Status for Partikelprojektet 2014-2016

Notat fra DCE - Nationalt Center for Miljø og Energi 30. September 2015

Jacob Klenø Nøjgaard, Andreas Massling og Thomas Ellermann

Institut for Miljøvidenskab

Rekvirent:
Miljøstyrelsen
Antal sider: 13

Faglig kommentering: Ole Hertel
Kvalitetssikring, centret: Vibeke Vestergaard Nielsen

AARHUS
UNIVERSITET
DCE - NATIONALT CENTER FOR MILJØ OG ENERGI

Indhold

Status for the Particle Project 2011-2013

An increasing part of the population migrates to larger cities. For example, the population in Copenhagen has increased by about 10,000 inhabitants each year from 2008-2013. However, the air quality and thereby human exposure to pollution in larger cities is not similar to that of rural background. A denser population implies more sources of incomplete combustion products from industry, residential heating and traffic, e.g. nitrogen oxides and soot, though improved technology has greatly lowered individual emissions over time. While some of the chemical products are monitored on a routine basis in urban background and on urban kerbside, more knowledge is needed on the spatial distribution of EC and the increment from rural background to urban background. At present, the *Danish Air Quality Monitoring Programme* (NOVANA LMP) provides knowledge on EC in rural background and on urban kerbside. Daily variations in the concentration of Elemental Carbon (EC) "soot" correlates with cardiovascular mortality and hospitalization in relation to heart and lung diseases. Furthermore, cohort studies reveal a relationship between long-term exposure to EC and mortality related to heart and lung diseases. Health effects associated with exposure to $PM_{2.5}$ and PM_{10} is typically also associated with EC and vice versa, but the association is stronger for EC. This indicates that EC is a better indicator for hazardous compounds from combustion processes. Although EC is not necessarily the hazardous species itself, it may serve as a carrier for such substances or formed along with hazardous substances.

The Particle Project 2014-2016 is funded by the Danish EPA, Miljøstyrelsen, and serves as a supplement to the *Danish Air Quality Monitoring Programme* with detailed physical and chemical measurements of atmospheric particles. The objectives of this fifth *Particle Project* is to

i) continue the measurement activities of particle size distributions, which started in urban background (H.C. Ørstedsinstituttet, HCOE) primo 2011. Long and continuous time series are important not only with respect to air quality issues but also to evaluate the effect of new emission standards for particle number concentrations for vehicles.

ii) evaluation of the $PM_{2.5}$ and PM_{10} TEOM (Tapered Element Oscillating Microbalance) time series, which were initiated in the first Particle project from 2001 -2004. The TEOM instrument has a time resolution of ½ hour and has the potential to elucidate mechanistic information, though not in compliance with PM standards.

iii) provide a review and a research based apportionment of urban EC to contributing sources based on available monitoring data and a dataset of EC in urban background, which is provided by this project. In order to do so, a low volume sampler (LVS) is installed on the roof of the H.C. Ørsteds Institute (urban background). The data forms the basis for the study of year-year variation and annual variation as well as urban background versus urban rural background, e.g. the urban increment.

Elemental Carbon is a better indicator for hazardous compounds

The air quality and thereby human exposure to pollution in larger cities is not similar to that of rural background. A denser population implies more sources of incomplete combustion products from industry, residential heating and traffic, e.g. nitrogen oxides and soot, though improved technology has greatly lowered individual emissions over time. While some of the chemical products are monitored on a routine basis in urban background and on urban kerbside, more knowledge is needed on the spatial distribution of Elemental Carbon (EC) and the increment from rural background to urban background. At present, the *Danish Air Quality Monitoring Programme* (NOVANA LMP) provides knowledge on EC in rural background and on urban kerbside.

Daily variations in the concentration of EC "soot" correlates with cardiovascular mortality and hospitalization in relation to heart and lung diseases. Furthermore, cohort studies reveal a relationship between long-term exposure to EC and mortality related to heart and lung diseases. Health effects associated with exposure to $PM_{2.5}$ and PM_{10} is typically also associated with EC and vice versa, but the association is stronger for EC. This indicates that EC is a better indicator for hazardous compounds from combustion processes. Although EC is not necessarily the hazardous species itself, it may serve as a carrier for such substances or formed along with hazardous substances.

Elemental Carbon (EC): 2011 versus 2014/2015

In the previous particle project 2011 – 2013, particulate matter with aerodynamic diameter smaller than 2.5 µm ($PM_{2.5}$) has previously been collected on filters in urban background during two four-weeks-campaigns in winter 2011 and summer 2012. Since September 1st 2014, a LVS has been installed on the same location to collect filters continuously. In Table 1 and the results from the previous Particle Project 2011-2013 (Nøjgaard et al., 2015) are compared with results from the present project 2014-2016.

Table 1. Overview of $PM_{2.5}$ as measured by ß-attenuation and its carbon fractions: Organic (OC), Elemental (EC) and Total Carbon (TC) during winter 2011 and summer 2013 campaigns (µg/m^3).

	$PM_{2.5}$	OC	EC	TC	EC/TC
Urban background, summer	7.7	1.36	0.25	1.62	0.15
Urban background, winter	16.0	1.88	0.48	2.35	0.20
Urban kerbside, summer	11.0	2.16	2.11	4.27	0.49
Urban kerbside, winter	19.8	2.74	2.82	5.56	0.51

The results from the campaigns indicated that rural background is influenced by the heating season, where EC roughly doubled from summer to winter (Nøjgaard et al., 2015). EC is formed during incomplete combustion and emitted from mainly biomass combustion and traffic, which also produce Organic Carbon (OC). OC shows a smaller increase than EC, i.e. 38% between the two campaigns, since more sources contribute including natural ones. Thus the EC fraction of Total Carbon (TC) also in-

creased from 0.15 to 0.20. Similar differences are observed at the kerbside station, but they are not as pronounced due to the strong influence from the traffic source. As a result, the EC shares are almost similar in the two seasons. However, these conclusions were based on data representing only 16% of the year. Continous data from the three stations will be provided by the present Particle Project 2014-2016 and the *Danish Air Quality Monitoring Programme.*

Table 2. Overview of $PM_{2.5}$ (µg/m^3) as measured by gravimetric analysis and its carbon fractions: Organic (OC), Elemental (EC) and Total Carbon (TC) from September 1st 2014 - March 31st 2015. OC is an estimated concentration - see text. OC is estimated, OC*, see text.

	$PM_{2.5}$	OC*	EC	TC	EC/TC
Urban background	14.7	1.84	0.47	2.30	0.22
Rural background	13.8	1.57	0.33	1.90	0.19
Urban kerbside	19.6	2.88	1.78	4.65	0.40

In the previous Particle project, the urban background OC was corrected from positive artifacts by use of a second filter (tandem sampling). In the present Particle Project, OC in urban background is estimated by use of a correction established at rural background, which is considered to be close to the one prevailing in urban background, see appendix A. However, OC* is an estimated concentration and should be treated as such - in particular at low OC concentrations, where the correction is relatively high.

The urban background concentrations of $PM_{2.5}$, OC, EC and TC, which represents autumn - spring, are in accordance with the results from the winter campaign in 2011 (Table 1 - 2). Whereas autumn - spring 2014/2015 OC at urban kerbside are in the same order as the winter 2011 concentration, EC is roughly 1 µg/m^3 lower in 2014-2015 compared with 2011 levels. Accordingly, the EC share of TC is clearly smaller in 2014-2015. A general improvement of the car fleet with respect to emission of pollutants, probably only accounts for a fraction of the observed difference in EC. More likely is the observed difference a result of different meteorological conditions and random variation. Table 2 is based on 7 months of measurements in 2015 and is thereby more reliable than 4 weeks of data supporting the winter concentrations 2011 in Table 1.

Elemental Carbon increment in urban background

EC in urban background is 42% higher in urban background, relative to rural background based on 7 months on measurement from September to March (Table 2). Sources of EC are predominantly wood combustion and traffic emissions (Szidat et al., 2009). Although traffic is expected to be more or less uniform over the year, wood combustion is mainly confined to the heating season. In the previous Particle Project 2011-2013, biomass combustion was found to contribute to ambient $PM_{2.5}$ in urban background by 1.5 µg/m³ during the heating season and only 0.3 µg/m³ in addition to this. The average EC concentration measured in this project includes an almost full heating season. By the time a full year of data is available, the EC increment in urban background is expected to be somewhat smaller.

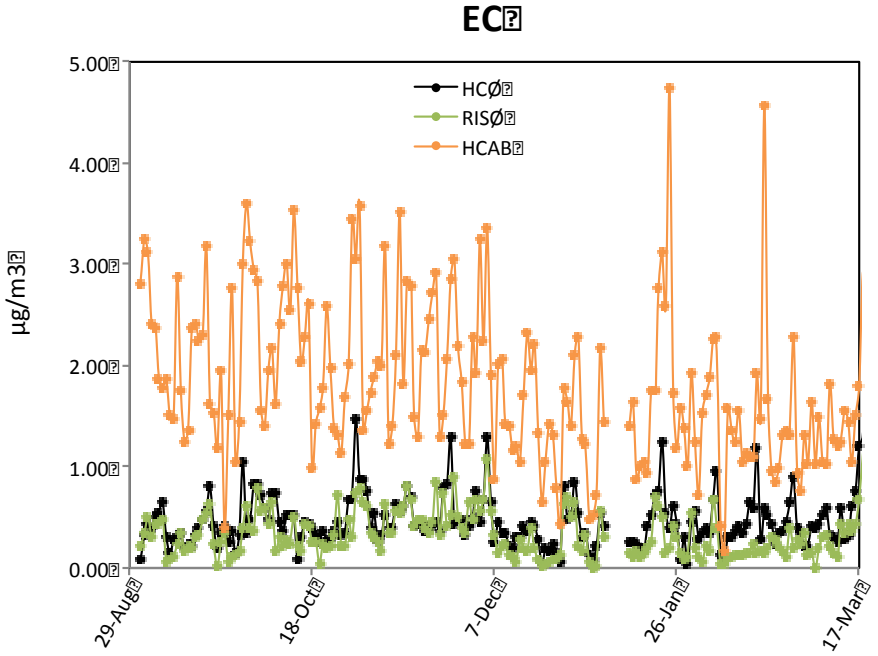

Figure 1. Ambient concentrations of Elemental Carbon (EC) in urban background (HCØ), rural background (Risø) and urban kerbside (HCAB) from September 2014 - March 2015.

Figure 1 illustrates the strong traffic source of EC, which prevails at urban kerbside, where the EC share of TC is 40%. On the other hand, rural background and urban background EC covariate, though urban background concentrations are generally higher, in particular during successive days in December and February/March (Figure 1). Zooming in on the winter months in Figure 1 reveals days with similar EC concentrations at both background sites, and successive days where urban background is 2-3 times higher than rural background, e.g. 9-21 February (Figure 2). According to DMI, this is taking place simultaneously with a change in wind direction from West to East and an associated temperature decrease to sub-zero Celcius degrees, which could enhance the daily use of wood stoves.

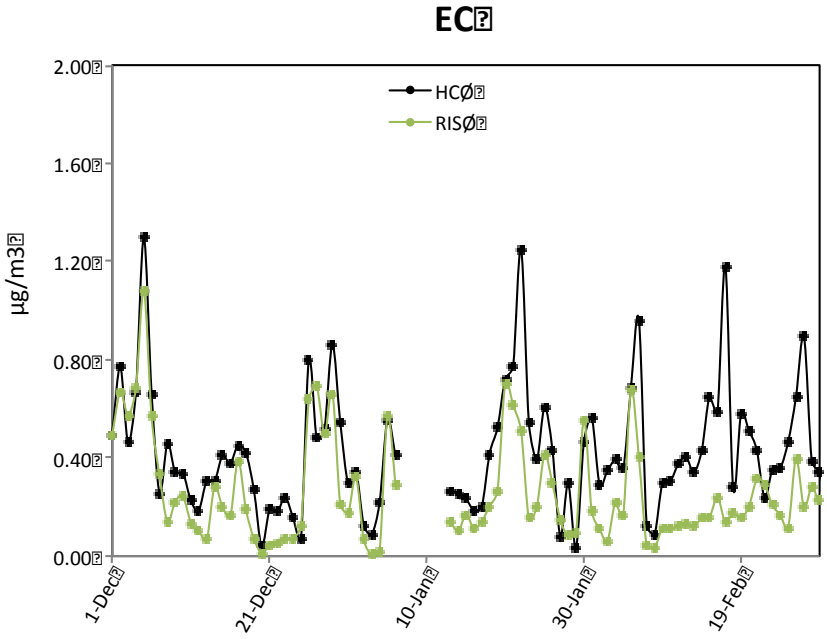

Figure 2. Ambient concentrations of Elemental Carbon (EC) in urban background (HCØ), and rural background (Risø) from December 2014 - February 2015

Evidently, the urban background concentration of EC is higher than observed in rural background - even if the concentrations at the two background sites are similar during the remaining 5 months of the calendar year.

Sources of urban EC

The sources of urban air pollution are partly reflected in concentrations of air quality parameters between kerbside and background sites. Nitrogen oxides, NO_X, of which traffic is a major source are far more abundant at the kerbside station HCAB compared to the background stations.

NO_X ratio (rural background : urban background : kerbside) = 1 : 2 : 13

EC ratio (rural background : urban background : kerbside) = 1 : 1.5 : 5

Traffic, in particular diesel fuelled vehicles, is also a significant source of EC. However, wood combustion is a major source of EC, which is typically 5-20 % of the particle mass originating from wood stoves. The differences in EC ratios between kerbside and background are therefore smaller than for NO_X, since wood stoves are well distributed over the country.

Sources of urban EC will be evaluated in the main report based on a literature study and a source apportionment based on EC, OC, and elements and ion data from the *Danish Air Quality Monitoring Program* 2014 - 2016.

TEOM measurements

Within the particle project 2014–2016, $PM_{2.5}$ and PM_{10} were measured using TEOM (Tapered Element Oscillating Microbalance). The TEOM instrument has a time resolution of ½ hour. Based on the measurement method, the sample is heated to 50 degree Celsius implying that some of

the volatile mass collected on the filter in the sensor unit may evaporate (Nøjgaard, et al., 2015). Thus, it has to be considered that the mass reported by TEOM is lower than measured with the reference method (Nøjgaard, et al., 2015).

$PM_{2.5}$ and PM_{10} were measured at the regional background station RISO and the urban Kerbside station HCAB. In Table 3 the data coverages are summarized for 2014.

Table 3. Data coverages for TEOM-$PM_{2.5}$ and TEOM-PM_{10} measurements at regional background (RISO) and urban kerbside (HCAB) in 2014.

	RISO	HCAB
TEOM-$PM_{2.5}$	65 %	58 %
TEOM-PM_{10}	56 %	69 %

Daily averages of the measured parameters are shown in Figure 3 and Figure 4. At RISO, some problems with the instrumentation explain the relatively low data coverage. At HCAB, both instruments were sent to service including calibration in the end of 2014.

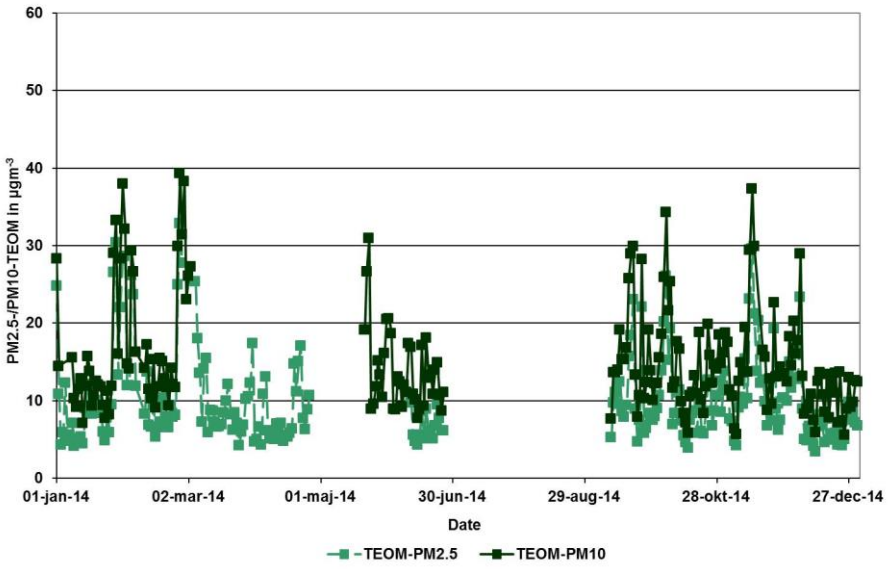

Figure 3. Time series of TEOM-$PM_{2.5}$ and TEOM-PM_{10} daily averages at regional background (RISO) in 2014.

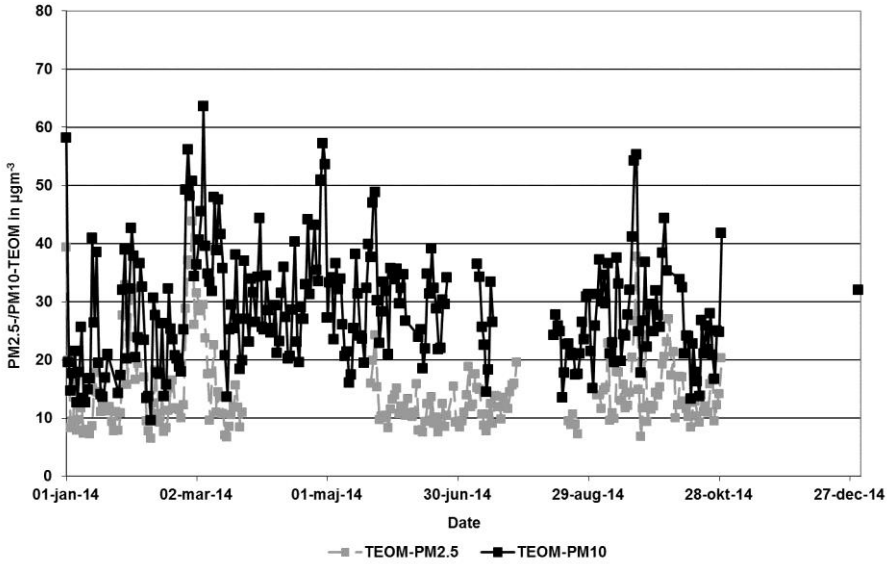

Figure 4. Time series of TEOM-$PM_{2.5}$ and TEOM-PM_{10} daily averages at urban kerbside (HCAB) in 2014.

As expected, the mass concentrations of TEOM-PM_{10} at RISO and HCAB are higher compared to TEOM-$PM_{2.5}$ of the corresponding station.

At RISO, TEOM-$PM_{2.5}$ and TEOM-PM_{10} is expected to be composed to a very large extent by aerosols that originate from long-range transported air masses. Aerosols are composed by a mixture of inorganic and organic matter and to a lower extent by EC. Depending on season, also local agricultural activities may contribute directly to TEOM-$PM_{2.5}$ and TEOM-PM_{10} in addition to regional emissions contributing with e.g. secondary organic aerosol (SOA) to the regional background at RISO (Nøjgaard et al., 2013).

TEOM-$PM_{2.5}$ and TEOM-PM_{10} averaged 10.1 µg/m³ and 15.2 µg/m³, respectively, at RISO in 2014. In comparison, the 2011-2013 average concentration during the last particle project period for TEOM-$PM_{2.5}$ was 8.4 µg/m³ and for TEOM-PM_{10} it was 12.9 µg/m³ at RISO (Nøjgaard et al., 2015). This means that for both size ranges, a slight increase in particulate mass is observed in 2014 compared with the average value of the previous particle project period from 2011 to 2013.

Exhaust and non-exhaust traffic related emissions influence TEOM-PM2.5 at HCAB in addition to long-range transported aerosols as observed at the regional background RISO. TEOM-PM_{10} at the urban Kerbside station HCAB has large contributions from traffic which are not related to exhaust emissions, but rather originate from break dust, road dust and road salt during the winter period labelled as non-exhaust emissions (Nøjgaard et al., 2015).

TEOM-$PM_{2.5}$ averaged 14.3 µg/m³ at HCAB in 2014, which is slightly higher compared with the 2011-2013 average of 12.9 µg/m³ observed during the previous particle project period. However, TEOM-PM_{10} decreased to about 28.5 µg/m³ in 2014 compared to the 2011-2013 average of 30.0 µg/m³.

In general, TEOM-PM_{25} and TEOM-PM_{10} values show a slight increase in 2014 compared to the average values during the previous particle project period from 2011 to 2013 except for TEOM-PM_{10} at the urban kerbside station HCAB where a slight decrease is observed.

Particle number size distribution measurements

Particle number size distributions were measured with a time resolution of ½ hour at RISO, HCOE and HCAB using a DMPS system stepping the size regime between 6 and 700 nm. In Table 4 the data coverages are summarized for 2014.

Table 3. Data coverages for the DMPS measurements at rural background (RISO), urban background (HCOE) and urban kerbside (HCAB) in 2014.

	RISO	HCOE	HCAB
DMPS	84 %	73 %	84 %

Yearly averages of the particle number size distributions at the three measurement stations for 2014 are shown in Figure 5.

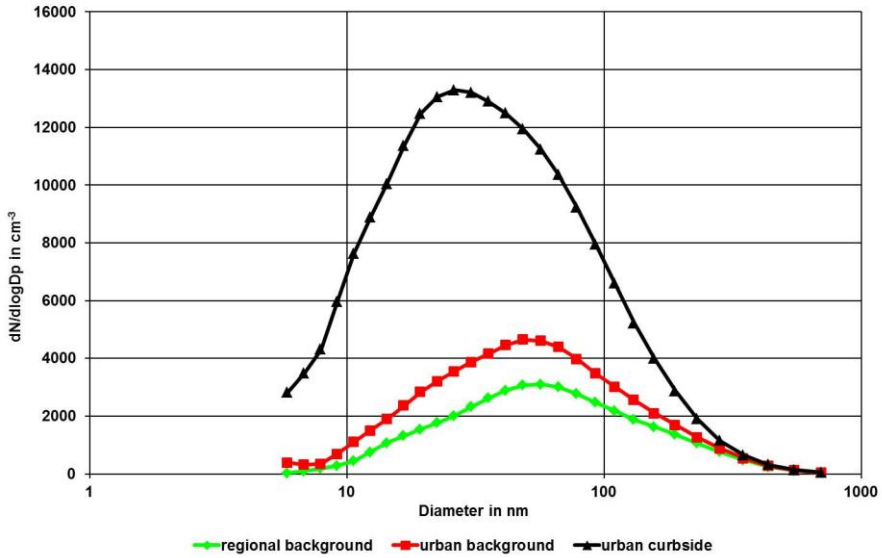

Figure 5. Yearly average particle number size distributions at regional background (RISO), urban background (HCOE) and urban kerbside (HCAB) in 2014.

In general, the total particle number concentrations increase when the local impact of urban emissions increases. The yearly average total number concentrations were 2960 cm^{-3}, 4510 cm^{-3}, and 13960 cm^{-3} in 2014 compared to average values of 3080 cm^{-3}, 4980 cm^{-3} and 15160 cm^{-3} in the previous particle project period from 2011 – 2013 at RISO, HCOE, and HCAB, respectively. Hence, the particle number is notably lower in 2014 at the urban background station HCOE and the urban kerbside station HCAB compared to the previous project period.

The measured mean diameter of the particle number size distributions is about 50-70 nm at RISO, 40-60 nm at HCOE, and 20-40 nm at HCAB as observed in the previous project period (Nøjgaard et al., 2015). The small mean diameters at the urban kerbside station are due to the presence of ultrafine particles that originate from vehicle exhaust emissions at HCAB.

For a further analysis, the particle number concentrations were determined in specific size regimes, namely particles with diameters of Dp_{F1} = 6–40, Dp_{F2} = 40–110, and Dp_{F3} = 110–700 nm at all three stations. The results are presented in Figure 6.

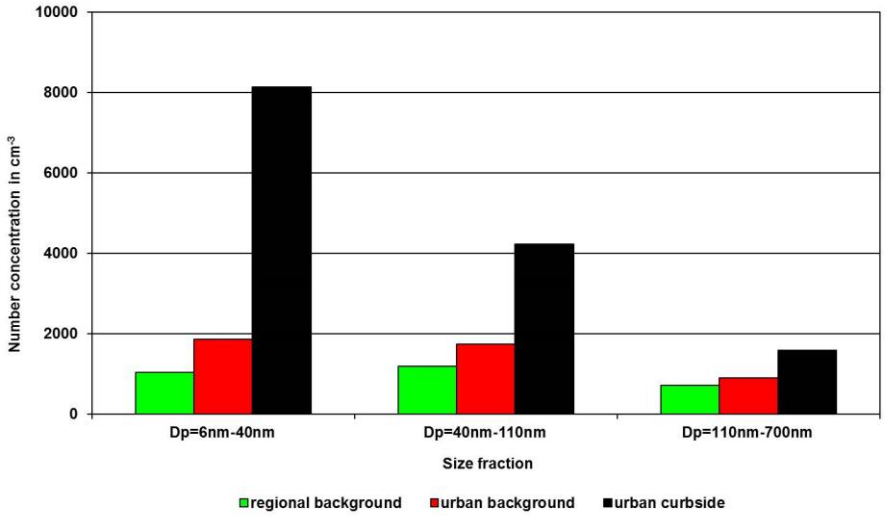

Figure 6. Yearly average particle number concentrations in specific size regimes Dp_{F1} = 6–40 nm, Dp_{F2} = 40–110 nm, and Dp_{F3} = 110–700 nm at regional background (RISO), urban background (HCOE), and urban kerbside (HCAB) in 2014.

In all three size regimes, it is shown that particle number concentrations are elevated for the stations where the impact of urban emissions is high compared to those stations where this impact is lower. Thus, an increasing trend in particle number is observed from RISO to HCOE and HCAB for all size regimes.

The number concentrations of Dp_{F1} = 6–40 nm particles has an average value of about 8140 cm^{-3} in 2014 at the urban kerbside station HCAB compared to 8980 cm^{-3} during the previous particle project period from 2011 to 2013. The corresponding value observed at the urban background station HCOE is 1860 cm^{-3} in 2014 compared to 2170 cm^{-3} for the previous project period and this size regime. A notable decrease in particle number was also observed for Dp_{F2} = 40–110 nm particles at HCAB and HCOE, when comparing 2014 with 2011-2013 average values.

References

Massling, A., Nøjgaard, J. K., Ellermann, T., Ketzel, M., Nordstrøm, C. (2011) Particle project report 2008 – 2010: Particulate contribution from traffic in Copenhagen, NERI Technical Report No. 837, 62 p.

Nøjgaard, J. K., Massling, A., Ellermann, T. (2013) Status for Partikel-projektet 2011 – 2013, DCE Technical Report, 10 p.

Nøjgaard, J. K., Massling, A., Christensen, J. H., Nordstrøm, C., & Ellermann, T. 2015. The Particle Project 2011-2013. Aarhus University, DCE – Danish Centre for Environment and Energy, 55 pp. Scientific Report from DCE – Danish Centre for Environment and Energy No. 156 http://dce2.au.dk/pub/SR156.pdf

Szidat, S., Ruff, M., Perron, N., Wacker, L., Synal, H.A., Hallquist, M., Shannigrahi, A.S., Yttri, K.E., Dye, C., Simpson, D., 2009. Fossil and non-fossil sources of organic carbon (OC) and elemental carbon (EC) in Goteborg, Sweden. Atmospheric Chemistry and Physics 9, 1521–1535

Appendix A: Estimation of Organic Carbon (OC*) in urban background

In the *Danish Air Quality Monitoring Programme,* OC is monitored in rural background and urban kerbside with a time resolution of 1 day. Quantification of OC and EC are based on tandem filter sampling by use of Low Volume Samplers (LVS). Samples are collected on two stacked filters in order to correct for positive artifacts, i.e. adsorption of Volatile Organic Compounds (VOC) on the filter material. These species add to the filter mass, but are not particulate matter as such. These species distribute themselves between the gas phase and particle phase. However, after some hours of sampling, the amount of VOC on the first and the second filter are assumed to be similar: continuously new VOC adsorp and desorp from each filter. Following analysis of both filters, OC on the second filter is subtracted from the first filter to yield the artifact corrected OC mass on the first filter. In reality, evaporation of VOC from filters also depends on the composition of the gaseous matrix and may not necessarily be identical from both filters. Still, the tandem filter approach is a simple way of correcting positive artifacts, though it doubles the number of analyses and thus increases the cost of analysis.

The Particle Project 2014 - 2016 focuses on sources to Elemental Carbon (EC), and hence tandem filter sampling and analysis of OC is not included. However, if the VOC in urban background and rural background is assumed to be similar, the positive artifact formation should be similar in these two environments. One could argue that ambient concentrations of anthropogenic VOC is higher in the urban background. Conversely, the concentration of biogenic VOC could be higher in rural background. In conclusion, OC* on HCØ is an estimate and should be treated as such. A validation of this approach is scheduled for 2015.