequently, measurement of the light flux to estimate the EC content [13].

# Annex B2: Emission factors of EC and OC for urban and highway traffic.

*Annex B2.1a: Emission factors for highway traffic in the Netherlands [10].*

| Type of vehicle | % highway traffic | exhaust pipe EC/OC (mg.VKT) | tire wear* EC/OC (mg.VKT) | road dust** EC/OC (mg.VKT) |
|---|---|---|---|---|
| *light duty* | | | | |
| petrol + converter | 40 | 1/2 | 1/2 | 1/2 |
| petrol | 18 | 5/15 | 1/2 | 1/2 |
| diesel + converter | 8 | 40/25 | 1/2 | 1/2 |
| diesel | 8 | 80/55 | 1/2 | 1/2 |
| LPG | 10 | 1/2 | 1/2 | 1/2 |
| *medium duty* | | | | |
| petrol + converter | 0,5 | 2/4 | 2/3 | 2/3 |
| petrol | 1 | 7/21 | 2/3 | 2/3 |
| diesel + converter | 3 | 60/40 | 2/3 | 2/3 |
| diesel | 6 | 125/80 | 2/3 | 2/3 |
| LPG | 1 | 1/2 | 2/3 | 2/3 |
| *motor* | 0,5 | 20/60 | 1/2 | 1/2 |
| *heavy duty* | 4 | 300/200 | 8/16 | 8/16 |

* tire wear: $PM_{10}$ emission is 100% allocated to $PM_{2.5-10}$;

** road dust: National Institute for Statistics (CBS) estimates road dust re-suspended from paved roads equal to tire wear. The emission is 100% allocated to $PM_{2.5-10}$.

*Annex B2.1b: Emission factors for urban traffic in the Netherlands [van den Brink].*

| type vehicle | % urban traffic | exhaust pipe EC/OC (mg.VKT) | tire wear* EC/OC (mg.VKT) | break lining* EC/OC (mg.VKT) | road dust** EC/OC (mg.VKT) |
|---|---|---|---|---|---|
| *light duty* | | | | | |
| petrol + converter | 24 | 2/3 | 1/2 | 3/6 | 1/2 |
| petrol | 28 | 12/20 | 1/2 | 3/6 | 1/2 |
| diesel + converter | 7 | 55/35 | 1/2 | 3/6 | 1/2 |
| diesel | 8 | 110/70 | 1/2 | 3/6 | 1/2 |
| LPG | 9 | ½ | 1/2 | 3/6 | 1/2 |
| *medium duty* | | | | | |
| petrol + converter | 1 | 3/6 | 2/3 | 3/6 | 2/3 |
| petrol | 2 | 10/30 | 2/3 | 3/6 | 2/3 |
| diesel + converter | 6 | 80/50 | 2/3 | 3/6 | 2/3 |
| diesel | 10 | 175/110 | 2/3 | 3/6 | 2/3 |
| LPG | 1 | 3/6 | 2/3 | 3/6 | 2/3 |
| *buses* | 1 | 360/950 | 6/12 | 3/6 | 6/12 |
| *heavy duty* | 2 | 550/350 | 8/16 | 3/6 | 8/16 |

* tire wear and break lining: $PM_{10}$ emission is 100% allocated to $PM_{2.5-10}$;

** road dust: National Institute for Statistics (CBS) estimates road dust re-suspended from paved roads equal to tire wear. The emission is 100% allocated to $PM_{2.5-10}$.

# Concluding remarks: Relation between ultrafines and carbon in traffic emissions

It would be a expected that that emission and dispersion of ultrafine particles from road traffic would be correlated with carbon. In that case black-carbon or black-smoke could be used as a proxy for the ultrafines. It was concluded in part A of the study that there is insufficient information on emissions and concentration of the number of ultrafine particles. Therefore data to warrant a direct relation between the number of particles emitted and the amount of carbon relation are not present. Therefore emission data combined with insight in the particle processes was used to more theoretically assess a possible relation between particle number and carbon mass in emission and dispersion. It is shown on the basis of particle dynamics that such a relation should not by necessity exist. An example is that of LPG-fueled vehicles, which are an important factor in Dutch road traffic. These emit large numbers of ultrafine particles, comparable to that by diesels, but the amount of carbon is several orders of magnitude less. Even for diesel-fueled vehicles, most of the carbon mass is in a few particles of a quite large size which are thus being produced via a different way than the much smaller and more numerous ultrafines the which the production is not by necessity related to that of the numerous small ones. Thus a relation between number of particles and mass of carbon emitted is even not warranted in diesel traction, but might exist. It is thus concluded that a relation therefore questionable and needs further investigation

***Direct measurements***

Correlations between particle number and emitted carbon (mass) have been studied on test-banks for vehicles. There is not a consistent pattern because of the limited number of data available (in open literature). The general conclusion is that the ultrafines contain very little mass and that most of the carbon is concentrated in particles of a larger size.

The authors performed co-operative experiments in a highway-tunnel with separate ducts for heavy duty and light duty vehicles. Both number of ultrafines and carbon mass were determined. This test provided unique data on the relation between carbon emissions and particle number under more realistic traffic condition than on a test-bank. The very preliminary emission results, which provide insight in the average number and concentration of carbon (not to be quoted yet) are summarised in table 1.

TABLE 1

| | *Number /km* | *EC*) mg/km* |
|---|---|---|
| Light-duty vehicles | 7 (±2) $\cdot 10^{14}$ | 18 (±3) |
| Heavy-duty vehicles | 200 (±1) $\cdot 10^{14}$ | 160 (±15) |

*) EC = Elemental Carbon; for the definition of EC see part B of this report

## *Indirect data*

In the mentioned ULTRA projects [10] both particle number and black smoke have been measured, but results have not been published. In Erfurt, Helsinki and recently in Amsterdam the relation between particle number and fine particle mass has been investigated; only older data from Erfurt, measured over a period of years, have been analysed. They show a very poor correlation between PM and number. In Brisbane a good correlation was found, but the study was of a much shorter duration. A crucial problem in using road-side measurements for assessment of a relation between particles and mass emitted by traffic is that other sources significantly contribute to both parameters [9].

It should further be realized that mass is a conservative aerosol parameter, that is, it does not change after emission while the number of particles changes from source to measuring site because of the microphysical processes discussed in chapter A4 above.

Summarizing, there is as yet insufficient experimental proof for presence or absence of a relation between number of particles and mass of carbon in emission and near roads, but emission studies and theoretical reasoning indicate that such a relation is not to be expected.

**Urban versus rural concentrations**

There is a possibility of making a rough estimate of the relation between carbon mass and number of ultrafines from traffic by comparing data in cities and at more remote sites in connecting air flows. We are aware of such data and preliminary analysis in the Manchester area in the UK and also now have own data. We were not able to analyze any of these unpublished data because of the limited time available for this study.