

On the variability of Black Smoke and carbonaceous aerosols in the Netherlands

M. Schaap*, H.A.C. Denier van der Gon

TNO, Business unit Environment, Health and Safety, PO Box 342, 7300 AH Apeldoorn, The Netherlands

Received 27 September 2006; received in revised form 12 March 2007; accepted 16 March 2007

Abstract

The study addresses the characteristics of elemental carbon (EC) and organic carbon (OC) distributions in the Netherlands by using Black Smoke (BS) data in combination with dedicated measurements and modelling. The BS levels indicate a large-scale background concentration over the Netherlands with low spatial variability and a gradient with highest levels ($\sim 9 \mu\text{g m}^{-3}$) in the south gradually decreasing to the north-west ($\sim 5.5 \mu\text{g m}^{-3}$). The BS concentrations at rural sites in the Netherlands are highly correlated due to common (diffuse) sources and large-scale meteorology. Superimposed on the regional background are the contributions of local/urban sources. Urban and rural BS levels show a distinct variation over the week with minimum levels on Sundays.

BS levels do not reflect a real concentration as they are obtained via an optical measurement in combination with an outdated calibration curve to arrive at total suspended particles (TSP). We have found that the relation between BS and EC in the Netherlands is linear and highly correlated but dependent on station type. Application of these relations to the BS time series yields a gradient in the rural background EC concentration from $0.5 \mu\text{g m}^{-3}$ in the north to $0.7 \mu\text{g m}^{-3}$ in the south of the Netherlands. The relationship between OC and BS appears to be location specific and is determined by the BS–EC relation in combination with a characteristic OC/EC ratio. OC/EC ratios are ~ 5 at regional background sites and ~ 2 at traffic locations. Minimum OC/EC ratios at the traffic sites reflect the primary OC/EC ratio of traffic. We argue that estimation of secondary organic aerosol by assuming the minimum OC/EC ratio to be a proxy for the primary OC/EC is not allowed since this approach does not account for sources with high OC/EC ratios. Based on European scale modelling and the measured data, we estimate that national sources contribute ~ 40 – 60% to Dutch EC levels.

The rather costly and laborious EC measurements provide a better indicator of the carbonaceous fraction in ambient particulate matter (PM) but the cheap BS method may provide valuable information on spatial distribution of EC when used in combination with validation sites to characterise the EC–BS relationship.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Black Smoke; Carbonaceous aerosol; Netherlands; Elemental carbon

1. Introduction

In the last two decades, the relationship between exposure to particles and adverse health effects has been under close scrutiny (e.g., Pope et al., 1995). There is growing evidence of associations of adverse

*Corresponding author. Tel.: +31 55 5493385;
fax: +31 55 5493252.

E-mail address: martijn.schaap@tno.nl (M. Schaap).

health effects with those particles originating from combustion sources, most notably traffic (e.g., Hoek et al., 2002). Particulate emissions from combustion sources such as traffic are known to contain a large fraction of carbonaceous material, consisting of elemental carbon (EC) and organic carbon (OC). Black Smoke (BS), an indicator for black carbon (BC) rather than PM₁₀, was associated with daily mortality in Amsterdam (Verhoeff et al., 1996). All of the above-mentioned studies and many others highlight the importance of the carbonaceous fraction of particulate matter (PM) in relation to adverse health effects.

Ambient concentrations of carbonaceous particles at a continental scale influence the radiation budget of the earth and thus have an impact on climate change. BC has recently been identified as an important contributor to radiative heating of the atmosphere (Haywood et al., 1997; Myhre et al., 1998; Jacobson, 2001). OC, which is often emitted along with EC, has a cooling effect on climate and may act to offset some of the global warming impact of EC emissions (Hansen and Sato, 2001). In case of biomass burning aerosol, OC is thought to completely compensate the warming potential of EC (Penner et al., 1998; Grant et al., 1999), because biomass burning emissions are characterised by high OC/EC ratios. However, for fossil fuel-derived (primary) emissions this is not the case and a net positive forcing remains (Penner et al., 1998; Cooke et al., 1999).

The above-mentioned issues highlight the need for a thorough knowledge on the concentrations and role of carbonaceous particles in our atmosphere in the past, present and future. However, major uncertainties are present in emission estimates, concentration data as well as the atmospheric lifetime of OC and EC in the atmosphere.

The carbon species (BC, EC, OC) are defined by the way they are measured. BC is obtained from methods measuring the light-absorbing properties of aerosols and reflects the sum of EC and “tarry” OC compounds. EC and OC are defined by their thermo-chemical behaviour. OC is chemically defined as carbonaceous material gasified at low temperatures in an inert environment whereas EC does not volatilise in an inert atmosphere at temperatures as high as 650 °C. Although there are sampling artefacts for OC, the uncertainties in OC and EC measurements are mostly determined by the analysis procedures (e.g., ten Brink et al., 2004). Total carbon (TC = EC + OC) can be analysed with an accuracy of ~10% (Schmid et al., 2001).

However, there is a large uncertainty in the discrimination between EC and OC as part of the OC may be pyrolysed (into EC). The different analysis procedures using a variety of temperature ranges, pyrolysis correction methods and oxidation circumstances (e.g., Cachier et al., 1989; Birch and Cary, 1996) may result in systematic differences for OC and especially EC of a factor 2 and more (Schmid et al., 2001). Hence, reported data on the OC and EC content are prone to be inconsistent due to the choice of analysis procedure. For a review of EC/OC sampling and analytical methods we refer to ten Brink et al. (2004) and Schmid et al. (2001).

As discussed above, measurements of OC and EC are difficult, labour intensive and therefore costly. Hence, only a few (short-term) OC and EC data series for the Netherlands and its surrounding exist. On the other hand, time series of BS and PM are available for various locations at regional, urban background and hotspot locations in the Netherlands (Roemer and van Wijnen, 2001; van Elzakker, 2001). In principle, these optical BS measurements are related to the actual EC content of particulate matter. Indeed, well-defined relations have been presented in the past (e.g., Erdmann et al., 1993; Adams et al., 2002; Cyrus et al., 2003), but these relations may be time and location specific due to spatial and temporal variation in aerosol composition. Liousse et al. (1993) showed that variation exists between optical and thermal measurements of BC aerosol content in different environments. Furthermore, EC (and therefore indirectly BS) represents a fraction of the PM mixture but measurements of PM₁₀ and BS across Europe showed that the PM₁₀/BS ratio may vary widely across sites, suggesting different source contributions (Hoek et al., 1997). Hoek et al. (1997) described a tendency of lower PM₁₀/BS ratios in the urban areas consistent with the contribution of (diesel) motor vehicle emissions.

Our hypothesis is that a thorough evaluation of BS as a proxy for EC in combination with specific data on the carbon content of PM may reveal important aspects of the carbonaceous aerosol distribution in the Netherlands that are presently obscured by a lack of OC and EC data. In this study, we aim to gain more knowledge on the distribution of EC and OC in the Netherlands by using BS data in combination with dedicated measurements and modelling. The following questions are addressed:

1. What is the Black Smoke distribution of the Netherlands?

2. Can we use Black Smoke as a proxy for EC?
3. What is the relation between OC and EC in the Netherlands?
4. What is the Dutch contribution to BS and EC levels in the Netherlands?

To address these questions we have gathered BS monitoring data for the Netherlands. The main characteristics of these data are presented in Section 3.1. In Section 3.2 we search for calibration curves to estimate EC concentrations from BS using Dutch campaign data on carbonaceous particles. Special attention is given to the relative levels of OC and EC in Sections 3.3 and 3.4. In Section 3.5 we present budget calculations for the Netherlands as performed with the LOTOS-EUROS model (Schaap et al., 2007) to assess the background levels of primary carbonaceous material from a theoretical perspective.

2. Data sources

To address the BS levels in the Netherlands we compiled data from various operational air quality networks. The stations used in this study are shown in Fig. 1 and listed in Table 1. The largest data set is obtained from the Dutch national air quality network as operated by the National Institute for Public Health and Environment (RIVM) (van Elzakker, 2001). These data are complemented with a data set for Amsterdam and the province Noord Holland operated by the Municipal Health Service (GG&GD) of Amsterdam. In Amsterdam and Noord-Holland 24-h concentrations of BS are measured with SX-200 BS continuous monitors (ETL, Hereford, England) operating with a sampling flow of 1.38 L min^{-1} through Whatman No. 1 paper filters with inverted funnels as sampling inlet. Sampling of particles, reflectance measurements, and calculation to mass concentrations were done according to specifications of the European community (OECD, 1964; Christolis et al., 1992). For a detailed description of the sites and methods, we refer to Roemer and van Wijnen (2001).

In the RIVM network, BS was measured until December 2000 using an active sampler fabricated by RIVM according to the OECD requirements. Samples were taken with Whatman No. 1 paper filters and analysed using the EEL-type 43 reflectometer. Calculation of mass concentrations were done according to specifications of the European community (OECD, 1964). From December 2000 onwards, the RIVM uses the same methodology as



Fig. 1. Locations of the measurement sites used in this study.

described above for Amsterdam and Noord-Holland. For a detailed description of the methods used in the national network we refer to van Elzakker (2001). The comparability between the old and new method was good, which warrants the comparability of the data in time (Hijink, 2002).

Two studies are available to compare the concentrations of carbonaceous aerosol with BS data. Visser et al. (2001) investigated the composition and origin of airborne particulate matter in the Netherlands by collecting samples of the fine fraction ($\text{PM}_{2.5}$) and the coarse fraction ($\text{PM}_{2.5-10}$) at six sites during 1 year (1998–99). The second study, the HEAVEN project (Spoelstra et al., 2002), measured BS, EC and OC at four sites in Rotterdam. These studies provide data for the regional and urban background as well as urban traffic locations (see Table 2, Fig. 1). For a detailed description of the measurement procedures we refer to Visser et al. (2001) and Spoelstra et al. (2002). Comparison between the data obtained in these two studies is warranted since both studies have used very similar sampling strategies and, more importantly, have used the same laboratory, following the

Table 1
Annual statistics of daily average Black Smoke levels averaged over 2000–2002

Station	Code	Type	Mean	Minimum	p05	p50	p95	Maximum	n
Wieringerwerf	Wie	R	5.4	0	0	4	16	46	961
DeZilk	Dez	R	5.5	0	0	3	17	55	1066
Braakman	Bra	R	7.6	0	0	5	22	82	1076
Houtakker	Hou	R	9.4	1	2	7	26	66	1068
Vredepeel	Vre	R	8.0	0	2	6	19	55	1025
Wijnandsrade	Wij	R	8.6	1	2	7	22	66	1071
Wageningen	Wag	R	7.9	0	1	5	21	54	1020
Eibergen	Eib	R	6.2	0	1	4	16	45	1018
Hoofddorp	S_ho	RS	7.2	0	1	5	20	59	1054
Badhoevedorp	S_ba	RS	10.5	0	2	8	28	67	973
Oude Meer	S_ou	RS	13.2	1	3	11	30	82	1065
Amsterdam-Overtoom	A_ov	UB	7.9	1	2	6	19	48	974
Utrecht-Universiteitsbibliotheek	U_ub	UB	11.3	1	3	9	27	69	1075
Amsterdam-Stadhouderskade	A_st	UT	19.6	2	9	17	40	75	1038
Utrecht-K.de Jongweg	U_kj	UT	19.4	1	4	17	43	85	1035
Utrecht-Wittevrouwenstraat ^a	U_wv	UT	28.5	2	7	25	61	110	1082
Vlaardingen	vla	UT	16.2	1	3	13	38	107	1085

The station types are rural (R), rural Schiphol (RS), urban background (UB) and urban traffic (UT). The mean, minimum, percentiles (5, 50, 95), maximum and the number of observations are shown.

^aTraffic densities have fluctuated during the selected period.

procedure by Birch and Cary (1996), to analyse the OC–EC content of the filter loading.

3. Results and discussion

BS is expressed as a concentration ($\mu\text{g m}^{-3}$), since the reflection of a filter measured with the BS monitor was used to assess the concentration of total suspended particles (TSP). The calibration curve to translate the reflection to TSP mass units used in the BS method was developed in the sixties when coal was the dominant source of carbon particles. Since the sixties, sources and their relative contributions have changed dramatically, influencing the composition, size distribution and optical properties of atmospheric PM. As a consequence, the BS calibration curve derived in the sixties is not valid for present day samples. Hence, it is important to keep in mind that the BS levels do not reflect a real concentration.

3.1. What is the BS distribution of the Netherlands?

At rural sites in the Netherlands the annual average BS concentrations range between 5.4 and $9.4 \mu\text{g m}^{-3}$ (Table 1). Lowest levels are found in the north-west of the country and the measured concen-

trations tend to increase going to the south(east), away from the coast. Considering the primary nature of the EC that is measured as BS, the variability between the sites is low. Median concentrations show a similar picture over the Netherlands. The median values are significantly lower than the averages reflecting the episodic nature of BS and the importance of the peak values for the annual average concentration. The latter is also evident from the large difference in the 95 percentile and the maximum value.

The urban background sites show BS levels of $8\text{--}11 \mu\text{g m}^{-3}$. Hence, the combined urban emissions result in an urban background which is 10–40% higher than the rural background. Near sources, busy roads/street canyons, BS levels are elevated up to four times the regional background level. The range of BS levels at the urban traffic stations indicate that the variability of BS levels within a city is larger than the difference between urban background and rural locations. These patterns are in line with observations for a wide range of European cities as presented by Hoek et al. (1997).

The sites dedicated to assess the influence of the national airport Schiphol are presented separately in Table 1. The concentrations at the three stations show a range of $7\text{--}13 \mu\text{g m}^{-3}$. The Hoofddorp site

shows concentrations comparable to the regional background, whereas the concentrations at the Oude Meer and Badhoevedorp sites are comparable to urban background levels. As these sites are located relatively near the highways around Schiphol airport, a significant traffic signal in the latter sites is expected. This is in line with a study directed to investigate VOC's concentrations around Schiphol which confirmed that the surrounding highways, and not so much the airport itself, have a large impact on the pollution levels at these two sites (Thijsse, 2005, personal communication).

BS concentrations show a pronounced seasonal behaviour with strong similarity in the seasonal pattern at all sites (Fig. 2). Concentrations are relatively low during the warm season and high during winter. The seasonal pattern of the rural and urban sites is highly correlated, as it is driven by the large-scale meteorological variability as well as common seasonal variability in source strengths over the country. The correlation among the sites of BS time series on a daily basis over the period 1998–2002 has been investigated (data not shown). The two coastal (or near-coastal) sites de Zilk (dez) and Wieringerwerf (wie) correlate well with each other ($R^2 = 0.89$) but less with the other, more inland, rural sites such as Braakman, Houtakker, Vredepeel, Wijnandsrade, Wageningen and Eibergen (range of $R^2 = 0.64$ – 0.84). However, these non-coastal rural sites correlate well among each other (range of $R^2 = 0.80$ – 0.94) which can be explained by the absence of local emissions and the (common) large-scale meteorological situation which drives the variability at all stations. The

BS concentrations at the rural sites correlate poorly with the heavily traffic-affected sites such as Utrecht Wittevrouwenstraat (range of $R^2 = 0.48$ – 0.61) and Stadhouderskade in Amsterdam (range of $R^2 = 0.43$ – 0.60).

The variation of the BS concentrations over the day of the week was explored by comparing the concentrations relative to the levels on Sundays (Fig. 3). For rural locations the concentrations are on average $\sim 50\%$ higher in the Tuesday–Friday period. For both Saturday and Monday, the enhancement is ~ 25 – 30% . At the urban background locations, the variation between the weekdays was similar to the variation at rural locations. During the week, BS concentrations at the urban traffic locations are enhanced by about 100% compared to the Sunday. Interestingly, the concentrations at the urban traffic locations on a Monday are higher than those on Saturday and appear to be more in line with the Tuesday–Friday levels. Hence, there appears to be a shift in response time between the urban and rural locations. The street locations directly respond to the emission changes in the street, whereas the city as a whole (urban background) and the rural area need more time to respond.

3.2. Can we use BS as a proxy for EC?

BS is an optically measured quantity, i.e., the reflectance of a loaded filter, which accounts for particles that absorb light. The main fraction of ambient aerosol that absorbs light is BC. Since a causal relationship exists between the BS and EC, it

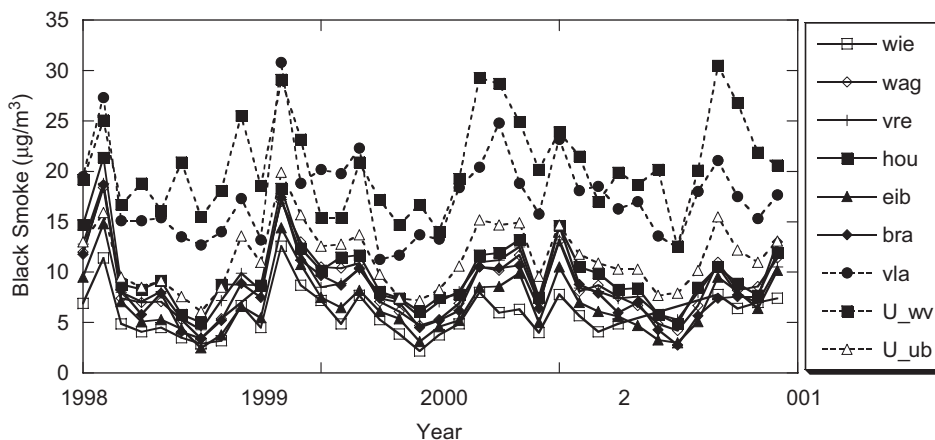


Fig. 2. Monthly mean concentrations of Black Smoke concentrations at a number of rural (solid line) and urban (dashed line) sites over the period 1998–2000 (see Table 1 for legend to station abbreviations).

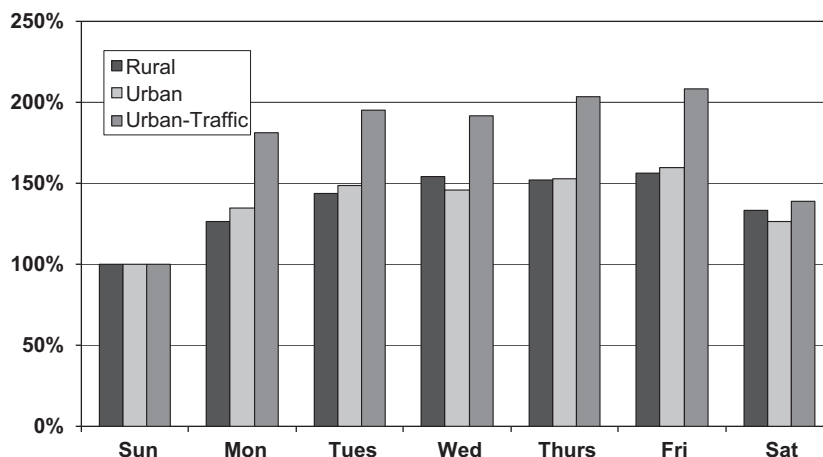


Fig. 3. Variability of BS concentration during the week relative to Sundays (Sunday = 100%).

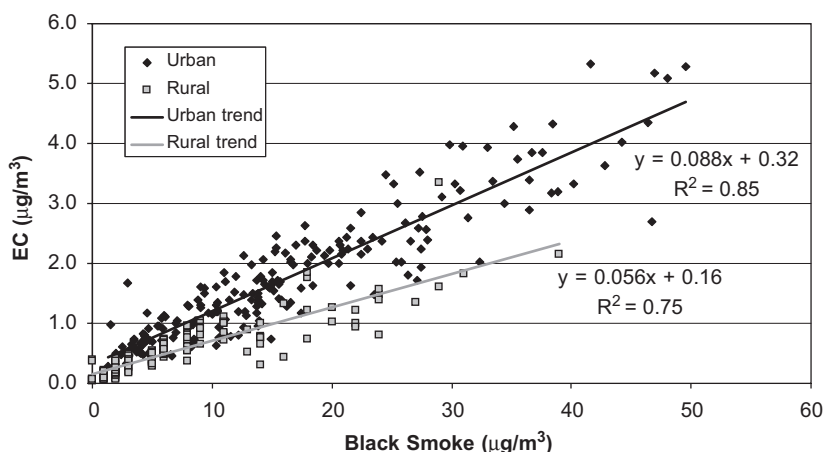


Fig. 4. Elemental carbon as a function of Black Smoke at rural and urban locations.

is possible to use BS as a proxy for EC (e.g., Edwards et al., 1983). However, it is known that the relationship between BS and EC is not constant over time and space due to differences in source contributions and source profiles. The analysis of ambient particulate matter for its EC content has evolved over the years (although systematic differences between methods still exist (e.g., ten Brink et al., 2004)) and relationships derived in the past cannot be used for the Netherlands in the year 2000. So, to quantitatively estimate EC and possibly OC concentrations based on BS data, relevant calibration curves are required. The major fraction of carbon is generally present in fine particles (e.g., Putaud et al., 2004; Visser et al., 2001). Therefore, all EC is sampled by the BS monitor, which

eliminates the issue of the poorly defined cut-off of a BS monitor and allows a direct comparison. Below we describe the relation between BS and EC for data obtained in the Netherlands.

EC has been plotted as a function of BS for locations where simultaneous analysis data are available (Fig. 4). The sites cover two rural stations (De Zilk, Vredepeel) and the seven urban locations in Amsterdam and Rotterdam. A linear relationship between BS and EC is observed for low concentration regimes in De Zilk and Vredepeel as well as the high-concentration regimes at urban (traffic) sites. However, the BS–EC relation is different for the rural stations compared to the urban locations. Linear relations ($EC = aBS + b$), derived using a least-square method, that describe rural stations and

urban stations separately give a better representation of the EC–BS relationship than one fit through all data (Fig. 4). The rural data points are consistently below the urban data points in Fig. 4. The relations and the variation explained by the fit are presented in Table 2. For the regional sites De Zilk and Vredepeel, the slopes are very similar, 0.056 and 0.054, respectively. In Amsterdam, 0.070 and 0.074 are found for the urban background site and urban traffic site, respectively. The fits through the relatively small data sets for Rotterdam yield steeper slopes, but are quite sensitive to outliers. The slope for the urban locations is steeper than for the rural locations (Fig. 4). This implies that the same blackness of a filter at an urban site is associated with more EC than at a rural location. A possible explanation for the higher absorption per unit mass at rural sites may be associated with the mixing state in which the BS occurs. Near sources there is more pure soot than at rural sites where the soot is mostly aged and present as a mixture with other aerosol components. Various studies (e.g., Jacobson, 2001; Lioussse et al., 1993) illustrated that the absorption per unit mass of a pure soot particle was lower than the absorption of soot particles which are present as a core of an aerosol droplet. This can be explained by reflections on the aerosol–air interface, increasing the amount of light that falls upon the soot particle. We speculate that a similar effect may be present for particles on a loaded filter.

Using the derived EC–BS relationships, we estimated the annual average EC concentrations at a number of Dutch locations from the Dutch BS time series (Table 3). Estimated EC levels at rural locations range from $0.5 \mu\text{g m}^{-3}$ in the north-west to $0.7 \mu\text{g m}^{-3}$ in the southern part of the country. This is in good agreement with the results of the EMEP EC–OC campaign for Kollummerwaard, a background station in the north of the Netherlands, where a mean concentration of $0.5 \mu\text{g m}^{-3}$ was measured (with the same analytical procedure as used here) during 2002–2003 (EMEP, 2004). Urban background concentrations are $1\text{--}1.5 \mu\text{g m}^{-3}$, whereas levels at urban traffic locations may be considerably higher. These values fall within the range of measured data in central Europe as compiled by Putaud et al. (2004).

Although the difference between rural and urban sites is robust, the dependency on location, i.e., station type, is a potential disadvantage. Firstly, in reality there will be a smooth transition between the regimes. Secondly, station classification is not always straightforward. An incorrect classification would lead to an error of about 35%, which also reflects the range of slopes found for the urban sites. One could argue that this estimate is too conservative. Nevertheless, the uncertainties induced by applying these relations are significantly lower than the uncertainty induced by the choice of a specific analysis method for EC, which induces an

Table 2
Fit parameters for the BS–EC relation using $\text{EC} = a\text{BS} + b$

Type/site	Slope a	Intercept b	R^2	n
<i>Regional sites</i>				
De Zilk	0.056	0.12	0.82	73
Vredepeel	0.054	0.22	0.67	70
<i>Average regional</i>	0.056	0.16	0.75	143
<i>Urban sites</i>				
Amsterdam-Overtoom	0.070	0.42	0.63	61
Amsterdam-Stadhouderskade	0.074	0.59	0.70	71
Rotterdam E1	0.104	0.07	0.78	19
Rotterdam E2	0.093	0.70	0.89	6
Rotterdam E3	0.074	0.32	0.76	26
Rotterdam E4	0.098	0.10	0.90	21
Overschie ^a	0.071	0.37	0.61	59
<i>Average Urban</i>	0.088	0.32	0.85	263

^aBS data stem from a nearby location, only to be used as indicative results.

Table 3
Annual average Black Smoke concentrations and derived elemental carbon concentrations at a number of Dutch locations based on daily average Black averaged over 2000–2002

Station	Type	BS	$a\text{BS} + b$
Wieringerwerf	R	5.4	0.5
DeZilk	R	5.5	0.5
Braakman	R	7.6	0.6
Houtakker	R	9.4	0.7
Vredepeel	R	8.0	0.6
Wijnandsrade	R	8.6	0.7
Wageningen	R	7.9	0.6
Eibergen	R	6.2	0.5
Hoofddorp	R	7.2	0.6
Badhoevedorp	UB	10.5	1.2
Oude-meer	UB	13.2	1.5
Vlaardingen	UT	16.2	1.8
Amsterdam-Overtoom	UB	7.9	1.0
Amsterdam-Stadhouderskade	UT	19.6	2.0
Utrecht-K.de Jongweg	UT	19.4	2.0
Utrecht-Wittevrouwenstraat	UT	28.5	2.8
Utrecht-Universiteitsbibliotheek	UB	11.3	1.3

uncertainty of about 200–300% (ten Brink et al., 2004).

3.3. What is the relation between OC and EC in the Netherlands?

The ratio of OC and EC differs considerably by source and fuel type (e.g., Bond et al., 2004). For example, diesel EC emissions are associated with low OC levels, whereas burning of wood or biological waste is associated with a high OC/EC ratio. A further understanding of composition and origin of carbonaceous aerosol may be obtained through the variability of the specific ratio of OC to EC in relation to source profiles, site characteristics and atmospheric chemistry. The information compiled for the Netherlands is discussed in this section.

The OC/EC ratios in the Netherlands typically range between 1 and 8, with higher OC/EC ratios of 5–6 at the rural background sites and lower OC/EC ratios of 2–3 at the traffic dominated sites (Table 4). The urban sites Overtoom and Rotterdam E3 have OC/EC ratios of ~ 4 and can be described as rural background with urban background excursions. The minimum OC/EC ratios observed at street stations approach the theoretic OC/EC ratio of 1.1 for exhaust emissions (Kleeman et al., 2000). Despite the limited number of locations and observations, the most important features of the OC and EC dynamics in the Netherlands are captured by the data in Table 4.

Various recent studies have tried to estimate the secondary fraction of organic carbonaceous aerosol by assuming that the lowest OC/EC ratio found for a location is representative for the primary OC/EC ratio. Provided that this is true, the primary OC contribution can be estimated from the measured

EC concentrations. The difference between total OC and primary OC must then be, by definition, secondary OC aerosol. This approach has mostly been proposed and used for urban (traffic) locations with a lowest value of 1.1 for the OC/EC ratio (e.g., Viidanoja et al., 2002; Salma et al., 2004), comparable to our observations for traffic-dominated sites (Table 4). Thus, these studies find the OC/EC ratio of the local source, i.e., traffic as is nicely illustrated by Viidanoja et al. (2002) who found that the ratio approached 1.1 when the wind speed goes to zero. However, emission data (Bond et al., 2004; Kupiainen and Klimont, 2007) show that OC and EC emissions in Europe are dominated by at least 2–3 different sources, most notably residential combustion and road transport, which differ considerably in OC/EC ratio. Hence, extrapolation of the minimum value to the whole time series as a proxy for the primary OC/EC ratio is not allowed since it does not account for non-traffic sources with high OC/EC ratios that may contribute significantly to the measured OC levels. Consequently, the estimated contribution of secondary organic aerosol to total OC will be overestimated.

3.4. Can we use BS as a proxy for OC?

BS also correlates well with OC at some individual stations (Table 5). However, there is a large variation in combinations of slope (a), intercept (b) and the explained variability for the locations. The pairs De Zilk/Vredepeel, Stadhouderskade/Overschie and E1/E4 behave very similar. These station pairs are of the same type and have in common that they are associated with very similar OC/EC ratios (see Table 4). The urban background location Amsterdam-Overtoom does not show a slope in

Table 4

Elemental carbon (EC) and organic carbon (OC) concentrations ($\mu\text{g m}^{-3}$), average ratio between OC and EC, ratio between average OC and average EC, minimum OC/EC ratio and number of observations for nine locations from the bronstof study and TNO_Rotterdam study

Site	EC	OC	Average OC/EC	Average OC/ Average EC	Minimum OC/EC	<i>N</i>	Classification
De Zilk	0.5	2.8	8.55	5.6	3	73	Marine/rural background
Vredepeel	0.7	3.9	5.8	5.6	1.7	70	Rural background
Amsterdam—Overtoom	0.9	3.6	4.5	4.0	2	72	Urban background
Rotterdam E3	1.4	5.5	4	3.9	2.4	16	Urban background
Amsterdam- Stadhouderskade	1.9	4.7	2.6	2.5	1.1	73	Street/traffic dominated
Overschie	1.6	4.2	2.9	2.6	1.1	62	Street/traffic dominated
Rotterdam E1	3.5	6.5	2.2	1.9	1	14	Street/traffic dominated
Rotterdam E4	3	6.3	2.9	2.1	1.4	14	Street/traffic dominated

Table 5
Fit parameters for the BS–OC relation using $OC = aBS + b$

Type/site	Slope <i>a</i>	Intercept <i>b</i>	<i>R</i> ²	<i>n</i>
<i>Regional sites</i>				
De Zilk	0.24	1.26	0.86	73
Vredepeel	0.23	1.74	0.62	70
<i>Urban sites</i>				
Amsterdam-Overtoom	0.29	1.66	0.64	61
Amsterdam-Stadhouderskade	0.19	1.20	0.57	71
Rotterdam E1	0.08	3.78	0.15	19
Rotterdam E2	0.10	3.21	0.09	6
Rotterdam E3	0.13	3.77	0.32	26
Rotterdam E4	0.08	3.76	0.47	21
Overschie ^a	0.19	1.20	0.74	59

^aBS data stem from a nearby location, only to be used as indicative results.

between those of the rural and urban traffic locations, which was to be expected in case of systematic behaviour as we found for EC. We conclude that the BS–OC relationship is more complicated than that of BS–EC and that the data do not justify a station-type classification to estimate OC levels from BS. Qualitatively, this can be explained by different sources with different OC/EC ratios dominating at various locations. Moreover, we feel that the BS–OC relation is defined by the combination of a well defined BS–EC relation and site-specific OC/EC ratios.

3.5. What is the Dutch contribution to BS and EC levels in the Netherlands?

The assessment of the national contribution to the ambient levels in the Netherlands is highly relevant for policy support. The high correlation between the rural sites reported in Section 3.1 may indicate a large (common) influence of long-range transport or an important contribution of well-spread and highly correlated diffuse sources, such as traffic. To discriminate between these issues one needs a model. We have used the 3D chemistry transport model LOTOS-EUROS (Schaap et al., 2007) to calculate the Dutch national contribution to rural EC concentrations. The EC emission data are described by Schaap et al. (2004). Model results of an earlier model version using this inventory have been evaluated against measurements by Schaap et al. (2004). The results of the present model underestimate measured EC concentrations by about a factor of 2. This is similar to the results

reported by Schaap et al. (2004) and we refer to this paper for a discussion on the emissions, the model and its performance.

In the simulation EC, tracers derived from Dutch and non-Dutch emissions are being used. In Fig. 5 we show the annual mean concentrations in the boundary layer as well as the modelled national contribution. In the mixing layer, the contribution of Dutch activities to the total EC concentration is highest (50–60%) in the densely populated Western part of the Netherlands (Randstad area). Over the central part of the Netherlands the contribution is higher than 40%. The relative contribution declines towards the borders and off the coast. In the surface layer of the model the influence of local emissions is about 20% higher than in the mixing layer. Low-level sources are emitted into this surface layer and then mixed into the boundary layer. Hence, there is a time delay before the surface emissions are mixed into the boundary layer. The mixing layer data represent relatively well-mixed conditions and can therefore be compared to rural conditions. The surface layer, on the other hand, reflects the average Dutch contribution including source areas such as cities.

The analysis of the model results shows that the national contribution is high (~80%) with westerly winds, independent of the wind speed. This is explained by the absence of sources upwind and the inflow of relatively clean air. Vice versa we find low national contributions up to about 50% in the “Randstad” for situations with strong easterly winds. Slow wind speed conditions from the east increase the importance of local emissions drastically, showing the importance of highly correlated surface sources in combination with atmospheric mixing conditions.

That the national contribution to ambient EC concentrations must be substantial is confirmed by the pattern of the BS concentrations over the week (Fig. 3). Concentrations on working days are ~30% higher than Sundays at the rural stations. Soot emissions on working days are higher than on Sundays but if sources at large distances would dominate the BS measured in the Netherlands then the day by day variability should be smoothed out, which is not the case (Fig. 3). A large part of the combustion particles must be emitted within an atmospheric transport distance of half a day to obtain the patterns shown in Fig. 3. Using a wind speed of 5 m s^{-1} , typical for winds from the east, and an average transport time of 12 h a distance of 180 km is estimated. This means that the variability at the sites in the western part of the Netherlands is

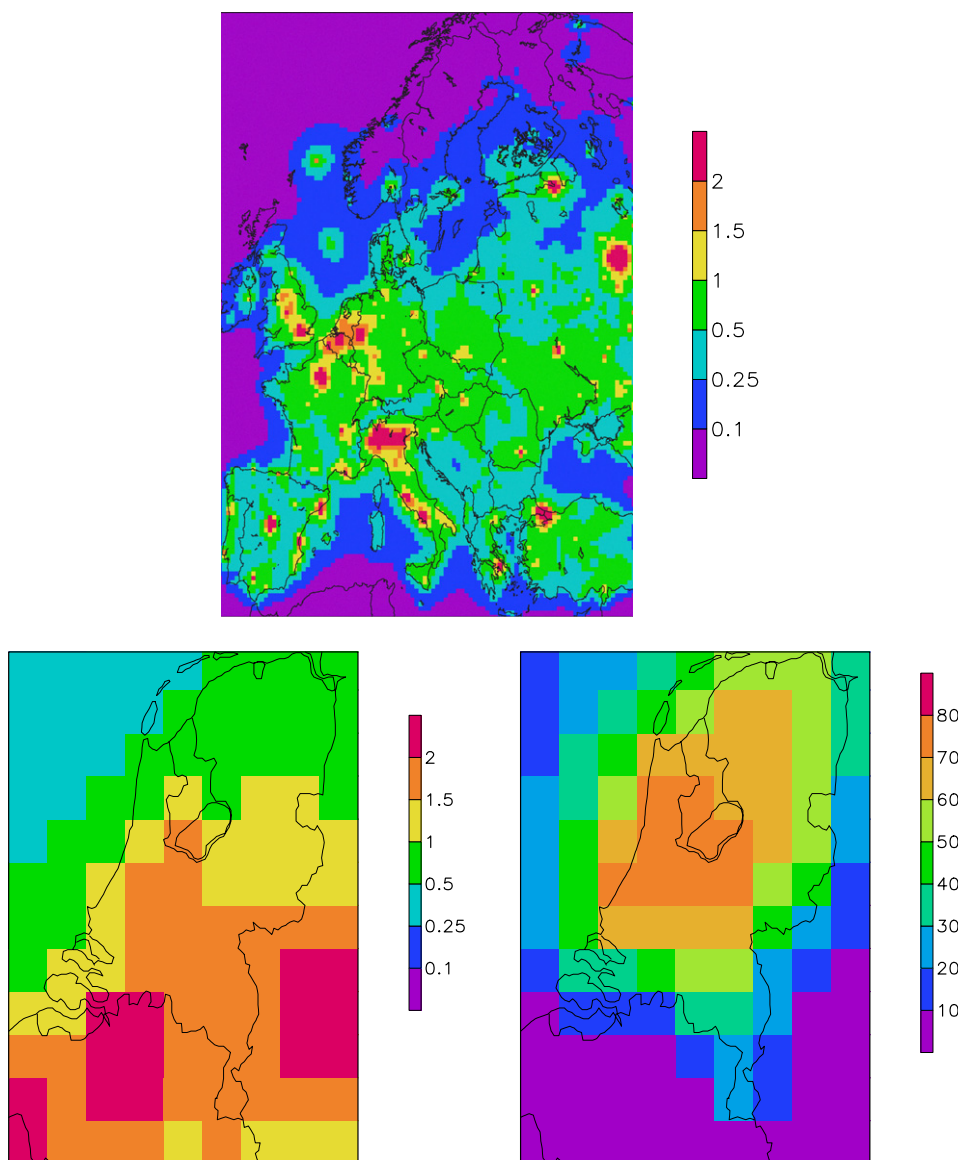


Fig. 5. Concentration field ($\mu\text{g m}^{-3}$) (upper panel and lower left panel) and Dutch contribution (%) (lower right panel) for the surface layer.

mainly due to Dutch emission sources. Hence, the percentage ($\sim 30\%$) given above should be interpreted as a minimum contribution due to Dutch emissions. The actual percentage is expected to be considerably higher since the Dutch emissions on a Sunday are far from negligible. This reasoning is inline with the modelling results.

4. Discussion and conclusions

Black smoke concentrations over the Netherlands consist of a large-scale background showing low spatial

variability with highest levels ($\sim 9 \mu\text{g m}^{-3}$) in the south gradually decreasing to the north-west ($\sim 5.5 \mu\text{g m}^{-3}$). The BS concentrations at rural sites in the Netherlands are highly correlated due to common (diffuse) sources and large-scale meteorology. Superimposed on the regional background are the contributions of local/urban sources. The variability of BS levels within a city due to urban emissions is larger than the concentration gradient between urban background and rural locations. BS levels in the Netherlands show a distinct variation over the days of the week with maximum concentration levels during the working days.

The relation between BS and EC is linear and highly correlated but dependent on station type. EC can be predicted using the following relationships for rural and urban locations:

$$EC = \begin{cases} 0.056 \times BS + 0.16 & \text{(rural),} \\ 0.088 \times BS + 0.32 & \text{(urban).} \end{cases}$$

These findings are in line with Cyrus et al. (2003) who found a significant difference in the regression slopes relating absorbance and EC for background and traffic sites. The dependency on location, i.e., station type, is a disadvantage because station classification is not always straightforward. Nevertheless, due to the large number of data points available to us we could find robust relationships for both types. Indeed, a number of studies have shown a robust relation between EC and BS or filter absorbance for single locations (e.g., Edwards et al., 1983; Erdmann et al., 1993; Liousse et al., 1993). Unfortunately, it is not possible to integrate the available relationships because studies have used different EC analysis procedures and/or different filter types for their absorbance measurements. It is important to acknowledge the influence of the analysis procedures and filter types for a consistent site-specific methodology to quantify the particle concentrations from incomplete combustion (EC).

Estimated EC levels based on BS measurements at rural locations in the Netherlands range from $0.5 \mu\text{g m}^{-3}$ in the north-west to $0.7 \mu\text{g m}^{-3}$ in the south. Urban background concentrations are $1\text{--}1.5 \mu\text{g m}^{-3}$ but EC levels at street locations can be considerably higher. The relationship between OC and BS appears to be site specific and determined by the BS–EC relation in combination with a characteristic OC/EC ratio. The relation of OC and EC in the Dutch atmosphere is complex showing a high variability as function of location and time. OC/EC ratios are lowest at the urban traffic stations and minimum values approach the OC/EC ratio for diesel car emissions at these locations. At the rural sites, the OC/EC ratio is highest, 5–6 on average, most likely due to contribution of sources with high OC fractions such as animal husbandry and wood burning.

Dutch sources contribute 35–70% to the regional background levels of BS/EC in the Netherlands. Model calculations show values at the high end of this range, whereas the lower values are obtained through simple estimates of the minimum contribution.

This study has shown that the cheap BS method may provide valuable information on EC in the atmosphere, especially the spatial distribution patterns. We therefore advise to keep and/or even expand BS monitoring to derive the EC component in PM₁₀ monitoring which is an indicator of exposure to combustion sources. In a discussion on the usefulness of BS as a surrogate for PM₁₀ in health studies Horvath (1996) stated correctly (in our opinion) that BS is not a good surrogate for PM₁₀ but might well be suited as an indicator of the health effect component of the aerosol, since BS will mainly be related to EC and, hence, to combustion sources. However, Horvath (1996) also asks the rhetorical question whether science cannot come up with a better alternative than the 50 (now 60!) year old BS method. Is it necessary to use this archaic BS method? The answer is “No”. EC measurements are to be preferred as they directly relate to a (weight) fraction of our legislative aerosol measures (PM₁₀ and PM_{2.5}). However, as long as the funding for environmental monitoring is limited, a cheap measurement like BS will still be valuable at satellite sites if used with care and properly cross-referenced at several sites to characterise the EC–BS relationship in time and space.

Acknowledgements

We are grateful for the data and/or support we obtained from Ernie Weijers (GG&GD Amsterdam), Jan Matthijssen (MNP), Harry ten Brink (ECN) and Michiel Roemer (TNO).

References

- Adams, H.S., Nieuwenhuijsen, M.J., Colville, R.N., Older, M.J., Kendall, M., 2002. Assessment of road users' elemental carbon personal exposure levels, London, UK. *Atmospheric Environment* 36, 5335–5342.
- Birch, M.E., Cary, R.A., 1996. Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. *Aerosol Science and Technology* 25, 221–241.
- Bond, T.C., Streets, D.G., Yarber, K.F., Nelson, S.M., Woo, J.-H., Klimont, Z., 2004. A technology-based global inventory of black and organic carbon emissions from combustion. *Journal of Geophysical Research* 109, D14203.
- Cachier, H., Bremond, M.P., Buat-Menard, P., 1989. Determination of atmospheric soot carbon with a simple thermal method. *Tellus* 41B, 379–390.
- Christolis, M., Clayton, P., Hecq, P., Payrissat, M., Petit-Coviaux, F., 1992. Instruction manual for air pollution monitoring. Vol II: Black Smoke Monitoring. Report EUR

- 14550/II EN. Joint Research Centre, Commission for the European Communities, Brussels, 1992.
- Cooke, W.F., Lioussse, C., Cachier, H., Feichter, J., 1999. Construction of a $I \times I$ fossil fuel emission data set for carbonaceous aerosol and implementation and radiative impact in the ECHAM4 model. *Journal of Geophysical Research* 104, 22137–22162.
- Cyrys, J., Heinrich, J., Hoek, G., Meliefste, K., Lewne, M., Gehring, U., Bellander, T., Fischer, P., Van Vliet, P., Brauer, M., Wichmann, H., Brunekreef, B., 2003. Comparison between different traffic-related particle indicators: elemental carbon (EC) PM_{2.5} mass, and absorbance. *Journal of Exposure Analysis and Environmental Epidemiology*, 1–10 doi:1053-4245/03.
- Edwards, J.D., Ogren, J.A., Weiss, R.E., Charlson, R.J., 1983. Particulate air pollutants: a comparison of British 'Smoke' with optical absorption coefficient and elemental carbon concentration. *Atmospheric Environment* 17, 2337–2341.
- EMEP, 2004. Measurements of particulate matter: status report 2004, Jan Schaag, EMEP/CCC-Report 3/2004, Oslo, Norway.
- Erdmann, A., Israël, G.W., Ulrich, E., 1993. Vergleich des Black-Smoke-Verfahrens mit absolutmessungen der atmosphärischen Russimmission. *Staub—reinigung der Luft* 53, 187–191.
- Grant, K.E., Chuang, C.C., Grossman, A.S., Penner, J.E., 1999. Modeling the spectral optical properties of ammonium sulfate and biomass aerosols: parametrization of relative humidity effects and model results. *Atmospheric Environment* 33, 2603–2620.
- Hansen, J.E., Sato, M., 2001. Trends of measured climate forcing agents. *Proceedings of the National Academy of Sciences of the United States of America* 98 (26), 14778–14783.
- Haywood, J.M., Roberts, D.L., Slingo, A., Edwards, J.M., Shine, K.P., 1997. General circulation model calculations of the direct radiative forcing by anthropogenic sulfate and fossil-fuel soot aerosol. *Journal of Climate* 10, 1562–1577.
- Hijink, B.M., 2002. Acceptance report of 17 SX200 black smoke monitors. RIVM-report 723101066, RIVM, Bilthoven, the Netherlands.
- Hoek, G., Forsberg, B., Borowska, M., Hlawiczka, S., Vaskoövi, E., Welinder, H., Branis, M., Benes, I., Kotesovec, F., 1997. Wintertime PM₁₀ and black smoke concentrations across Europe: results from the PEACE study. *Atmospheric Environment* 31, 3609–3622.
- Hoek, G., Brunekreef, B., Goldbohm, S., Fischer, P., van den Brandt, P.A., 2002. Association between mortality and indicators of traffic-related air pollution in the Netherlands: a cohort study. *The Lancet* 360, 1203–1209.
- Horvath, H., 1996. Discussion. Black Smoke as a surrogate for PM₁₀ in Health studies. *Atmospheric Environment* 30, 2649–2650.
- Jacobson, M.Z., 2001. Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols. *Nature* 409 (6821), 695–697.
- Kleeman, M.J., Schauer, J.J., Cass, G.R., 2000. Size and composition distribution of fine particulate matter emitted from motor vehicles. *Environmental Science and Technology* 34 (7), 1132–1142.
- Kupiainen, K., Klimont, Z., 2007. Primary emissions of carbonaceous particles in Europe. *Atmospheric Environment* 41, 2156–2170.
- Lioussse, C., Cachier, H., Jennings, S.G., 1993. Optical and thermal measurements of black carbon aerosol content in different environments: variation of the specific attenuation cross-section, sigma (σ). *Atmospheric Environment* 27A, 1203–1211.
- Myhre, G., Stordal, F., Restad, K., Isaksen, I.S.A., 1998. Estimation of the direct radiative forcing due to sulfate and soot aerosols. *Tellus* 50B, 463–477.
- OECD, 1964. Methods of measuring air pollution. Report of the working party on methods of measuring air pollution and survey techniques. Organization for Economic Cooperation and Development, Paris, 1964.
- Penner, J.E., Chuang, C.C., Grant, K., 1998. Climate forcing by carbonaceous and sulfate aerosols. *Climate Dynamics* 14, 839–851.
- Pope, C.A., Thun, M.J., Namboodiri, M.M., Dockery, D.W., Evans, J.S., Speizer, F.E., Heath, C.W., 1995. Particulate air pollution as a predictor of mortality in a prospective study of US adults. *American Journal of Respiratory and Critical Care Medicine* 151, 669–674.
- Putaud, J.-P., Raes, F., Van Dingenen, R., Brüggemann, E., Facchini, M.C., Decesari, S., Fuzzi, S., Gehrig, R., Hüglin, C., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N., Müller, K., Querol, X., Rodriguez, S., Dchneider, J., Spindler, S., ten Brink, H.M., Torseth, K., Wiedensohler, A., 2004. A European aerosol phenomenology Part 2: chemical characteristics of particulate matter at Kerbside, urban, rural and background sites in Europe. *Atmospheric Environment* 38, 2579–2595.
- Roemer, W.H., van Wijnen, J.H., 2001. Differences among black smoke, PM₁₀, and PM_{1.0} levels at urban measurement sites. *Environmental Health Perspectives* 109, 151–154.
- Salma, I., Chi, X., Maenhaut, W., 2004. Elemental and organic carbon in urban canyon and background environments in Budapest, Hungary. *Atmospheric Environment* 38, 27–36.
- Schaap, M., Denier Van Der Gon, H.A.C., Dentener, F.J., Visschedijk, A.J.H., Van Loon, M., Ten Brink, H.M., Putaud, J.-P., Guillaume, B., Lioussse, C., Bultjes, P.J.H., 2004. Anthropogenic black carbon and fine aerosol distribution over Europe. *Journal of Geophysical Research* 109, D18201.
- Schaap, M., Sauter, F., Timmermans, R.M.A., Roemer, M., Velders, G., Beck, J., Bultjes, P.J.H., 2007. The LOTOS-EUROS model: description, validation and latest developments. *International Journal of Environmental Pollution*, in press.
- Schmid, H., Laskus, L., Abraham, H.J., et al., 2001. Results of the "carbon conference" international aerosol carbon round robin test stage I. *Atmospheric Environment* 35, 2111–2211.
- Spoelstra, H., Hollander, J.C.T., Verhagen, H.L.M., Wesseling, J.P., Teeuwisse, S.D., 2002. HEAVEN project: report on the TNO measuring and modelling results in 2000 and 2001 for use of the development of a new atmospheric dispersion model, TNO report R2002/377, TNO-MEP, Apeldoorn, the Netherlands.
- ten Brink, H.M., Maenhaut, W., Hitzemberger, R., Gnauk, T., Spindler, G., Even, A., Chi, X., Bauer, H., Puxbaum, H., Putaud, J.-P., Tursic, J., Berner, A., 2004. Comparability of methods in use in Europe for measuring the carbon content of aerosol. *Atmospheric Environment* 38, 6507–6519.
- Thijssse, T., 2005. Personal communication.
- van Elzaker, B.G., 2001. Monitoring activities in the Dutch national air quality monitoring network in 2000 and 2001. RIVM report 723101 055, RIVM, Bilthoven, the Netherlands.

- Verhoeff, A.P., Hoek, G., Schwartz, J., van Wijnen, J.H., 1996. Air pollution and daily mortality in Amsterdam. *Epidemiology* 7, 225–230.
- Viidanoja, J., Sillanpaa, M., Laakia, J., Kerminen, V.-M., Hillamo, R., Aarnio, P., Koskentalo, T., 2002. Organic and black carbon in PM_{2.5} and PM₁₀: 1 year of data from an urban site in Helsinki, Finland. *Atmospheric Environment* 36, 3183–3193.
- Visser, H., Buringh, E., van Breugel, P.B., 2001. Composition and origin of airborne particulate matter in the Netherlands. RIVM report 650010029, RIVM, the Netherlands.