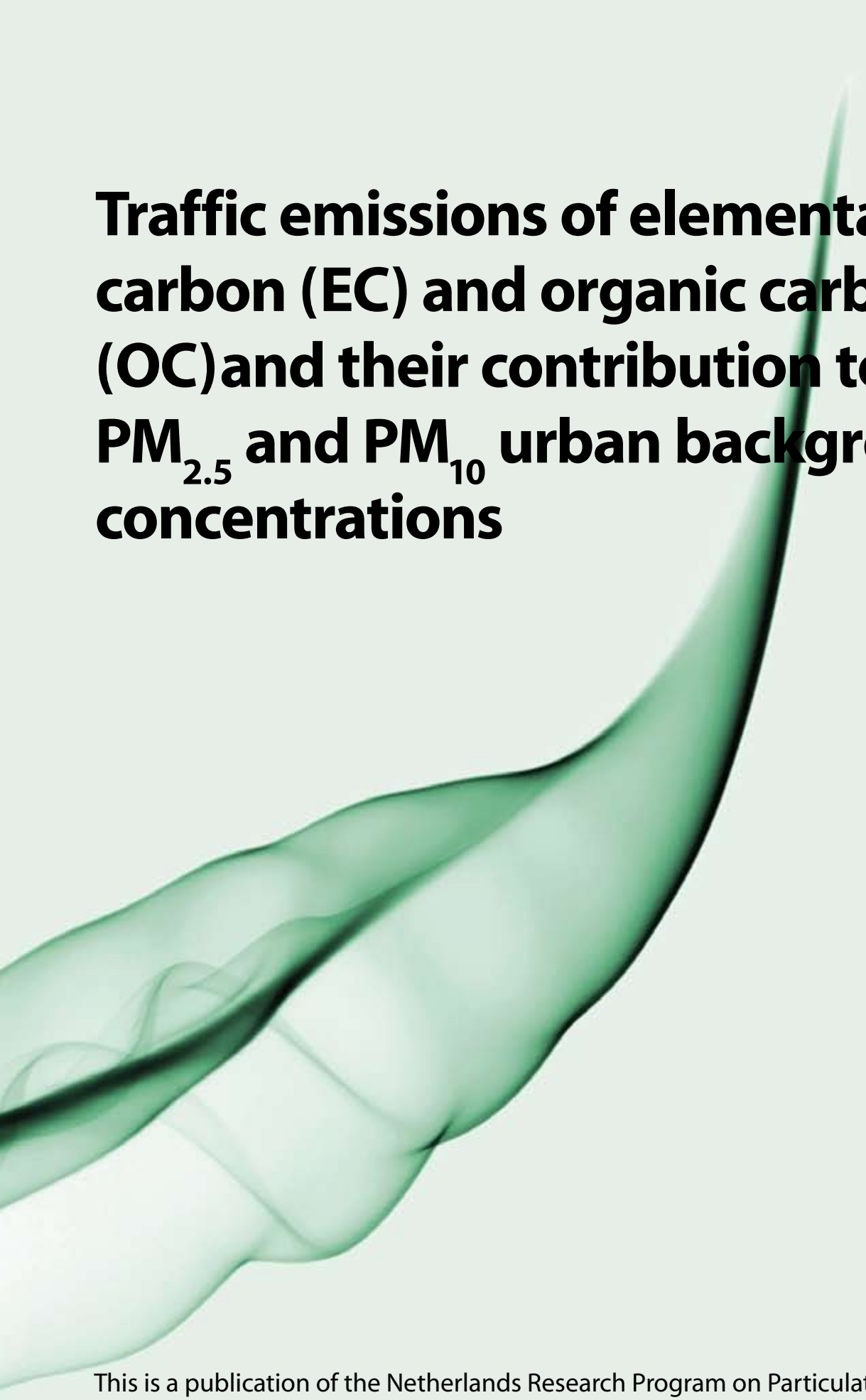
Traffic emissions of elemental carbon (EC) and organic carbon (OC)and their contribution to $PM_{2.5}$ and PM_{10} urban background concentrations



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

Netherlands Environmental Assessment Agency

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TNO

BOP report

Traffic emissions of elemental carbon (EC) and organic carbon (OC) and their contribution to $PM_{2.5}$ and PM_{10} urban background concentrations

M. P. Keuken, TNO; H.M. ten Brink, ECN

Netherlands Environmental Assessment Agency

ECN Energy research Centre of the Netherlands

TNO

rivm National Institute for Public Health and the Environment

Traffic emissions of elemental carbon (EC) and organic carbon (OC) and their contribution to PM2.5 and PM10 urban background concentrations

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

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Rapport in het kort

In het Nederlandse Beleidsondersteunend Programma Fijnstof (BOP) is onderzoek uitgevoerd naar de bijdrage van elementair koolstof (EC) en organisch koolstof (OC) aan de stedelijke achtergrond van $PM_{2.5}$ en PM_{10}. Hieruit is geconcludeerd dat de toename van EC en OC in de stedelijke achtergrond het gevolg is van verkeersemissies. Deze jaargemiddelde toename is in de orde van 0.5 µg/m³. Rekeninghoudend met de gemiddelde jaarlijkse concentratie van $PM_{2.5}$ en PM_{10} is het potentieel om de stedelijke achtergrond te reduceren door het terugdringen van uitlaatemissies van autoverkeer minder dan 5%.

Contents

Executive summary

The Netherlands Research Program on Particulate Matter (BOP) is a national programme on $PM_{2.5}$ and $PM_{10,}$ funded by the Netherlands Ministry of Housing, Spatial Planning and the Environment (VROM), and implemented by TNO, the Energy Research Centre of the Netherlands (ECN), the National Institute for Public Health and the Environment (RIVM) and the Netherlands Environmental Assessment Agency (PBL). The programme aims to reduce uncertainties regarding concentration levels of particulate matter (PM), and to gain a better insight into the different sources which contribute to PM concentrations in ambient air. BOP started in February 2007 and was finalized in March 2009.

One of the aspects studied in the BOP programme is the contribution of elemental carbon (EC) and organic carbon (OC) to the urban background concentrations of $PM_{2.5}$ and PM_{10}. Knowledge about anthropogenic sources controlling the composition and urban background concentrations of especially $PM_{2.5}$ is important, as under the new EU Air Quality Directive, there is a requirement to reduce the urban background concentrations of $PM_{2.5}$ in 2020 against 2010. Reduction in road traffic emissions of EC and OC, potentially, may be important for reducing urban background concentrations of $PM_{2.5}$. Presently, there is a gap in knowledge on 1) the increment in EC and OC in urban background concentrations, compared to those in regional background concentrations, and 2) EC and OC emission factors for urban traffic, to model the contribution from urban traffic to EC and OC concentrations.

Research carried out in this part of the BOP programme has the following objectives:

1. to determine the increment in EC and OC concentrations, from the regional to the urban background, the so-called "urban increment";
2. to establish EC and OC emission factors for urban traffic, and
3. to estimate the contribution of traffic-related EC and OC to urban background concentrations of PM.

Specific research on EC and OC was performed in the Rotterdam-Rijnmond area, in three monitoring campaigns: the *first* campaign, held in 2006 to 2007, was directed at identifying urban sources contributing to EC, and looked at the trend for black smoke (BS) at urban background locations, between 1989 and 2006; the *second* campaign, in March 2008, was directed at the regional/urban/street increment in EC, and the *third* campaign, in Oktober 2008, at establishing EC and OC emission factors for urban traffic. Furthermore, this report presents EC and OC data from the monitoring campaign in the BOP research programme, in 2007 and 2008.

The main findings and conclusions from this study are summarised as follows:

- *EC;* The annual *regional* background concentration of EC was 2.1 ± 1.2 µg C/m³, and the annual urban increment was 0.3 ± 0.2 µg C/m³ (BOP). The annual average EC concentration at heavy-traffic inner-urban roads was 4 ± 2.2µg C/m³ (BOP). The study in Rotterdam indicated that other sources than road traffic, such as industry, refineries, aviation and shipping, did *not* contribute significantly to the urban background concentrations of EC;
- *OC;* The annual *regional* background concentration of OC was 1.6 ± 0.5 µg C/m³, and the annual urban increment was 0.1 ± 0.2 µg C/m³ (BOP). Thus, the urban background concentration was *not* significantly elevated against that of the regional background. The annual average OC concentration at heavy-traffic inner-urban roads was 1.9 ± 0.8 µg C/m³ (BOP). These results illustrate that urban and street OC concentrations were mainly controlled by regional OC background concentrations. The regional level was controlled by primary emissions (e.g. combustion processes) and secondary organic aerosol. The latter was attributed to biogenic precursors, such as terpenes released by vegetation and photochemical ageing of diesel engine emissions. The contributions to OC from biogenic and combustion sources was estimated at 60% and 40%, respectively [Harrison, 2008]. The study in Rotterdam indicated *no* significant increment in OC at the traffic locations, contrary to at the urban background locations. Other urban sources, such as industry, refineries, aviation and shipping, also did not significantly contribute to the urban background concentration of OC;
- *Contribution of EC and OC emissions from road traffic to urban background concentrations of $PM_{2.5}$ and PM_{10};* From the study in Rotterdam could be concluded that the increment in EC and OC at the urban background locations was mainly related to road-traffic emissions. To compute the contribution of *OC* to the $PM_{2.5}$ and PM_{10} background concentrations, OC was expressed as the mass of organic compounds 'OCom'. This was performed by multiplying OC by a factor of 1.6 [Bae, 2006]. For the urban increment in OC, in the Netherlands, this resulted in a contribution of organic compounds of 0.2 µg/m³ to $PM_{2.5}$ and PM_{10}. Consequently, the contribution of EC and OCom emissions from road traffic to the urban background concentrations of $PM_{2.5}$ and PM_{10} was 0.3 (EC) plus 0.2 (OCom), which is 0.5 µg/m³. The

average urban background concentrations of $PM_{2.5}$ and $PM_{10,}$ in the Netherlands, were in the range of 15 to 20 and 20 to 30 µg/m³, respectively (BOP). *It was concluded, that the potential for reducing urban background concentrations of $PM_{2.5}$ and PM_{10} by reducing exhaust emissions from road traffic, would be less than 5%*;

- *EC as traffic-related PM indicator;* The hourly increments in EC at street locations compared to urban background locations – measured by automated monitors in Rotterdam – were in good agreement with the traffic intensity during weekdays and weekends. The EC emission factor for urban traffic was established at 10 mg C/km, which is at the low end of the range of values 8 to 20 mg C/km presented in the literature. For OC, *no* increment could be measured and, thus, *no* emission factor for OC was established. In the literature, a ratio of 4:1 is indicated for EC and OC in road-traffic emissions [Harrison, 2008], which, in our study in Rotterdam, would have resulted in an increment below the detection limit of the monitoring method. This indicated that traffic emissions of EC and OC were dominated by EC, which is in agreement with the BOP results for the Netherlands, in this report. Subsequently, an annual EC concentration map for Rotterdam was modelled, by using the dispersion model 'URBIS'. The modelled contrast between EC concentrations near heavy road-traffic and at background locations, was much higher than that for $PM_{2.5}$ and PM_{10}. This confirms, that EC is a sensitive indicator for the dispersion of traffic-related PM emissions;
- *Black Smoke (BS) as proxy for EC trend;* The results for Rotterdam confirmed the results from earlier studies, that BS measurements – presented in optical units without conversion to mass units – have a linear correlation with EC (R^2 =F 0.93), but *not* with OC. Both BS and EC reflect the contribution of (incomplete) combustion emissions to PM. From measurements of BS at an urban background location in Rotterdam and a regional location, in the period from 1989 to 2006 – as a proxy for EC concentrations – could be concluded that EC concentrations, especially those after 2001, have been decreasing significantly, by 5% per year. This shows the impact from cleaner vehicles on urban air quality. When using PM_{10} as an indicator for air quality, this trend could not be detected. Differences in road-traffic composition, and other local factors, would have to be considered before the results from Rotterdam could be generalised for the Netherlands as a whole;
- *Note on the EC and OC measurements;* Major problems in research on EC and OC are the lack of an agreed standardised analytical procedure, and the uncertainty about the artefacts that occur by adsorption of volatile OC compounds to filters. The use of field blanks for correction is the approach used here to correct for the artefact, but this approach should be further supported. Two analytical methods are widely applied to determine EC and OC: the 'Sunset method' and the 'Cachier method'. The BOP programme applied a method developed by ECN, based on the Cachier method, to measure the average annual EC and OC at street, urban and regional locations in the Netherlands [ten Brink et al, in preparation]. In the study in Rotterdam on the EC and OC contributions from traffic, the Sunset method was used, as well as automated methods for hourly measurements of EC and OC. From a comparison of filters that were collected in the BOP programme, it was concluded that results from the Sunset method, systematically, were lower by a factor of 0.4 for EC, compared to those from the Cachier method. The field blank for OC, in BOP, was 1.2 µg C/m³, while, in Rotterdam, the field blank was 0.7 µg C/m³. The relevant results for OC were corrected in accordance to the field blanks. In the findings and conclusions is indicated whether the results refer to the Cachier analysis ('BOP') or the Sunset analysis ('Rotterdam'). Because of the fact that the Cachier method measures a higher EC content also differences in EC are more pronounced in this method as compared with the Sunset approach.
- It is recommended to :
  - develop, improve and standardise sampling and analytical procedures for monitoring EC and OC ambient air concentrations and
  - perform more research on EC as an indicator for traffic-related particulate matter, in health studies.

1 Introduction

1.1 Background

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

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

These objectives are approached through the integration of mass and composition measurements of PM_{10} and $PM_{2.5}$, emission studies and model development. In addition, dedicated measurement campaigns have been conducted to research specific PM topics.

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

The urban background concentration of PM consists of 1) a regional background concentration which depends on the contributions from large-scale transport of pollutants, and 2) a contribution from urban sources. Presently, there is a lack of knowledge on 1) the increment in EC and OC at urban background locations, compared to that at the regional background locations, 2) the impact from local combustions sources (e.g. shipping, industries and road traffic) on urban background concentrations of EC and OC, and 3) EC and OC emission factors for urban traffic, to model its contribution to EC and OC concentrations.

In general, EC is emitted from incomplete combustion of fossil fuels and natural fires. OC originates from a wide range of sources, including combustion processes, re-suspension of road dust and secondary organic aerosol. Secondary OC originates from biogenic precursors, such as terpenes released by vegetation and photochemical ageing of diesel engine emissions. The ratio between biogenic and combustion sources of OC is estimated at 60% to 40% [Harrison, 2008]. The sum of EC and OC emissions from combustion processes is known as 'soot'.

A study on these EC and OC aspects has been carried out on the city of Rotterdam, by ECN and TNO, supported by the Environmental Protection Agency Rijnmond (DCMR) and RIVM. Prior to this study, TNO performed research, in cooperation with DCMR, on EC and black smoke (BS) in Rotterdam, in 2006 and 2007, the results of which are also presented in this report.

1.2 Objectives

The study carried out in this part of the BOP Programme has the following objectives:

1. to determine the increment in EC and OC concentrations, from the regional to the urban background;
2. to establish EC and OC emission factors for urban traffic, and
3. to estimate the contribution of traffic-related EC and OC to the urban background concentrations of PM.

2 Methodology and results

2.1 EC and OC and black smoke measurements

2.1.1 EC and OC measurements

The content of carbonaceous material in PM can be distinguished in elemental carbon (EC) and organic carbon (OC), which are defined according to analytical method. Quite often, the terms EC and 'black carbon' (BC) or 'black smoke' (BS) are also mixed. The terms BC and BS are used when *optical* methods are applied to quantify the light-absorbing fraction of PM, while the term EC is used when *thermal* methods have been applied for distinguishing EC and OC.

The total carbon content of PM shows good agreement between various methods, but large uncertainties are encountered for the ratio between EC and OC. This is attributed to artefacts associated with *sampling of OC*, especially adsorption of volatile OC (also in field blanks) and analytical difficulties of *separating EC from OC*. At present, the most widely applied methods for analysing EC and OC are the thermal methods. These methods are based on heating the sampled filter in a non-oxidising environment (e.g. helium atmosphere) to measure OC, followed by heating the filter in an oxidised environment (e.g. oxygen atmosphere) to measure EC. During the heating of the filter for the OC analysis, artificial EC is generated and, if not accounted for, this will positively bias the 'true' EC of the sample. Basically, two types of thermal methods were applied: the Sunset method and the Cachier method [Chow, 1993]. The former method resulted in lower EC and higher OC than the latter. Lower values for EC in the Sunset method related to the thermal-optical correction for the artificially generated EC, *which was not corrected for in the Cachier method*.

Currently, there is no consensus within the scientific community on how to sample OC while taking artefacts into account; neither of the above-mentioned analytical methods should be applied to quantify EC and OC. Within the EU-funded project EUSAAR (*European Supersite for Atmospheric Aerosol Research*), a unified protocol for sampling and analysing EC and OC is being developed. Also, the Commission of European Standardisation prepares a protocol for EC and OC measurements, for which the Sunset method is likely to be adopted.

In the BOP programme, EC and OC were analysed by using a method developed at ECN, based on the Cachier method, while in the Rotterdam study the Sunset method was applied. To derive EC and OC emission factors for urban traffic, automatic monitoring on an hourly basis was applied in Rotterdam, with equipment developed by ECN (see Annex 2).

Another issue of EC and OC measurements concerns the contribution of OC to the mass of PM. For EC and OC, the analysis results in mass carbon per m^3. For EC, this is the contribution to PM, but for OC, the carbon content is associated with organic compounds containing hydrogen, nitrogen and oxygen. The mass of these organic compounds (OCom) depends on the time and location. To compute the mass of organic compounds, studies indicate multiplication by a factor of 1.3 to 1.6 for urban OC, and 1.5 to 1.9 for regional OC [Bae, 2006]. In this report, in Section 2.5, multiplication by a factor of 1.6 was used to correct the OC data to OCom data, to compute the contribution of OC to the urban background.

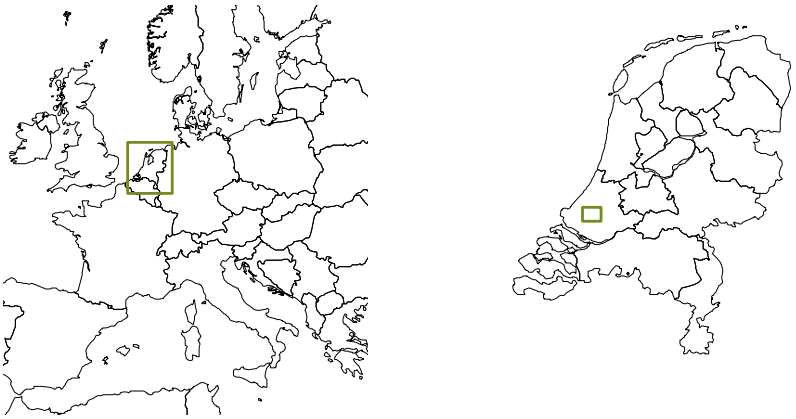
2.1.2 Black smoke measurements

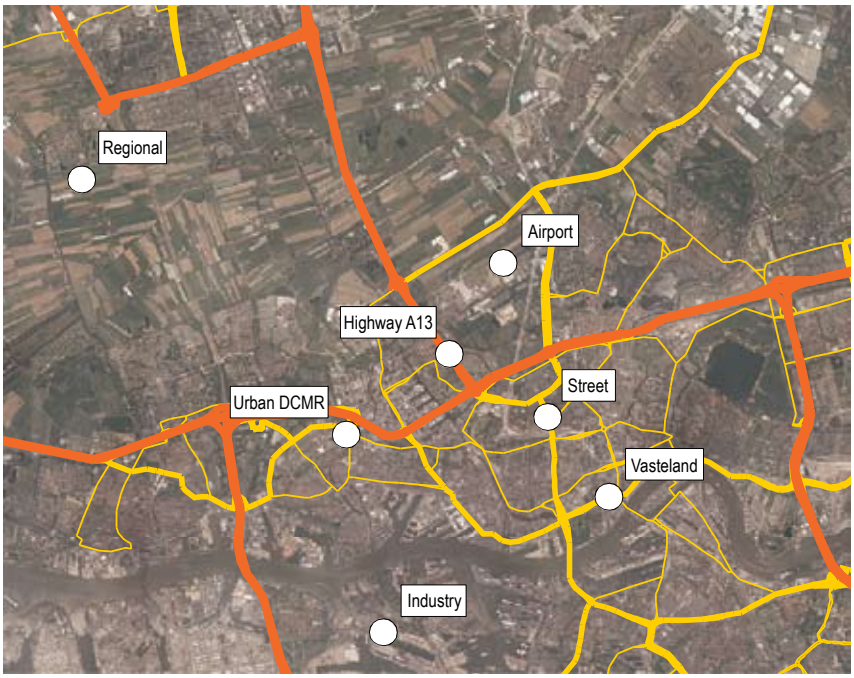
In the past, BS has been determined, as an indicator for particulate matter originating from incomplete combustion of fossil fuels (e.g. fly-ash particles). BS measurements to establish *mass concentration* of 'black particles' are now regarded semi-quantitative, due to the time and location specific conversion of absorbance coefficient units to mass units [Erdmann, 1993; Hamilton, 1995; Muir, 1995]. Today, the *optical* BS method has widely been replaced by EC and OC measurements, to achieve quantitative m*ass* units for carbonaceous PM. However, there are long time-series of BS, which may be used for studying the trend of black particles in ambient air. For example, in the Rijnmond area, DCMR and RIVM have been monitoring BS since the 1960s. In this report, first the correlation of BS with EC is investigated, followed by a trend analysis of BS, as a proxy for the trend in EC, in Section 2.2.4.

2.2 Monitoring EC, OC and Black Smoke in 2006 and 2007, and Black Smoke from 1989 to 2006

2.2.1 Monitoring locations for EC, OC and black smoke in 2006 and 2007

From November 2006 to September 2007, TNO, in cooperation with DCMR (the Rijnmond Environmental Protection Agency), executed a monitoring programme for EC, OC and Black Smoke (BS) in Rotterdam, the Netherlands. The objec-





Monitoring location

Road type

Highway

Main road

Other roads

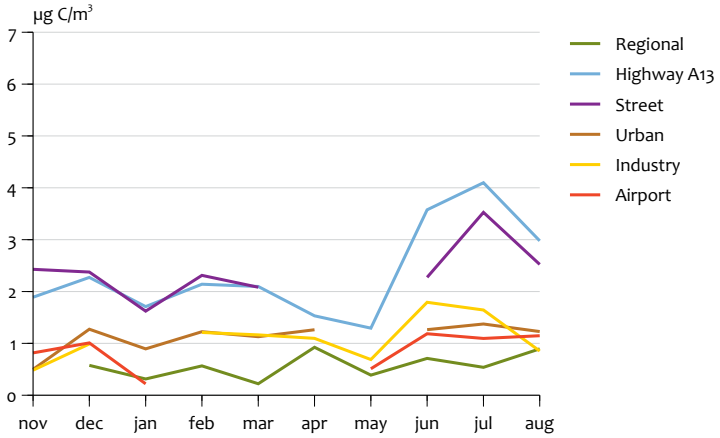
Six sampling locations for EC, OC and BS, in Rotterdam, between 2006 and 2007, and the urban background location (Vasteland) with BS measurements in the period from 1989 to 2006.

tives of this study were directed at 1) the contribution from local sources to the urban background concentrations of EC and OC, 2) the correlation between BS and EC, and 3) the trend of BS in the period from 1989 to 2006, as a proxy for the trend of EC.

At six sampling locations, fortnightly PM samples were taken between November 2006 and March 2007, and monthly samples were taken between April and September 2007; they were analysed for BS, EC and OC. The sampling volume was of the order of 4 m³ on QMA filters, and field blanks were included during each sampling period. The BS measurements were performed with an EEL 43 Smoke Stain Reflector [ISO 9835, 1993], and for EC and OC measurements the Sunset method was used [Chow, 1993]. The six locations are shown in Figure 2.1. Also, the urban background location ('Vasteland') is shown, where in the period from 1986 to 2006 BS measurements were performed by DCMR. In this period, BS measurements were also executed by RIVM, at the regional location at Westmaas, which is located 10 kilometres south of Rotterdam. This regional location is outside of the area shown in Figure 2.1.

EC concentrations in Rotterdam **Figure 2.2A**

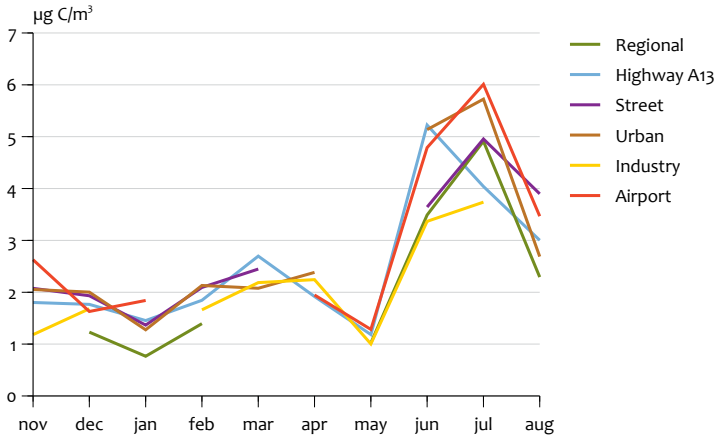
During the period from November 2006 to September 2007



EC concentrations (µg C/m³) at the six locations in Rotterdam, during the period from November 2006 to September 2007.

OC concentrations in Rotterdam **Figure 2.2B**

During the period from November 2006 to September 2007



Similar to Figure 2.2A, but for OC (µg C/m³).

The six locations for monitoring EC, OC and BS, in 2006 and 2007, were selected with the following monitoring objectives:

- 'regional': the regional background concentration near Rotterdam;
- 'urban DCMR': the urban background concentration in Rotterdam;
- 'industrial': the impact of industrial/refineries emissions;
- 'street': the impact of traffic emissions at a street location, Bentinckplein in Rotterdam (of the National Air Quality Monitoring Network);
- 'motorway A13': the impact of traffic emissions from the motorway A13 and
- 'airport': the impact from Rotterdam airport 'Zestienhoven'.

2.2.2 Regional-urban-street gradient of EC and OC, in 2006 and 2007

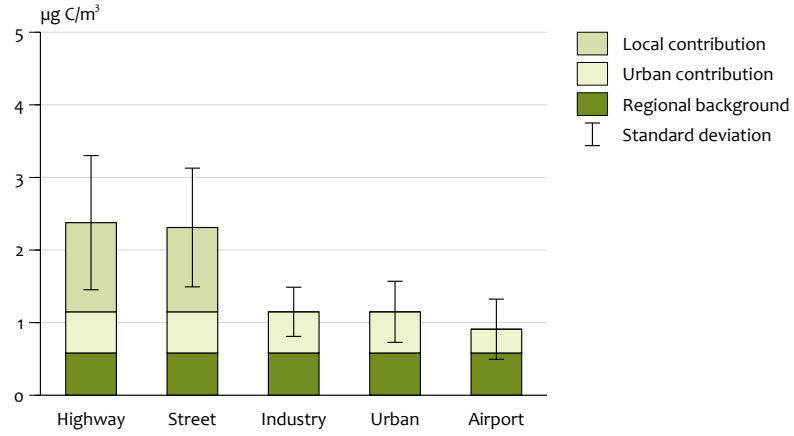
The monitoring results for EC and OC at the six locations in Rotterdam are presented in Figure 2.2A and 2.2B.

The results in Figure 2.2A show, that there is no seasonal variation in the regional background concentrations of EC. This is in line with other research [Bae, 2006]. Figure 2.2A illustrates the importance of traffic emissions to EC, by the elevated levels near traffic impacted locations 'street' and 'motorway'. Increased levels of EC near the traffic locations in the summer period are difficult to explain, as one expects *lower* values due to increased dispersion in the summer, and less emissions due to summer holidays.

The results in Figure 2.2B have been corrected for a field blank of 0.7 µg C/m³, as established by the Sunset method. Figure

Annual average EC concentration **Figure 2.3A**

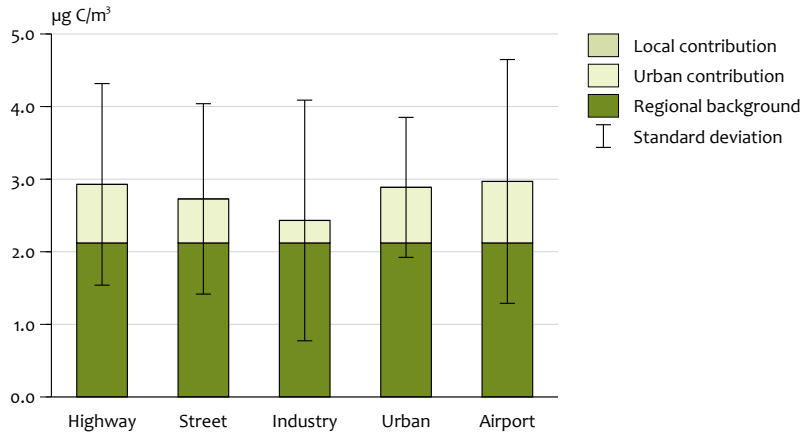
at the six locations in Rotterdam during the period from November 2006 to September 2007



Annual average of EC concentrations (µg C/m³) and standard deviation, at the six locations in Rotterdam, during the period from November 2006 to September 2007.

Annual average OC concentration **Figure 2.3B**

at the six locations in Rotterdam during the period from November 2006 to September 2007



Similar to Figure 2.3A, but for OC (µg C/m³).

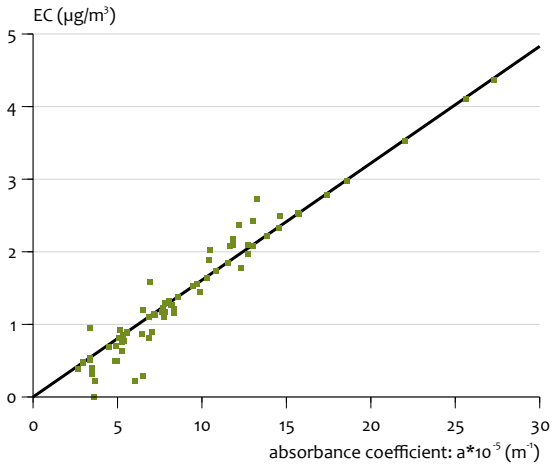
2.2B shows a seasonal variation of OC at all locations, with elevated OC levels in the summer period. This is in agreement with other research [Bae, 2006]. Contrary to EC, *no* elevated levels were measured at the traffic locations. These results illustrate that urban OC concentrations are mainly controlled by the regional background concentrations of OC. The latter is the result of primary emissions (e.g. from combustion processes) and secondary organic aerosol (SOA). SOA is attributed to photochemical ageing of biogenic precursors, such as terpenes released by vegetation, and carbonaceous compounds emitted by anthropogenic sources, for instance, diesel engines. The elevated levels of OC in summertime may reflect increased biogenic emissions during the growing season [Bae, 2006], and may be caused by enhanced photochemical ageing of diesel emissions.

Figures 2.3A and 2.3B present the annual average results for EC and OC at the six locations.

Figure 2.3A illustrates the following issues:

- *EC urban increment;* the average, annual urban background concentration was elevated against the regional background concentration. This urban increment was 0.6 +/- 0.2 µg C/m³. The annual average urban background of 1.1 ± 0.3 µg C/m³ was in good agreement with studies done in Ghent in 2004 and 2005 with 1.0 µg C/m³, in Amsterdam in 2005 and 2006 with 1.8 µg C/m³, and in Birmingham in 2004 and 2005 with 1.7 µg C/m³. [Viana, 2007; Harrison, 2008]. However, caution is required when comparing EC monitoring results, in view of the variation in sampling/measurement procedures.
- *EC roadside concentration;* there was a strong roadside to urban to regional gradient, which illustrated the impor-

Correlation of black smoke versus EC concentrations **Figure 2.4A**



Correlation between BS (10^{-5} m^{-1}) and EC concentrations (µg C/m³), at six locations in Rotterdam, for all fourteen periods from November 2006 to September 2007.

tance of traffic emissions to EC concentrations. The annual concentration at the street location and near a motorway was 2.3 ± 0.7 µg C/m³. The elevated EC levels near traffic locations agreed with the findings from the study in Birmingham [Harrison, 2008].

- *EC emissions from other sources;* other sources than road traffic hardly contributed to the urban background concentration of EC. At the airport location, no impact from aviation on EC concentrations was identified, and even the urban background contribution was lower at this location, because of its proximity to the rural region. Also, at the industrial location, no impact on EC concentrations was found from industrial/refinery emissions, at the monitoring location. Probably, this was the result of the height of the emission stacks. High emission stacks allow for dilution of the emitted substances before they reach ground level. Consequently, these concentration levels are expected to be lower at the surface, than when emissions would have been emitted more closely to the surface.

Figure 2.3B illustrates the following issues:

- *OC urban increment;* the average, annual urban background concentration of OC was slightly elevated against the regional background concentration. The regional and urban increment was of the order of 0.7 +/- 0.4 µg C/m³. The annual, average urban background concentration of 2.8 ± 1.7 µg C/m³ was low, compared to studies in Ghent in 2004 and 2005 with 4.1 µg C/m³, in Amsterdam in 2005 and 2006 with 5.4 µg C/m³, and in Birmingham in 2004 and 2005 with 3.8 µg C/m³. [Viana, 2007; Harrison, 2008]. However, as discussed for EC, also for OC caution is required when comparing OC monitoring results from various studies.
- *OC roadside concentrations;* contrary to EC, there was hardly any roadside to urban to regional gradient. The annual concentration at the street location and near the motorway is of the order of 2.6 ± 1.4 µg C/m³. This illustrates the importance of the regional OC background concentrations, on which limited OC traffic emissions are superimposed. In our study, *no* increment at the traffic locations was measured compared to the urban background. However, in the study in Birmingham, an increment of 0.6 µg C/m³ was determined at an urban roadside [Harrison, 2008].
- *OC emissions from other sources;* similar to EC, no other sources apart from road traffic (e.g. refineries and airport) contribute significantly to the urban background concentrations of OC. The differences between the average OC concentrations at the six locations, in Figure 3B, are not significant, in view of the annual variation at these locations.

2.2.3 Correlation between black smoke, EC and OC, in 2006 and 2007

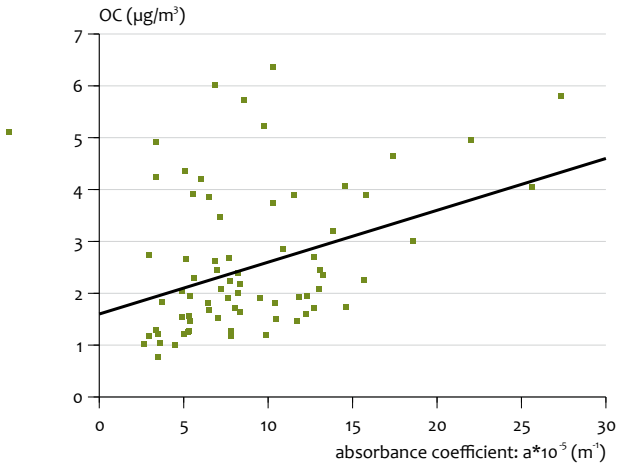
To investigate the application of BS trends as a proxy for EC and OC trends, first the correlation between BS and EC and OC measurements was investigated. In the BS method, the measured absorbance was computed in the absorbance coefficient and than converted into µg black carbon per m³. However, as discussed in Section 2.1, this absorbance/mass conversion is no longer valid, due to the shift in fossil-fuel consumption, since the 1950s. Therefore, in this study, the absorbance coefficient was directly applied, without mass conversion. For all locations, during all periods, BS absorbance coefficients were plotted against the EC and OC concentrations in Figure 2.4A and 2.4B.

Figure 2.4A indicates a linear relation between EC and BS, which is in agreement with earlier findings [Quincey, 2007; Schaap, 2007]. However, Schaap found a different relation between EC and BS for each of the regional and urban locations. In Rotterdam, there was no indication of a different fit between EC and BS at the regional and urban locations.

Figure 2.4B shows that there is *no* useful linear relation between OC and BS.

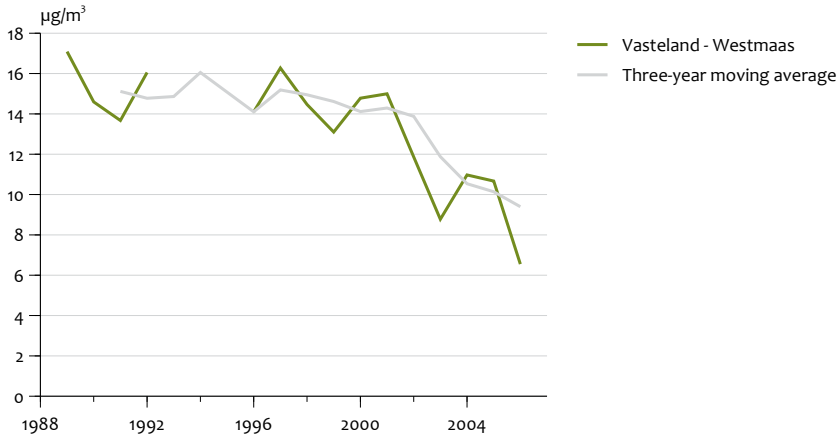
From these findings, presented in Figure 2.4A and 2.4B, was concluded that BS *is an adequate proxy for EC concentrations and, thus, BS trends may be used as a proxy for EC trends.*

Correlation of black smoke versus OC concentrations **Figure 2.4B**



Similar to Figure 2.4A but for OC (µg C/m³).

Concentration difference annual black smoke **Figure 2.5**



The difference between annual BS at the urban background location in Rotterdam (Vasteland; DCMR) and at a regional location (Westmaas; RIVM), for the period from 1989 to 2006, including a three-yearly moving average trend line.

2.2.4 BS trend as proxy for EC trend from 1989 to 2006

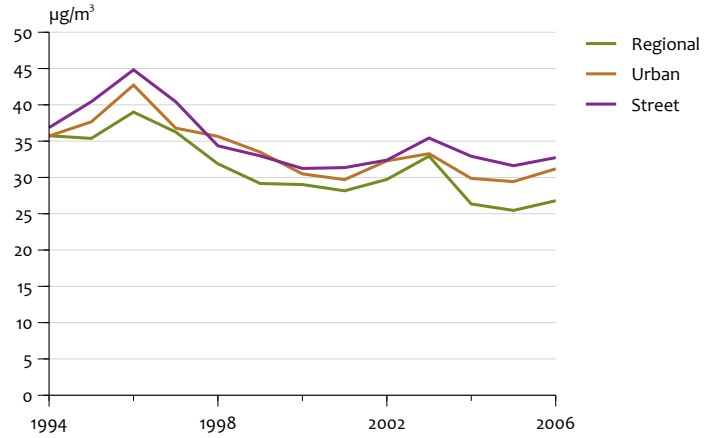
For the Netherlands, there are time series of BS measurements available over periods of more than 30 years, which have been applied in health studies [Fischer, 2009]. In view of the increasing use of EC and OC measurements, instead of BS measurements, and the correlation between EC and BS, these BS trends may be used as a proxy for EC trends. In Figure 5, the delta between the urban background concentrations in Rotterdam and regional background concentrations near Rotterdam for BS, are shown for the period from 1989 to 2006.

Figure 2.5 shows a declining difference in the BS concentrations between the regional and urban background locations, especially after 2001. This indicates that BS emissions and (in view of the correlation between BS and EC) also EC emissions from the road traffic, in Rotterdam, were decreasing faster than the long-range contribution of BS and EC to regional background concentrations. It is assumed that, for the last 20 years, BS and EC in the urban background concentration, in Rotterdam, predominantly have come from road traffic emissions and, thus, confirm the correlation between BS and EC, established in 2006 and 2007 (see Section 2.2.2).

[Note: A personal communication from the GGD in Amsterdam indicated that, contrary to Rotterdam, BS concentrations have *not* declined since 2001. In general, in the Netherlands BS concentrations decreased with 0.3 – 0.5 µg BS/m³ per year in rural areas and 0.7-0.8 µg BS/m³ per year in urban areas in the period 1984 – 2006 [Bloemen et al., 2007]. Similar, as in Amsterdam no decreasing trend has been measured since 2000. Hence, differences in road-traffic composition, and other local factors, would have to be considered before the results from Rotterdam could be generalised for the Netherlands as a whole.]

The trend in annual average PM_{10} concentrations **Figure 2.6**

Measurements of the National Air Quality Monitoring Network



The trend in annual average PM_{10} concentrations at regional, urban and street locations, from measuring stations of the National Air Quality Monitoring Network 1994 to 2006 (source: RIVM/PBL).

It is interesting to note that this decreasing trend of BS was not measured by RIVM's regular monitoring network for PM_{10}. The results for PM_{10} at regional, urban and street locations are shown in Figure 6.

Figure 2.6 illustrates that, since 2000, the trend for PM_{10} at urban and street locations has remained constant. This has been the case not only in the Netherlands, but also in other European countries. PM_{10} is a less sensitive indicator for these traffic-related PM contributions, as PM_{10} at urban background locations is dominated by long-range transport and (partly) by the contribution of road dust from resuspension. This dominant impact of regional concentrations on the urban and street locations is also valid for OC. The comparison of Figure 6, and the trend of BS en EC in Figure 5, *confirms that BS and EC are more adequate indicators than PM_{10} for measuring the impact of exhaust emissions from road traffic on urban background concentrations of PM.*

2.3 Monitoring EC, OC and Black Smoke, in March 2008

2.3.1 Monitoring locations for EC, OC and Black Smoke, in March 2008

In the framework of the BOP programme, in March 2008, at eleven locations in Rotterdam, fortnightly PM samples were collected to measure EC, OC and BS. The objectives of this study were directed at: 1) the spatial variation in urban background concentrations of EC, OC and BS, 2) the regional-urban gradient of EC, OC and BS, and 3) EC, OC and BS contributions to $PM_{2.5}$ and PM_{10}.

The eleven locations are detailed in Figure 2.7, four of which (6, 9, 10 and 11) are similar to the locations 'regional background', 'urban background DCMR', 'street location' and 'motorway A13', presented in Figure 1. At five (of the eleven) locations separate $PM_{2.5}$ and PM_{10} samples were collected to differentiate EC in $PM_{2.5}$ and PM_{10}, while at the remaining six locations, no particle size separation was performed during sampling. The BS analysis was performed by TNO, and the EC and OC analysis by ECN. More details on the ECN method are provided in Annex 1.

The eleven locations were selected for research on the urban background of $PM_{2.5}$ and PM_{10} [Voogt *et al.*, 2009]. The objectives of these locations are presented in Table 2.1.

The locations 2, 3, 4, 5 and 9, in Table 2.1, were regarded 'true' urban background locations – in accordance with EU guidelines [Larsen, 1999] – to study the variability in the urban background concentrations of EC, OC and BS. The gradient from regional to urban background concentrations was studied at locations 6, 1 and 9. Station 7 was characterised as an urban background location, but because of the relatively close proximity to the river 'Nieuwe Maas' and the harbour 'Leuvehaven', its results may have been influenced by emissions from inland shipping, during wind directions from south to east. Analogously, location 8 may have been affected by industrial emissions during westerly winds, while location 11 monitored the impact of motorway emissions. Finally, location 10 was a traffic location, located at Bentinckplein in Rotterdam.

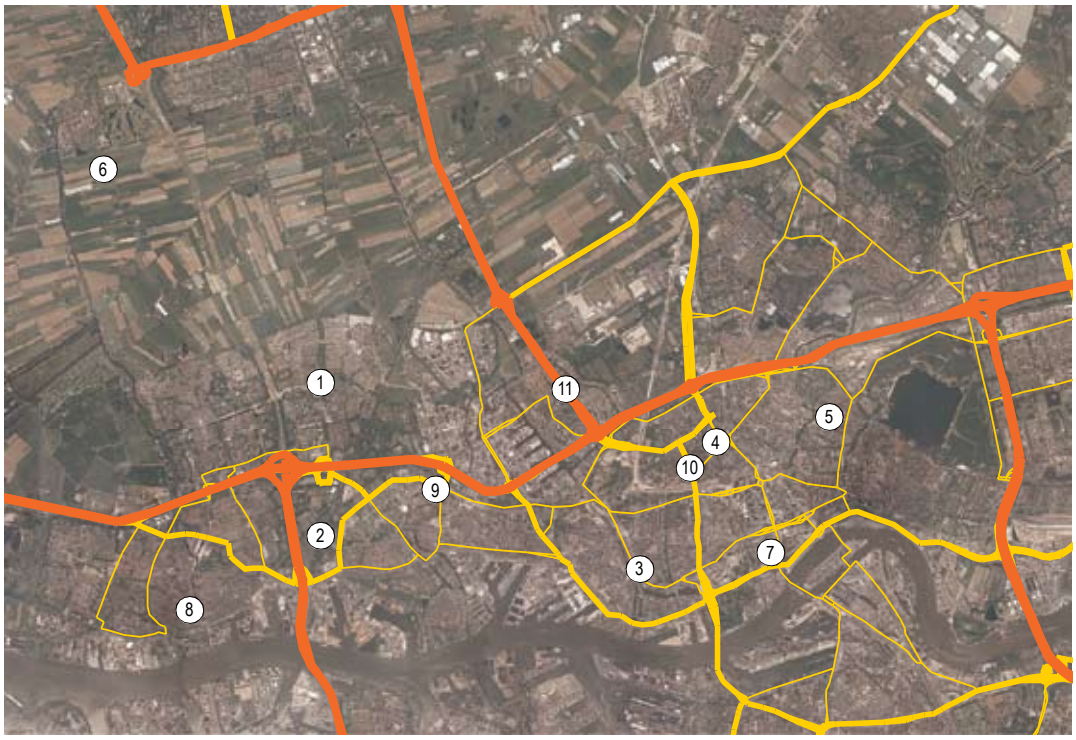
2.3.2 Spatial variability of EC in Rotterdam, in March 2008

The sampled filters at the eleven locations did not produce adequate results for EC and OC, for reasons unknown. Therefore, the objective of studying the spatial variability of EC and OC and the regional-urban gradient in Rotterdam could not be achieved. However, the filters were successfully analysed for BS, and the EC concentrations were derived from these BS results, by using the correlation between BS and EC established in Section 2.2.3. Therefore, this study reports on the results for BS and EC, only. The results for EC from the five locations with $PM_{2.5}$ and PM_{10} samples and from the six locations with no size fraction, are presented in Table 2.

Monitoring locations and specific objectives Table 2.1

Nr	Monitoring objective
1	Suburban background: regional-urban gradient
2	Urban background
3	Urban background
4	Urban background
5	Urban background
6	Regional background: regional-urban gradient
7	Urban background: impact inland shipping?
8	Urban background: impact industry/harbour or urban traffic?
9	Urban background: regional-urban gradient
10	Inner-urban traffic
11	Motorway traffic

Sampling locations for EC/OC and BS in Rotterdam in the period March 2008 Figure 2.7



Eleven sampling locations for EC, OC and BS in Rotterdam, in March 2008.

The agreement in the EC results for $PM_{2.5}$ and PM_{10} in Table 2.2 (between locations 2, 5, 6, 10 and 11), confirm the results from earlier measurements, showing that *no size fraction* is required to measure EC in ambient air. EC originates from incomplete combustion processes of fossil fuels, and these emissions are in the sub-micron size fraction: hence, differentiation in $PM_{2.5}$ and PM_{10} samples is not required. This is confirmed by research performed in Birmingham with size fractions of PM_1, $PM_{2.5}$ and PM_{10} [Harrison, 2008].

The urban background concentrations of EC for the locations 2 to 5 and 9 was 0.6 ± 0.3 µg C/m³. Therefore, the spatial variation in the urban background concentrations of EC, during March 2008, was less than the uncertainty in the EC measurement. The latter is of the order of 50%. Similar to the results in Figure 3A, for EC, no significant impact on the urban background concentration was identified from shipping or industrial emissions at locations 7 and 8, respectively. The increment in EC at traffic locations 10 and 11, against measurements at the urban background locations, is of the order of 1.2

Monthly EC concentrations (µg C/m³) Table 2.2

		EC		
Nr	Monitoring objective	$PM_{2.5}$	PM_{10}	No size fraction
1	Suburban			0.7
2	Urban	0.3	0,2	
3	Urban			0.9
4	Urban			0.8
5	Urban	0.8	0.7	
6	Regional	0.3	0,5	
7	Urban: impact inland shipping?			0.6
8	Urban: impact industry/harbour?			0.9
9	Urban			0.5
10	Traffic	1.8	1.8	
11	Urban: impact motorway traffic?	1.9	1.9	

March 2008, at eleven monitoring locations in Rotterdam.

Traffic intensity for light and heavy-duty vehicle Table 2.3

	Weekday	Saturday	Sunday
# private cars/24 h	29852	25280	23864
# trucks/buses/ 24 h	1897	929	647
Total	31749	26209	24511
Percentage trucks/buses	6.4%	3.7%	2.7%

September to October 2008, at the street location in Rotterdam.

µg C/m³. This agrees well with the annual average increment in EC, in Figure 2.3A.

An average urban increment, in March 2008, was determined at 0.1 µg ± 0.3 µg C/m³, which is not significant. The annual urban increment for 2006 and 2007, in Section 2.2.2., was 0.6 ± 0.3 µg C/m³. The lack of a significant increment, in March 2008, could be attributed to the domination of south-westerly winds. Consequently, the urban increment was expected to be low, for this period, as urban emissions are transported in the direction of the regional locations (see Figure 2.7).

2.4 EC and OC emission factors for urban traffic (September to October 2008)

Regulatory EC and OC emission factors for road traffic are *not* available by dynamometer test cycles. Estimates for EC and OC emission factors have been established by research in road tunnels or roadside measurements [Ning *et al*, 2008]. The objectives of the study in the BOP programme were directed at 1) establishing EC and OC emission factors for urban traffic and 2) preparing a map with annual average concentrations of EC and OC, for the Rotterdam-Rijnmond area.

EC and OC emission factors were determined by measurements performed at an urban background location and a traffic location. Hourly EC and OC measurements were performed by ECN, using an OC monitor (Sievers) and an EC monitor developed by ECN (for the technical details of this experimental configuration, see Annex 2). The monitoring period lasted from 18 September to 23 October 2008. The instruments that were used, were compared before and after this campaign, to account for the reproducibility of the instruments. It was found that EC and OC data values deviated by 10 and 4%, respectively. Here, it was assumed that the increment measured at the traffic location, compared with measurement results from the background location, was a proxy for the additional contribution to EC and OC due to traffic emissions.

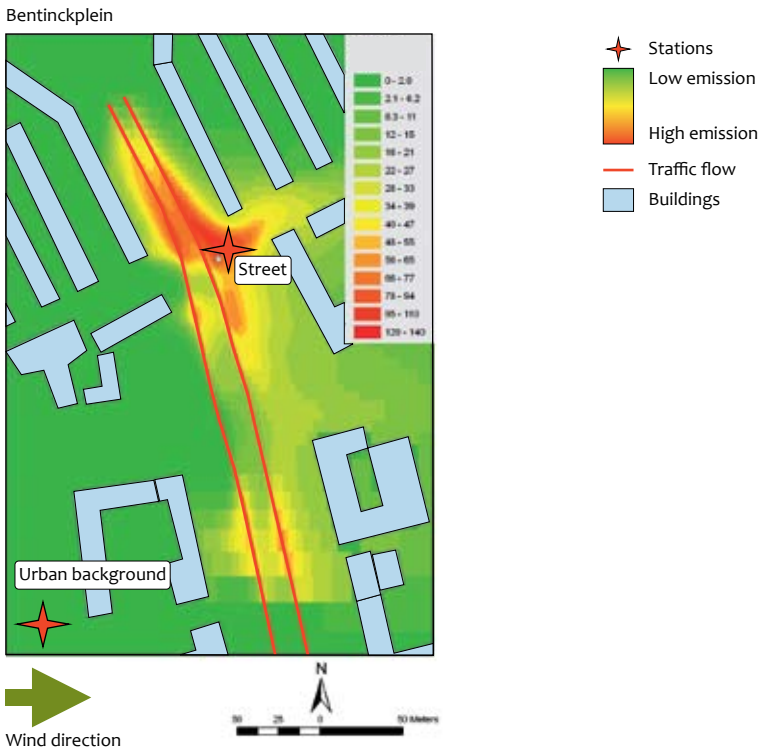
In addition to air quality data, hourly traffic data were collected near the traffic location, by automatic traffic counting (e.g. the number of vehicles and the average speed). Meteorological data on wind speed and wind direction are monitored routinely at Rotterdam airport, at less than 3 kilometres from the monitoring locations. Monitoring, meteorological data and traffic data were input for a CFD (Computational Fluid Dynamics) model, to compute the emission factors for EC and OC by inverse modelling. These emission factors were applied as input for TNO's urban dispersion model, Urbis, to compute the annual average concentrations of EC and OC in the Rotterdam-Rijnmond area.

2.4.1 Monitoring locations (September to October 2008)

In the period from 18 September to 23 October 2008, at the street location '10' (Figure 2.2) and at an urban background location at less than 500 metres from the street location, EC and OC concentrations were measured by ECN, using automatic equipment (see Annex 2). The locations are presented in Figure 8.

The distance between the urban background monitoring location and the traffic north of the location (not indicated in Figure 8) was more than 50 meters across open field. The traffic intensity at this street, north of the urban background location, was significantly lower than near the street location. Therefore, location 1 was considered an adequate background location for this study. In addition to the monitoring locations, Figure 2.8 also shows the dispersion of traffic emissions as computed by the CFD model (WinMISKAM: www.etcaq.rivm.nl/databases/mds.html) at a westerly wind.

Dispersion of traffic emissions near monitoring locations in Rotterdam **Figure 2.8**



The urban background location (1) and the street location (2) in Rotterdam, as well as buildings (blue), traffic flow (red lines) and the dispersion of traffic emissions at westerly winds (green-yellow-red).

2.4.2 Traffic intensity near the street location

The traffic intensity near the traffic location is presented in Table 2.3.

The traffic near the traffic monitoring location is representative for an inner-urban road with high traffic intensity, in the Netherlands.

2.4.3 Monitoring data on EC and OC (October 2008)

The collected monitoring data, from both locations, were used to compute the hourly EC and OC concentration differences between the background location and the street location. The automatic monitoring data, from the period between 8 and 20 October 2008, were used to present the diurnal increment in the concentrations of EC and OC at Bentinckplein, both for weekdays and weekends. The results are presented in Figures 2.9 and 2.10.

Figure 2.9 illustrates that the typical morning and evening rush hours during weekdays, resulted in larger increments in EC at the street location, while Figure 10 shows that, typically, at the weekend, significant increases in EC at the street location only occurred in the afternoons and evenings. Both, during weekdays and at weekends, no increment in OC was measured at the street location, contrary to the urban background location. This indicated that the increment in OC emissions from traffic was at least smaller than the variability during the monitoring method, which was established by parallel measurements at 0.5 µg C/m³.

Table 2.4 presents the average EC and OC concentrations from the monitoring period, at the street location and the urban background location.

The levels measured with the automated monitoring equipment during the October 2008 campaign at the street location were 2.8±1.8 µg C/m³ for EC, and 2.5±1.2 µg C/m³ for OC. Both levels are in agreement with the annual average range for EC and OC in 2006 to 2007 (see street location in Figures 2.3A and 2.3B).

The urban-street increment in EC of 1.0±0.7 µg C/m³ was only significant for weekdays, which have a significant amount of (heavy-duty) traffic (see: Table 2.3). During the weekend, the emissions from road traffic were too low to result in a significant increment at the street location, in contrast to the urban background location. For OC, *no* increment was measured; either during weekdays or at weekends, and, consequently, *no* emission factor for OC could be established.

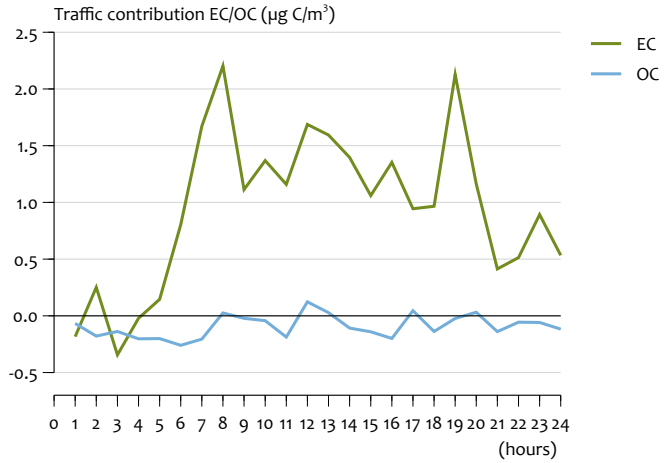
2.4.4 Establishing the EC emission factor

Hourly increments in concentrations of EC, hourly averaged meteorological data, and hourly averaged traffic data were stored in a database. Subsequently, certain hours were selected to compute the emission factors for EC. As no significant increments in OC were measured, this method was only applied for EC. The criteria for selecting hours, were as follows:

- *Traffic volume*; for a significant contribution of traffic emissions, only the hours were selected with more than 750

The diurnal variation of the increment EC/OC **Figure 2.9**

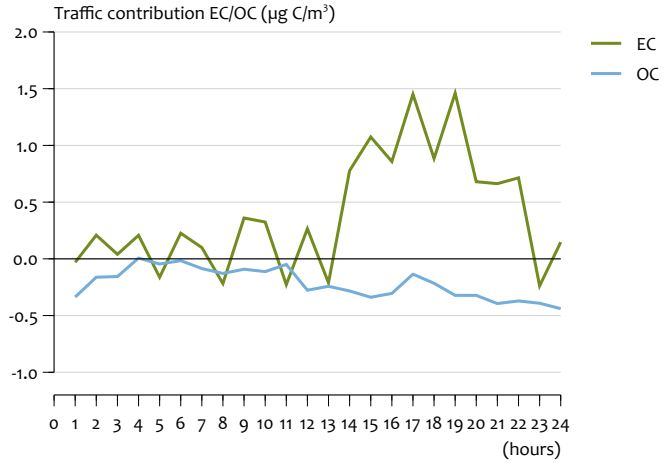
street location against the urban background in Rotterdam for working days



The diurnal variation of the increment in EC and OC (µg C/m³), on weekdays, at the street location, against the urban background location, in Rotterdam.

The diurnal variation of the increment EC/OC **Figure 2.10**

street location against the urban background in Rotterdam for weekend days



Similar to Figure 2.9, but for weekends.

vehicles. This resulted in day-time hours between 7 a.m. and 8 p.m.;

- *Monitoring data;* only those hours were selected for which the data on concentrations of EC and OC at both the traffic and the background location were available. This narrowed down the available period to between 8 and 20 October 2008. For this period, the increment in EC and OC at the traffic location was established for weekends and weekdays.
- *Meteorological conditions;* to have a representative contribution of traffic emissions during a monitoring hour, without remaining contribution from the previous hour, a certain amount of ventilation of the street-canyon would be required. Only those hours were selected with wind speeds of more than 1 m/s. In addition, only the hours were selected with a wind direction transporting traffic emissions towards the traffic location: from west to north-northeast.

For the selected number of hours, the EC and OC emission factors for urban traffic were determined. The criteria for selecting suitable hours from within the monitoring period, yielded 199 weekday hours and 77 weekend hours. Subsequent selection, by applying the criteria for suitable meteorological conditions, narrowed down the number of hours to 21. For these hours, inverse modelling was applied with the WinMISKAM model, as well as data input on hourly increments in EC, traffic intensity and meteorology.

The input data for this exercise are presented in Annex 3, while the range and the average values are summarised in Table 2.5.

Average EC and OC concentrations and variability (µg C/m³) Table 2.4

	Weekdays		Weekend		Total	
	EC (µg C/m³)	OC (µg C/m³)	EC (µg C/m³)	OC (µg C/m³)	EC (µg C/m³)	OC (µg C/m³)
Bentinckplein	3 ± 2	2.1 ± 1	2.6 ± 1.3	3.1 ± 1.1	2.8 ± 1.8	2.5±1.2
Urban	2 ± 1.7	2.2 ± 1.1	2.2 ± 0.9	3.4 ± 1.4	2.1±1.8	2.6±1.2
Delta	1.0±0.7	-0.1±0.1	0.4±0.5	-0.2±0.1	0.8±1.3	-0.1±0.4

At the monitoring locations in Rotterdam from 8 to 20 October 2008.

Average data input for inverse modelling by WinMISKAM, on hourly increments Table 2.5

	Wind direction (°)	Traffic intensity (#/h)	Traffic speed (km/h)	Delta EC (µg C/m³)	EF EC (mg C/km)
Range (21 hours)	270-290	1000-2500	45-50	0.2-4.6	2-25
Average (21 hours)	277	1838	48	2.0	12±6

Traffic intensity and meteorology between 8 and 20 October 2008, in Rotterdam, and the resulting average emission factor for EC (mg C/km).

The average emission factor for EC was established for each hour, and averaged over the range of values. Another option would be to determine this emission factor from a linear regression of the data in Annex 4, which is presented in Figure 2.11.

The slope of the linear regression of the data presented in Figure 2.11 provides an EC emission factor for urban traffic of 10 mg C/km. Linear regression is a more appropriate method for determining the emission factor and variability, than that of the arithmetic mean, as presented in Table 2.4. *Based upon linear regression, an emission factor for EC of 10±6 mg C/km was established.*

2.4.5 Concentration map of EC for Rotterdam

An annual average concentration map was computed for EC, by using the Urbis model of TNO. This model calculates the contribution from local traffic to air pollution with Plume Motorway, a line-source model for motorway traffic, and CAR, a statistical street-canyon model for inner-urban traffic[Boeft, 1996]. These contributions were added to the regional background concentrations, taking into account the dispersion of local traffic emissions towards the urban background location.

As input for the Urbis model, meteorological data, the regional background concentrations of pollutants, and the emission factors for traffic, all from the previous year, were provided by the Netherlands Environmental Assessment Agency (PBL) (http://www.mnp.nl/nl/themasites/gcn/index.html). Traffic data were made available by the Regional Environmental Agency DCMR. However, the regional background concentrations and emission factors for EC were *not* available. Therefore, the measured value of 0.5 µg C/m³ for the annual regional background concentration of EC, based on the Rotterdam study (Sunset method), was applied (see: Section 2.2.2). The EC emission factor for urban traffic of 10 mg C/km was used, as determined in the previous section. For emission factors for motorway traffic, the results from a separate study by TNO, in 2008 [Keuken *et al*., 2009], were applied: 5 mg C/km (for light-duty vehicles) and 25 mg C/km (for heavy-duty vehicles). These last two emission factors were established in a motorway tunnel with a separate tunnel tube for heavy-duty vehicles.

These emission factors agreed with a recent source-apportionment study, in a motorway tunnel in the UK, on the emissions from motorway traffic [Lawerence *et al.,* 2009]. For PM_{10}, an emission factor of 40 mg/km was established for motorway traffic, with 65% non-exhaust emissions (e.g. from road wear due to breaking, tire wear and resuspension), 10% un-accounted for, and 25% exhaust emissions. The last of which, consisted of EC plus OC with a ratio of 4:1 [Harrison, 2008]. Hence, this resulted in an emission factor for EC of 8 mg C/km. With a traffic composition of 95% in light-duty vehicles and 5% in heavy-duty vehicles, the aforementioned emission factors of 5 mg C/km and 25 mg C/km, respectively, provide an overall emission factor of about 6 mg C/km. However, studies in Japan [Naser *et al.*, 2009] and Switserland [Hueglin *et al.*, 2006] indicate emission factors for EC in the order of 20 mg per kilometer per vehicle for motor ways. Hence, the value of 6 mg C/km in BOP is regarded rather low, as compared to other studies.

The annual concentrations in Rotterdam were computed with traffic data from 2006, meteorology from 2006, and the above mentioned regional background concentrations and emission factors for EC. The results are presented in Figure 12.

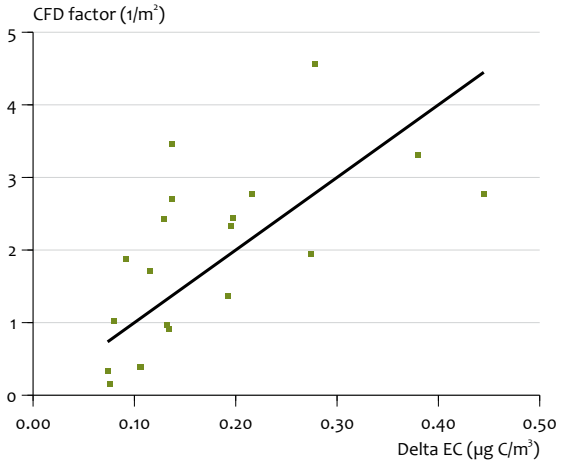
Figure 2.12 illustrates elevated concentrations of EC near heavy-traffic inner-urban roads and the motorways around the centre of Rotterdam. For PM_{10} and $PM_{2.5}$, similar maps were modelled, which showed relatively fewer elevated concentrations near traffic locations. This illustrates that $PM_{2.5}$ and PM_{10} concentrations are more dominated by large-scale transport. To illustrate that EC concentrations were relatively higher (than those of $PM_{2.5}$ and PM_{10}) compared to background concentrations, a contrast map was made. This map, produced by dividing concentrations according to regional background concentration, is presented in Figure 13.

The map in Figure 2.13 shows that EC is a more sensitive indicator for traffic-related PM emissions. It is assumed that EC is probably a better indicator than $PM_{2.5}$ and PM_{10}, for monitoring

Linear regression of the WINMISKAM data and the delta EC

Figure 2.11

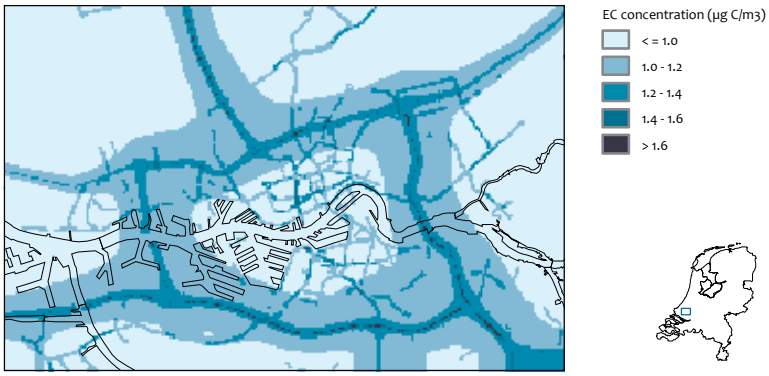
Measured at the street location and urban background from 8-20 October 2008 in Rotterdam



Linear regression of the WINMISKAM data and the delta EC, as measured at the street location and the urban background location, between 8 and 20 October 2008, in Rotterdam.

Annual concentrations of EC in Rotterdam (2006 traffic data and meteorology)

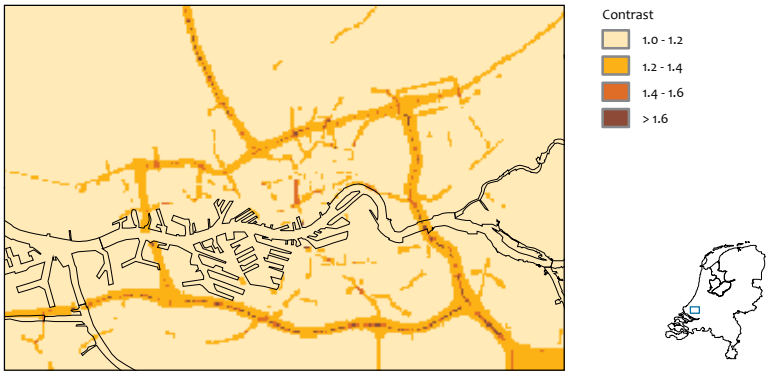
Figure 2.12



Annual concentrations of EC (µg C/m³), with traffic and meteorological data from 2006, in Rotterdam.

Annual contrast of EC in Rotterdam

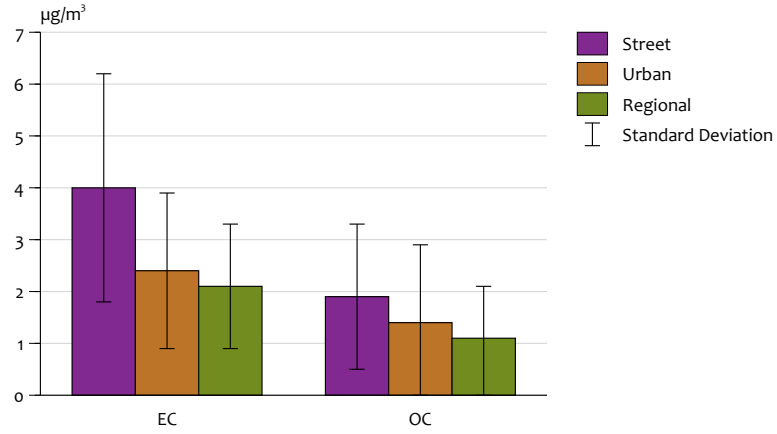
Figure 2.13



Annual contrast concentrations of EC in Rotterdam.

Annual average concentration of EC and OC **Figure 2.14**

the Netherlands 2007 - 2008



Average concentrations, and standard deviation, of EC and OC (µg C/m³) at street, urban and regional locations in the Netherlands, during the period from august 2007 to september 2008 [Arkel et al., 2009].

the effectiveness of emission reduction measures directed at exhaust emissions. Also, the results for EC may be used in epidemiological studies more effectively than the more general parameters, such as $PM_{2.5}$ and PM_{10}, specifically when directed at the role of traffic-related PM emissions.

2.5 The contribution of EC and OC to urban background concentrations

In this section, the contribution of EC and OC traffic emissions to urban background concentrations is assessed. This was based on the results from the monitoring campaign in the BOP programme, in the Netherlands. In the year 2007 to 2008, $PM_{2.5}$ and PM_{10} samples were collected at street, urban and regional locations and analysed for EC and OC. These analyses were performed by the Cachier method, which resulted in systematically higher values for EC (see Annex 1). The annual average concentrations of EC and OC at street, urban and regional locations are presented in Figure 2.14. Only the results for EC and OC in PM_{10} are shown, but the results for $PM_{2.5}$ were similar, which confirmed the conclusion, drawn in Section 2.2.3, that '*no size fraction* is required to measure EC in ambient air'.

Figure 2.14 shows that, in the Netherlands, the average street-urban increment in EC was 1.6 ± 0.8 µg C/m³, and for OC this was 0.5 ± 0.2 µg C/m³. These results were in agreement with the study in Rotterdam, taking into consideration the differences in analytical method. The average EC and OC roadside increments resulted from road-traffic emissions. Thus, for road-traffic emissions, in the Netherlands, the ratio for EC and OC is approximately three, which is consistent with the study in Birmingham, where the ratio between EC and OC is 4:1 [Harrison, 2008]. This ratio depends on the road-traffic composition (e.g. ratio in heavy-duty traffic and diesel vehicles).

Figure 2.14 shows that, in the Netherlands, the average urban-regional increment in EC was 0.3 ± 0.2 µg C/m³, and for OC this was 0.2 ± 0.2 µg C/m³. This indicates that superimposed on the regional background emissions of EC and OC, was an urban increment in mainly EC, and *no* significant increment in OC. The urban-regional EC and OC increment was mainly related to road-traffic emissions, as other urban sources (e.g. industries, refineries, shipping) do *not* contribute significantly to urban background concentrations (see Figure 3A). From the ratio of 4:1 for EC and OC for road-traffic emissions, was computed that the urban-regional EC increment of 0.3 µg C/m³ (as a result of road-traffic emissions) is associated with an OC increment of 0.1 µg C/m³. However, this computed increment in OC is *not* measurable against the regional background of OC, due to the uncertainty of the monitoring method.

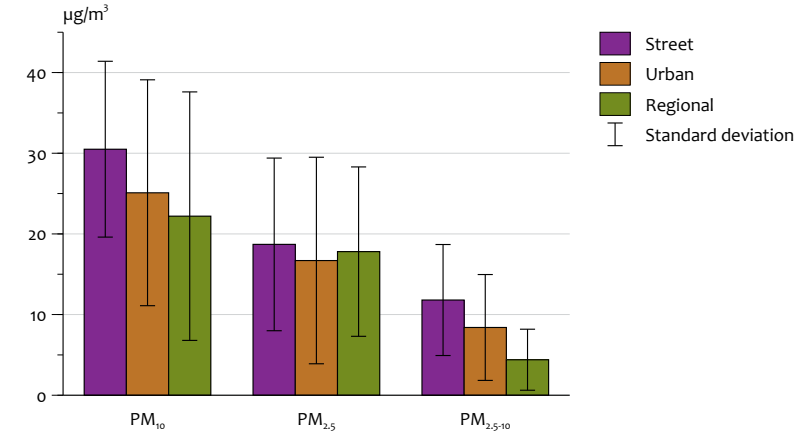
In the next step, the contribution of EC and OC in road-traffic emissions to the *urban* background concentrations of $PM_{2.5}$ and $PM_{10,}$ in the Netherlands, was estimated. As indicated by the BOP results, the urban-regional increment in EC of 0.3 ± 0.2 µg C/m³ was associated with a computed increment in OC of 0.1 µg C/m³. To estimate the contribution to $PM_{2.5}$ and PM_{10}, the mass of organic carbon (OC) had to be computed as the mass of organic compounds (OCom). Studies indicate a factor 1.3 to 1.6 for urban OC and 1.5 to 1.9 for regional OC, to compute the mass of organic compounds [Bae, 2006]. For the urban increment in OC, in the Netherlands, this resulted in a contribution of organic compounds to $PM_{2.5}$ and PM_{10} of 1.6* 0.1 µg C/m³, which is 0.2 µg OCom/m³. Consequently, the contribution of EC and OCom emissions from road traffic to the urban background concentrations of $PM_{2.5}$ and PM_{10} is 0.3 (EC) plus 0.2 (OCom), which is 0.5 µg/m³.

Figure 2.15 shows the results from the BOP programme for $PM_{2.5}$, PM_{10} and (calculated $PM_{2.5\text{-}10}$) in the Netherlands..

Figure 2.15 shows that the average urban background concentrations for $PM_{2.5}$ and $PM_{10,}$ in the Netherlands, was in the range of 15 to 20 and 20 to 30 µg/m³, respectively. Hence, the contribution of EC and OCom from road-traffic emissions to the urban background concentrations of $PM_{2.5}$ and PM_{10}

Annual average concentration of PM_{10}, $PM_{2.5}$ and $PM_{2.5-10}$ **Figure 2.15**

the Netherlands 2007 - 2008



Average concentrations and standard deviation of $PM_{2.5}$, PM10 and $PM_{2.5-10}$ (µg/m³) at street, urban and regional locations in the Netherlands, during the period from august 2007 to september 2008 [Arkel et al., 2009].

was maximally 2.5 and 3%, respectively. *It is concluded that the potential for reducing the urban background of $PM_{2.5}$ and PM_{10} by reduction of exhaust emissions, is less than 5%.* Hence, policies directed at reducing exhaust emissions from vehicles, will hardly reduce the urban background of $PM_{2.5}$ and PM_{10}. From a health point of view, it may be effective to reduce EC and OCom levels near heavy-traffic locations. However, more epidemiological research is required on the relation between population exposure, EC and OCom levels and health effects.

Figure 2.15 also shows that there was *no* significant street-urban-regional gradient for $PM_{2.5}$, and only a limited street-urban-regional gradient for PM_{10}. For $PM_{2.5}$, this illustrates that the urban background concentration of $PM_{2.5}$ was dominated by the regional background concentrations, and that local measures for reducing these background concentrations would *not* be effective. For PM_{10}, this illustrates that increments in PM_{10}, mainly at street level, but also at urban level, were the result of an increase in $PM_{2.5-10}$. These particles are *not* emitted in exhaust emissions, but are mainly related to resuspension of road dust, tire wear and other friction processes. These emissions are difficult to control, other than by reducing traffic volumes.

3 Conclusions and recommendations

The main findings and conclusions from this study are summarised as follows:

- *EC and OC measurements;* Major problems in research on EC and OC are the lack of an agreed standardised analytical procedure, and the uncertainty about field blanks of OC. Two analytical methods were widely applied to determine EC and OC: the so-called 'Sunset method' and the 'Cachier method'. The BOP programme applied a method developed by ECN, based on the Cachier method, to measure the average annual EC and OC at street, urban and regional locations in the Netherlands. In the study in Rotterdam on the EC and OC contribution from traffic, the Sunset method was used, as well as automated methods for hourly measurements of EC and OC. From comparison of filters that were collected in the BOP programme, was concluded that the results from the Sunset method, were systematically lower by a factor of 0.4 for EC, compared to those from the Cachier method. The field blank for OC, in BOP, was 1.2 µg C/m3, while, in Rotterdam, the field blank was 0.7 µg C/m³. The relevant results for OC were corrected in accordance to the field blanks. In the findings and conclusions is indicated whether the results refer to the Cachier analysis ('BOP') or the Sunset analysis ('Rotterdam');
- *EC;* The annual *regional* background concentration of EC was 2.1 ± 1.2 µg C/m³, and the annual urban increment was 0.3 ± 0.2 µg C/m³ (BOP). The annual average EC concentration at heavy-traffic inner-urban roads was 4 ± 2.2µg C/m³ (BOP). The study in Rotterdam indicated that other sources than road traffic, such as industry, refineries, aviation and shipping, did *not* contribute significantly to the urban background concentrations of EC;
- *OC;* The annual *regional* background concentration of OC was 1.6 ± 0.5 µg C/m³, and the annual urban increment was 0.1 ± 0.2 µg C/m³ (BOP). Thus, the urban background concentration was *not* significantly elevated against the regional background concentration. The annual average OC concentration at heavy-traffic inner-urban roads was 1.9 ± 0.8 µg C/m³ (BOP). These results illustrate that urban and street OC concentrations were mainly controlled by regional OC background concentrations. The regional level was controlled by primary emissions (e.g. combustion processes) and secondary organic aerosol. The latter was attributed to biogenic precursors, such as terpenes released by vegetation and photochemical ageing of diesel engine emissions. The contributions to OC from biogenic and combustion sources was estimated at 60% and 40%, respectively [Harrison, 2008]. The study in Rotterdam indicated *no* increment in OC at the traffic locations, contrary to the urban background locations, Other urban sources, such as industry, refineries, aviation and shipping, also did not significantly contribute to the urban background concentration of OC;
- *Contribution of EC and OC emissions from road traffic to urban background concentrations of $PM_{2.5-10}$;* From the study in Rotterdam could be concluded that the increment in EC and OC at the urban background locations was mainly related to road-traffic emissions. To compute the contribution of *OC* to the $PM_{2.510}$ background concentrations, OC was expressed as the mass of organic compounds 'OCom'. This was performed by multiplying OC by a factor of 1.6 [Bae, 2006]. For the urban increment in OC, in the Netherlands, this resulted in a contribution of organic compounds of 0.2 µg/m³ to $PM_{2.5}$ and PM_{10}. Consequently, the contribution of EC and OCom emissions from road traffic to the urban background concentrations of $PM_{2.5}$ and PM_{10} was 0.3 (EC) plus 0.2 (OCom), which is 0.5 µg/m³. The average urban background concentrations of $PM_{2.5}$ and $PM_{10,}$ in the Netherlands, were in the range of 15 to 20 and 20 to 30 µg/m³, respectively (BOP). *It was concluded that the potential for reducing urban backgroundconcentrations of $PM_{2.5}$ and PM_{10} by reducting exhaust emissions from road traffic, would be less than 5%*;
- *EC as traffic-related PM indicator;* The hourly increments in EC at street locations compared to urban background locations – measured by automated monitors in Rotterdam – were in good agreement with the traffic intensity during weekdays and weekends. The EC emission factor for urban traffic was established at 10 mg C/km, which is at the low end of the range of values 8 to 20 mg C/km presented in the literature. For OC, *no* increment could be measured and, thus, *no* emission factor for OC was established. In the literature, a ratio of 4:1 is indicated for EC and OC in road-traffic emissions [Harrison, 2008], which, in our study in Rotterdam, would have resulted in an increment below the detection limit of the monitoring method. This indicated that traffic emissions were dominated by EC, which is in agreement with the BOP results for the Netherlands. Subsequently, an annual EC concentration map for Rotterdam was modelled, by using the dispersion model 'URBIS'. The

contrast between EC concentrations near heavy road-traffic and at background locations was much higher than that for $PM_{2.5}$ and PM_{10} . This confirms, that EC is a sensitive indicator for the dispersion of traffic-related PM emissions;

- *Black Smoke (BS) as proxy for EC trend;* The results from Rotterdam confirmed the results from earlier studies, that BS measurements – presented in optical units without conversion to mass units – have a linear correlation with EC (R^2 =F 0.93), but *not* with OC. Both BS and EC reflect the contribution of (incomplete) combustion emissions to PM. From measurements of BS at an urban background location in Rotterdam and at a regional location, in the period from 1989 to 2006 – as a proxy for EC concentrations – could be concluded that EC concentrations, especially those after 2001, have been decreasing, significantly, by 5% per year. This shows the impact from cleaner vehicles on urban air quality. When using PM_{10} as an indicator for air quality, this trend could not be detected. Differences in road-traffic composition, and other local factors, would have to be considered before the results from Rotterdam could be generalised for the Netherlands as a whole.
- It is recommended to :
  - develop, improve and standardise sampling and analytical procedures for monitoring EC and OC ambient air concentrations and
  - perform more research on EC as an indicator for traffic-related particulate matter, in health studies.

Annex 1 EC and OC analysis of filter samples in BOP

Field blank for OC

The content of carbon was determined from the PM samples collected with quartz-fibre filters, every fourth day, since the start of the campaign. This means that close to 200 filters were analysed for any given location, both PM_{10} and $PM_{2.5}$ samples. In total, 151 (random) field blanks, and over 30 blanks as received from the manufacturer, were analysed. It is here that a serious complication was noticed: the average field blank for carbon is 1.4 +- 0.6 µg C/m³, which is virtually all OC. The average value for the factory blanks was, on average, substantially lower, however, it was consistently observed that the top filter in a stack had a higher value than the average field blank. With this in mind, it should be realised that there are some uncertainties in the individual data, while the total average is affected less by the blank problems. For a detailed discussion, the reader is referred to the technical report on the sampling and analysis procedure for carbon, in the BOP programme.

Analysis of EC and OC

Filters, as received from RIVM, were stored in a refrigerator until analysis. Immediately before analysis, the filters were cut in half (the other half was analysed for 'SIA'). Analysis of the carbon content was performed in a so-called 'Coulomat'. In short, the analysis is quite simple: the sample is combusted in, pure, oxygen. An analysis takes 15 minutes and the analysis is divided in 2 steps. In the first step, the sample is oxidised at a temperature of 340 °C. The carbon which is released in this step, is OC. In the second step, the rest is combusted at 750 °C, the released carbon of which, is EC – according to a procedure used in the commercial ACPM [Ten Brink *et al.*, 2005]. This method is known as 'T2S', meaning *T*hermographic (oxidative) analysis in *2S*teps, which is a variation of the 'Cachier method'.

The distinction of the carbon in OC and EC depends on the method used. The filters from the study in Rotterdam, by TNO, were analysed at the GGD Amsterdam, according to the 'Sunset method'. To assess the comparability of the methods used by ECN and GGD, a series of samples (65 in total) were analysed at both institutions. The analyses were done by using spare BOP filters (not used in the regular analysis, every fourth day). Early on in the comparison study, filters sampled by the GGD were used. These had been obtained in a quite similar collection procedure as in the BOP campaign. Each filter were halved, after which one batch of halves was analysed at ECN. The other batch was analysed at the GGD.

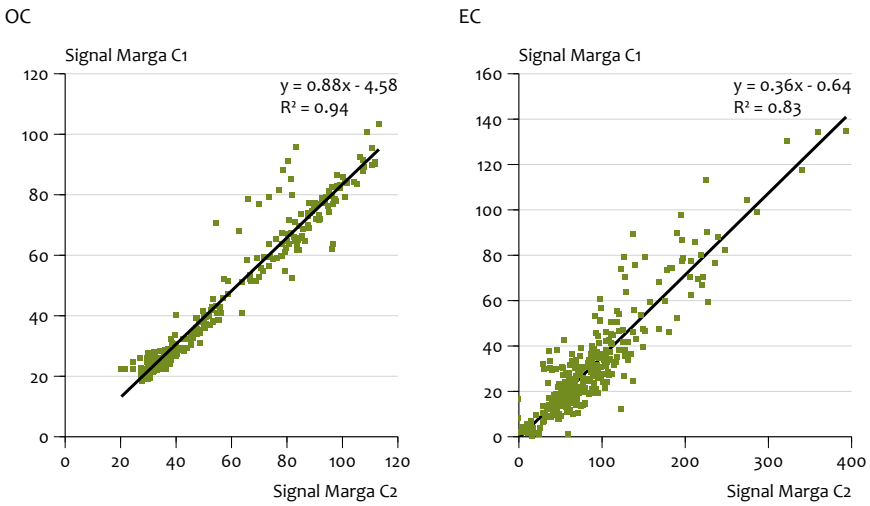
The main findings are: Total Carbon (the sum of EC and OC) results from the 'ECN method' and the 'Sunset method' correlated very well, but there was an average difference of 15%, with the results from the GGD being the lowest. With respect to EC, we found a good correlation between GGD and ECN results, with GGD being 0.4 of that of ECN.

Annex 2 Automatic EC and OC monitor

The automatic EC and OC monitors, applied in the study in Rotterdam, were developed and deployed by ECN. The monitors offer a time resolution of 10 minutes and are referred to as MARGA-C (C- stands for Carbon), using a wet chemical sampling and detection technique. PM_{10} heads were used for size-selective sampling. The sampling is established by a SJAC (Steam Jet Aerosol Collector, Khlystov 1995) after absorption of potential gaseous interferences by means of a wet rotating denuder. The acquired sample solution is on-line divided over 2 analysers: one for photometric detection of EC. and one for conductometric detection of OC after oxidation and membrane diffusion (Sievers 900). The monitor is described in a status report [Weijers *et al.,* 2008]. Immediately after the measurement were taken, both monitors were positioned at the street location for 3 consecutive days, to determine their systematic deviation.

The intercomparison showed correlation coefficients of 0.94 for OC, and 0.83 for EC, indicating reliable measurement series. The regression coefficient for OC of 0.88 was good, while the regression coefficient for EC was considered as poor, indicating losses of EC in the monitor. Therefore, the optimal situation was sought by normalising the Marga C1 to C2, instead of using the average. Under these conditions, the precision obtained was 0.1 µg C/m³ for OC, and 0.2 µg C/m³ for EC, the standard deviation being around 1 µg C/m³ level (n=10). The inlets were 10 metres away from each other, due to local obstructions which could possibly lead to additional noise, especially for EC. The detectors were frequently calibrated by means of standard solutions (EC LBNL Berkeley, and OC Glucose PA Baker).

X-Y plots of Marga C1 and C2 time series during the sampling period **Figure A2.1**



X-Y plots of Marga C1 and C2 time series (time resolution 10 min) during the co-located sampling period used for normalisation. Marga C1 was originally located at Bentinckplein and Marga C2 at the urban background location.

Annex 3 Data input for inverse modelling emission factor EC

Data input for inverse modelling emission factor ECi Table A3.1

date (yyyy/mm/dd)	Time (previous hour)	wind direction	traffic (#.h)	speed (km/h)	delta EC (ug/m³)	EF EC (mg/km)
20081016	19	270	1838	47.3	1.0	13
20081008	10	270	1696	47.7	0.3	4
20081017	11	290	1103	49.8	0.2	2
20081008	6	270	2053	45.5	0.4	4
20081008	9	270	2022	46.9	0.4	4
20081009	18	280	1806	48.6	2.4	19
20081017	14	270	1770	48.0	1.9	20
20081014	14	280	2157	45.7	1.4	7
20081014	11	290	2109	47.1	2.8	13
20081008	21	270	2058	46.7	0.9	7
20081009	1	270	2032	47.2	1.0	7
20081008	8	270	1767	48.9	1.7	15
20081009	19	280	2304	44.6	1.9	7
20081009	17	270	2279	46.2	2.4	12
20081017	17	270	1578	49.4	3.5	25
20081017	16	270	1527	48.6	2.8	21
20081017	15	270	2140	46.1	4.6	16
20081017	13	280	2126	47.1	3.3	9
20081008	7	280	1093	50.1	2.3	12
20081014	12	270	1055	49.4	2.7	20
	Average	275	1826	48	1.9	12

October 2008, at the street location and urban background location in Rotterdam

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In the Netherlands Research Programme on Particulate Matter (BOP), the contribution of elemental (EC) and organic carbon (OC) to urban background concentrations of $PM_{2.5}$ and PM_{10} has been studied. The increment of EC and OC in urban background concentrations was concluded to be mainly related to road traffic emissions. The annual total contribution was 0.5 µg/m^3. Considering average urban background concentrations of $PM_{2.5}$ and PM_{10}, it was concluded that the potential for reducing urban background concentrations by reducing exhaust emissions from road traffic would be less than 5%.

This study is a BOP publication produced under the auspices of TNO and ECN.

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