BOPII - report

The MAAP as a monitoring instrument for combustion aerosol near road traffic: an explorative study

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This report is a publication in the framework of the Netherlands Research Program on Particulate Matter II (BOP II) performed by the Energy research Centre of the Netherlands (ECN), the Environment and Safety Division of the National Institute for Public Health and the Environment (RIVM) and TNO. The research of BOP II is supervised by a steering committee which consists of Menno Keuken (TNO), Ronald Hoogerbrugge (RIVM), Ernie Weijers (ECN), Eric van der Swaluw (RIVM), Klaas Krijgsheld (Ministry of Infrastructure and the Environment) and Jan Matthijsen (PBL Netherlands Environmental Assessment Agency).

Summary

Combustion aerosol is a more health relevant and a better indicator for dispersion of traffic-related exhaust emissions than $PM_{2.5}$ and PM_{10}. Therefore, monitoring combustion aerosol is proposed to assess the effects of traffic measures (environmental zoning; reduction of exhaust emissions; dynamic traffic management) on air quality and health. In present national and local monitoring networks, combustion aerosol is mainly measured automatically by the ETL SX-200 Black Smoke monitor. However, the resulting mass concentrations are semi-quantitative and the ETL SX-200 instrument is no longer commercially available. Hence, there is a need for an alternative method to monitor combustion aerosol.

Combustion aerosol mainly consists of a mixture of elemental carbon (EC) and organic compounds (OC). EC is regarded an appropriate indicator for combustion aerosol. For air quality monitoring networks, the (intended) EU reference method - based on sampling of filters and thermal analysis of EC in the laboratory – is too time-consuming and too laborious. The Multi-Angle Absorption Photometer (MAAP) – already deployed by the DCMR in Rijnmond area - seems a more convenient option to measure automatically EC in ambient air. TNO, in collaboration with the GGD Amsterdam, has studied the applicability of the MAAP. Our study was performed in the framework of the Netherlands Policy Support Program on PM ("BOPII"), financed by the Ministry of Housing, Physical planning and Environment.

The MAAP measures light transmitted through and reflected by a filter tape which continuously samples particulate matter. The optical measurement is internally converted to EC concentrations. Our study indicated that EC concentrations are a factor three higher downwind of the motorway A10 as compared to upwind concentrations. This is a significant increase when compared to PM_{10} which in general increases less than 20% downwind of motorways. Also, at inner-urban roads with heavy traffic intensity, a similar increase of a factor three for EC concentrations was measured as compared to the urban background. The relatively low EC concentrations during the weekend are attributed to the limited number of heavy duty vehicles as compared to working days. This illustrate that EC concentrations may be applied to evaluate the impact of traffic measures on air quality and health.

It is concluded that the MAAP is an appropriate, automatic instrument to measure EC as a *proxy* for the mass of combustion aerosol. From this explorative study, it is recommended:

- to perform more parallel measurements between the MAAP and thermal analysis over a longer period and at various locations to validate the calibration of the MAAP in accordance to a thermal protocol;
- to further harmonize thermal measurements of EC in the Netherlands and to support the European working group to establish a reference method;
- to establish EC emission factors for road traffic with the MAAP which will facilitate combination of MAAP measurements with modelling.

In addition to EC, explorative research on OC concentrations indicated a limited contribution of traffic emissions. In view of the toxicity of traffic-related OC, despite its relatively small contribution it may have significant health effects. In the framework of the Netherlands Policy Support Program on PM (BOPII) further research in 2010-2011 and international collaboration on EC/OC is envisaged.

Samenvatting

Verbrandingsaerosol is een betere indicator voor de verspreiding van uitlaatemissies van wegverkeer en gerelateerde gezondheidseffecten dan $PM_{2.5}$ en PM_{10}. Daarom wordt voorgesteld om verbrandingsaerosol te meten voor het vaststellen van de gevolgen van verkeersmaatregelen (milieuzones; terugdringen van uitlaatemissies; dynamisch verkeersmanagement) voor luchtkwaliteit en gezondheid. In de huidige nationale en lokale meetnetten wordt verbrandingsaerosol voornamelijk gemeten met de ETL SX-200 Black Smoke monitor. Echter, de gemeten massa concentratie van verbrandingsaerosol is semikwantitatief en de ETL SX-200 monitor is niet meer commercieel verkrijgbaar. Er is daarom behoefte aan een alternatieve methode om verbrandingsaerosol te meten.

Verbrandingsaerosol bestaat voornamelijk uit een mengsel van elementair koolstof (EC) en organische componenten (OC). EC wordt beschouwd als een geschikte indicator voor verbrandingsaerosol. De verwachte referentie methode in de EU is gebaseerd op het verzamelen van fijnstof op een filter en thermische analyse van EC in het laboratorium. Deze methode is echter minder geschikt voor een luchtkwaliteit meetnet want deze methode is te arbeidsintensief en neemt teveel tijd in beslag. De "Multi-Angle Absorption Photometer (MAAP)"die al wordt toegepast door de DCMR in het Rijnmond gebied is een meer geschikte optie om automatisch EC in de buitenlucht te meten. TNO, in samenwerking met de GGD Amsterdam, heeft de inzet van de MAAP onderzocht. Deze studie is uitgevoerd binnen het Nederlands Beleidsondersteunend Programma naar Fijnstof ("BOPII") en gefinancierd door het Ministerie van Infrastructuur en Milieu.

De MAAP meet de transmissie van licht door en gereflecteerd van een filter tape waarop continue fijnstof wordt bemonsterd. Deze optische meting wordt intern omgezet naar EC concentraties. Onze studie laat zien dat EC concentraties een factor drie zijn verhoogd benedenwinds van de snelweg A10 ten opzichte van bovenwindse concentraties. Dit is een significante verhoging in vergelijking met PM_{10} dat in het algemeen minder dan 20% benedenwinds van een snelweg is verhoogd. Ook langs binnenstedelijke wegen met intensief wegverkeer wordt een vergelijkbare verhoging van een factor drie gemeten vergeleken met de stedelijke achtergrond. De relatieve lage EC concentraties in het weekend worden toegeschreven aan het beperkt aantal zware vrachtvoertuigen in vergelijking met werkdagen. Dit laat zien dat EC concentraties bruikbaar zijn om de gevolgen van verkeersmaatregelen op luchtkwaliteit en gezondheid te evalueren.

Het wordt geconcludeerd dat de MAAP een geschikt, automatische instrument is om EC te meten als indicator voor verbrandingsaerosol. De aanbevelingen op basis van deze verkennende studie zijn als volgt:

- de MAAP te kalibreren volgens de (referentie) thermische analyse door gelijktijdige metingen van een MAAP en thermische analyse gedurende een langere periode en op verschillende locaties;
- de themische analyses in Nederland te harmoniseren en de werkgroep in Europa te ondersteunen voor Europese harmonisatie van een themische analyse van EC;
- emissiefactoren van EC voor wegverkeer op te stellen op basis van MAAP metingen zodat de combinatie van metingen en modellen wordt ondersteund.

Naast EC is verkennend onderzoek uitgevoerd naar OC. Dit laat zien dat wegverkeer een beperkte bijdrage levert aan OC emissies. Gezien de giftigheid van verkeersgerelateer organische verbindingen is het mogelijk dat zelfs een geringe bijdrage mogelijke gezondheidseffecten heeft. In het raamwerk van het Nederlands Beleidsondersteunend onderzoek naar Fijnstof (BOPII) wordt in de periode 2010-2011 vervolgonderzoek naar EC en OC uitgevoerd.

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1 Introduction

Elevated ambient levels of particulate matter have adverse health effects. Therefore, in the EU air quality standards have been established to which the Netherlands has to comply for PM_{10} in 2011 and for $PM_{2.5}$ in 2015. These standards do not consider the composition of particulate matter, but only take into account the total mass of particulate matter. However, research shows that particles emitted by road traffic are more harmful than other particles (Laden et al., 2000; Lanki et al., 2006). In Figure 1 the health impact of particles from different sources are compared: re-suspended soil ("crustal"); "long-range transport"; "oil-combustion"; "sea salt" and "local traffic". In Figure 1 also the health impact of different parameters of particles are presented: "$PM_{2.5}$" the mass of particles smaller than 2.5 µm, "ultrafine" the number of particles and "absorbance" the amount of combustion aerosol.

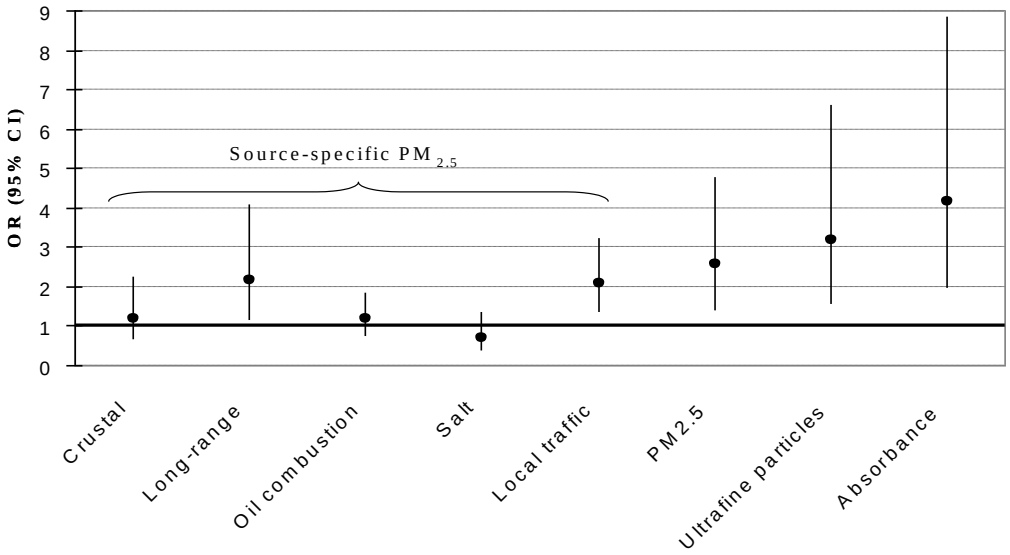

Figure 1: Risk for the prevalence of ischemia (risk factor for cardio-infarct) for sources/components related to particulate matter [Lanki et al., 2006]. OR is "Odds Ratio": the ratio of the relative risk at the 75 versus 25 percentile of the concentration distribution of a source contribution (*crustal, long-range, oil-combustion, salt* and *local traffic*) or physical/chemical property of PM (*$PM_{2.5}$, ultrafine particles* and *absorbance*). "Absorbance" is an optical measurement by the Black Smoke method of the carbonaceous content in PM.

Figure 1 shows that exposure to local road traffic emissions and particles from "long-range transport" provide a higher health risk than particles from other sources. Figure 1 also illustrates that carbonaceous particles, measured as "absorbance" and the number of ultrafine particles, which are smaller than 100 nm, have a higher health risk than $PM_{2.5}$. Exhaust emissions by road traffic are an important source for both carbonaceous and ultrafine particles in urban areas. In general, in the Netherlands, the mass contribution of exhaust emissions to PM is less than 10% as compared to the background concentrations of PM_{10} en $PM_{2.5}$ [Keuken and van den Brink, 2009].

Consequently, the concentrations of PM_{10} and $PM_{2.5}$ near heavy traffic locations are hardly increased as compared to the background concentrations. This is contrary to the mass of carbonaceous particles and the number of particles, as illustrated in Figure 2 with carbon monoxide (CO) as an indicator for the dispersion of exhaust emissions.

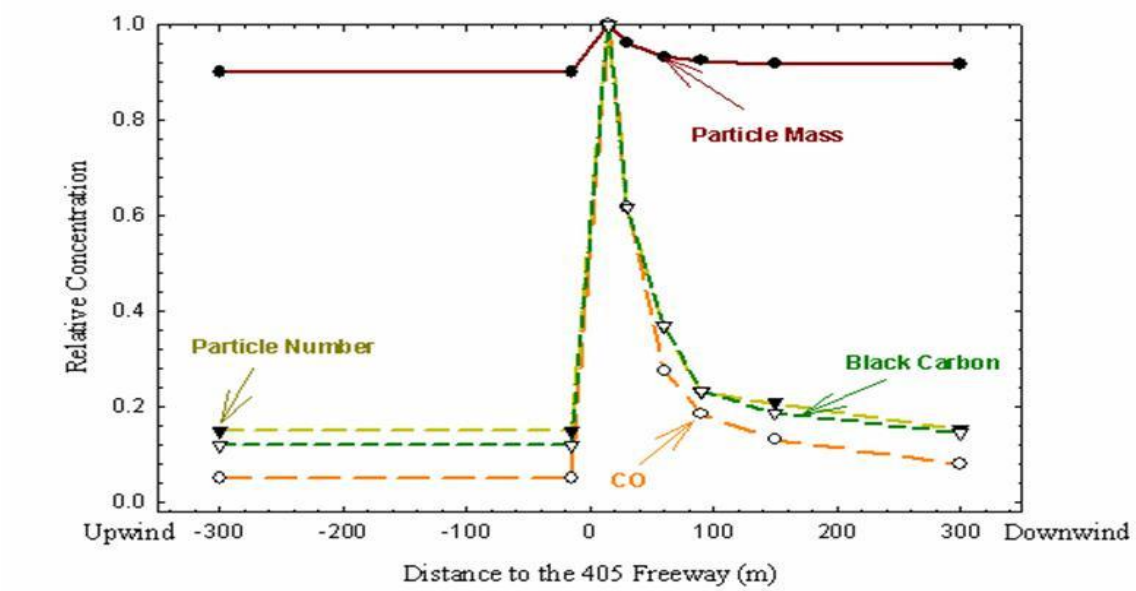

Figure 2 The relative concentrations of the particle mass, the particle number, the mass of "black carbon" and carbon monoxide (CO), as a function of the up- and down-wind distances to the road with the concentration of these components at the road is "1". [Zhu et al., 2002].

Figure 2 shows that downwind of a motorway the concentrations of CO, the mass of "black carbon" and the number of particles are significantly higher as compared to the background concentrations upwind of the motorway. Contrary, the downwind *total* mass of PM is less than 10 % increased as compared to background concentrations. From Figure 2 , it is concluded that PM_{10} and $PM_{2.5}$ are less adequate indicators to monitor the effects of local traffic emissions on air quality and health. The number of particles and the mass of "black carbon" seem more appropriate indicators for traffic-related PM emissions. The focus in this paper is on the measurement of the mass of combustion aerosol to study the effect of traffic-related PM on air quality and health.

Carbonaceous particles are formed due to incomplete combustion of carbon-containing fuels (biomass, coal, gasoline/diesel and natural gas) and lubricants. These particles mainly consist of a mixture of elemental carbon (EC) and organic compounds (OC) and less than 5% in mass of sulfate and traces of metallic ash [Maricq, 2007]. Elemental carbon is chemically characterized as "graphite". Organic compounds in exhaust emissions encompass hundreds of substances. OC aerosol is formed by *condensation* of semi-volatile hydrocarbons on the solid EC and background particles and/or as separate droplets. Formation of OC aerosol takes place in the exhaust pipe but mainly during the first seconds after dispersion of exhaust emissions in ambient air. Figure 3 schematically presents the various particles in diesel exhaust.

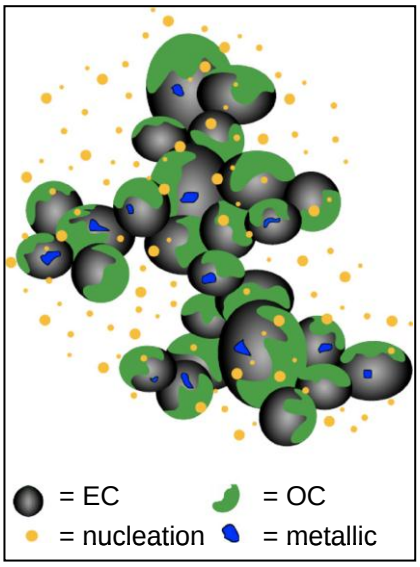

Figure 3: Schematically presentation of particles in diesel emissions: agglomerates of solid EC (black) primary particles of 15-30 nm aggregated with metal particles from friction in engine parts and catalytic convertor (blue) and condensed OC (green) plus a large number of nano-particles ("nucleation mode") in yellow of condensed OC and sulfate. [Maricq, 2007].

Figure 3 illustrates the complex mixture of particles in diesel exhaust, which is also relevant for exhaust emission by road traffic in general. Figure 4 presents the typical aerosol size distributions for diesel emissions.

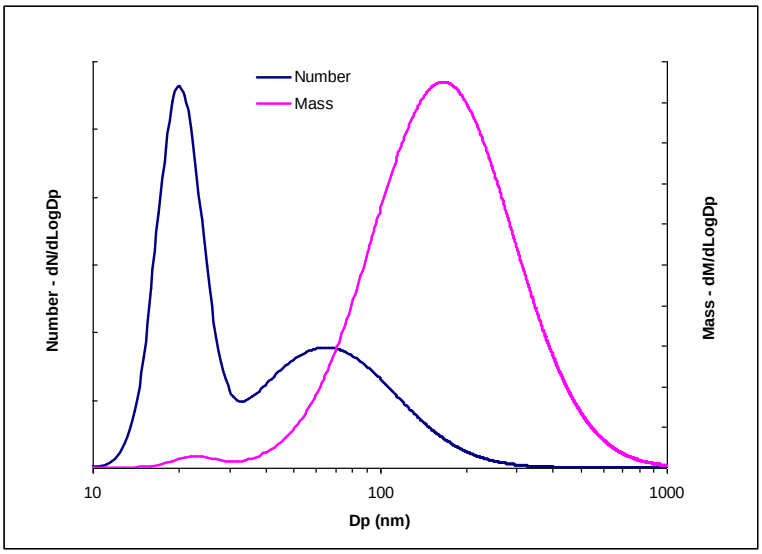

Figure 4: Typical size distribution in aerosol of diesel emissions related to mass and particle number [Kittelson et al., 2001].

Figure 4 shows that particles with size diameters between 25 nm and 1µm (agglomerates of EC with condensed OC and traces of metals in Figure 3) mainly

contribute to the mass of exhaust emissions[1] while the largest number of particles is smaller than 100 nm: the ultrafine particles. Particles smaller than 25 nm, are known to be semi-volatile as a major part of these particles disappear when heated at 200-300 ^{o}C. These particles are dominantly OC from unburned lubricating oil, while a minor part are traces of metal particles and sulphate [Sakurai et al., 2003].

Carbonaceous particles or "soot"are known as "Black Smoke - BS", "Black Carbon - BC" and "Elemental Carbon - EC". These names refer to a measurement method of elemental carbon and *not* to organic compounds (OC). The indicators BS, BC and EC are all highly correlated [Chow et al., 2009]:

- *Black Smoke - BS;* This method is based on the measurement of the *reflectance* of light by a filter on which particulate matter has been sampled. The reflection reduces with increasing EC content in particulate matter, while the content of OC hardly influences the reflectance. The measured reflectance is converted into the *total* mass concentration ($\mu g.m^{-3}$) of total particulate matter by the Black Smoke Index [ISO 9835, 1993]. The BS conversion dates back to the 1950s and since then the relation between reflectance and mass has changed drastically. In addition, the automated BS instrument SX200, which is applied in local and national air quality monitoring networks [Hijink, 2002], is no longer commercially available. Therefore, the BS method is not recommended to assess the mass contribution of combustion aerosol. However, time series of BS measurements in the Netherlands from the 1970s onwards may be used to analyze the *trend* in concentrations of combustion aerosols;
- *Black Carbon - BC;* "Black carbon" is measured optically by an absorption photometer by attenuation of the *transmission* of light through a filter with sampled particulate matter. There are several automated instruments commercially available such as the RP8100, Magee aethalometer type AE21 and the MAAP [Green et al., 2007]. The measured absorption coefficients are converted into "black carbon" mass concentration which are highly correlated due to calibration with EC concentrations;
- *Elemental Carbon - EC;* Elemental carbon is measured by a thermal method. An advantage of the thermal method - as compared to Black Smoke and Black Carbon methods - is that total carbon is determined in separate fractions of EC and OC. The thermal method is based on two-step heating of a quartz filter with sampled particulate matter and detection of carbon dioxide. In the first step, organic compounds are measured and in the second step EC. The temperature gradient protocol for these two steps and the composition of the combustion aerosol determines the ratio of EC/OC as OC may be partially converted into variable *artefact* EC depending on the type of protocol. Both in the USA and Europe, thermal protocols have been developed [Chow et al., 2001; ten Brink et al., 2004; Cavalli and Putaud, 2007; CEN/TC 264 2010] which are the basis for an (intended) reference method of EC in ambient air. However, an important disadvantage is that most EC/OC measurements are *off-line* analysis of EC. This makes most thermal methods time-consuming, labour-intensive and with a low time resolution.

[1] The EURO 5/6 emission standards - effective from 2011/2014 for personal gasoline and diesel vehicles – have a mass-based limit of 5 mg per km per vehicle. These standards also include a limit for the number of particles *larger than 23 nm* to $6 * 10^{11}$ particles per km. The number-based limit was introduced to prevent that particulate filters may be developed which may meet the mass limit but allow high numbers of particles to pass.

EC is considered as an adequate indicator for dispersion of combustion aerosol in general and exhaust-related PM emissions by road traffic in particularly [Schauer et al., 2003]. Absorption photometers, such as the MAAP (next to the RP8100 and Magee AE21) automatically measures black carbon as an indicator for EC. This report describes a study in June – September 2010 in collaboration with the Amsterdam Municipal Health Service (GGD Amsterdam) on the applicability of the MAAP to measure combustion aerosol. In section 2, the objective of the study and the approach are elaborated, followed by section 3 where the experimental setup is described. The experimental results are presented and discussed in section 4 and finally, in section 5 the conclusions and recommendations are provided.

2 Objective and Study approach

The objective of this study is to investigate the applicability of the MAAP as an instrument to measure the concentration of combustion aerosol near traffic locations.

Two MAAP instruments were simultaneously deployed at an urban location and near a motorway (A10). PM_{10} was also collected at these locations by 24-hourly sampling. The sampled PM_{10} was analyzed for EC/OC in two laboratories (TNO and GGD) by a thermal method with two temperature protocols (EUSAARII and NIOSH). Comparison of MAAP measurements with thermal EC concentrations provides information on the impact of various protocols on the EC concentration and (possibly) on a location-specific relation between the MAAP and thermal EC. Comparison of EC and Black Smoke measurements is directed to establish a relation between the widely applied Black Smoke method and EC measurements.

The MAAP measurements at the urban and motorway locations were used to determine the average EC concentration per wind direction. At the motorway location A10, the measured contribution of the motorway emissions of EC was compared to the modelled contribution. The modelled contribution of traffic emission was calculated with the "HEAVEN" model of TNO. This is an hour-to-hour version of the regulatory reference line-source model in the Netherlands.

Finally, OC concentrations measured in the 24-hourly samples of particulate matter collected at the urban and A10 location are presented. This provides information on the contribution of traffic emissions to OC concentrations.

3 Experimental approach

3.1 Sampling period and -locations

In the period between 16 June and 14 July 2010, measurements have been performed at an urban background location “A’dam” and a location south of Amsterdam near the A10 motorway “A10”. The two locations are part of the air quality monitoring network of the GGD-Amsterdam. Black Smoke measurements with the ETL SX-200 from these GGD locations and the street locations “Stadhouderskade” and the “Jan van Galenstraat” have been included in this study. The locations are presented in Figure 5.

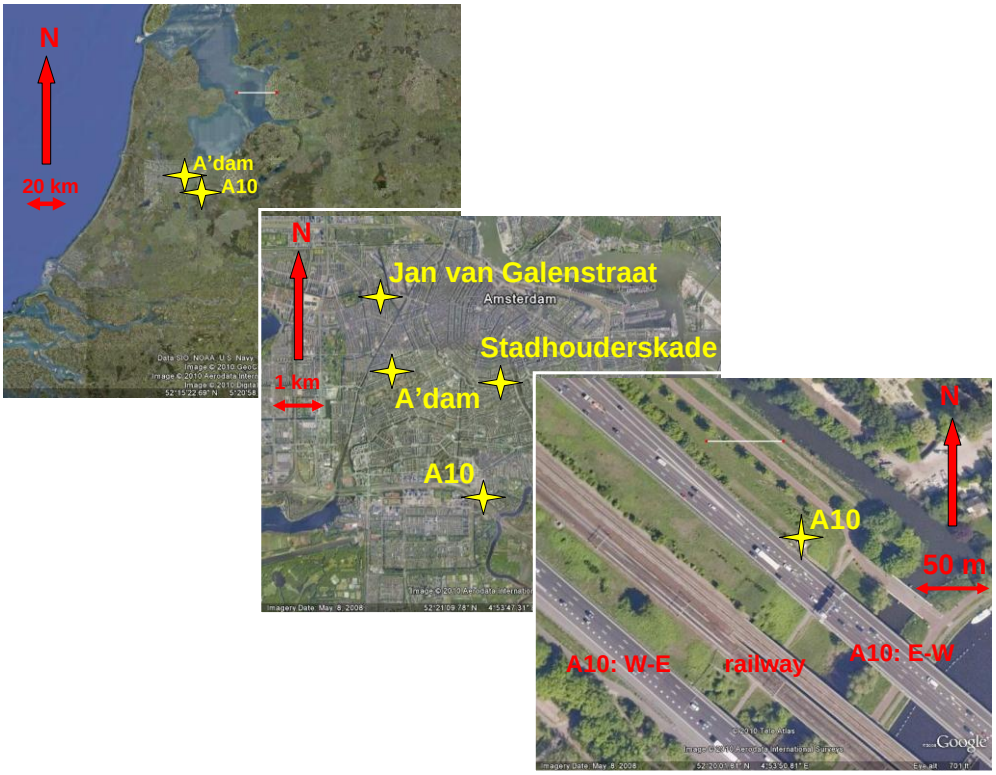

Figure 5: The sampling locations at Amsterdam and near the A10.

“A’dam” is an urban background location next to the Vondelpark in the centre of Amsterdam. “A10” is a traffic-exposed location at 15 m north of the east-west driving lanes and at 100 m north of the west-east driving lanes of the motorway A10.
In previous years, the GGD Amsterdam has performed automatic ETL SX-200 Black Smoke measurements at the locations A’dam, A10 and a street location “Stadhouderskade”. In addition, GGD has performed thermal EC/OC measurements in June - July 2010 on the locations A’dam and a street location “Jan van Galenstraat”, and near the A10.

3.2 Monitoring instruments and sampling

Black carbon monitoring with the MAAP (Thermoscience Model 5012) are based on measurements of both the transmission and reflectance of light (670 nm) by particulate matter collected on filter tape [Petzold and Schönlinner, 2004]. This mode of detection of the MAAP is schematically presented in Figure 6.

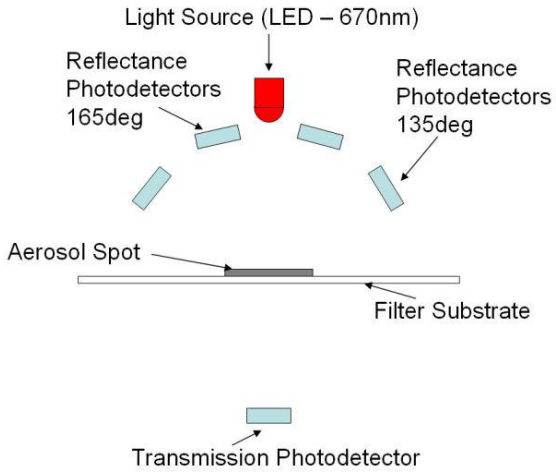

Figure 6: Schematic setup of the MAAP.

The MAAP samples particulate matter at a sampling flow of 16.7 $l.min^{-1}$ without a size-selective sampling inlet. The amount of EC in the sampled particulate matter is continuously monitored by the decreasing transmission of detected light via the sampled particulate matter on the filter tape, as well as the reflectance by the filter tape. The combined measurement of transmission and reflectance is an important difference of the MAAP as compared to other less sophisticated absorption photometers such as the aethalometer and the Black Smoke photometer. The MAAP enables correction for internal reflectance of light within the filter material and by "white" secondary particles in particulate matter. The filter tape is automatically transported when the transmission of the aerosol spot in Figure 6 is reduced to 20% (or another preset value). The optical measurements by the MAAP of the absorption coefficient (m^{-1}) are internally converted into EC concentrations ($g.m^{-3}$) by a mass specific absorption coefficient of 6.6 m^2 per g EC [Petzold and Schönlinner, 2004]:

concentration ($g.m^{-3}$) = absorption coefficient (m^{-1})/ 6.6 ($m^2.g^{-1}$) equation 1

From theoretical considerations, the mass specific absorption coefficient is estimated at 7.5 $m^2.g^{-1}$ for spherical carbonaceous particles at 550 nm [Petzold and Schönlinner, 2004]. However, the matrix of particulate matter may interfere with the optical measurement of the absorption of EC for example by "white" particles of secondary inorganic aerosol, sea salt and soil or "brown" particles of organic compounds. These interferences increase by ageing of combustion aerosol during long-range transport and internal mixing of particles [Vester et al., 2007]. Consequently, the mass absorption coefficient of EC measured by optical methods may vary up to 10 $m^2.g^{-1}$ at 550 nm for aged combustion aerosol. The *default* mass specific absorption coefficient of 6.6 $m^2.g^{-1}$

in equation 1 is directed to EC measurements in urban areas with “fresh” combustion aerosol and hence for rural areas the MAAP may overestimate EC concentrations.

The *default* mass specific absorption coefficient in the MAAP has been established by comparison with EC measurements based on a German VDI thermal protocol. The VDI protocol is different from the aforementioned EUSAARII/NIOSH thermal protocols. The main differences between EUSAARII/NIOSH protocol and the VDI protocol is that the former two protocols correct for the artefact EC formation, while in the VDI protocol no correction is applied. Consequently, the VDI protocol (*and thus the MAAP*) overestimates EC concentrations as compared to measurements by EUSAARII/NIOSH by a factor 1.15 – 1.35 [Petzold and Schönlinner, 2004]. Further details on these protocols are provided in Annex 2.

In addition to continuous EC measurements with the MAAP, particulate matter was simultaneously sampled at the three locations by Low Volume Samplers – LVS (Leckel, Berlin) with a sequentially sampler set at 24-hour sampling period. A size selective inlet for PM_{10} was mounted on the LVS with a sampling flow of 2.3 $m^3.h^{-1}$. The filters were quartz (Pallflex membrane filter with a diameter of 47 mm. The LVS filters were analyzed in the laboratory for EC/OC by the EUSAARII protocol [Cavalli and Putaud, 2007] and a thermal instrument (Sunset Lab., USA).

The GGD-Amsterdam in their monitoring network measures Black Smoke automatically by the SX200 (ETL, Hereford, UK). This automated method provides $\mu g.m^{-3}$ for values of the “BS index” following the ISO 9835 protocol [ISO 9835, 1993]. The GGD-Amsterdam employs a thermal method for EC/OC analysis based on the NIOSH (National Institute for Occupational Safety and Health) protocol [Chow et al., 2001].

Hence, in this research combustion aerosol measurements have been compared based on analysis following the automated SX200 Black Smoke method and the thermal EUSAARII and NIOSH protocols. In Annex 2 more details are provided of both protocols.

3.3 Quality Assurance and Quality Control

The reproducibility of the MAAP was tested by parallel measurements of 2 MAAPs before the monitoring period during two days at a regional background location. The results are presented in Figure 7.

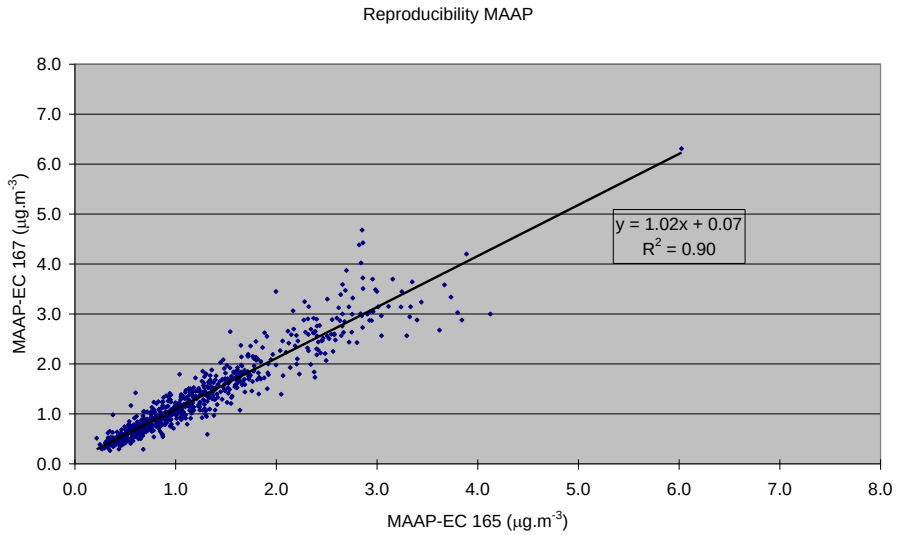

Figure 7: The reproducibility of two MAAPs tested for four days by parallel measurements at the same location.

Figure 7 illustrates that the reproducibility of the MAAP is better than 90% in the concentration range of 0.1 – 6 µg EC per m^3. The detection limit of the MAAP is 0.1 µg EC per m^3. The average value for the MAAP "167" was 7% higher than for the MAAP "165". Hence, MAAP 167 measures 7% too high or *vice versa* MAAP 165 measures 7% too low. After this study is was measured that the flow of the MAAP 167 was 7% higher than the MAAP 165, while the latter had the "correct" flow of 16.7 $L.min^{-1}$. The MAAP number 167 was employed at the urban background at A'dam, while the MAAP 165 was applied near the motorway A10. The systematic difference of 7% between both instruments is considered in the data analysis.

Before sampling with the LVS, the applied quartz filters were heated at 900 ^oC during 2 hours to remove traces of OC in the filters. For each sampling location, a field blank was included and the results were corrected for the field blanks. The values of the field blanks were 0.1 $\mu g.m^{-3}$ EC en 1 $\mu g.m^{-3}$ OC which have been used to correct the actual measurements.

The samples in A'dam and near the A10 have been analyzed by TNO following both the EUSAARII and NIOSH protocol. Also, samples collected near the motorway A10 have been analyzed both by TNO and the GGD. From these results, it is concluded that the results from the EUSAARII protocol agrees with the NIOSH protocol when analyzed in the same laboratory but are systematically higher (~ 20%) when analyzed in different laboratories. In Annex 2, the results of these tests are presented. It is noted that this comparison only comprised of a small set of samples and more research is required to decide on a harmonized protocol [GGD, 2009]. In Europe a working group of the international standardization commission (CEN/TC 264 "Air quality" WG35) has been involved in harmonization of the analytical protocol for EC/OC with a focus on EUSAARII and NIOSH. Due to lack of funds, this working group has temporarily finalized its activities with a technical document [CEN/TC 264; 2010] without a decision for a specific protocol.

4 Results

4.1 Daily average automated ETL SX-200 Black Smoke in A'dam, Stadhouderskade and A10

The results of Black Smoke measurements in mass units at the GGD locations: urban background ("A'dam"), a street location ("Stadhouderskade") and near a motorway ("A10") in 2008 are presented in Figure 8.

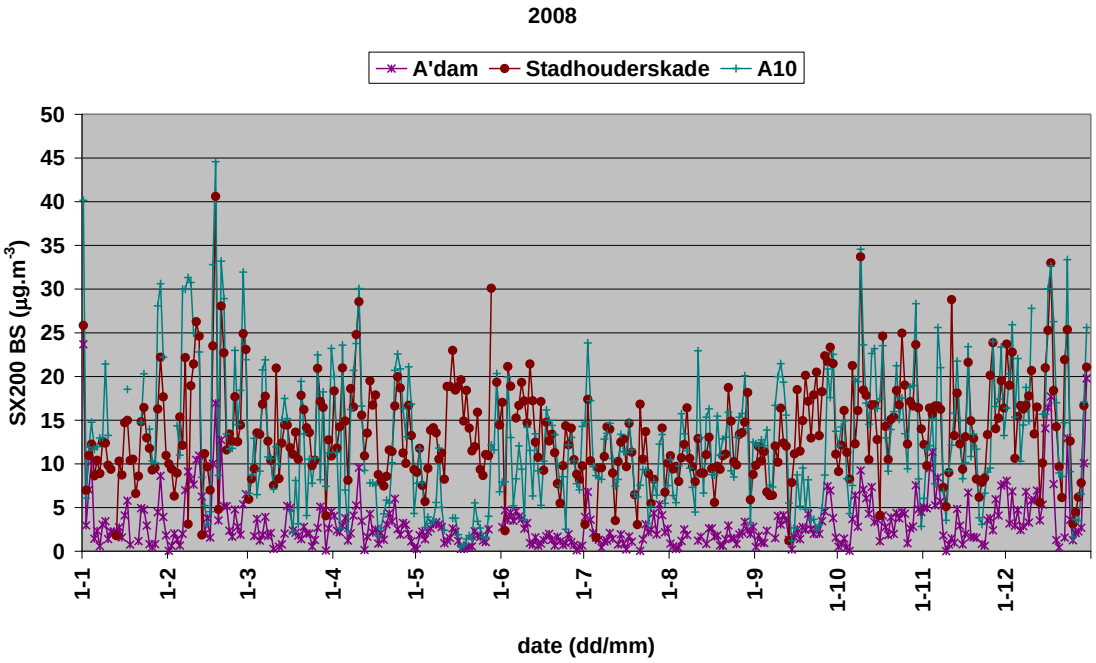

Figure 8: Daily average concentrations of the Black Smoke Index ("µg.m^{-3}") in 2008 measured at an urban background location (A'dam), in a street (Stadhouderskade) and near a motorway (A10).

Figure 8 shows that Black Smoke Index, as an indicator for combustion aerosol, has the highest concentrations at traffic-exposed locations in the street location Stadhouderskade and near the motorway A10. The annual average concentrations at the locations in Amsterdam are presented in Table 1.

Table 1: Annual average and standard deviation of Black Smoke Index in "µg.m^{-3}" in A'dam, Stadhouderskade en A10.

	Black Smoke Index (SX200 "µg.m^{-3}")		
	A'dam	Stadhouderskade	A10
Average ± Standard deviation	3.2±3.1	13.6±5.7	12.8±7.6
Number of days	345	359	343

Table 1 shows that the annual average concentration of Black Smoke Index is fourfold higher at both the traffic locations as compared to the urban background. This demonstrates that combustion aerosol is significant higher near heavy traffic locations as compared to the background. The Stadhouderskade is an urban road with one-sided buildings in the centre of Amsterdam, while the motorway is constructed on a 10 m elevated embankment in an open area. The similar increase in Black Smoke Index – despite traffic intensity at the Stadhouderskade and the A10, of respectively, 24.000 and 170.000 vehicles per 24 h - illustrates the impact of limited dispersion at an urban road on air pollution. It is acknowledged that the Black Smoke Index provides a too high estimate for the mass concentration of combustions aerosol. Recent research in the Netherlands at urban background and urban roads indicates a concentration range in the order of 1-3 (urban) and 2-5 (urban roads) µg EC per m^3 [Keuken and van den Brink, 2009].

The relation between Black Smoke measurements and concentrations of thermal EC has been studied by the GGD-Amsterdam. This was done by simultaneous Black Smoke measurements by the SX200 near the A10 motorway and thermal analysis in the period 2006-2007. The results are presented in Figure 9.

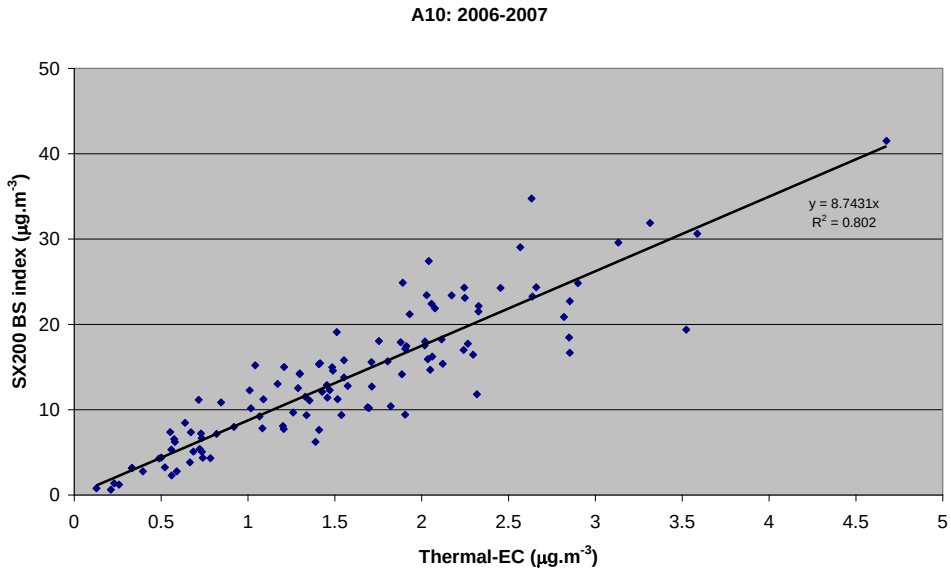

Figure 9 : Scatter plot of the BS index ("µg.m^{-3}") measured by the SX200 and thermal-EC (µg.m^{-3}) measured by the NIOSH protocol in daily average particulate matter at A10 in the period 2006-2007.

Figure 9 shows that BS index and thermal EC have a linear range up to 5 µg.m^{-3} EC. The correlation of 0.8 means that 80% of the variability in thermal EC is explained by the variability in Black Smoke and hence, thermal EC is a good proxy for Black Smoke. The slope of 8.3 in Figure 9 means that EC concentrations may be derived from Black Smoke measurements by dividing results of the BS index by a factor 8.7. This factor is similar with other studies comparing Black Smoke with thermal EC at regional, urban and traffic locations [Cyrys et al., 2003; Schaap and van der Gon, 2007].

4.2 Comparison of MAAP-EC and thermal-EC at A'dam and A10

The possible location-specific dependency of the MAAP is studied by comparing the MAAP measurements and thermal-EC measurements at the locations A'dam and A10. De results for the whole period are presented in Table 3.

Table 3: The average and standard deviation in the daily average MAAP-EC and thermal-EC in A'dam and A10 in the period 16/06-14/07/2010.

	EC (µg.m^{-3})	
	A'dam (n=26)	A10 (n=28)
MAAP-EC	1.3±0.7	2.8±1.7
Thermal-EC	0.9±0.4	2.1±1.2

The data in Table 3 indicate that the MAAP at the urban background and near the motorway A10 overestimates the EC concentrations as compared to the thermal EUSAARII method. This was expected in view of the discussion in section 3.2 which predicted 15 – 35 % higher MAAP-EC results as compared to thermal EC analysis following the EUSAARII protocol. The results of MAAP-EC and thermal-EC EUSAARII for all three locations are plotted in Figures 10 A-B.

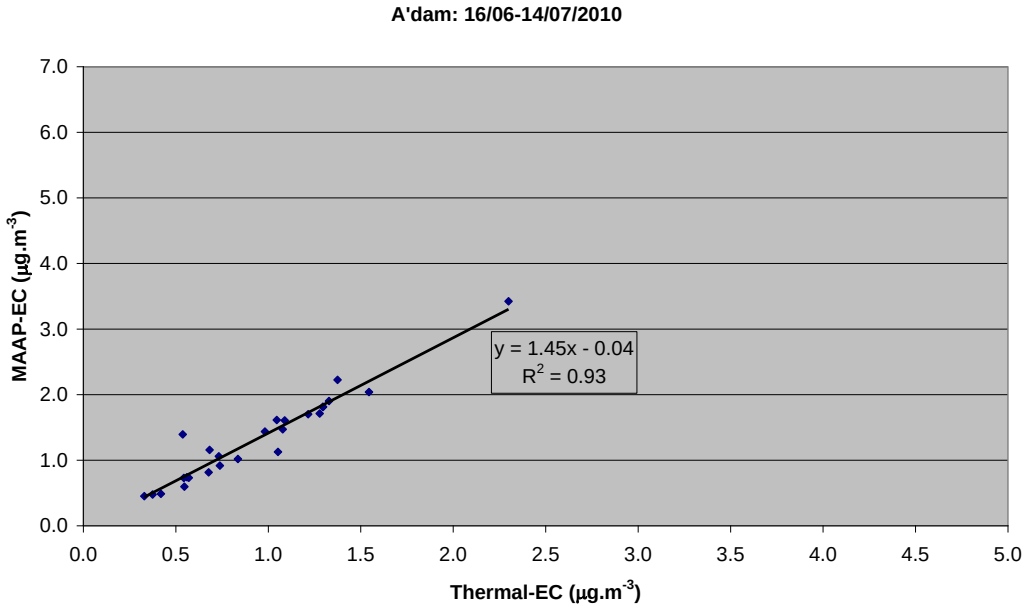

Figure 10A: Comparison of MAAP-EC and thermal-EC at A'dam in the period 16/06-14/07/2010.

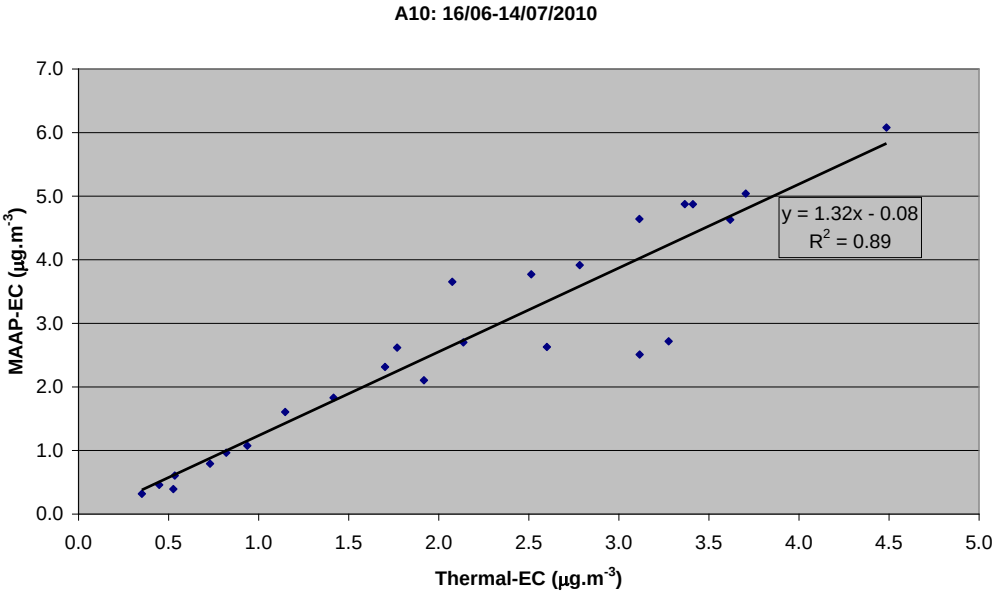

Figure 10B: Similar as Figure 10A for A10 in the period 16/06-14/07/2010.

For the urban background and near the motorway A10, figures 10A-B show that MAAP measurements are highly correlated with the thermal-EC. The correlation coefficient (R^2) is 0.93 for A'dam and 0.89 for A10. Figures 10A-B further illustrate that the MAAP overestimates EC concentrations in Amsterdam and near the A10, respectively 45% en 32% as compared to the thermal-EC by the EUSAARII protocol. The differences between A10 and A'dam are attributed to 7% overestimation by the MAAP at A'dam (see: section 3.3). Hence, the overestimation at the urban background A'dam is actually 38%. The overestimation of 32% near the A10 and 38% at the urban background A'dam is reasonable in agreement with the predicted value of 15-35% due to calibration of the MAAP by the thermal VDI protocol (see: section 3.2).

Figures 10A-B show a similar linear relation for the MAAP against the thermal method in the concentration range of 0.5 - 7 µg EC per m^3 for both the urban background and a traffic-exposed location. Consequently, it is concluded in urban and traffic-exposed locations, the MAAP seems "fit for purpose" as an automated instrument to measure EC in a monitoring network.

It is recommended to continue parallel measurements at various locations and a longer period with the MAAP and the thermal EUSAARII/NIOSH method. This would enable to calibrate the MAAP in accordance to the EUSAARII/NIOSH method (as the intended reference thermal protocol) instead of the VDI protocol.

4.3 Hourly average MAAP measurements at A'dam and A10

The results of hourly average MAAP-EC in the study period at the locations A'dam and A10 are presented in Annex 1. The average value over the study period and minimum and maximum are shown in Table 4.

Table 4: The average, minimum and maximum MAAP-EC concentration (µg.m^{-3}) in 16/6-14/07/2010 in A'dam en A10.

	MAAP-EC (µg.m^{-3})	
	A'dam	A10
Average	1.4	2.8
Minimum-Maximum	0.2-7.9	0.1-14.1

Table 4 presents, that the average concentrations of MAAP-EC are a factor two higher near the A10 than at the urban background in Amsterdam. The variation in the hourly concentrations, as given in Annex 1 shows that the variation of the MAAP-EC is highest near the A10. Next to variation in traffic intensity and composition, this is mainly caused by variation in wind direction and consequently variation in transport of air pollution from the A10 to the sampling location. The MAAP-EC concentrations on the two sampling locations are presented in Figure 11.

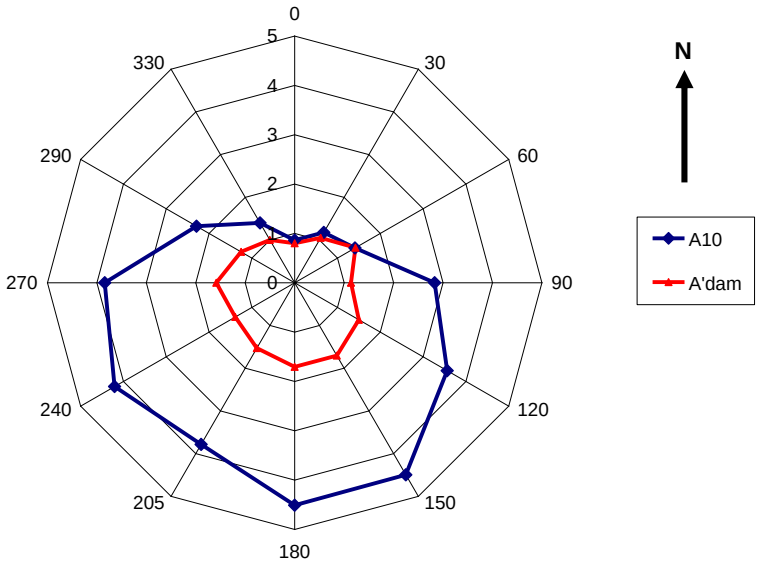

Figure 11: Hourly average concentrations of MAAP-EC (µg.m^{-3}) at various wind directions at A'dam and A10 in June-July 2010 (n = 639 hours).

Figure 11 illustrates that during south-easterly wind directions the concentrations of MAAP-EC at the two locations are elevated: this is caused by continental air with higher soot concentrations due to combustion emissions by traffic, industry and energy generation at the continent, while north-westerly winds are characterized by relative

clean air from the North Sea. Further, Figure 11 clearly shows that the highest MAAP-EC concentrations at the location A10 are measured during south and south-westerly wind directions. This is related to transport of combustion aerosol to the sampling location from the motorway A10 (see: Figure 5). This contribution is further quantified by comparison of modelled and measured contribution of the A10 emissions to EC concentrations at the sampling location in the next section.

4.4 Measured and modelled contribution to EC on the sampling location A10

The *measured* contribution of traffic emissions to the EC concentrations at the sampling location A10 has been estimated for wind directions in between 120^{o} and 270^{o}. The measured contribution is computed from the differences between the measured concentrations at the A10 and A'dam locations during these wind directions.

The *modelled* contribution of traffic emissions to EC at A10 is computed by model calculations for hours with wind directions in between 120^{o} and 270^{o} and at wind speeds higher than 2 $m.s^{-1}$. The related traffic volume, composition and speed have been collected from the National Road Authority. For these hours (n= 117), the meteorological conditions (e.g. wind direction and wind speed) measured at Schiphol by the Royal National Meteorological Institute at less than 10 km from the location A10 have been applied. Subsequently, the HEAVEN model – an hour-to-hour application of the National Reference Model for dispersion of traffic emissions from a motorway - has been used. The model takes into account the distances of the sampling location to the motorway for the east-west lanes at 15 m and the west-east lanes at 100 m (see Figure 5). EC emission factors for road traffic on a motorway were based on data from the literature for EC as fraction of $PM_{2.5}$ in exhaust emissions [Ntziachristos L and Samaras Z., 2009]. These fractions are provided for three vehicle categories: heavy duty (> 20 ton), light duty (3.5-20 ton) and passenger cars (< 3.5 ton). This resulted for *heavy and light duty trucks* in 50 – 140 mg EC per km per vehicle for respectively, free flowing traffic at 80 – 100 $km.h^{-1}$ and congested traffic, while for *passenger cars* to 7 mg EC per km per vehicle both for free-flowing and congested traffic. The emission factor for passenger cars takes into account the present, average composition of 20% diesel and 80% petrol cars on the Netherlands motorways. The results of the measured and modelled contribution of EC on the monitoring location A10 are presented in Figure 12.

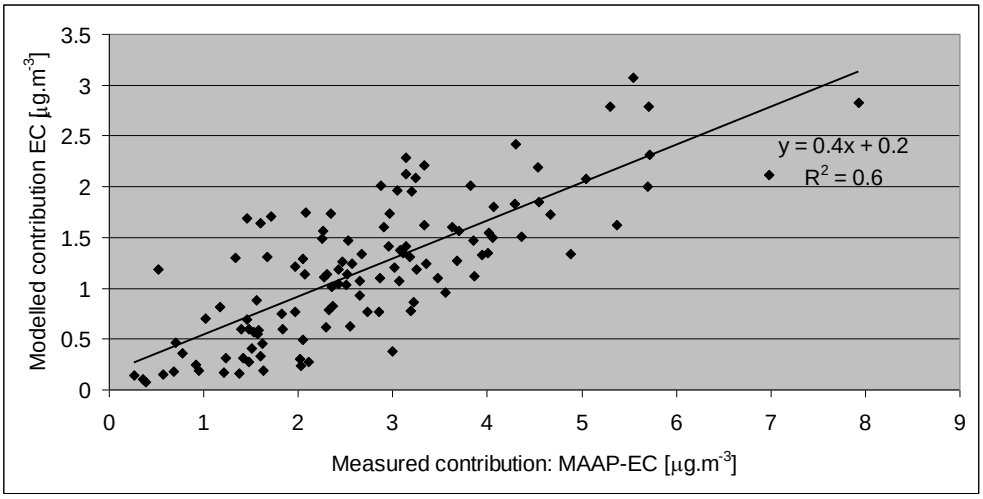

Figure 12: Measured and modelled hourly contribution to EC concentrations ($\mu g.m^{-3}$) at the monitoring location A10 (n=117).

Figure 12 shows that the modelled and measured contribution during hours with wind directions transporting combustion aerosol from the motorway A10 to the sampling location is correlated with a R^2 of 0.6. This correlation indicates that 60% of the variation in the measured EC may be explained by emissions of EC by road traffic on the motorway A10. The modelled contribution is a factor 2.5 lower than measured. If the measured contribution by the MAAP is corrected with a factor 1.3 (to account for the overestimation of measured EC due to calibration with the VDI protocol) still a factor two remains between the modelled and measured contribution of EC. In similar studies with NO_x the modelled contribution is typically 80% of the measured contribution [Wesseling and Visser, 2003]. This suggests that uncertainties in the input parameters for the model related to traffic (e.g. volume, composition, speed and congestion) and meteorology (e.g. wind speed and direction) should have resulted in a similar range of uncertainty for EC. The larger discrepancy for EC then for NO_x may be attributed to uncertainties in the EC emission factors for road traffic. However, these factors for free-flowing traffic on a motorway (7 $mg.km^{-1}$ for passenger cars and 50 $mg.km^{-1}$ for heavy duty vehicles) agree very well with experimental data established in the Drechttunnel in the Netherlands in 2008 with 5 (±3) and 30 (±10) mg $EC \cdot km^{-1}$ for respectively, passenger cars and heavy duty vehicles [Keuken and ten Brink, 2009].

The most likely explanation for the discrepancy between modelling and measurements is the complex dispersion of traffic-related pollution behind the safety screen of 2.5 m height between the motorway and the monitoring station. Calculations with a Computational Fluid Dynamics model indicate that the wind speed may drop by half at 3 m height behind the safety screen where the sampling inlets for the measurements are located. As a consequence, the modelling results may indeed underestimate the monitoring results by a factor two.

Based on the results of this explorative study, it is recommended to compare modelling with measurements at a less complex situation and to measure EC in exhaust emissions by the MAAP. The advantages of a MAAP for exhaust emissions are 1.) continuous

measurements [Moosmüller et al., 2001], as compared to laborious filter sampling and off-line thermal EC analysis, 2.) information on EC emissions of specific parts of a driving cycle (cold-start, congestion, high load) and 3.) integration of dispersion modelling based on established EC emission factors by the MAAP with ambient monitoring by the MAAP.

4.5 Comparison of OC at A'dam and A10

Next to EC, exhaust emissions are a source of semi-volatile organic compounds in ambient air. However, natural emissions of volatile hydrocarbons followed by conversion into semi-volatile compounds in the atmospheric processes are probably a dominant source of OC in aerosols [Harrison and Yin, 2008; Mauderly and Chow, 2008]. The contribution of OC by traffic emissions has been studied by the thermal analysis of the daily average OC concentrations in collected particulate matter at A'dam and A10. The results are presented in Table 5.

Table 5: The daily average and standard deviation of OC ($\mu g.m^{-3}$) in A'dam and A10 in 16-28/06/2010 (1ste period) and 29/06-14/07/2010 (2^{nd} period).

	OC ($\mu g.m^{-3}$)	
	A'dam	A10
1^{ste} period (n=13)	2.1±1.3	2.0 ±1.4
2^{de} period (n=13)	2.8±1.4	3.1±1.3
total period (n=26)	2.4±1.4	2.6±1.4

Table 5 shows that during the first period, OC concentrations at the urban background were similar with concentrations near the motorway. This can be explained by the dominant wind directions from the north during the first period – with the exception of the last four days – and consequently, the monitoring location A10 was hardly exposed to traffic emissions. In the second period, the average OC concentration at the motorway location is 10% elevated against the urban background. This illustrates the limited impact of local traffic emissions on local OC concentrations as these are dominated by the regional background.

The differences in impact of traffic emissions on local OC and EC concentrations are illustrated by measurements at the urban background A'dam, a traffic location in the Jan van Galenstraat ("JvG") in Amsterdam and near the motorway A10. These measurements were performed by the GGD in the period June-July 2010 and presented in Figure 13A and B.

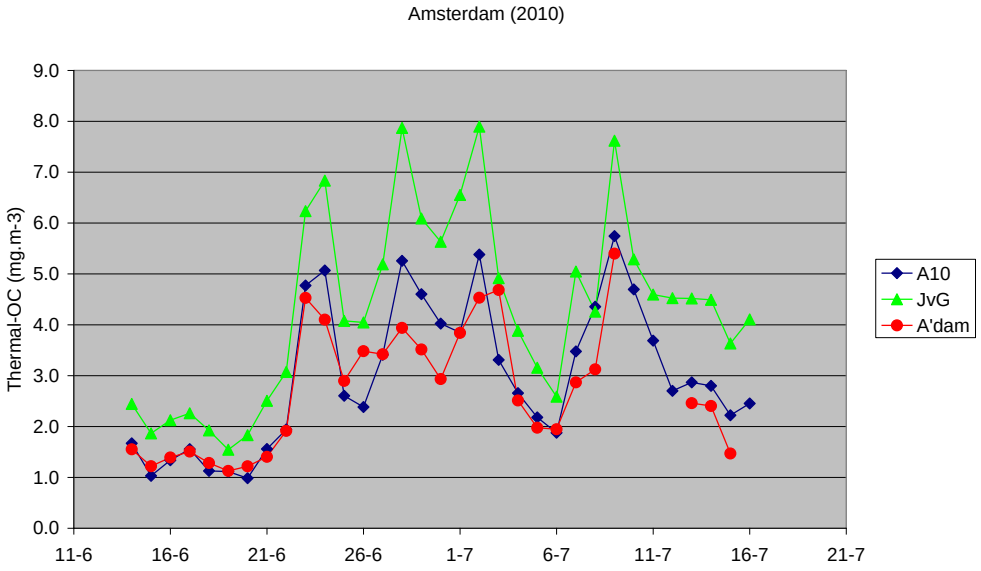

Figure 13A: Daily average OC (µg.m^{-3}) measured at the urban background (A'dam), an inner urban road (JvG) and near a motorway (A10) in June-July 2010.

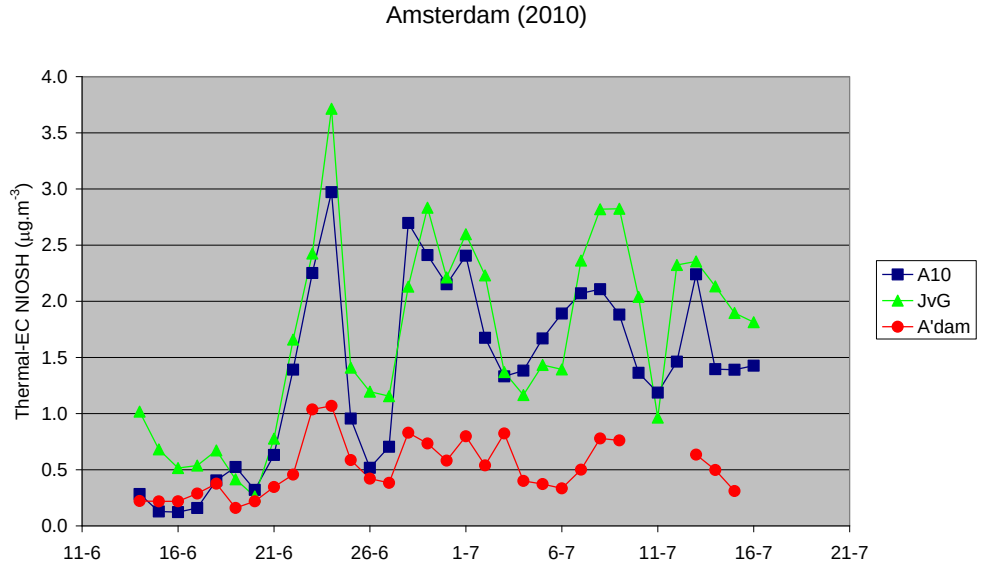

Figure 13B: Similar as figure 15A for EC.

The results presented in Figure 13A, confirm the limited contribution of traffic emissions to OC levels as presented in Table 5. Only at the inner-urban road Jan van Galenstraat are OC levels increased as compared to the urban background A'dam. Figure 13B confirms that EC concentrations are an adequate indicator for combustion aerosol of road traffic. Similar to the results for Black Smoke as shown in Figure 8, it is noted that the levels of EC are in the same range in an inner-urban road with a traffic intensity of 15-20.000 per 24 h with 3% heavy duty vehicles as compared to the motorway A10 with more than 150.000 vehicles per 24 h with 3% heavy duty vehicles. The impact of lower traffic intensity, *especially reduction of the number of heavy duty vehicles during the weekend* on EC concentrations is clearly visible at both locations on

19/20-6, 26/27-6, 03/04-7 and 10/11-7. The latter is an illustration for application of EC concentrations to evaluate the impact of traffic measures on air quality.

It is noted that despite the relatively small *traffic* contributions to the mass of OC may still have significant health impacts as these emissions concern toxic organic compounds such as (nitro)polycyclic aromatic hydrocarbons [Mauderly and Chow, 2008]. In view of the limited period and number of samples, the presented results on OC are regarded "explorative". More extensive research on the contribution of road traffic and other urban sources to OC in ambient air is envisaged in 2010 – 2011 within the framework of the Netherlands Policy Support Program on Particulate Matter ("BOPII") financed by the Ministry of Housing, Physical planning and Environment.

5 Conclusions and recommendations

Studies indicate that combustion aerosol in ambient air is a better indicator for health effects of particulate matter (PM) than $PM_{2.5}$ and PM_{10}. Till present, combustion aerosol is mainly monitored by the automated Black Smoke method in local and national monitoring networks in the Netherlands. However, this method does not provide a reliable mass of combustion aerosol and the applied SX200 automatic monitor is no longer commercially available.

The mass of elemental carbon (EC) is regarded a more appropriate indicator for combustion aerosol and to assess the effects of traffic measures (environmental zoning; reduction of exhaust emissions; dynamic traffic management) on air quality and health. EC may be measured by thermal analysis but there is still no consensus on a reference method. In the Netherlands, currently the GGD Amsterdam uses the NIOSH protocol, while TNO applies the EUSAARII protocol. In our study, an average of ~ 20% higher EC was measured by the EUSAARII protocol as compared to the NIOSH protocol when analyzed in different laboratories. It is recommended to further harmonize both protocols for EC measurements in the Netherlands. However, for monitoring networks the thermal method is too time-consuming and labour-intensive. Hence, there is a need for an automatic instrument to measure EC in ambient air as a successor of the SX200 Black Smoke monitor.

The recently developed Multi Angle Absorption Photometer (MAAP) seems an appropriate automatic instrument to monitor EC in ambient air and is already deployed by DCMR in the Rijnmond area since 2007. Our research at an urban background (A'dam) and near a motorway (A10) in June-July 2010 indeed demonstrates the applicability of the MAAP. Though, similar to the Black Smoke method also the MAAP requires conversion of the optical "black carbon" measurements to the mass units of EC. The MAAP overestimates EC concentrations as compared to thermal analysis 15 to 35% due to calibration of the MAAP with the VDI protocol.

The results in our study indicate that the mass of combustion aerosol is a factor 3 higher downwind of a motorway with more than 150.000 vehicles per 24-h as compared to upwind concentrations. This is a significant increase of combustion aerosol as compared to PM_{10} with in general an increase less than 20% downwind of motorways. Also, at inner-urban roads with traffic intensity in the range of 15-20.000 vehicles per 24-h a similar increase of a factor three for EC concentrations was measured as compared to the urban background. The relatively low EC concentrations during the weekend near these heavy traffic locations are attributed to the limited number of heavy duty vehicles as compared to working days. This illustrates that EC concentrations may be applied to evaluate the impact of traffic measures (e.g. environmental zoning) on air quality and health.

From this explorative study it is concluded that the MAAP may be used as an automatic instrument to measure EC as a *proxy* for the mass of combustion aerosol. Due to the relative short monitoring period in this study, it is recommended to perform comparative measurements between the MAAP and the (intended) reference method during various seasons and locations. These comparative measurements should also be focused on agreeing on an European protocol to be used in the reference method. It is also recommended to combine the MAAP measurements with modelling (street canyon

model, line-source model and point sources) in order to improve the spatial coverage of EC in ambient air. This requires EC emission factors established with the MAAP or based on an agreed thermal protocol to determine the EC concentrations in exhaust emissions.

Finally, explorative research on OC concentrations in ambient aerosol by thermal analysis indicates that OC concentrations are dominated by the regional background. However, in view of the toxic characteristic of OC emitted by road traffic, despite this relatively small contribution in mass traffic-related OC may have significant health effects. In the Netherlands Policy Support Program on PM (BOPII) further research on EC/OC is envisaged in 2010-2011

6 Authentication

Contractor:

The study was financed by the Ministry of Housing, Physical planning and Environment in the framework of the Netherlands Policy Support Program on Particulate Matter (“BOPII”)

Name and role of TNO participants:

Marcel Moerman (field measurements),
Aleksandra Jedynska (chemical analyses),
Sander Jonkers (model calculations),
Marita Voogt (data analysis)
Bas Henzing (reporting) and
Menno Keuken (project leader and reporting)

Name and role of external participants:

Dave de Jonge (GGD Amsterdam) contributed by results of measurements at a street location and an urban background location in Amsterdam and near the motorway A10. Gerard Hoek of IRAS (University Utrecht) provided background information on health effects of particulate matter. Meteorological data was collected at the location Schiphol of the National Meteorological Institute (KNMI) and traffic data of the motorway A10 was provided by the National Roadway Authority (RWS) of the Ministry of Transport and Water management.

Research period:

June – November 2010

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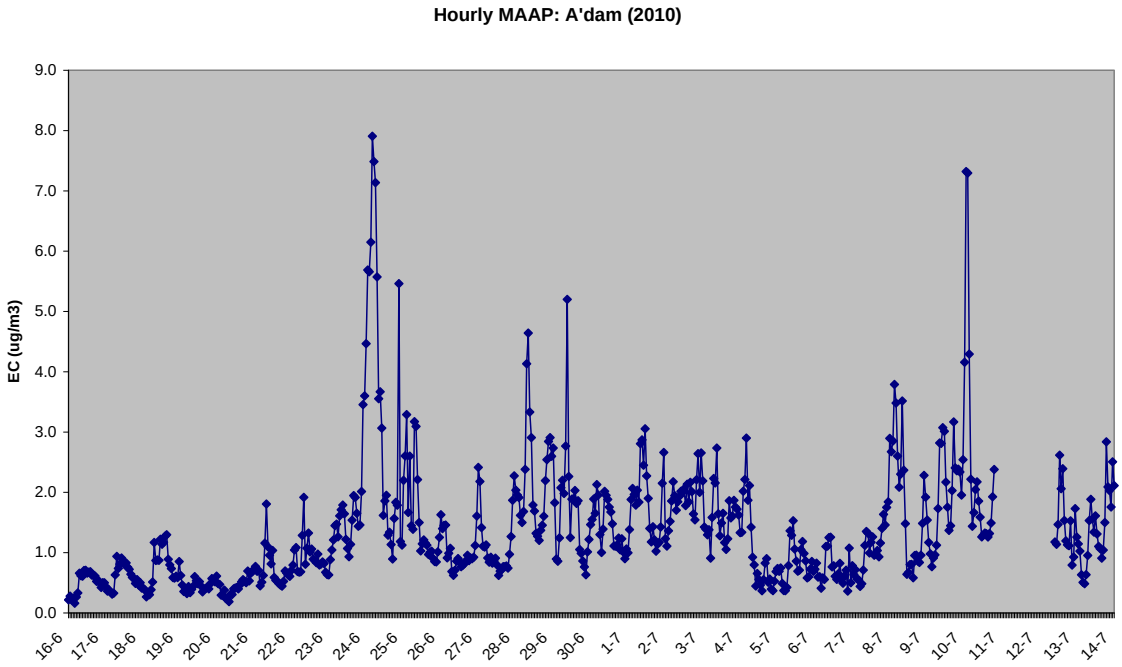
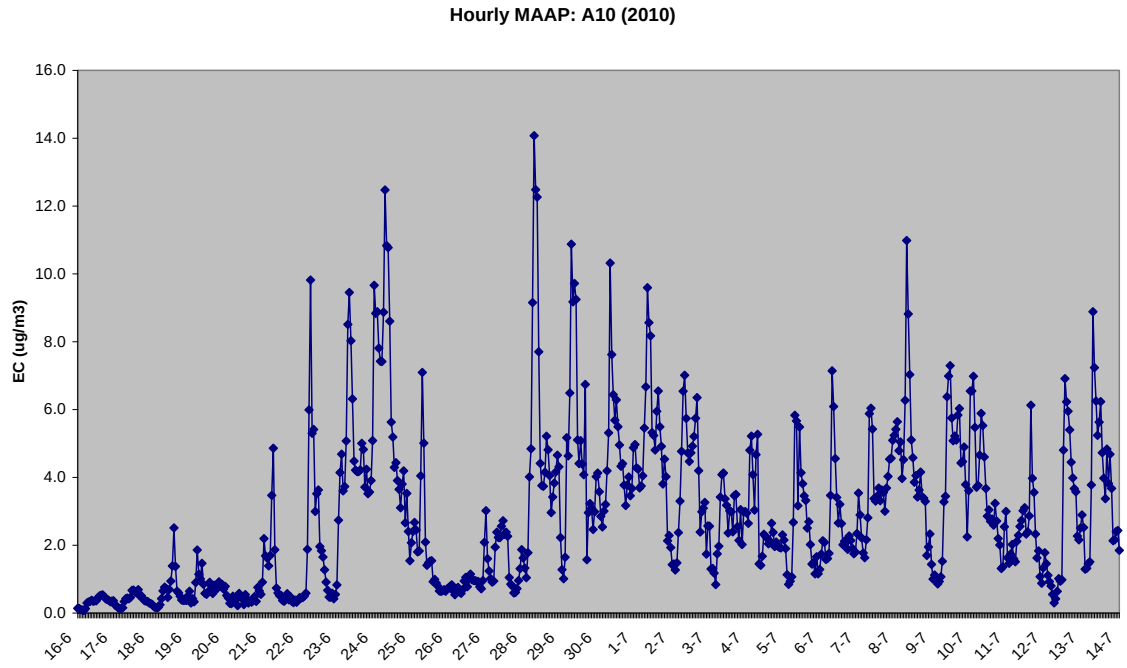
Annex 1: Hourly average MAAP results (June – July 2010) at an urban background (Amsterdam) and motorway (A10)





Annex 2: Thermal analysis by NIOSH and EUSAARII protocol

GGD applies the NIOSH protocol, while TNO uses the EUSAARII protocol. The two methods are presented in the following table [GGD, 2009].

	NIOSH		EUSAARII	
	Seconds	^{o}C	Seconds	^{o}C
Carrier gas	70	310	120	200
Helium	60	475	150	300
Helium	60	615	180	450
Helium	90	870	180	650
analysis time	*4,66 min*		*10,5 min*	
Oxygen in Helium	45	550	120	500
Oxygen in Helium	45	625	120	550
Oxygen in Helium	45	700	70	700
Oxygen in Helium	45	775	80	850
Oxygen in Helium	45	850	80	850
Oxygen in Helium	120	890	-	-
analysis time	*5,75 min*		*6,5 min*	
Total analysis time	*10,4 min*		*17 min*	

As it can be seen in the table, the EUSAARII protocol uses lower temperature and longer duration for the organic carbon analysis than NIOSH. The oxygen phase analysis in time and temperature is not so different, except for a 40°C higher maximum for the NIOSH method. This results in a longer analysis time for the EUSAARII protocol, but also a possibly higher ratio of the elemental carbon to the total carbon (EC/TC), as compared to NIOSH. Also, in some samples the carbon signal did not return to zero when analyzed by the EUSAARII protocol, which indicates that some of the elemental carbon was not analyzed. However, the NIOSH protocol may result in a higher variability in EC analysis as the cut-off between EC and OC is during a fast increasing temperature gradient of the protocol. Hence, a slight difference in timing may result in relatively large differences in EC/TC ratio for the NIOSH protocol. *Hence, in both protocols there seems room for improvement before one may agree on a reference method.*

As part of the quality control procedure, samples collected near the motorway A10 were analyzed at TNO applying both the EUSAARII and NIOSH protocol, while these samples were also analyzed at GGD by the NIOSH protocol. The results are presented below in differences of EC (%) with “EUII” (EUSAARII), “N-TNO” (NIOSH-TNO) and “N-GGD” (NIOSH-GGD).

	EUII/N-TNO	EUII/N-GGD	N-TNO/N-GGD
Filter code	EC (%)	EC (%)	EC (%)
A10 1	3	20	17
A10 2	4	11	7
A10 4	-4	10	14
A10 10	-3	39	42
A10 12	10	21	12
A10 13	6	63	57
A10 14	-1	10	10
A10 16	-4	24	28
average	**1**	**25**	**23**

From these results it is concluded that the differences within the laboratory of TNO applying different protocols (EUSAARII and NIOSH) are smaller than the differences between the laboratories of TNO and GGD applying a similar protocol (NIOSH). However, it is noted that this comparison only comprised of a small set of samples and more research is required to decide on a harmonized protocol. It is therefore recommend to start this process in the Netherlands as well as to restart the Working Group of the international standardization commission (CEN/TC 264 “Air quality” WG35) in order to agree on a reference method.