# THE PARTICLE PROJECT 2011-2013

Scientific Report from DCE - Danish Centre for Environment and Energy No. 156

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# Data sheet

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Abstract:	The Particle Project 2011-2013 continues the record of particle mass and number measurements on urban and rural locations. Anthropogenic and natural sources to PM2.5 were evaluated using receptor models based on detailed chemical composition of particulate samples collected during two intense campaigns in the urban background of Copenhagen. Furthermore, scenario calculations of PM2.5 in 2020, 2025 and 2030 were conducted to evaluate if Denmark will be able to meet future reduction targets.
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# Contents

Ab	brevia	tions	5
Su	mmary	Ŷ	6
1	Intro	duction	9
2	Parti	cle mass and number	11
	2.1	TEOM measurements	11
	2.2	Particle number size distribution measurements	14
	2.3	Conclusion	17
3	Sour	ces to urban PM <sub>2.5</sub>	18
	3.1	Source apportionment of rural background	18
	3.2	Urban Campaigns 2011-2012	18
	3.3	Chemical composition of urban PM <sub>2.5</sub>	19
	3.4	Methods	20
	3.5	Particle Mass, Total Carbon and fossil Carbon	21
	3.6	Source-specific organic tracers	23
	3.7	Comparison of urban background and urban curbside	25
	3.8	Polycyclic Aromatic Hydrocarbons (PAH)	29
	3.9	Source apportionment of urban background	29
	3.10	Conclusion	34
4	Scen	ario calculations for $PM_{2.5}$ in 2020, 2025 and 2030	36
	4.1	Introduction	36
	4.2	The Danish Average Exposure Target	37
	4.3	Model calculations and emission scenarios	37
	4.4	Results from the model calculations	40
	4.5	Comparison with the proposal for the new EU-directive on National Emission Cailings for the EU member states	44
	4.6	Conclusions	47
5	Refe	rence	49

# Abbreviations

AMS	Aerosol Mass Spectrometry
AVOC	Anthropogenic (man-made) VOC
BVOC	Biogenic VOC
BB	Biomass burning, which includes residental wood burning.
BC	Black carbon
Coal	A source profile for coal combustion in mainly coal-fired power plants
COPREM	The Constrained Physical Receptor Model
DMPS	Differential Mobility Particle Sizer
EC	Elemental carbon, which is comparable to black carbon (BC) and soot
fC	Mass concentration of fossil carbon related to anthropogenic activity.
Marine	A source profile for sea salt emissions, either primary or aged, where Cl is evaporated and substituted by $NO_3$
OC	Organic carbon, only the mass of carbon it self
ОМ	Organic matter equal to the total mass of the compounds that contain OC
Oil	A source profile for oil combustion
PBAP	Primary Biological Aerosol Particles, e.g. decomposed plant material and microorganisms
PM	Particulate matter is the term for particles found in the air
PM <sub>2,5</sub>	Particles less than 2.5 micrometers in diameter refered to as fine particles
$PM_{10}$	Particles less than 10 micrometers in diameter
PMF	Positive Matrix Factorisation - a receptor model like CO-PREM
SIA	Secondary Inorganic Aerosols comprising nitrates and sul- phates of ammonium
SOA	Secondary Organic Aerosols, i.e. particulate species formed during atmospheric oxidation of VOCs
TC	Total carbon = $OC + EC$
TEOM	Tapered Element Oscillating Microbalance
VOC	Volatile Organic Compounds, including anthropogenic emissions of benzene, and natural compounds, e.g. isoprene

#### Summary

In addition to the measurements included in the *Danish Air Quality Monitoring Programme*, detailed physical and chemical measurements of atmospheric particles have been conducted in a series of research projects on atmospheric particles since 2001. The objectives of this fourth *Particle Project* was to i) continue the record of particle mass and number measurements, ii) evaluate the sources to urban PM<sub>2.5</sub>, and iii) to provide scenario calculations of PM<sub>2.5</sub> in 2020, 2025 and 2030 to evaluate if Denmark will be able to meet future reduction targets.

 $PM_{10}$  and  $PM_{2.5}$  were measured with TEOM (Tapered Element Oscillating Microbalance) at the different stations (rural background, urban background and urban curbside) in and around Copenhagen between 2002 and 2013. For TEOM-PM<sub>2.5</sub> the data show a slow decreasing trend over the years. In general, regional and long-range transported aerosols dominate the  $PM_{2.5}$  mass at the background stations, while the urban curbside is also impacted by exhaust and non-exhaust emissions from traffic. The decreasing trend in  $PM_{2.5}$  reflects the general situation in Europe, where both precursors to particle formation and primary particle emissions are decreasing, which lowers ambient mass levels at the background sites. A decreasing trend in TEOM-PM<sub>10</sub> has as well been observed at the urban background, while the data series at the rural background is too short to make any conclusions.

Particle number size distributions were measured with DMPS (Differential Mobility Particle Sizer) at the different stations (rural background, urban background and urban curbside) in and around Copenhagen during the time period 2002-2013. Particle numbers show a slight decreasing trend for the rural background and urban background stations. This decrease is much more pronounced at the urban curbside, which is highly influenced by traffic exhaust emissions. This is also indicated by the small particle mean diameter compared to the other stations. The number of particles in the lowest size regime (diameter between 6 and 40 nm) is about four times higher at the urban curbside compared with the urban background. In the middle size regime (diameter between 40 and 110 nm) the values are still twice as high at the urban curbside as at the urban background, which is showing the high traffic contribution in this size class. In general, the decreasing trend in particle number is in accordance with improvements in engine exhaust technologies and past changes in fuel composition, which lead to lower particulate emissions.

Sources to urban PM<sub>2.5</sub> were evaluated based on campaigns during the winter 2011 and summer 2012 by use of the receptor model COPREM. Particle samplers were placed in an urban street and urban background from which a traffic source profile was derived by subtraction of the measured species' concentrations at the two sites. Apportionment of the carbonaceous fraction was accomplished by use of source specific chemical markers, e.g. radiocarbon (<sup>14</sup>C) to track anthropogenic sources of fossil carbon (combustion of gasoline, diesel, oil and coal). Secondary Organic Aerosols (SOA) was tracked by specific markers for biogenic volatile organic compounds (BVOC), which are oxidized to form aerosol particles in the atmosphere. SOA is also formed by oxidation of anthropogenic volatile organic compounds (AVOC), which are composed of fossil

carbon and thus included in the sources *Ship emissions, Coal* or *Oil*. One exception is VOCs released during residential wood burning. A part of this is oxidized in the atmosphere to form SOA, which cannot be separated from BSOA. *Biomass Burning* (BB), of which the largest source is believed to be residential wood burning in Denmark and neighbour countries, is traced by use of four organic tracers in addition to inorganic potassium.

The applied tracers were used to successfully track their specific sources. Concentrations of elemental carbon (EC, "soot") was highest during the winter campaign, where the activity of residential wood combustion is highest, but with a clear signal all year due to traffic emissions and other combustion processes. SOA tracers were highest during the summer campaign, though products from coniferous trees were also measured during the winter campaign. Also, most tracers for biological aerosol particles (PBAP) particles such as decomposition of leaves and other plant materials were only detected during the summer campaign. Markers for residential wood combustion were only vaguely present during the summer campaign.

 $PM_{2.5}$ , EC and OC differed largely between the two campaigns and sites, which was particular evident for the winter 2011/summer 2012 concentrations of  $PM_{2.5}$ . However, increased PM concentrations were measured at all Danish sites in 2011. Absolute winter concentrations of  $PM_{2.5}$ , EC and OC were all higher than summer concentrations. The fraction of fossil carbon, on the other hand, showed only 4% variation with season. In contrast, a large difference was observed between urban background (30%) and urban street (50%).

In the winter campaign, Polycyclic Aromatic Hydrocarbons (PAH) were measured in the urban background and urban street in the  $PM_{2.5}$  and  $PM_{10}$  fractions during the winter campaign. On average, two thirds of benzo[a]pyrene were found in the  $PM_{2.5}$  fraction. Furthermore, urban curbside concentrations of benzo[a]pyrene were generally higher than urban background concentrations, evident of traffic being a source of urban PAH.

Source apportionment of urban background  $PM_{2.5}$  identified Secondary Inorganic Aerosols (SIA) to be the most abundant aerosol fraction averaging 4.3 µg/m<sup>3</sup> over the two campaigns (36%). SOA accounted for 1.2 µg/m<sup>3</sup>, which was less than expected and could be a consequence of the relatively few applied tracers for SOA, which do not encompass all SOA sources and thus possibly underestimates this source. Primary emissions included marine emissions "sea salt" (1.0 µg/m<sup>3</sup>; 8%) and the minor crustal and primary biological Aerosol Particles. Ship emissions accounted for 0.62 µg/m<sup>3</sup> (5%). Other fossil sources were *Coal* (0.81 µg/m<sup>3</sup>; 7%), *Oil* (0.03 µg/m<sup>3</sup>; 0.3%) and *Vehicular Traffic* (0.26 µg/m<sup>3</sup>; 2%).

Sources of particles from BB are believed to be mainly residential wood burning. However, contributions other than national sources are likely also to play a role. According to the source apportionment analysis BB accounts for  $0.88 \ \mu g/m^3$  of PM<sub>2.5</sub> averaged over the winter and summer campaigns. However, the source contribution is not evenly distributed over the year, for which reason the mitigation potential is higher during the heating season. On average, this source contributed by  $1.5 \ \mu g/m^3$  of PM<sub>2.5</sub> during the winter campaign, but only  $0.3 \ \mu g/m^3$  during the summer campaign.

Dominating sources to EC are BB (36%) and *Traffic* (44%). *Ship emissions, Oil* and *Coal*, are responsible for 12%, 1% and 7% of EC, respectively.

Organic carbon mass was attributed to SOA (44%), BB (22%) and *Traffic emissions* (9%). Furthermore, *Ship emissions* accounted for another 22% of organic carbon. Minor contributions were attributed to biological sources (PBAP) such as microorganisms and decomposition of leaves. These findings agree with other European studies of organic carbon in PM<sub>2.5</sub>.

The major uncertainty related to the present source apportionment analysis is a result of the fact that annually averaged source contributions are estimated from only 8 weeks of measurements campaigns, representing only 15% of the year. Due to the high cost of chemical measurements, however, it is very expensive to carry out longer campaigns using conventional laboratory analysis of chemical markers. A more promising approach is Aerosol Mass Spectrometry (AMS), from which continuous measurement series of organic and inorganic compounds can serve as input for source detailed apportionment analysis. AMS instruments have been purchased (with funding from the Villum Foundation) and installed temporarily at Risø in 2014 - 2015.

A national exposure reduction target of 2.1  $\mu$ g/m<sup>3</sup> was derived for Denmark based on an average exposure indicator of 14  $\mu$ g/m<sup>3</sup> for the reference year 2010. This reduction target is based on the measurements in urban background in Copenhagen, Aarhus and Aalborg.

The model calculated reduction in  $PM_{2.5}$  from 2010 to 2020 will most probably be slightly too low, due to limitations in the model applied. First, a likely decrease in SOA cannot be accounted for. Second. a reduction in particle-bound water cannot be addressed by the model. However, a simple estimate based on the results from the measurements has been used to take the reductions of water into account. This leads to a slightly larger reduction in  $PM_{2.5}$ .

When particulate bound water is taken into account, the Gothenburg 2020 scenario will lead to a reduction of  $PM_{2.5}$  of 1.6 µg/m<sup>3</sup>. The EC baseline scenarios for 2025 and 2030 will lead to a reduction of 2.0 µg/m<sup>3</sup> and the EC scenario 2025A will lead to a reduction of 2.9 µg/m<sup>3</sup>. Therefore, it is only EC scenario 2025A, which will lead to a reduction exceeding the national emission reduction target for Denmark of 2.1 µg/m<sup>3</sup>. The EC baseline scenarios for 2025 and 2030 leads to a reduction just below the target, while the Gothenburg scenario is well below the target.

The proposal from the EU Commission for a new directive on national emission ceilings suggest more stringent emission commitments from the EU member states for 2025 and 2030 than the base line emissions scenarios applied in this project (Amann, 2013). The emission scenarios are estimated to lead to reductions in PM<sub>2.5</sub> of 1.6, 2.3 and 2.9  $\mu$ g/m<sup>3</sup> for 2020, 2025 and 2030, respectively. Hence, it is estimated that the national exposure reduction target can be met in 2025 and may be somewhere between scenario 2020 and scenario 2025 since the calculated reductions in PM<sub>2.5</sub> do not account for reductions in the secondary organic particles.

# 1 Introduction

The DCE - Danish Centre for Environment and Energy have conducted detailed physical and chemical measurements of atmospheric particles since 2001(Palmgren et al., 2005; Wåhlin, 2008; Massling et al., 2011), in addition to those included in the National Monitoring programme (Ellermann et al., 2013).

The preceding three research projects have focused on detailed measurements designed for determining the microphysical properties of particles mainly in the urban environment. The parameters that have been measured are particle mass, volume, number and size distribution since these parameters are important for the microphysical properties of the particles as well as they affect the associated health effects. The measurements were carried out with high time resolution (typical ½ hourly averages) because this gives the possibility to determine the diurnal variations of the microphysical parameters. This information can again be used to estimate the sources of the particles based on knowledge of the typical diurnal variations of for example traffic emissions. In the previous particle reports, it was found, that a large part of the particulate air pollution in Copenhagen especially at street level was due to traffic emissions.

Where all projects have focused on detailed measurements designed for determining the microphysical properties of particles, the two latest projects have sought to provide a more sophisticated understanding of particle chemistry and associated sources. In the previous particle project the rural environment was subject to intense campaigns to chemically characterise ambient aerosols (Massling et al., 2011).

The measurements have mainly been conducted at the H.C. Ørsted Institute (HCØ, urban background), and H.C. Andersens Boulevard (HCAB, street station). The measurement stations have been selected with the aim of characterising physical and chemical properties of:

- The particles in urban background air in Copenhagen i.e. the particles at some distance from busy roads.
- The ambient air particles at curbside in one of the busiest streets in Copenhagen. Particles come to a large extent from the traffic in the street itself, however the long-range transported particles contributes also significantly depending on the exact particle parameter.

The main objectives of the Particle Project 2011-2013 were (1) the continuation of the time series of PM and ultrafine particles in rural background, urban background and urban curbside; (2) to provide the scientific knowledge on chemical composition and sources to urban PM<sub>2.5</sub>; and finally (3) to provide the necessary data for evaluation of the trend in PM<sub>2.5</sub> from 2008 - 2020. PM and particle size distributions were monitored and evaluated using TE-OM and DMPS particle size distribution measurements. Chemical composition and sources to urban PM<sub>2.5</sub> were evaluated based on two campaigns each of duration of four weeks during winter 2011 and summer 2012. Sources were quantified using two different source-receptor model approaches, i.e. Positive Matrix Factorization (PMF) and Constrained Physical Receptor Model (COPREM) by application of 62 chemical compounds, of which a number were defined as source-specific tracers that are necessary for the model analysis. Source apportionment in combination with scenario calculations serves as input to political abatement strategies for PM<sub>2.5</sub>.

### 2 Particle mass and number

#### 2.1 **TEOM measurements**

Within the Particle Project 2011-2013,  $PM_{2.5}$  and  $PM_{10}$  were measured using the TEOM (Tapered Element Oscillating Microbalance). The TEOM measurements have a time resolution of half an hour. A part of the procedure in the method is that the sample is heated up to 50 degree Celsius implying that some of the mass collected on the filter in the sensor unit may evaporate. Thus, it has to be considered that the mass reported by TEOM is lower than the one measured with the reference method (Massling et al., 2011).

 $PM_{2.5}$  and  $PM_{10}$  were measured at RISØ and HCAB during the entire project period. In Table 2.1 the data coverage is summarized for the years 2011, 2012 and 2013.

**Table 2.1**. Data coverage for TEOM-PM<sub>2.5</sub> and TEOM-PM<sub>10</sub> measurements at rural background (RISØ) and urban curbside (HCAB) during the project period.

	Ru	Rural background			Urban curb	oside
	2011	2012	2013	2011	2012	2013
TEOM-PM <sub>2.5</sub>	55 %	86 %	87 %	93 %	86 %	93 %
TEOM-PM <sub>10</sub>	60 %	66 %	80 %	87 %	87 %	87 %

The relatively low data coverage at rural background for both size regimes in 2011 is due to extensive technical problems with the instruments. Daily averages of the measured parameters are shown in Figure 2.1 and Figure 2.2 for the different mass fractions and different locations.



**Figure 2.1.** Time series of TEOM-PM<sub>2.5</sub> and TEOM-PM<sub>10</sub> daily averages at rural background (RISØ) in 2011, 2012 and 2013.

As a general finding, the mass concentrations of TEOM-PM<sub>10</sub> at rural background are higher compared to TEOM-PM<sub>2.5</sub> at the corresponding site. At rural background, TEOM-PM<sub>2.5</sub> and TEOM-PM<sub>10</sub> is to a very large extent the result of long-range transported aerosols.



**Figure 2.2.** Time series of TEOM-PM<sub>2.5</sub> and TEOM-PM<sub>10</sub> daily averages at urban curbside (HCAB) in 2011, 2012 and 2013.

For some periods, local agricultural activities may contribute at the rural background site. These emissions have a strong seasonal cycle. But also other local emissions are expected to contribute to the rural background as there are traffic emissions from a major road in a distance of about 1 km or e.g. wood stove emissions in the surrounding area during the winter time.

TEOM-PM<sub>2.5</sub> and TEOM-PM<sub>10</sub> averaged 8.4 and 12.9  $\mu$ g/m<sup>3</sup>, respectively, at rural background (RISØ) during the project period. In comparison, the 2008-2010 average for TEOM-PM<sub>2.5</sub> was 8.6  $\mu$ g/m<sup>3</sup> at Lille Valby (LVBY), which is located about 3 km west of RISØ. Please note that the present rural background site at RISØ replaced the previous LVBY site in the summer 2010. TEOM-PM<sub>10</sub> measurements were initiated at the rural background RISØ in 2011 and do not exist for the LVBY site.

Long-range transported aerosols as well as local emissions from traffic (exhaust and non-exhaust) directly from the street influence TEOM-PM<sub>2.5</sub> at the urban curbside. In comparison, TEOM-PM<sub>10</sub> is highly influenced by non-exhaust traffic related emissions from break dust and road dust in addition to road salt during the winter period at this site (Massling et al., 2011).



**Figure 2.3**. Yearly trend of TEOM-PM<sub>2.5</sub> at rural background (LVBY/RISØ), urban background (HCØ) and urban curbside (HCAB).

TEOM-PM<sub>2.5</sub> averaged 12.9  $\mu$ g/m<sup>3</sup> at urban curbside during the project period, which is in full accordance with the 2008-2010 average of 12.8  $\mu$ g/m<sup>3</sup>.

In Figure 2.3 and Figure 2.4, the yearly average values of TEOM-PM<sub>2.5</sub> and TEOM-PM<sub>10</sub> are displayed for the rural background LVBY/RISØ and the urban curbside HCAB. Measurements were also carried out in previous projects at HCØ, so they are also displayed here. Data are available from 2001/2002 and ongoing for some of the stations and parameters.

In general, a slow decrease of TEOM-PM<sub>2.5</sub> is observed from the middle of the last decade and onwards. A slight increase as e.g. observed in 2011 can be explained by a higher number of long-range transport episodes in this specific year. The concentration at the urban curbside is about 20-40 % higher compared with rural background, indicating that urban emissions together with some curbside emissions significantly contribute to TEOM-PM<sub>2.5</sub> at the urban curbside station. The meteorology is important here, because there were periods with low wind that would cause curbside concentrations to increase.

TEOM-PM<sub>2.5</sub> has been measured between 2002 and 2010 at the urban background station. Also for this station and size fraction a decreasing trend has been observed during the entire measurement period.

At HCAB the TEOM-PM<sub>10</sub> is highly impacted by non-exhaust traffic emissions. Thus, the contribution of non-exhaust traffic emissions to TE-OM-PM<sub>10</sub> is expected to be very high at this station. In general, TEOM-PM<sub>10</sub> shows a slight decreasing trend over the years. It is interesting that the difference between TEOM and the reference method for PM<sub>10</sub> is decreasing over the years. This unexpected trend will be investigated in more detail in future reports. TEOM-PM<sub>10</sub> at the urban background station was only measured up to 2010 and shows a decreasing trend from 2005 and onwards, which reflects the general situation in Europe, where both precursors to particle formation and particle emissions are decreasing, which lowers ambient mass levels at the background sites. Data points at the rural background only exist for three years and show almost constant values.



**Figure 2.4**. Yearly trend of TEOM-PM<sub>10</sub> at rural background (LVBY/RISØ), urban background (HCØ) and urban curbside (HCAB).

#### 2.2 Particle number size distribution measurements

Particle number size distributions were measured with a time resolution of half an hour at 3 locations (RISØ, HCØ, HCAB) using a DMPS system scanning the size regime between 6 and 700 nm in diameter. In Table 2.2 the data coverage is summarized for 2011, 2012 and 2013.

 Table 2.2. Data coverage for the DMPS measurements at rural background (RISØ), urban background (HCØ) and urban curbside (HCAB) in 2011, 2012 and 2013.

	Rural background	Urban background	Urban curbside
2011	53 %	62 %	45 %
2012	44 %	70 %	83 %
2013	64 %	73 %	64 %

Yearly averages of the particle number size distributions at the three measurement stations RISØ, HCØ and HCAB from 2011 to 2013 are shown in Figure 2.5.



**Figure 2.5.** Yearly average particle number size distributions at rural background (RISØ), urban background (HCØ) and urban curbside (HCAB) in 2011, 2012 and 2013.

The measured mean diameter of the particle number size distributions is about 50-70 nm at rural background, 40-60 nm at urban background and 20-40 nm at urban curbside, respectively. The 20-40 nm particles dominate the urban aerosol nearby busy streets, which is in full agreement with previous findings (Massling et al., 2011). The differences in mean particle diameter have to do with the differences in particle age.

For a further analysis, the particle number concentrations were determined in specific size regimes, namely particles with diameters of 6–40 nm, 40–110 nm and 110–700 nm at all three stations RISØ, HCØ and HCAB. The results are presented in Figure 2.6.



**Figure 2.6.** Yearly average particle number concentrations in specific size regimes, namely between 6 and 40 nm, 40 and 110 nm, and 110 and 700 nm in diameter at rural background (RISØ), urban background (HCØ) and urban curbside (HCAB) during the project period 2011 – 2013.

It is shown that particle number concentrations are elevated in all three size regimes at the urban curbside compared to urban and rural backgrounds. The rural station RISØ represents mainly long-range transported aerosols apart from some local emissions as e.g. local wood burning in private households during winter or transported particles from urban emissions nearby. Number concentrations of particles between 6–40 nm are still by a factor of about two higher in the urban background compared to the rural background. In general we find that the smaller the size regime the larger is the difference in number concentration between rural background and urban background and urban curbside indicating the influence of urban emissions on the number of particles in the small size regimes.

In Figure 2.7, the total particle number concentration in the size range from 6 to 700 nm is displayed for all three stations and from 2002–2013.



**Figure 2.7**. Yearly trend of total particle number concentrations for particles between 6 and 700 nm at rural background (LVBY/RISØ), urban background (HCØ) and urban curbside (HCAB) from 2002 to 2013.

We generally observe a strong decreasing trend in particle number at the urban curbside, which seems to stabilize at a more or less constant level in the last five years. One of the main reasons for this decrease is the change in vehicle exhaust emission technologies and some past changes in the fuel composition. Simultaneously, number concentrations at the urban background and rural background have also been very constant or only been slightly decreasing over the last five years.

In Figure 2.8, the particle number concentration for nucleation mode + Aitken mode particles (diameter from 6 to 110 nm) is displayed at the three locations. The number of accumulation mode particles (diameter from 110 to 700 nm), which is not presented here, is dominated by regional and long-range transport at the rural and urban background and has shown to be fairly constant over the years. Even at HCAB this number shows nearly constant values over the last few years. In contrast, the number of nucleation and Aitken mode particles (Figure 2.8) has been decreasing substantially at the urban curbside station from about 26,000 cm<sup>-3</sup> in 2002 and about 21,000 cm<sup>-3</sup> in 2006 to about 15,000 cm<sup>-3</sup> in 2013.



**Figure 2.8.** Yearly average particle number concentrations for particles between 6 and 110 nm (nucleation mode + Aitken mode particles) at the rural background (LVBY/RISØ), the urban background (HCØ) and the urban curbside (HCAB) from 2002 – 2013.

#### 2.3 Conclusion

 $PM_{10}$  and  $PM_{2.5}$  were measured with TEOM (Tapered Element Oscillating Microbalance) at the different stations (rural background, urban background and urban curbside) in and around Copenhagen between 2002 and 2013. For TEOM-PM<sub>2.5</sub> the data show a slowly decreasing trend over the years. In general, regional and long-range transported aerosols dominate the  $PM_{2.5}$  mass at the background stations, while the urban curbside is also affected by exhaust and non-exhaust emissions from traffic. The decreasing trend in  $PM_{2.5}$  reflects the general situation in Europe, where both precursors to particle formation and particle emissions are decreasing, which lowers ambient mass levels at the background sites. A decreasing trend in TEOM-PM<sub>10</sub> has also been observed at the urban background and the urban curbside, while the data series at the rural background is too short to make any conclusions.

Particle number size distributions were measured with DMPS (Differential Mobility Particle Sizer) at the different stations (rural background, urban background and urban curbside) in and around Copenhagen between 2002 and 2013. Particle numbers show a slightly decreasing trend for the rural background and urban background stations. This decrease is considerably more pronounced at the urban curbside, which is highly influenced by primary particles from traffic exhaust emissions. This is also indicated by the small particle mean diameter compared to the other stations. The number of particles in the lowest size regime (diameter between 6 and 40 nm) is about four times higher at the urban curbside compared to the urban background. In the middle size regime (diameter between 40 and 110 nm) the values are still twice as high at the urban curbside compared with urban background, which is showing the high traffic contribution in this size class. In general, the decreasing trend in particle number is in accordance with improvements in engine exhaust technologies and past changes in fuel composition lowering particulate emissions.

### **3** Sources to urban PM<sub>2.5</sub>

Sources to atmospheric particles can be derived from the chemical composition of source-specific tracers. A source apportionment in this context attributes the share of the particle mass to specific sources. Following, the potential impact of mitigating pollutant emissions from a particular source, e.g. residental wood combustion, can be evaluated. In the previous Particle Project 2008-2010, sources to ambient particles were apportioned in the rural background, which represents a lower estimate of the basic exposure of the Danish population. In the present Particle Project, sources are apportioned to urban background particles, which often are used as an estimate for the exposure of a large and growing part of the population in urban areas. Well-planned measurement campaigns of sufficient duration are a prerequisite for a successful source apportionment analysis. Campaigns are, however, also expensive, which on the other hand calls for shorter campaigns and fewer samples. Furthermore, the campaigns must include different seasons over the year in order to account for annual variation in the tracer species.

#### 3.1 Source apportionment of rural background in the previous Particle Project 2008 - 2010

Sources to PM in rural background were evaluated in the Particle Project 2008-2010 (Massling et al., 2011). The source apportionment study was based on data from two intensive EMEP campaigns, conducted in autumn/winter 2008 and winter/spring 2009, and analyzed using the source receptor model COPREM (Wåhlin, 2003). PM<sub>10</sub> and PM<sub>2.5</sub> (inorganic composition, only) samples were collected and analyzed with respect to elements, ions and elemental/organic carbon. PM<sub>2.5</sub> accounted for 78% of PM<sub>10</sub>, and the compounds of PM<sub>2.5</sub> was ammonium sulphates and ammonium nitrate, that is Secondary Inorganic Aerosols (SIA) (3.80  $\mu g/m^3$ , 28%), biomass burning (BB) (1.27  $\mu g/m^3$ , 10%) and Secondary Organic Aerosols (SOA) (2.10  $\mu$ g/m<sup>3</sup>, 16%). No specific tracers were available to estimate the SOA source. Rather, it was calculated from unexplained organic carbon in PM<sub>10</sub> (Massling et al., 2011), which also includes Primary Biological Aerosol Particles (PBAP) and anthropogenic sources of carbon. Furthermore, carbon analysis was conducted on the PM<sub>10</sub> samples, not in PM<sub>2.5</sub>. All Organic Carbon (OC) and Elemental Carbon (EC) in PM<sub>10</sub> was assumed to be in the PM<sub>2.5</sub> fraction. Therefore, the apportioned rural SOA source was most likely overestimated. Of the natural sources, crustal dust, accounted for 0.3  $\mu$ g/m<sup>3</sup> (2%), which is comparable to the sum of primary and aged marine particles (0.31  $\mu$ g/ m<sup>3</sup>, 2%). Oil including Ship emissions and Coal sources added up to 1.32  $\mu g/m^3$  (10%), and *Vehicular Traffic* accounted for only 0.09  $\mu g/m^3$  (0.7%).

#### 3.2 Urban Campaigns 2011-2012

In the present project, two comprehensive urban measurement campaigns were conducted during winter 2011 (14.11.11-14.12.11) and summer 2012 (28.06.12-28.07.12) in Copenhagen. Simultaneous samplings were conducted at an urban curbside station at H.C. Andersens Boulevard (HCAB), and at urban background on the roof top of the H.C. Ørsted Institute (HCØ). Both sites are part of the National Air Quality Monitoring Program (NOVANA LMP) and equipped with additional analytical instruments to support the campaign measurements. The objectives of the urban campaigns were to:

- (1) Derive a traffic source profile for urban background based on the data from the curbside station subtracted by the urban background.
- (2) Determine natural and anthropogenic sources to PM<sub>2.5</sub> in urban background using receptor models. The potential to mitigate residential wood burning as a source of ambient PM<sub>2.5</sub> is based on the source apportionment result.

#### 3.3 Chemical composition of urban PM<sub>2.5</sub>

The chemical composition of  $PM_{2.5}$  was evaluated from analysis of 62 chemical species in addition to Volatile Organic Compounds (VOC) and gasses (Table 3.1). Individual species were following grouped into classes of compounds, for the purpose of comparison between the urban sites (Section 3.7 and Figure 3.8). In a source apportionment study of urban background, the chemical composition was simplified to 38 particulate species of  $PM_{2.5}$ , 2 VOCs and nitrogen oxides ( $NO_X = NO + NO_2$ ) in addition to 3 size classes of ambient particles.

**Table 3.1.** Sample program for the campaigns. PAHs were analyzed during the winter campaign, only, and VOCs were only sampled at HCØ. SO<sub>2</sub> is only analyzed at curbside.

PM <sub>2.5</sub> Inorganic ions (4)
Cl <sup>-</sup> , NH <sub>4</sub> <sup>+</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>
PM <sub>2.5</sub> Elements (28)
Al, Mn, Ga, Pb, Sb, K , Fe, As, Na, Ba, Ca, Ni, Se, Cd, Mg, Ti, Cu, Rb, Mo, Cl, V, Zn, Sr,
Co, Cr, Mn, Ga, Pb
PM <sub>2.5</sub> Organic compounds (17)
2-methylerythritol, pinic acid, cis-pinonic acid, $\beta$ -caryophyllinic acid, D-(+)-glucose, D-
mannitol, D-arabitol, D-glycerol, D-(+)-trehalose, D-sorbitol, adonitol (ribitol), myo-Inositol,
levoglucosan, mannosan, vanillic acid, $\beta$ -sitosterol, 1,2-benzenedicarboxylic acid,
PM <sub>10</sub> and PM <sub>2.5</sub> Carbon analysis (3)
<sup>14</sup> C (carbon-14 isotope), Organic Carbon (OC), Elemental Carbon (EC), Total Carbon (TC)
PM <sub>10</sub> and PM <sub>2.5</sub> PAHs (10)
chrysene, benzo(a)anthracene, dibenz(a,h)anthracene, benzo(ghi)perylene, indenopyrene,
benzo(e)pyrene, benzo(a)pyrene, benzo(b+j)fluoranthene, benzo(k)fluoranthene, perylene
Ultra fine particles eller nano particles
Particle size distributions 10-700 nm
Gasses
NO <sub>X</sub> , O <sub>3</sub> , CO, SO <sub>2</sub> (5)
VOC (17)
1-pentene, n-pentane, trans-2-pentene, isoprene, 2-methylheptane, n-hexanbenzene, n-
heptane, isooctane, toluene, n-octane, ethylbenzene, m,p-xylene, o-xylene, 1,2,3-
trimethylbenzene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene

Inorganic ions account for a large mass fraction of PM<sub>2.5</sub>, i.e. in the form of the inorganic salts NH<sub>4</sub>NO<sub>3</sub>, NH<sub>4</sub>SO<sub>4</sub> and NH<sub>4</sub>HSO<sub>4</sub> which are designated SIA. In addition, marine particles being essentially NaCl, sulphates and NaNO<sub>3</sub>.

The elements serve as tracers for a number of sources, e.g. selenium for coal combustion and vanadium for oil combustion, which relates to e.g. industrial processes and generation of power. However, advanced cleaning technologies removes these tracers to a large extent, which has made it more difficult to accurately track these sources. Still, these processes rely on combustion of fossil fuels in which case the isotope <sup>14</sup>C serve as a specific tracer, since fossil fuels are characterized by a zero content of <sup>14</sup>C in contrast to "modern" carbon sources, which have well-defined <sup>14</sup>C content.

Source apportionment of BB mainly residential wood combustion, has in the past solely relied on potassium, K. However, modern source apportionment utilizes several organic tracers, i.e. ß-sitosterol, levoglucosan, mannosan and vanillic acid.

Other sources are characterized by specific ratios of elements, e.g. the Crustal source being natural dust (Al, Ti, Mn, Fe, Ca), Primary Marine Particles (K, Na, Cl, Sr, Br, Mg,  $SO_4^{2-}$ ) and the traffic source (Fe, Co, Cu, Zn, Ga, Cd, Ba and Pb), in addition to EC and OC.

In the previous Particle Project, the carbonaceous particles were measured and differentiated into OC and EC, as well as Total Carbon TC = OC + EC. In the present Particle Project, a number of organic tracers served as specific tracers for SOA and BB. This was important to more correctly apportion the carbon mass to BB. Furthermore, the <sup>14</sup>C isotope unambiguously differentiated anthropogenic from natural sources. SOA tracers were divided into 2-methylerythritol from atmospheric oxidation of isoprene emitted by deciduous trees, and pinic acid, cis-pinonic acid from coniferous trees. While 2-methylerythritol was almost exclusively present during the summer campaign, the later was observed in both campaigns. Presumably both local and long transported SOA from coniferous trees contributed. BB was tracked using tracers for different species of trees, i.e. levoglucosan, mannosan, vanillic acid,  $\beta$ -sitosterol in addition to inorganic potassium (Rogge et al., 1998).

Of the volatile organic compounds, only benzene and toluene were included in the source apportionment to trace BB and traffic, which are major sources hereof.

In addition to the chemical measurements, particle numbers differentiated into 3 size classes (10-40 nm; 40-110 nm; 110-700 nm) were included to support the Traffic profile.

#### 3.4 Methods

Two high-volume samplers (Digitel DHA-80, Switzerland) with PM2.5 inlets, and one with PM<sub>10</sub> inlet, were placed at the urban background and curbside measurement stations from 14 November - 14 December 2011 and 28 June - 28 July 2012 to collect ambient particles on quartz filters. PM<sub>2.5</sub> was measured using a beta gauge particle mass monitor (OPSIS SM200, Sweden). Bulk inorganic ions were analysed by Ion Chromatography; elements by Ion Coupled Plasma Mass Spectrometry; elemental and organic carbon by thermal-optical analysis (Sunlab, CA) using the EUSAAR2 protocol; organic tracers for BB, Primary Biological Aerosol Particles (PBAP), Secondary Organic Aerosols (SOA) and anthropogenic sources were extracted, derivatised using N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) and analysed using Gas Chromatography Mass Spectrometry (GC-MS) according to Fu et al., 2009. 14C measurements for tracking of fossil fuel combustion were analysed using Accelerator Mass Spectrometry (AMS) at Lund University. PAHs were extracted from filter samples and measured by GC-MS (Ellermann et al., 2013).

Particle size distributions from 10-700 nm were obtained from two DMPS systems (Winkelmayer et al., 1991).

#### 3.5 Particle Mass, Total Carbon and fossil Carbon

Figure 3.1 and 3.2 illustrate the TC and fC fraction of  $PM_{2.5}$ , where fC is the part of TC that origins from fossil oil. Please note, that organic matter (OM) accounts for a larger fraction of  $PM_{2.5}$  than TC. OM is about twice the concentration of organic carbon (OC) in the urban background, where OC is the major part of TC. At the urban curbside, the OM/OC conversion factor is lower due to the more reduced or hydrogen-rich nature of vehicular emissions (Aitken et al., 2008).



Figure 3.1. PM<sub>2.5</sub>, Total carbon TC = OC+EC and fossil carbon, fC, during winter and summer campaigns in urban background.



**Figure 3.2.**  $PM_{2.5}$  as measured by ß-attenuation, total carbon TC = OC+EC and fossil carbon, fC, during winter and summer campaigns at urban curbside.

fC is a highly-specific tracer for combustion of fossil fuels. fC is lower in the urban background, relative to urban curbside which is strongly affected by contributions from the traffic source (Figures 3.1-3.2,). These results are in accordance with measurements in Sweden (Szidat et al., 2009).

	PM <sub>2.5</sub>	OC	EC	TC	OM+EC	fC
Urban background, summer	7.7	1.36	0.25	1.62	3.11	0.45 (28%)
Urban background, winter	16.0	1.88	0.48	2.35	4.43	0.75 (32%)
Urban curbside, summer	11.0	2.16	2.11	4.27	6.10	2.11 (49%)
Urban curbside, winter	19.8	2.74	2.82	5.56	7.87	2.82 (51%)

**Table 3.2.** Overview of PM<sub>2.5</sub> as measured by ß-attenuation and its carbon fractions during winter and summer campaigns ( $\mu$ g/m<sup>3</sup>).

The concentration of PM<sub>2.5</sub> was subject to great variation in the two campaigns (Table 3.2), and to a smaller extent its carbon fractions OC, EC, TC and fC. The carbonaceous particles, i.e. the mass of organic carbon species and EC "soot" are estimated from EC and OC. EC is by definition pure carbon in the form of graphite-like structures, soot or other highly reduced substances, but in reality some other species such as hydrogen and oxygen are also present (Andrea and Gelencser, 2006). OC carbon is mainly bound to oxygen, nitrogen and hydrogen, depending on the origin of the carbonaceous material and the time it has been aged in the atmosphere. Aging of carbonaceous particles builds in oxygen in the carbon chains, which increases the carbonaceous mass. Therefore, a factor of 1.4 is used for the conversion of OC to OM for fresh traffic/industrial emissions, while a factor of 2.1 is used for aged particulate OC such as SOA (Turpin and Lim, 2011).

In Table 3.2, the mass of carbonaceous particles OM+EC is calculated for the different campaigns and sites. In order to calculate OM, the street contribution (HCAB-HC $\emptyset$ ) is converted from OC using a conversion factor of 1.4, while a factor of 2.1 is used for the remaining (aged) OC.

The high concentrations of EC at curbside compared to urban background in Figure 3.3 show that traffic is a major source of EC, which is also apparent from Figure 3.9. During the campaigns, the urban background was somewhat higher than rural background, which is probably due to the impact from traffic. From 16 to 17 November 2011 rural background EC concentrations approximately doubled those in urban background, which could be due to local sources, e.g. intensive biomass burning.



**Figure 3.3.** Elemental carbon (EC) during the winter and summer campaigns in rural background RISØ, urban background HCØ and urban curbside HCAB.

A longer measurement period is however necessary for an accurate estimate of urban background increment in EC.



Figure 3.4. Organic carbon (OC) during winter and summer campaigns in rural background RISØ, urban background HCØ and urban curbside HCAB.

Except for a few data points, urban background OC (Figure 3.4) is higher than rural background, but lower than urban curbside, which reflects local urban sources, e.g. traffic.

#### 3.6 Source-specific organic tracers

In order to apportion anthropogenic and biological sources with a higher accuracy, quantitative methods for source-specific organic tracers were developed in the project. The temporal variation in the individual tracer concentrations (Figure 3.5 - 3.7), and the covariation of these is the fundamental property that enables the receptor models to apportion the sources contribution to  $PM_{2.5}$  (Wåhlin, 2003).



Figure 3.5. Temporal profiles of tracers for Secondary Organic Aerosols (SOA) in urban background during the campaigns in winter 2011 and summer 2012.

Tracers for SOA included oxidation products of isoprene (2-methylerythritol), which is emitted from deciduous trees. Thus, the winter concentrations were virtually zero. Small contributions origin from traffic and long-range transport from warmer regions. Other markers were emitted from coniferous trees (pinic acid and cis-pinonic acid) and were present during both campaigns. The sesquiterpene oxidation product ßcaryophyllene represents a third group of natural SOA. In addition to emissions from e.g. pine trees, sources also include oxidation of terpenes volatilized during biomass combustion. This is not observed for isoprene, which cannot be stored in biomass.



Figure 3.6. Temporal profiles of tracers for BB in urban background during the campaigns of winter 2011 and summer 2012.

The opposite trend is observed for tracers of BB (Figure 3.6). Levoglucosan, mannosane and potassium were high during winter and virtually absent during the summer campaign, except for a few days in the end of July. The reason for this later event is not known, however it might be due to local fires (i.e. field burning) or long-range transported particles from wildfires although this has not been specifically analysed. The concentrations of the BB tracers vanillic acid and beta-sitosterol were much lower than the other tracers of BB, but still important for tracking BB.



Figure 3.7. Temporal profiles of tracers for Primary Biological Aerosol Particles (PBAP) in urban background during the campaigns of winter 2011 and summer 2012.

PBAP was recently found in significant amounts in Nordic background aerosols, accounting for 20-32% of the organic carbon in  $PM_{10}$  (Yttri et al., 2011). Examples of PBAP are degraded plant material and fungal spores. Although PBAP is known to be considerably lower in the  $PM_{2.5}$  fraction relative to  $PM_{10}$  (Yttri et al., 2007), their markers were included in the campaigns to differentiate biological sources to  $PM_{2.5}$ . In particular, glucose, arabitol and mannitol showed a pronounced seasonal variation (Figure 3.7). As for the SOA tracers, however, part of the markers may be due to unburned material during BB.

#### 3.7 Comparison of urban background and urban curbside

The chemical compositions of PM<sub>2.5</sub> at urban curbside and urban background are shown in Table 3.3 and Figure 3.8. The urban curbside was 26% higher than urban background averaged over the two campaigns. A number of species differed markedly at the two sides, which evidenced local sources at the urban curbside, i.e. *Vehicular Traffic*.



**Figure 3.8.** Chemical composition of  $PM_{2.5}$  at urban curbside HCAB and urban background HCØ averaged over the campaigns in winter 2011 and summer 2012.  $PM_{2.5}$  averages of the two campaigns were 15.3 µg/m<sup>3</sup> and 11.8 µg/m<sup>3</sup>, respectively.

OC was 56% higher at urban curbside, which is heavily impacted by traffic. Note in Figure 3.8 that OC is converted to OM, which is less different at the two sites, because OM from fresh traffic emissions is less dense (section 3.5).

*Elemental carbon (EC)* is more than 6 times higher at urban curbside, compared with urban background, which demonstrates the source strength of traffic emissions, in particular those from diesel vehicles. EC has received a lot of attention recently, because recent findings indicates that soot is strongly associated with health effects (Jansen et al., 2011).

Urban curbside  $NH_4^+$  was 27% higher than in urban background. However, this finding has not been observed in the annual statistics confirming that the urban sources of  $NH_4^+$  are very small.

CO, NO<sub>X</sub> and Aitken mode particles smaller than 40 nm are higher at urban curbside compared to urban background, because of the traffic source. The same is also true for resuspension of crustal matter or dust from the road (Ca, Ti, Mn, Fe), and a number of elements otherwise related to traffic (Cu, Fe, Zn, Ba, Pb).

**Table 3.3.** Chemical composition of  $PM_{2.5}$  at urban curbside (HCAB) and urban background (HCØ) as averaged over the campaign seasons and year. A Traffic profile is calculated from subtraction of the average concentrations at the two measurements sites. All concentrations are  $\mu g/m^3$ , except for CO (ppm), NO<sub>X</sub> (ppb) and particle number (cm<sup>-3</sup>).

Species	HCAB	HCAB	HCAB	HCØ	HCØ winter	HCØ	Traffic	Traffic	Traffic
PM <sub>2.5</sub> (ß-attenuation)	19.8	11.0	15.3	16.1	7.7	11.8	3.7	3.3	3.3
OC	2.74	2.16	2.45	1.73	1.38	1.57	1.01	0.77	0.88
EC	2.82	2.11	2.46	0.46	0.26	0.37	2.36	1.85	2.10
fC	3.00	2.44	2.72	0.69	0.47	0.59	2.31	1.96	2.14
Na	0.33	0.13	0.23	0.38	0.15	0.27			
Mg	0.037	0.013	0.025	0.041	0.016	0.028			
CI	0.301	0.082	0.190	0.404	0.088	0.243			
К	0.093	0.015	0.054	0.089	0.019	0.054			
NH4	1.79	0.95	1.36	1.30	0.85	1.07	0.49	0.10	0.29
NO3	2.45	1.10	1.76	2.92	1.00	1.94			
SO4	1.97	1.78	1.87	1.64	1.73	1.69	0.33	0.05	0.18
Al	0.025	0.023	0.024	0.010	0.030	0.020	0.016		0.004
Са	0.097	0.049	0.072	0.032	0.038	0.035	0.065	0.011	0.037
Ti	0.003	0.003	0.003	0.002	0.001	0.001	0.001	0.002	0.001
V	0.0015	0.0021	0.0018	0.0012	0.0022	0.0017	0.0003	1	0.0001
Mn	0.004	0.002	0.003	0.001	0.001	0.001	0.003	0.001	0.002
Fe	0.272	0.213	0.241	0.072	0.040	0.056	0.200	0.174	0.186
Co	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ni	0.003	0.001	0.002	0.005	0.002	0.003			
Cu	0.016	0.014	0.015	0.010	0.004	0.007	0.006	0.010	0.008
Zn	0.020	0.010	0.015	0.015	0.005	0.010	0.005	0.005	0.005
Ga	0.0001	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
As	0.0009	0.0003	0.0006	0.0005	0.0003	0.0004	0.0004	0.0000	0.0002
Se	0.0006	0.0003	0.0005	0.0006	0.0005	0.0006			
Rb	0.0003	0.0001	0.0002	0.0004	0.0001	0.0002			
Sr	0.0006	0.0002	0.0004	0.0005	0.0002	0.0004			
Мо	0.0011	0.0005	0.0008	0.0008	0.0001	0.0005	0.0002	0.0004	0.0003
Cd	0.0004	0.0001	0.0002	0.0001	0.0001	0.0001	0.0003	0.0000	0.0001
Sb	0.0020	0.0011	0.0015	0.0015	0.0008	0.0011	0.0006	0.0002	0.0004
Ва	0.007	0.006	0.006	0.001	0.001	0.001	0.006	0.004	0.005
Pb	0.0057	0.0020	0.0038	0.0050	0.0019	0.0034	0.0007	0.0002	0.0003
Glycerol	0.048	0.028	0.037	0.001	0.002	0.001			
meso-Erythriol	0.001	0.004	0.003	0.004	0.001	0.003			
β-Caryophyllinic acid	0.006	0.004	0.005	0.000	0.010	0.005			
2-methyl-erythritol	0.001	0.012	0.007	0.008	0.015	0.011			
cis-Pinonic acid	0.007	0.007	0.007	0.003	0.005	0.004			
Pinic acid	0.003	0.003	0.003	0.009	0.006	0.008			
Phthallic acid	0.019	0.006	0.012	0.033	0.004	0.018			
Mannosan	0.035	0.005	0.019	0.001	0.007	0.004			
Arabitol	0.001	0.015	0.008	0.213	0.030	0.120			
Levoglucosan	0.259	0.039	0.143	0.002	0.000	0.001			
Vanillic acid	0.002	0.000	0.001	0.001	0.006	0.004			
D-Mannitol	0.002	0.016	0.009	0.001	0.006	0.004			

#### Table 3.3. Continued.

D-Sorbitol	0.001	0.002	0.002	0.001	0.002	0.001			
D-Glucose	0.010	0.047	0.029	0.006	0.015	0.011			
myo-Inositol	0.001	0.009	0.006	0.001	0.002	0.001			
D-Trehalose dihydrate	0.001	0.018	0.010	0.001	0.005	0.003			
β-Sitosterol	0.002	0.001	0.002	0.002	0.002	0.002			
СО	0.37	0.32	0.35	0.20	0.22	0.21	0.18	0.11	0.14
NO <sub>X</sub>	73.4	62.7	68.1	14.4	8.1	11.3	59.0	54.6	56.8
Particles 110-700 nm	754	421	619	771	699	735			
Particles 40-110 nm	2540	1009	1922	1553	1826	1690	987		232
Particles 10-40 nm	4661	1942	3563	1887	2217	2052	2775		1511

One of the objectives of the campaigns was to establish a PM<sub>2.5</sub> traffic source profile representative of the current 2011-2012 car fleet for the city of Copenhagen. Previously, a PM<sub>10</sub> traffic source profile has been calculated from subtraction of urban background from urban curbside concentrations of selected species (Oliviera et al., 2007) based on a study in 2003-2004.



**Figure 3.9.** Traffic profiles derived for  $PM_{10}$  (Oliviera et al., 2007; shown in green for a limited number of parameters) and  $PM_{2.5}$  (shown in blue; the present project). The profiles are calculated from subtraction of measured concentrations at urban background from concentrations at urban curbside in Copenhagen, Denmark.

Traffic is a major source of EC and Aitken mode particles from 6-40 nm. In fact, OM and EC account for the vast majority of traffic PM<sub>2.5</sub> by mass, which is almost exclusively fossil carbon. The Traffic profile in Figure 3.9 shows the ratio of the species, which are emitted or otherwise associated with traffic. An example of the later is the crustal elements Al, Ca, Ti, Mn and Fe, which origin from resuspended road dust. In particular Cu and Zn are important tracers for vehicular traffic, which is also an important source of OC and EC with almost all carbon being fossil. Moreover, particles are emitted in high number concentrations from this source.

#### 3.8 Polycyclic Aromatic Hydrocarbons (PAH)

Polycyclic Aromatic Hydrocarbons (PAH) are formed during incomplete combustion, e.g. from traffic and wood stove emissions. PAH from these sources are currently, or have been evaluated in the Danish Air Quality Monitoring Program and additional air quality projects supported by The Danish Ministry of Environment. However, no detailed information on background levels is available. The distribution of PAHs in  $PM_{2.5}$  and  $PM_{10}$  size fractions, as well as the urban curbside contribution was measured during the winter campaign (Table 3.4).

**Table 3.4**. Benzo[a]pyrene fine/coarse ratio ( $PM_{2.5}/PM_{10}$ ) at urban curbside, and weekly averaged  $PM_{2.5}$  benzo[a]pyrene concentrations at urban curbside and urban background during week days.

Week number	PM <sub>2.5</sub> /PM <sub>10</sub> curbside benzo[a]pyrene (%)	PM <sub>2.5</sub> curbside benzo[a]pyrene (ng/m³)	PM <sub>2.5</sub> background benzo[a]pyrene (ng/m³)
45	72	0.53	0.24
46	65	0.41	0.32
47	50	0.43	0.47
48	84	0.25	0.15
49	79	0.27	0.11
Average	66%	0.38	0.26

On average, two thirds of the  $PM_{10}$  benzo[a]pyrene was present in the fine fraction, i.e. particles with aerodynamic diameter less than 2.5 µm (Table 3.4). However, the curbside  $PM_{2.5}/PM_{10}$  ratio of benzo[a]pyrene was notably lowest during weeks 45 - 47, where comparisons of  $PM_{2.5}$  and  $PM_{10}$  at urban background, urban curbside and rural background evidenced periods of long-range transport that typically contains large fractions of SOA and hence relative lower concentrations of benzo[a]pyrene.  $PM_{2.5}$  mass concentrations were increased in urban curbside and background both due to long-range transport and low wind speeds.

The traffic contribution to benzo[a]pyrene in  $PM_{2.5}$  thus appears to be significant, about 1/3 on average, but other major sources to benzo[a]pyrene clearly impact the urban background. A recent study provides evidence for higher PAH and benzo[a]pyrene concentrations in a small village impacted by BB exceeding those of urban curbside in a similar measurement period (Ellermann et al., 2011).

#### 3.9 Source apportionment of urban background

A source apportionment study was conducted with the objective to determine the sources of  $PM_{2.5}$  in urban background air, based on the campaigns during winter 2011 and summer 2012. Two receptor models were applied. First, Positive Matrix Factorization (PMF) was utilized to identify contributing sources in the dataset using all analyzed species, and subsets hereof (Paatero, 1997). PMF clearly identified natural and anthropogenic sources, but the 8 campaign weeks represented too few data to separate all sources using PMF. Based on the PMF solutions, source profiles were therefore built for another receptor model, the COnstrained Physical REceptor Model (COPREM, Wåhlin, 2003). COPREM requires a detailed description of the source profiles, but is characterized by a higher resolving power for small data sets than PMF. *Fossil fuel sources.* Combustion of fossil fuels represents a major source of soot and organic particulate matter. These sources can be separated from e.g. BB using the carbon-14 isotope, <sup>14</sup>C, which is absent in fossil fuel. Inorganic ions and atomic elements furthermore characterize the individual sources of *Oil* and *Coal* as well as *Vehicular Traffic*.

- The Traffic source profile is based on the difference between the urban curbside and the urban background measurements in this study.
- The *Coal* source profile is constructed from the composite profile *Coal 3193*, which is representative of power plants fuelled by coal and derived from the US EPA database *Speciate* (EPA, 2014).
- The *Oil* source profile is representative of oil combustion and derived from the US EPA database *Speciate* (EPA, 2014).
- The share of carbon that origins from combustion of fossil fuel is unambigously calculated from measurements of the tracer <sup>14</sup>C. Since there is a discrepancy between the carbon mass apportioned to combustion of Oil, Coal and Traffic emissions and the carbon mass calculated from <sup>14</sup>C, we conclude that the used source profiles do not fully account for all sources of fossil fuel combustion. More efficient cleaning of exhaust emissions is one factor that puts a limitation to the application of source/specific tracers, e.g. selenium (Se) from coal and vanadium (V) from oil. In order to account for this discrepancy we analysed the data using Positive Matrix Factorization. PMF revealed an additional anthropogenic source, which is mainly composed of fossil carbon, sulphate and is strongly associated with the anthropogenic tracer phthallic acid as well as V and Ni indicative of crude oil. This points towards international ship emissions, see section 3.09, which are known to contribute to ambient particle concentrations in Denmark (Ellermann et al., 2014; Olesen et al., 2009). Therefore an additional source profile of Ship emissions were included in the COPREM analysis based on (Agrawai et al., 2008) from the european database of source profiles: SPECIEUROPE (profile 211).

Anthropogenic/natural sources. BB is predominantly related to anthropogenic activities such as residental wood combustion for heating appliances, though a minor contribution probably originates transboundary pollution in the form of wildfires, which was observed during the summer campaign. Several organic markers, including the sugar anhydride levoglucosan and organic acids were used as specific tracers, but potasium, benzene and toluene were also associated with this source.

*SIA* is mainly gas-particle conversion of ammonia from husbandry and sulphate or nitrate from industrial or otherwise anthropogenic emissions.

*Natural sources*. Particle profiles of either marine or crustal origin are taken from a receptor analysis in the Particle Project 2008-2010 (Massling et al., 2011).

*Biological sources.* Biological sources to OC include Primary Biological Aerosol Particles (PBAP) and Secondary Organic Aerosols (SOA). PBAP are traced by sugars, sugar alcohols and OC, whereas isoprene and terpene oxidation products are used as chemical tracers for SOA.

The source apportionment of the urban background in the present Particle Project generally agrees with the previous analysis of rural background in the Particle Project 2008-2010 (Massling et al., 2011). Measured  $PM_{2.5}$  was comparable in the two studies, i.e. 13.2  $\mu$ g/m<sup>3</sup> and 11.8  $\mu$ g/m<sup>3</sup> respectively. Rural background concentrations were about 1  $\mu g/m^3$ higher than urban background, which is ascribed to seasonal and annual variation in the two studies. In both studies, SIA is the major component with  $NH_4NO_3 > (NH_4)_2SO_4 > NH_4HSO_4$ . The crustal source is minor in the fine size fraction. The marine source is somewhat higher in the urban background and could be impacted by road salt. Sources relating to heating appliances were somewhat higher in the previously reported source apportionment of rural background in the former Particle Project 2008 -2010, which agrees with colder weather during the autumn/winter and winter/spring campaigns in that study, compared to the present study with a summer and winter campaign. As expected, the traffic source was higher in the urban background compared to the rural background. However, in the present project a new profile was derived applying also VOCs and particle number concentrations for a more accurate source profile.

SOA is significant lower in the urban background, compared to the rural background in the former Particle Project 2008 - 2010 for a number of reasons. First, the carbon speciation in the rural background was measured only in the PM<sub>10</sub> samples. EC and OC were assumed to be exclusively in the PM<sub>2.5</sub> fraction, which most likely overestimated OC in the rural PM<sub>2.5</sub>. This is supported by curbside PM<sub>2.5</sub>/PM<sub>10</sub> ratios of EC and OC in the present winter campaign, where the PM<sub>2.5</sub>/PM<sub>10</sub> ratio of EC was 100%, but the PM<sub>2.5</sub>/PM<sub>10</sub> ratio of OC was only 61% on average. This ratio was not measured in the urban background, but is believed to be higher than at urban curbside. The use of <sup>14</sup>C and organic tracers for BB, SOA, PBAP and anthropogenic sources in the present study furthermore increases the accuracy of OC apportionment to biological and anthropogenic sources. This is in contrast to the rural source apportionment study, where these tracers were not available and all unexplained OC was assumed to be SOA.

Sources to EC were mainly *Biomass burning* (0.13  $\mu$ g/m<sup>3</sup> – 36%) and *Traf-fic* (0.16  $\mu$ g/m<sup>3</sup> – 44%). The remaining 20% were attributed to the *Ship emissions* (0.04  $\mu$ g/m<sup>3</sup>), *Coal* (0.03  $\mu$ g/m<sup>3</sup>) and *Oil* (0.002  $\mu$ g/m<sup>3</sup>).

**Table 3.5.** Source apportionment of PM<sub>2.5</sub> in urban background during winter 2011 and summer 2012. PM<sub>2.5</sub> averaged 11.8  $\mu$ g/m<sup>3</sup> during the winter and summer campaigns. SOA is differentiated into two groups: one that is based on isoprene from deciduous trees (SOA\_ISO), and one based on pinenes from coniferous trees (SOA\_PINE).

Source/ Compound	Apportioned mass (µg/m³)
Marine, primary	0.36 (3%)
Marine, aged	0.65 (6%)
SIA, NH4NO3	2.4 (20%)
SIA, (NH4) <sub>2</sub> SO <sub>4</sub>	0.98 (8%)
SIA, (NH <sub>4</sub> HSO <sub>4</sub>	0.96 (8%)
Crustal	0.10 (1%)
SOA_ISO	1.0 (8%)
SOA_PINE	0.18 (2%)
РВАР	0.04 (<1%)
BB	0.88 (7%)
Ship emissions	0.62 (5%)
Coal	0.83 (7%)
Oil	0.03 (<1%)
Traffic	0.26 (2%)
Unexplained mass	2.5 (21%)
Total apportioned mass	9.3 (79%)

Sources related to combustion of fossil fuel added up to  $1.7 \,\mu g/m^3$ , excluding secondary sulphate and nitrate. Other anthropogenic sources were SIA 4.3  $\mu$ g/m<sup>3</sup> and BB 0.88  $\mu$ g/m<sup>3</sup>. In total, anthropogenic sources SIA, BB, and Coal, Oil, Traffic and Ship emission sources accounted for 6.9  $\mu g/m^{3}$ . Note however, that the anthropogenic influence on SOA formation from anthropogenic ozone formation are disregarded. Natural sources of marine and crustal  $PM_{2.5}$  accounted for 1.1  $\mu$ g/m<sup>3</sup>. The contribution from PBAP was minor as expected, since PBAP is mainly present in PM<sub>10</sub>. Biological sources accounted for  $1.26 \,\mu g/m^3$  and were almost exclusively SOA. This was less than expected and less than in the rural source apportionment in the former Particle Project 2008 - 2010 (Massling et al., 2011). In the present source apportionment, three tracers originating from atmospheric oxidation of the biogenic compounds isoprene and pinenes, were selected to track SOA. Whereas the tracers represent a substantial fraction of SOA, these tracers cannot represent all SOA. The result is therefore, that SOA is most likely underestimated. However, techniques have recently become available to measure the complete SOA mass, rather than a subset hereof, by use of Aerosol Mass Spectrometry (AMS). Note also that the source apportionment analysis is based on 4 weeks of sampling during winter and 4 weeks during summer, which represents 15% of the year. Furthermore, the equal weighting of summer and winter is assumed to represent the variation imposed by four seasons. Given these assumptions the urban background is dominated by anthropogenic sources over natural and biological ones. BB is believed to mainly origin from residential wood burning and accounts for 0.88  $\mu$ g/m<sup>3</sup>. The remaining 2.5  $\mu$ g/m<sup>3</sup> of PM<sub>2.5</sub> (21%) is assumed to be mostly

water and small amounts of silicon, oxides and hydroxides that was not determined in this campaign.

A limitation of the source apportionment analysis is the origin of SIA. While the ammonia part clearly origins from husbandry, the sources of sulphate and nitrate can for the major part be attributed to combustions sources in general but cannot be attributed to specific combustion sources, e.g. vehicular emissions, energy production, or industrial emissions. Sulphate has primary sources, but also origins from oxidation of gaseous precursors, e.g. SO<sub>2</sub> from combustion of fossil fuel. Any combustion reaction will form NO and NO<sub>2</sub>, which may further oxidize to nitrate, NO<sub>3</sub>. Thus, part of the nitrate in SIA is expected to origin from long-range transportation of combustion emissions that is being oxidized in the atmosphere, and this part is not included in the (local) vehicular traffic source. The BB source is almost four times stronger than the traffic source, if secondary nitrate formation is not considered. However, 85% of the BB source was attributed to the winter campaign and only 15% during the summer, which each represents two extreme conditions. The exposure to BB particles is thus not evenly distributed over the year, but more abundant during the heating season, which again depend on the ambient temperature. Thus, the urban background exposure to BB particles is  $1.5 \,\mu g/m^3$  on average during the heating season provided that the winter campaign is representative for these conditions. Similarly, the exposure is only  $0.3 \,\mu\text{g/m}^3$  on average where the summer campaign is representative.



**Figure 3.10.** Source variation during winter 2011(left) and summer 2012 (right) campaigns. For sources, please refer to Table 3.5. Please note the different scales on winter and summer plots.

 $PM_{2.5}$  measured using ß-attenuation averaged 11.8 µg/m<sup>3</sup> during the two campaigns. However, adding the concentrations of the measured species yields 9.5 µg/m<sup>3</sup> using an OM/OC conversion factor of 2.1 (Turpin and Lim, 2011). For these conditions the mass closure was thus 80%. Missing mass is believed to be mainly water and small amounts of Si, oxides and hydroxides, which were not analysed. The apportioned mass by CO-PREM is 9.3 µg/m<sup>3</sup>, which is close to the analysed mass. That is, 0.2 µg/m<sup>3</sup> could not be apportioned to sources. PM<sub>2.5</sub> differed markedly during winter (16.0 µg/m<sup>3</sup>) and summer (7.7 µg/m<sup>3</sup>), and so did their sources. BB (red in Figure 3.10) and SOA (green in Figure 3.10)

0.88 and 1.2  $\mu$ g/m<sup>3</sup> based on the two campaigns. While BB was almost exclusive present during winter, Secondary Organic Aerosols from coniferous trees e.g. spruce, pine and fir (SOA\_PINE) had a winter contribution from biogenic sources, while Secondary Organic Aerosols from decidous trees, e.g. birch, oak and beach (SOA ISO) were almost absent during winter (Figure 3.10). This is because SOA from this source is based on the precursor isoprene, that is emitted from the deciduous trees' leaves, which are lost in the autumn. Coal equalled 0.81  $\mu$ g/m<sup>3</sup>, whereas Oil and Traffic represented minor sources to PM2.5 in urban background. An additional anthropogenic source based on fossil fuels, sulphate and correlated well with phthallic acid and V, Ni indicative of oil combustion. The source is evenly distributed over the year (Figure 3.10), and thus not believed to be oil combustion from residential heating, but rather ship emissions. The apportioned mass concentration of 0.62  $\mu$ g/m<sup>3</sup> aggrees well with previous estimates of 1  $\mu$ g/m<sup>3</sup> PM<sub>2.5</sub> from Ship emissions (Olesen et al., 2009) of which 50% is believed to be sulfate (Petzold et al., 2010).

#### 3.10 Conclusion

The source apportionment of PM<sub>2.5</sub> in rural background (2008-2009; Massling et al., 2011) is generally in good accordance with urban background (2011-2012; this project). However, differences are in particular observed for BB and SOA. Average measured masses were comparable, 13.2  $\mu$ g/m<sup>3</sup> in rural background and 11.8  $\mu$ g/m<sup>3</sup> urban background. Please note, that these averages are based on different years and seasons, and thus not directly comparable. Primary and aged marine aerosols added up to 0.31 and 1.0  $\mu$ g/m<sup>3</sup> in rural and urban background, respectively. These estimates are in both cases based on two campaigns of four weeks duration. However, the seasons were colder during the rural campaigns, and the marine source is subject to annual and year-year variation. More comparable source contributions were expected, which however, calls upon longer campaigns or simultaneous campaigns in the rural and urban background. The crustal source was minor in the rural and urban  $PM_{2.5}$  fractions, 0.03 and 0.10  $\mu$ g/m<sup>3</sup>, respectively. The SOA source was estimated to account for 2.1  $\mu$ g/m<sup>3</sup> in the rural background based on a crude estimate (Massling et al., 2011). In the present project, specific chemical markers for SOA were analysed and included in the receptor model, which resulted in a much lower estimate for SOA of 1.2  $\mu g/m^3$  in urban background. SIA amounted to 3.80 and 4.3  $\mu g/m^3$ , respectively. BB was higher in the rural study, 1.3 versus  $0.88 \,\mu\text{g/m}^3$  in urban background. However, both campaigns in the rural study were probably influenced by BB. National non-industrial combustion sources, which includes BB, was modelled to  $0.87 \ \mu g/m^3$  in a recent report (Jensen et al., 2013). As for SOA, BB has been carefully evaluated using new organic markers in addition to potassium and the organic markers levoglucosan and mannosan, used in the former particle projects. The sum of fossil fuel combustion, mainly Oil and Coal amounted to 1.3 and  $1.7 \,\mu g/m^3$ . Vehicular transport was significantly lower in the rural campaigns, i.e 0.09 versus 0.26  $\mu$ g/m<sup>3</sup> in the urban campaign. The latter is in excellent agreement with a recent modelling of  $0.34 \,\mu\text{g/m}^3$  (Jensen et al., 2013). An additional source of fossil carbon accounts for 0.62  $\mu$ g/m<sup>3</sup> and is believed to be ship emissions. This apportionment aggrees with previous findings (Ellermann et al., 2014, Olesen et al., 2009; Petzold et al., 2010)

Organic carbon mass was mainly attributed to SOA (44%), *BB* (22%) and *Traffic emissions* (9%). Furthermore, *Ship emissions* accounted for 22% of organic carbon. Minor contributions were attributed to biological sources such as microorganisms and decomposition of leaves. These findings agree with other European studies of organic carbon in PM<sub>2.5</sub>, though large differences are observed from site to site (Genlencser et al., 2007). Sources to EC were mainly BB (0.13  $\mu$ g/m<sup>3</sup> – 36%) and *Traffic* (0.16  $\mu$ g/m<sup>3</sup> – 44%). The remaining 20% were attributed to mainly *Ship emissions* and *Coal*.

The sources of BB are believed to be mainly non-industrial combustion for heating appliances, i.e. residential wood burning. However, contributions other than national sources such as wildfires are likely to play a role, but typically in the summer season. The source apportionment estimate BB to account for  $0.88 \ \mu g/m^3$  as averaged over the winter and summer campaigns, but higher concentrations of BB particles were found in the urban background during the heating season, averaging 1.5  $\mu g/m^3$  during the winter campaign. Similarly, BB particles averaged 0.3  $\mu g/m^3$  during the summer campaign.

# 4 Scenario calculations for PM<sub>2.5</sub> in 2020, 2025 and 2030

#### 4.1 Introduction

Fine particulate matter ( $PM_{2.5}$ ) is responsible for significant negative impacts on human health. This is the background for the introduction of a "national exposure reduction target" in the EU directive on ambient air quality and cleaner air for Europe 2008/50/EC (EC, 2008). The aim of this new target is to reduce the exposure of the general population to  $PM_{2.5}$ . Moreover, the reduction target aims at a general reduction of particulate concentrations in the urban background air to ensure that large sections of the population benefit from improved air quality.

The national exposure reduction target is a percentage reduction of the average exposure of the population of a Member State set for the reference year (2010) with the aim of reducing harmful effects on human health, to be attained where possible over a given period – i.e. at the latest in the target year 2020.

The national exposure reduction target is defined in terms of the "average exposure indicator" (AEI) that is the mean average level determined on the basis of measurements at urban background locations throughout the territory of a Member State and which reflects population exposure.

The Average Exposure Indicator expressed in  $\mu$ g/m<sup>3</sup> (AEI) is based upon measurements in urban background locations in zones and agglomerations throughout the territory of a Member State. It is based on a 3calendar year running annual mean concentration averaged over all sampling points. The background for use of the mean over three years is that this will reduce the influence of the natural variations from year to year in the meteorological conditions.

The Average Exposure Indicator for the reference year 2010 is determined as the mean concentration of the years 2008, 2009 and 2010. The Average Exposure Indicator for the target year 2020 shall be the 3-year running mean concentration for the years 2018, 2019 and 2020.

The EU directive states also that the Commission in 2013 should review the provisions related to  $PM_{2.5}$ . More specifically, the review should be undertaken with a view to establish a legally binding national exposure reduction obligation in order to replace the national exposure reduction target. Hwever this review has been postponed by the EU Commission.

The aim of this part of the project is to carry out scenario calculations of the concentrations of  $PM_{2.5}$  in 2020, 2025 and 2030 using DCE's air quality model DEHM (Danish Eulerian Hemispheric Model) in order to evaluate whether or not Denmark will be able to fulfill the reduction target for Denmark. Hence this work will provide useful information as basis for the revision of the directive.

The model calculations include calculations of  $PM_{2.5}$  in Danish urban background for the reference year and emission scenarios for 2020, 2025 and 2030 (see section 4.3).

Moreover, in December 2013 the EU Commission published their proposal for the next stage of the EU-directive on the National Emission Ceilings (EC, 2013). This proposal includes suggestions for national emission ceilings for the EU member states for 2020 (similar to the targets in the Gothenburg protocol) and 2030. Besides this, the proposal suggests an interim though less binding target for 2025. If the proposals from the EU commission are finally adopted it will have large impact on the future development of the air quality and the average exposure indicator. This project has therefore been extended with a short preliminary comparison between the scenarios used in this project and the proposed new emission ceilings (see section 4.5).

#### 4.2 The Danish Average Exposure Target

The urban background measurement stations in the three largest cities in Denmark (Copenhagen, Aarhus and Aalborg) have been selected for the determination of the average exposure indicator, which is calculated as the measured average urban background concentration of PM<sub>2.5</sub> averaged over three calendar years. The measurements at the stations are carried out as part of the Danish Air Quality Monitoring Program under NOVANA (Ellermann et al., 2013). The results for the three first determinations of the average exposure indicator are shown in Table 4.1.

**Table 4.1.** The average exposure indicator in Denmark for the reference year 2010 and the following two years (Ellermann et al., 2013).

Year	Period	Average Exposure Indi- cator μg/m³
2010	2008-2010	14.1
2011	2009-2011	15.2
2012	2010-2012	14.2

The size of the national reduction target is based on the average exposure indicator in 2010. According to the EU directive (2008/50/EC, Annex XIV, section B; EC, 2008) an average exposure indicator of 14  $\mu$ g/m<sup>3</sup> in 2010 leads to a national reduction target of 15%. Therefore Denmark has to reduce the average exposure indicator with 2.1  $\mu$ g/m<sup>3</sup> from 2010 (average of 2008-2010) to 2020 (average of 2018-2020) in order to fulfill this target.

#### 4.3 Model calculations and emission scenarios

The model calculations of the concentrations of PM<sub>2.5</sub> has been carried out with the air quality model called DEHM (Dansk Eulersk Hemisfærisk Model) that since 2004 has been used as part of the monitoring of air quality in Denmark (Ellermann et al., 2013). DEHM is an Eulerian model, where emissions, air borne transport, chemical reactions and depositions of the various air pollutants are calculated to a three dimensional net of grit cells.

Information on the emissions of the air pollutants is based on the national emission inventories and international scenarios for the development in the emissions. These will be described in further details below.

The airborne transport and deposition is calculated on the basis of the meteorological conditions in 2012 for both the reference year and the

scenarios. Hence it is only the emission inventories that will be changed in the scenario calculations for 2020, 2025 and 2030. The meteorological data is prepared for the model using the meteorological model called MM5 (Grell et al., 1995) that are included as part of DCE's entire model system called THOR (Thor.DMU.dk).

DEHM covers the entire northern hemisphere because air pollutants can be transported more than 1,000 km via the air. Therefore the model also includes emissions for the entire model domain. However, in connection to this project it is the emissions for Denmark and the remaining Europe that are most important for the concentrations of air pollutants in Denmark.

The model has three levels of spatial resolution where the highest spatial resolution is used for Denmark. This variation of the spatial resolution is used in order to reduce the computing time for the model that otherwise could be very long. For Denmark the spatial resolution is 6 km x 6 km in the horizontal plane. This spatial resolution is sufficient to give reliable results for the air concentrations in urban background that is in focus in this project.

Vertically the model covers the lowest 15 km of the atmosphere. The model is divided in 29 vertical layers that are relatively thin at the bottom (60 m) and thick at the top (2,000 m).

Model calculations for the reference year are based on European emissions for 2008 (EMEP 2013) and Danish emissions for 2010 (Nielsen et al., 2013). These emissions were the most recently updated emissions available when the model calculations were carried out. The emission inventories include emissions of NH<sub>3</sub>, NO<sub>2</sub>, SO<sub>2</sub>, VOC and PM. The emission inventories include both land based sources and emissions from aviation and ship traffic.

Information on the spatial variation of the emissions has been collected from a number of different emission inventories. DCE's emission inventory on 6 km x 6 km is used for Denmark. This includes inventory for about 70 large point sources and a very detailed spatial distribution of the Danish emissions of ammonia on 100 m x 100 m. A detailed inventory on 17 km x 17 km is used for EU's member states, while EMEP's gritted inventory on 50 km x 50 km is used for the remaining European countries (EMEP, 2013).

Emissions from ship traffic in the Danish marine waters are based on the inventory carried out by DCE in 2009 (Olesen et al., 2009) that later has been updated to the inventory from 2011. Ship emissions for other European marine waters are based on EMEPs inventory with geographic resolution on 50 km x 50 km (EMEP, 2013).

In addition to the calculations for the reference year, there have been made model calculations for four different scenarios covering the years 2020, 2025, and 2030:

• **Gøteborg 2020.** This scenario for 2020 is based on the emission ceilings for 2020 in the newly accepted and revised Gothenburg protocol (UNECE, 2012) under the Geneva Convention on Long-Range Transboundary Air Pollution (CLRTAP).

- EU 2025. Scenario for 2025 that is a baseline scenario prepared by International Institute for Applied Systems Analysis (IIASA; Amann, 2013).
- **EU 2025A**. An alternative scenario for 2025 where additional reductions in the emissions has been anticipated. This scenario has been prepared by IIASA (Amann, 2013).
- EU 2030. Scenario for 2030 that is a baseline scenario prepared by IIASA (Amann, 2013).

The same spatial distribution of the sources has been assumed for all the years 2020, 2025 and 2030. Although some changes in the spatial distribution of the sources can be anticipated within a country, it is expected that this limitation in the model only will give minor impact on the validity of the scenario calculations, because PM<sub>2.5</sub> is long-range transported leading to a very uniform distribution in the concentrations of PM<sub>2.5</sub>.

The emissions for Denmark, EU and a number of neighboring countries for the reference year and the four scenarios are shown in Figure 4.1.



**Figure 4.1.** Emissions for Denmark, EU and a number of neighboring countries for the reference year (2008/2010) and the four scenarios (Gothenburg 2020, EU2025, EU2025A and EU2030) for the primary emissions of PM<sub>2.5</sub> and the gasses that will lead to formation of secondary particles via the chemical reactions in the atmosphere. The emissions are shown relative to the emissions in the reference year.

#### 4.4 **Results from the model calculations**

The results from model calculation of  $PM_{2.5}$  for the reference year and the four scenarios are shown in Figure 4.2 and Table 4.2.



**Figure 4.2.** The model calculated PM<sub>2.5</sub> for the reference year (2008/2010) and the four scenarios for the urban background stations in Copenhagen, Odense, Aarhus and Aalborg, the rural background station at Risø and the Average exposure indicator (indicator) averaged from these 5 stations.

**Table 4.2.** The model calculated PM<sub>2.5</sub> for the reference year (2008/2010) and the four scenarios for the urban background stations in Copenhagen, Odense, Aarhus and Aalborg, the rural background station at Risø and the Average exposure indicator (indicator). The average exposure indicator is the average of Copenhagen, Aarhus and Aalborg. The last column shows the reduction from the reference year to the scenario.

	Urban background				Rural	Average Exposure	Reduction
	Copenhagen	Odense	Aarhus	Aalborg	Risø	Indicator	
	µg/m³	µg/m³	µg/m³	µg/m³	µg/m³	μg/m³	µg/m³
Ref.	7.5	6.4	5.8	4.7	6.0	6.0	
2020	5.8	5.0	4.6	3.8	4.7	4.7	1.3
2025	5.5	4.6	4.3	3.6	4.4	4.5	1.6
2025A	4.4	3.8	3.6	3.2	3.7	3.8	2.3
2030	5.8	4.7	4.4	3.5	4.4	4.6	1.4

The differences between the urban background stations are relatively small and the reductions of  $PM_{2.5}$  in the four scenarios follow the same pattern as shown for the reductions in the emissions (Figure 4.1). Hence the largest reduction of the average exposure indicator, 2.3  $\mu$ g/m<sup>3</sup>, is seen for the scenario EC 2025A and the smallest reduction, 1.3  $\mu$ g/m<sup>3</sup>, is seen for the scenario Gothenburg 2020.

Figure 4.2 and Table 4.2 includes also the results from the rural background station Risø situated 6 km north of Roskilde. PM<sub>2.5</sub> at Risø is on the same level as the model calculated average exposure indicator.

The reductions of the different chemical components of  $PM_{2.5}$  are shown in Figure 4.3. Again the patterns look quite similar for the different stations. This is also expected since the majority of  $PM_{2.5}$  is long-range transported and hence a quite homogeneous spatial distribution of  $PM_{2.5}$ and the chemical constituents is expected.



Figure 4.3. The chemical composition of  $PM_{2.5}$  model calculated for the reference year (2008/2010) and the four scenarios.

Table 4.3 shows a comparison between the measured and model calculated  $PM_{2.5}$  at the urban background stations and at the rural station Risø. The results for the model calculations are on average 55% lower than measured at the urban background stations. This is mainly because the model calculations do not include a number of chemical constituents of  $PM_{2.5}$ :

- Water associated with the hygroscopic inorganic salts (mainly ammonium sulphates, ammonium nitrate, and sea salt)
- Secondary organic particles produced in the atmosphere from both manmade and natural emissions
- Particles produced due to natural emissions of sulphur containing compounds from the oceans (see below)

Note that there is a slight inconsistency in this comparison since the measurements are from 2012 and model calculations are based on emissions for Europe from 2008 and DK from 2010 and meteorology from 2012. Since the emissions have decreased slightly from 2008/2010 to 2012

there would have been a slightly larger difference between results from measurements and model calculations if all data had been from the same year.

Table 4.3. Comparison between model calculations and measurements (2012). Input data
for the model: Emissions for Europe from 2008 and DK from 2010. Meteorology from
2012. The average urban background is based on Copenhagen, Aarhus and Aalborg.

	Measurements	Model	Difference
	μg/m³	µg/m³	%
Copenhagen	11.4	7.5	66
Odense		6.4	
Aarhus	10.7	5.8	55
Aalborg	10.7	4.7	44
Urban background, average	10.9	6.0	55
Risø	9.6	6.0	63

Table 4.4 shows a comparison between the measured and model calculated chemical content of  $PM_{2.5}$  at the rural station Risø that is the only background station, where this kind of measurements are carried out in Denmark. This comparison shows that the model underestimates all the chemical constituents that can be compared directly to the measurements except for elementary carbon (EC).

The model underestimates the contribution from sea salt. This source of  $PM_{2.5}$  is very difficult to model since it requires that the model can calculate the wind dependent sea spray production. The contribution from sea salt to  $PM_{2.5}$  is small and the bias on sea salt is therefor of minor importance. Moreover, since sea salt comes from a natural source there will be no long term change in the concentration of sea salt. The bias will therefore not influence the estimate of the reduction of  $PM_{2.5}$  due to the reduction in the manmade sources.

The model underestimates the contribution from sulphate with 37%. This underestimation may be due to two different reasons:

- The model does not include sulphate coming from marine emissions of dimethyl sulfide (Hertel et al., 1994) that via the chemical transformations in the atmosphere will lead to production of sulphate. This source of sulphate has become increasingly important because of the very large reductions of the manmade sources of sulphate.
- The primary emissions of PM<sub>2.5</sub> are only determined by the mass of the particulate emissions and there is no speciation of the chemical content. However, it is known that ship emissions of primary PM<sub>2.5</sub> contain approximately 50% sulphate (Petzold et al., 2010). This sulphate is in the model calculations regarded as "Other primary" PM<sub>2.5</sub>, while it is part of the sulphate in the measurements.

Nitrate can be found both in the fine (< 2.5 mm) and coarse (> 2.5 mm) fraction of the particles. The description of the reactions forming particulate nitrate is somewhat uncertain and especially the partitioning of nitrate between fine and coarse particles is uncertain. This may explain

why the model underestimates the amount of nitrate in the fine fraction and overestimates for the coarse fraction. Moreover, the measurements of nitrate in  $PM_{2.5}$  may be slightly overestimated due to absorption of gas phase nitric acid on the particle filter.

Ammonium in the particles is bound to sulphate and nitrate and both sulphate and nitrate can be limiting for the amount of ammonium formed in the atmosphere. The underestimation of both sulphate and nitrate is likely the reason for the simultaneous underestimation of ammonium.

The amount of elementary carbon agrees very well between measurements and model calculations. In contradiction the mass attributed to organic mass (estimated from the amount of organic carbon) is much higher in the measurements than in the model. The reason for this is that the model only accounts for the primary emitted organic mass while the measurements are the sum of the primarily emitted and secondarily formed organic mass.

Moreover, the measurements show that  $PM_{2.5}$  contains a minor fraction of potassium and calcium that originates from both manmade and natural sources. These compounds are not included in the model calculations; however, their contribution is so small that they can be neglected in this context.

Finally, there is a difference of  $1.3 \,\mu\text{g/m}^3$  in the measured PM<sub>2.5</sub> and the sum of the chemical constituents determined by analysis of the collected particles. This mass consist most likely of water associated to the hygroscopic parts of the particles.

**Table 4.4.** The measured and model calculated chemical composition of  $PM_{2.5}$  at the rural background station at Risø, Roskilde. Measurements are annual mean for 2012. Input data for the model: Emissions for Europe from 2008 and DK from 2010. Meteorology from 2012.

	Measurements	Model	Difference
	µg/m³	µg/m³	%
PM <sub>2.5</sub>	10.0	6.0	60
Salt (NaCl)	0.6	0.3	54
Sulphate	1.6	1.0	63
Nitrate	2.4	1.7	73
Ammonium	1.2	0.9	74
Elementary carbon	0.3	0.3	98
Organic particles, primary		0.6	
Organic particles, primary and secondary	2.5		
Pottassium	0.1		
Calcium	0.1		
Others primary		1.1	
Others including water	1.3		

The particulate bound water is not included in the model calculations. A large fraction of this water is bound to the secondary inorganic salts (ammonium sulphate, ammonium nitrate) and since these inorganic salts are reduced in the four scenarios there will be a corresponding reduction of the water content of PM<sub>2.5</sub>. In order to account for this it has been as-

sumed that the amount of water is reduced proportionally to the reduction of the sum of sulphate, nitrate and ammonium.

When the particulate bound water is taken into account then the scenarios show that the Gothenburg 2020 scenario will lead to a reduction of  $PM_{2.5}$  of 1.6 µg/m<sup>3</sup>, the EC baseline scenarios for 2025 and 2030 will lead to a reduction of 2.0 µg/m<sup>3</sup> and the EC scenario 2025A will lead to a reduction of 2.9 µg/m<sup>3</sup>. It is therefore only the EC scenario 2025A that will lead to a reduction larger than the national emission reduction target for Denmark on 2.1 µg/m<sup>3</sup>. The EC baseline scenarios for 2025 and 2030 lead to a reduction just below the target while the Gothenburg 2020 scenario is well below the target.

The calculated reductions from the reference year (2008/2010) to the scenario years are in reality reductions from a mixed year since the used emissions for Europe are from 2008 and for DK from 2010 while the meteorology is from 2012. However, the reduction target defined in the EU directive for the reference year 2010 is based on the average emissions and meteorology for the three years 2008-2010. The reductions of  $PM_{2.5}$  will therefore be slightly smaller than calculated here.

**Table 4.5.** The model calculated  $PM_{2.5}$  and the reduction of  $PM_{2.5}$  from the reference year to the four scenarios. In addition the table shows the estimated amount of water,  $PM_{2.5}$  including the estimated water and the reduction when the water content is taken into account (right column).

	Estimated PM <sub>2.5</sub> + estimated				
	ΡΜ <sub>2.5</sub> μg/m <sup>3</sup>	Reduction µg/m³	Water µg/m <sup>3</sup>	PM₂.₅+Water µg/m³	Reduction including water µg/m <sup>3</sup>
Reference	6.0		1.3	7.3	
2020	4.7	1.3	1.0	5.7	1.6
2025	4.4	1.6	0.8	5.3	2.0
2025A	3.7	2.3	0.7	4.4	2.9
2030	4.4	1.5	0.8	5.2	2.0

# 4.5 Comparison with the proposal for the new EU-directive on National Emission Ceilings for the EU member states

The EU Commission has proposed new emission ceilings for 2020 and 2030, where the proposed ceilings for 2020 follow the reduction targets of the Gothenburg protocol (EC, 2013; ECE, 2012). The new EU emission ceilings for the EU member states are defined as a percentage reduction of the emissions relative to the annual national emission in the reference year 2005.

Beside this, an interim though less binding target for 2025 has been proposed. This interim target is in essence the average of the reduction targets for 2020 and 2030.

A comparison between the emission scenarios used in this project and the proposed emission ceilings are shown in Figure 4.4 and 4.5 for the compounds that are most important for PM<sub>2.5</sub>. Both the emissions from Denmark and the sum of the EU member states are shown. Because PM<sub>2.5</sub> for a large part is long-range transported to Denmark and the sum of the emissions from all the member states gives a reasonable picture of the average reductions although there are significant variations from member state to member state. Denmark is also included because the local emissions are also important; especially for the primary emitted PM<sub>2.5</sub> and for the secondary inorganic particles formed in the atmosphere from emission of ammonia and nitrogen oxides.

The proposed ceilings for 2020 are in agreement with the Gothenburg 2020 scenario used in this project and hence similar to the targets set in the Gothenburg protocol. There are some minor differences that are believed to be due to revisions of the nationally reported emissions for the reference year 2005.

The EU emissions for primary emissions of  $PM_{2.5}$  are an exception from the picture described above, since the emissions used in the scenario for Gothenburg 2020 is about 20% higher than the proposed national emissions ceiling for 2020 calculated from the official national emissions collected from the EMEP emission database (EMEP, 2013). This discrepancy is most likely due to a recent revision of the EU emissions that systematically has reduced the emissions of primary  $PM_{2.5}$  with about 20%. This revision has led to the generally higher emissions used in the model calculations compared to the newest data compiled from the database in January 2014. This discrepancy will give an overestimation of the primary  $PM_{2.5}$  from the EU member states except Denmark, but will only have little impact on the overall picture since the EU contribution from primary  $PM_{2.5}$  only accounts for a small part of  $PM_{2.5}$  in Denmark and the relative decrease in  $PM_{2.5}$  between the reference year shows the expected variations.

The proposed interim targets for 2025 are also in reasonable agreement with the EC 2025 scenario for nitrogen oxides, non-methane volatile organic compounds and primary PM<sub>2.5</sub> (except EU). For sulphur dioxide there is reasonable agreement for EU while the proposed target for Denmark is higher than in the EC 2025 scenario. For ammonia the proposed target are higher for Denmark and lower for EU than in the EC 2025 scenario.

The proposed ceilings for 2030 are in agreement with the EC 2030 scenario for nitrogen oxides and for the Danish emissions of sulphur dioxide and ammonia. For the EU emissions of sulphur dioxide and ammonia and the Danish and EU emissions of non-methane volatile compounds and primary PM<sub>2.5</sub> the proposed ceilings for 2030 are significantly lower than in the EC 2030 scenario.

Interestingly, the EC 2025a is in general in good agreement with the proposed ceilings for 2030 for all compounds and both for Denmark and EU as a hole (except EU PM<sub>2.5</sub>). The model calculations for EC 2025a will therefore give a reasonable estimate for the expected reductions in PM<sub>2.5</sub> assuming that the proposed new directive on National Emissions Ceilings will be fully implemented. It is therefore estimated that implementation of the proposed directive will lead to a 2.9  $\mu$ g/m<sup>3</sup> reduction of

 $PM_{2.5}$  from the reference year to 2030. Moreover, since the interim target for 2025 is the "average" of the ceilings for 2020 and 2030, it is estimated that the proposed directive will give a reduction of 2.3 µg/m<sup>3</sup> in 2025.



**Figure 4.4**. The emissions of sulphur, nitrogen oxides and ammonia used for the reference year (2008/2010), the four emission scenarios (Gothenburg 2020, EC 2025, EC 2030, EC 2025a) and the proposed national emission ceilings for 2020 and 2030 and the interim target for 2025 (EC 2013). In addition the official national emissions (EMEP, 2013) are shown for the period 2005-2011. Left figures show the emissions for Denmark and right figures show emissions for the sum of the EU member states.



**Figure 4.5.** The emissions of non-methane volatile organic compounds (NMVOC) and primary PM<sub>2.5</sub> used for the reference year (2008/2010), the four emission scenarios (Gothenburg 2020, EC 2025, EC 2030, EC 2025a) and the proposed national emission ceilings for 2020 and 2030 and the interim target for 2025 (EC 2013). In addition the official national emissions (EMEP, 2013) are shown for the period 2005-2011. Left figures show the emissions for Denmark and right figures show emissions for the sum of the EU member states.

#### 4.6 Conclusions

The concentrations of  $PM_{2.5}$  are on the same level in the urban background in the three largest Danish cities. The average exposure indicator is determined to 14 µg/m<sup>3</sup> for the reference year 2010 (average of 2008-2010) and this leads to a national exposure reduction target for Denmark of 2.1 µg/m<sup>3</sup> (see Chapter 4.2)

The model calculations underestimate the concentrations of  $PM_{2.5}$  compared to the measurements. This is mainly due to the fact that the model calculations do not include all the chemical constituents of  $PM_{2.5}$ . Hence, the model calculations will most likely lead to a too small reduction of  $PM_{2.5}$  from the reference year to the years of the four scenarios.

The model calculations do not include the secondary organic particles produced in the atmosphere from the manmade and biogenic emissions of volatile organic compounds. Since the emissions of volatile organic compounds are reduced in the four scenarios (Figure 4.1) it is most likely that there will be a reduction in the amount of secondary organic compounds. It has not been possible to estimate this reduction in PM<sub>2.5</sub>.

Moreover, the model calculations do not include water. A simple estimate based on the results from the measurements has been used to take the reductions of water into account. This leads to a slightly larger reduction in PM<sub>2.5</sub>.

When particulate bound water is taken into account, the Gothenburg 2020 scenario will lead to a reduction of  $PM_{2.5}$  of 1.6 µg/m<sup>3</sup>. The EC baseline scenarios for 2025 and 2030 will lead to a reduction of 2.0 µg/m<sup>3</sup> and the EC scenario 2025A will lead to a reduction of 2.9 µg/m<sup>3</sup>. Therefore, it is only EC scenario 2025A, which will lead to a reduction exceeding the national emission reduction target for Denmark of 2.1 µg/m<sup>3</sup>. The EC baseline scenarios for 2025 and 2030 leads to a reduction just below the target, while the Gothenburg scenario is well below the target.

The proposal from the EU Commission for a new directive on national emission ceilings suggest more stringent emission commitments from the EU member states for 2025 and 2030 than the base line emission scenarios applied in this project. A full implementation of the proposed directive is estimated to lead to reductions in  $PM_{2.5}$  of 1.6, 2.3 and 2.9  $\mu$ g/m<sup>3</sup> for 2020, 2025 and 2030, respectively. Hence, it is estimated that the national exposure reduction target can be met in 2025 and may be somewhere between scenario 2020 and scenario 2025 since the calculated reductions in  $PM_{2.5}$  do not account for reductions in the secondary organic particles.

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#### THE PARTICLE PROJECT 2011-2013

The Particle Project 2011-2013 continues the record of particle mass and number measurements on urban and rural locations. Anthropogenic and natural sources to  $PM_{2.5}$  were evaluated using receptor models based on detailed chemical composition of particulate samples collected during two intense campaigns in the urban background of Copenhagen. Furthermore, scenario calculations of  $PM_{2.5}$  in 2020, 2025 and 2030 were conducted to evaluate if Denmark will be able to meet future reduction targets.