THE PARTICLE PROJECT 2014-2016

Scientific Report from DCE – Danish Centre for Environment and Energy No. 233 2017

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Data sheet

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Abstract: The Particle Project 2014-2016 continues the record of particle mass and number measurements on urban and rural locations. Monitoring of Elemental Carbon (EC) has been extended from the rural site RISØ and the urban curbside station HCAB to furthermore include the urban background site HCØ and the suburban site HVID. In addition to traffic, wood combustion is known to be a major source of EC. The Particle Project 2014 - 2016 demonstrates how EC can be used as a marker of wood combustion to quantitatively evaluate primary wood combustion particle concentrations since autumn 2014 at HCØ and RISØ, and from October 2015 at HVID.

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Contents

Abbreviations/definitions

AMS	Aerosol Mass Spectrometry
BB	Biomass burning, which includes residential wood burning
BC	Black carbon
DMPS	Differential Mobility Particle Sizer
EC	Elemental carbon, which is comparable to black carbon (BC) and soot
EMEP	European Monitoring and Evaluation Programme
Degree days	Degree days are provided by the Technological Institute (in Danish: Teknologisk Institut) and shows the differences between actual daily temperature and 17 ˚C added up to monthly numbers.
HCAB	Urban busy street measurement site in Copenhagen
HCØ	Urban background measurement site at H.C. Ørsted Instituttet in Copenhagen
HVID	Suburban measurement site at Fjelstedvej in Hvidovre
OC	Organic carbon, only the mass of carbon it self
OM	Organic matter equal to the total mass of the compounds that contain OC
PM	Particulate in ambient air
$PM_{2.5}$	Particles less than 2.5 micrometers in diameter, i.e. fine particles
PBBA	Primary Biomass Burning Aerosols. Primary particles from biomass combustion in the $PM_{2.5}$ size fraction. SOA from BB is not included. The applied methods cannot differentiate different sources of BB, e.g. wildfires, bonfires and prescribed burning of agricultural waste from residential wood combustion, although the latter will certainly dominate in the colder season
PM_{10}	Particles less than 10 micrometers in diameter
RISØ	Rural measurement site at Risø, North of Roskilde
RWC	Residential Wood Combustion
SIA	Secondary Inorganic Aerosols comprising nitrates and sulfates of ammonium
SOA	Secondary Organic Aerosols, i.e. particulate species formed during atmospheric oxidation of VOCs, including VOCs from BB
TC	Total carbon = OC + EC
TJ	1 TJ = 10^{12} J
TEOM	Tapered Element Oscillating Microbalance
VOC	Volatile Organic Compounds

Dansk Resume

Partikelprojektet 2014-2016 omhandler dataanalyse af koncentrationen af luftbårne partikler mindre end 2,5 µm ($PM_{2.5}$) samt mindre end 10 µm (PM_{10}) på vores landlige målestation nord for Roskilde (RISØ) samt gadestationen (HCAB) i København målt med teknikken TEOM. Endvidere analyseres størrelsesfordelingen af partikler, antallet af partikeler samt sod målt som elementært kulstof (EC) på RISØ, HCØ, HCAB samt målestationen HVID i forstaden Hvidovre. Herudover indgår brænderøgspartikler som særligt tema, hvor koncentrationen af primære brænderøgspartikler (PBBA) er beregnet i perioden 2014-2016 på baggrund af EC.

Det seneste Partikelprojektrapport omhandlende perioden 2011-2013, mens det nuværende dækker perioden 2014-2016. Imellem disse to perioder er $PM_{2,5}$ målt med TEOM på RISØ blot aftaget fra 8,4 µg/m^3 til 8,2 µg/m^3. På HCAB er der derimod konstateret et fald fra 12,9 µg/m^3 til 11,9 µg/m^3 over samme periode. PM_{10} på HCØ steg fra 12,9 to 13,5 µg/m^3 målt med TEOM, mens der på HCAB blev observeret et mindre fald fra 30,0 µg/m^3 til 29,6 µg/m^3. PM_{10} er aftaget i koncentration siden 2001, hvor det første Partikelprojekt blev påbegyndt. Faldet i PM_{10} er dog mest tydeligt på HCAB. Alle målestationer har vist faldende $PM_{2,5}$, hvilket afspejler den generelle udvikling i Europa samt vigtigheden af langtransporteret luftforurening.

Regionale og langtransporterede partikler antages ligeledes at bidrage i overvejende grad til antallet af partikler og mest tydeligt på den landlige målestation RISØ, hvor afstanden til lokale kilder er stor. Samme partikler vil bidrage væsentligt på målestationerne HVID, HCØ samt HCAB. Dog er den relative betydning af langtransporterede partikler begrænset på HCAB på grund af det store bidrag fra trafikken i gaden. Partiklerne på RISØ, HVID og HCØ udviser næsten samme størrelsesfordeling med flest partikler i området 40-60 nanometer (nm). På HCAB derimod, ses også partikler omkring 20 nm, der stammer fra den lokale trafik. I perioden fra det første Partikelprojekt til 2016 har antallet af partikler været konstant aftagende, mest tydeligt for HCAB, men målbart for alle stationer. Således ses et fald i perioden for de mindste partikler (6-40 nm) fra 20.320 cm^{-3} – 7.820 cm^{-3} på HCAB samt et tilsvarende fald på HCØ fra 4.220 cm^{-3} til 1.660 cm^{-3} svarende til at de nuværende koncentrationer udgør hhv. 38% og 39%.

Monitorering af EC i bybaggrund og forstadskommunen Hvidovre påbegyndtes i hhv. september 2014 og oktober 2015. EC udgjorde 0,22 µg/m^3 på RISØ mod 0,37 µg/m^3 på HCØ i 2015. I 2016 blev der målt 0,26 µg/m^3 på RISØ, 0,33 µg/m^3 på HCØ og 0,44 µg/m^3 på HVID. Forøgelsen i bybaggrund udgjorde således gennemsnitligt 0,11 µg/m^3 baseret på toårsperioden 2015-2016 svarende til en bybaggrund på 0,33 µg/m^3. Forøgelsen var større på hverdage (0,12 µg/m^3) end weekender (0,08 µg/m^3), hvilket afspejler trafikkens bidrag til EC. Hvor trafikbidraget antages at være konstant over året, forholder det sig anderledes med brændeovne og anden afbrænding af biomasse. Et gentagent årligt mønster blev observeret med høje EC-koncentrationer om vinteren og lave koncentrationer om sommeren, hvilket formodes hovedsageligt at kunne tilskrives brændeovne. Dog var der ingen tydelig korrelation med temperatur eller graddage for dette foreløbige datasæt.

For at komme årstidsvariationen af EC nærmere blev flere af de kemiske stoffer, som måles i overvågningsprogrammet NOVANA, testet som markører for PBBA (Primary Biomass Burning Aerosols). EC blev fundet anvendelig efter fratrækning af trafikbidraget og multiplikation med en faktor, der beskriver forholdet mellem PBBA og EC. Trafikbidraget blev således fundet til 0,12 µg/m^3 for RISØ, og dette resultat blev valideret ved brug af to uafhængige metoder. Ved hjælp af denne teknik kunne daglige koncentrationer af PBBA beregnes for RISØ og HCØ (2014-2016) samt HVID (2016). Metoden blev valideret overfor PBBA bestemt ved en etableret og veldokumenteret markør i form af levoglucosan på RISØ (R^2 = 0,67) og HCØ (R^2 = 0,68). Følsomheden blev valideret ved at modellere oprindelsesstedet af luftmasser, som bidrog med PBBA højere end 3 µg/m^3 i udvalgte perioder. Dette viste en overvægt med oprindelse i det nordlige og østlige Europa samt de Baltiske lande, hvilket kan give falsk høje PBBA-koncentrationer forårsaget af langtransporteret EC fra disse egne. Ligeledes kan skovbrænde bidrage til PBBA i sommermånederne på den nordlige halvkugle. I perioden 2014-2016 var PBBA i bybaggrund (1,1 µg/m^3) højere end RISØ (0,9 µg/m^3) svarende til, at PBBA tegner sig for 48% af EC på HCØ mod 54% af EC på RISØ. Dette kan betyde, at befolkningen eksponeres for en 23% højere koncentrationer af primære brænderøgspartikler sammenlignet med folk i landlige miljøer. Her refererer "primære" partikler til den andel af brænderøgspartiklerne, som direkte udledes som partikler, i modsætningen til sekundære partikler, der udledes som flygtige stoffer eller gasser og først senere omdannes til partikler i atmosfæren. Sidstnævnte gruppe bestemmes ikke i dette projekt. I 2016 udgjorde PBBA således 0,83 µg/m^3 på RISØ, 0,93 µg/m^3 på HCØ mod 1,68 µg/m^3 på HVID. Heraf kan befolkningen i forstæderne eksponeres for dobbelt så høje brænderøgskoncentrationer som folk i landlige miljøer. De absolutte brænderøgskoncentrationer svarer dog til, hvad der tidligere er målt i danske undersøgelser (0,5-2 µg/m^3).

Metoden har muliggjort beregning af døgnmidlede PBBA-koncentrationer tilbage til 2010 for RISØ, efteråret 2014 for HCØ og efteråret 2015 for HVID, hvor EC-måledata er tilgængelig. Metoden har givet indsigt i sæson- og dag til dag-variation, men også at PBBA forekommer udenfor fyringssæsonen i foråret og efteråret, inklusive om sommeren. I Partikelprojektet er endvidere benyttet en metode til online-måling af bl.a. brænderøgspartikler. Skønt mere tidskrævende muliggjorde anvendelsen af aerosolmassespektrometri (AMS) måling af brænderøgspartikler med 20 min tidsopløsning. AMS viste over en kortere tidsserie forbigående høje koncentrationer af PBBA på alle ugedage og tidspunkter. Dette kan bruges i fremtidige projekter til evaluering bl.a. sundhedsaspekter af brænderøg.

Abstract

The Particle Project 2014-2016 covers data analysis of particle mass concentrations smaller than 2.5 µm ($PM_{2.5}$) and particles smaller than 10 µm (PM_{10}) at the rural site RISØ and curbside station HCAB using TEOM. Particle size distributions are furthermore analyzed at RISØ, HCØ, HCAB and the suburban site HVID. Elemental Carbon (EC) has been monitored at RISØ, HCØ and HVID and is a measure of airborne soot. As special issue, long time series of Primary Biomass Burning Aerosols (PBBA) mainly originating from residential wood combustion has been calculated for RISØ, HCØ and HVID from September 2014 to end of 2016.

$PM_{2.5}$ was virtually unchanged from 2011-2013 (8.4 µg/m^3) to 2014-2016 (8.2 µg/m^3) at RISØ. At HCAB however, $PM_{2.5}$ decreased from 12.9 µg/m^3 to 11.9 µg/m^3 during the same period. PM_{10} increased from 12.9 to 13.5 µg/m^3 at HCØ and from 30.0 µg/m^3 to 29.6 µg/m^3 at HCAB during the same period. Since the first Particle Project in 2001 a slight decrease in ambient concentrations has been observed for PM_{10} (most evident at HCAB) and $PM_{2.5}$ at all stations reflecting the general decreasing trend of $PM_{2.5}$ in Europe and furthermore the importance of long-range transport.

Regional and long-range transported aerosols were expected to contribute to a large extent to the particle number in the sub micrometer size range, most evident at the rural site RISØ. Consequently, long-range transported aerosols also contributed to HVID, HCØ and HCAB, but the relative contribution of these particles is lower at HVID and HCØ and especially much lower at HCAB. The processed aerosol at the regional, rural and urban background sites resulted in a nearly mono modal particle number size distribution with mean diameters of about 40-60 nm at RISØ, HVID and HCØ. As a general difference the particle number size distributions at HCAB appears somewhat bimodal as an additional peak can be observed at around 20 nm from vehicle exhaust emissions. As a general finding it has been observed that the total sub micrometer number concentration has been constantly decreased throughout the whole measurement period from 2002 to 2016, most evident at HCAB but noticeable for all measurement stations. The particle number concentration has decreased from 20,320 cm^{-3} during 2002-2004 to 7,820 cm^{-3} during 2014-2016 for the smallest particle sizes (6-40 nm). At HCØ the corresponding decrease was from 4,220 cm^{-3} 1,660 cm^{-3}, that is to 39% and 38% of its initial values.

Measurements of EC in urban background was initiated by September 2014. EC averaged 0.22 µg/m^3 at RISØ and 0.37 µg/m^3 at HCØ in 2015, and 0.26 µg/m^3 at RISØ, 0.33 µg/m^3 at HCØ and 0.44 µg/m^3 at HVID in 2016. Based on 2 years of data the urban increment was 0.11 µg/m^3 equal to an ambient concentration of 0.33 µg/m^3 at HCØ. The weekday average increment (0.12 µg/m^3) was higher than the weekend average increment (0.08 µg/m^3). Furthermore, a repeating annual pattern with higher absolute concentrations during winter and lower concentrations during summer was observed at all three stations. However, no apparent correlations between EC increment and ambient temperature or degree days were observed for the 2-year dataset.

Several chemical species obtained from the *Danish Air Quality Monitoring Programme*, including EC, were tested as markers for residential wood combustion. Following subtraction of non-biomass combustion sources, including traffic as the largest source, residual EC was converted to PBBA ($PM_{2.5}$) by a factor obtained from exposure studies on wood stove emissions. Traffic and other sources equaled 0.12 µg/m^3 EC at RISØ using two independent methods. Following, the daily concentrations of PBBA were calculated for RISØ and HCØ and validated against an established and well documented marker species (levoglucosan) for PBBA. PBBA derived from EC and levoglucosan correlated well at the rural site (R^2 = 0.67) as well as urban background (R^2 = 0.68). In order to test the sensitivity of the method, back trajectory analysis were performed for days, where PBBA exceeded 3 µg/m^3 in selected periods. Back trajectories with origin in Northern/Eastern Europe and the Baltic countries were overrepresented, which could lead to false high PBBA concentrations from long-range transport of EC. Furthermore, forest fires may contribute to part of the PBBA concentration in the summer months.

By use of this method daily PBBA concentrations were calculated for 2014 - 2016. Urban background PBBA averaged 1.1 µg/m^3 equal to 48% of ambient EC, compared to the rural site RISØ, where PBBA averaged 0.9 µg/m^3, which explained 54% of ambient EC. Implications are that the urban population could be exposed to 23% higher concentrations of primary particles from biomass burning than the rural population, excluding the populations living at hot spots close to sources of biomass burning. In this context, "primary" refers to particles directly emitted from wood stoves, unlike secondary particles formed in the atmosphere from volatile species or gasses. The latter is not evaluated in this report. During 2016, PBBA averaged 0.8 µg/m^3 at RISØ, 0.9 at HCØ and 1.7 µg/m^3 at HVID. Thus, the suburban population could be exposed to twice the PBBA concentration, the rural population is exposed to. The results are within the range of previous annual concentration estimates of 0.5 - 2 µg/m^3 PBBA.

The daily time resolution of PBBA illustrates the large variation from season to season and day to day, but also that PBBA not only occurs during the coldest months, but also in the spring and autumn. Even during the summer PBBA prevails, however mostly in lower concentrations. By use of a second, yet more time consuming technique using Aerosol Mass Spectrometry (AMS), a time resolution as low as of 20 min was achieved online. This technique revealed transient peak concentrations of PBBA on all weekdays at all hours. This observation is of relevance for e.g. health aspects of Wood Stove emissions and is a potential topic in future research projects.

1 Introduction

An increasing part of the population migrates to larger cities. Since 1990, the increase in population in Copenhagen has exceeded the National average, which is also true for Greater Copenhagen since 2010 (Danmarks Statistik, 2016). However, air quality and thus human exposure to pollution in larger cities is not similar to that of rural background. A denser population means more sources of incomplete combustion products from industry, residential heating and traffic, e.g. nitrogen oxides and soot, though improved technology has greatly reduced individual emissions over time. While some of the air pollutants are monitored on a routine basis in urban background and on urban curbside, more knowledge is needed on the spatial distribution of the pollutants and the increment from rural background to urban background. At present, Elemental Carbon (EC) as a measure of "soot" (see section 3) is monitored in the *Danish Air Quality Monitoring Programme* (Ellermann et al., 2015). A cohort study 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 (Janssen et al, 2011), though EC may not necessarily be the hazardous species itself.

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; Nøjgaard et al., 2015a), in addition to those included in the National Monitoring program (Ellermann et al., 2016).

The preceding research projects have focused on the continuation of detailed measurements of the microphysical properties of particles, including particle mass, volume, number and size distribution, mainly in the urban environment. These parameters are relevant for associated health effects and are conducted in high time resolution: typical 30 minute averages, which enables establishment of 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 projects, it was concluded, that a large part of the particulate air pollution in Copenhagen especially at street level, was due to traffic emissions. The Particle projects 2008-2010 (Massling et al., 2011) and 2011-2013 (Nøjgaard et al., 2015a) provided detailed chemistry of ambient aerosols, which was used for source apportionment in the rural and urban environment.

The main objectives of the present Particle Project 2014-2016 were (1) the continuation of the time series of PM and ultrafine particles in rural background, urban background and urban curbside by use of TEOM and DMPS particle size distribution measurements; and (2) to provide the scientific knowledge from existing monitoring data about residential wood combustion, which is among the main sources to urban EC in $PM_{2.5}$. The measurements have mainly been conducted at the H.C. Ørsted Institute (HCØ, urban background), and at Risø north of Roskilde (RISØ, rural site). The measurements at Risø are assumed to be representative of the regional background onto which sources in the urban environment are

superimposed to yield the urban background. That is, the difference between HCØ and RISØ for any given species should equal the sum of urban sources. The measurement stations have been selected based on these characteristics. Thus, the increment in EC at HCØ is used as a measure of urban sources of which we will focus on PBBA from residential wood combustion.

2 Particle physics and Elemental Carbon

2.1 TEOM measurements

The $PM_{2.5}$ and PM_{10} measurements of particle mass were carried out at the urban curbside station H.C. Andersens Boulevard (HCAB) and at the regional background station on the Risø peninsula (RISØ) throughout the project period from 2014 to 2016. A TEOM instrument (Tapered Element Oscillating Microbalance) was used to carry out these measurements on a half-hourly basis. The TEOM consists of a filter-connected oscillating unit, which is placed in a closet that is temperature-conditioned to 50 degree Celsius. The change in frequency of this oscillating unit can be related to a change of mass on the filter. From this information and the knowledge of the volume flow through the filter a mass concentration is determined.

Due to the relatively high temperature in the sensor unit, it cannot be guaranteed that the aerosol sample is stable. This means that losses from the filter can be induced by evaporation. It is therefore expected that mass concentrations originating from the TEOM are somewhat lower compared to measurements originating from reference methods (Nøjgaard, et al., 2015a). However the loss is highly dependent on the chemical composition of the sample and thus will also depend on location and season.

In Table 2.1 the data coverage of the TEOM measurements is summarized for the years 2014, 2015 and 2016:

Table 2.1. Data coverage of TEOM measurements for the years 2014-2016 at the regional background site RISØ and the urban curbside site HCAB.

	Regional background			Urban curbside		
	2014	**2015**	**2016**	**2014**	**2015**	**2016**
TEOM-$PM_{2.5}$	65 %	94 %	91 %	58 %	86 %	88 %
TEOM-PM_{10}	56 %	79 %	90 %	69 %	93 %	92 %

The relatively low data coverage in the year 2014 at the regional background station is mostly due to service of the TEOM instruments. This was carried out by the Swedish distributor, who delivers the kind of instrument. Additionally, instrumental and data comparisons were carried out in order to check the instruments for malfunction.

2.1.1 TEOM measurements - Daily averages

Daily averages of the measured TEOM-$PM_{2.5}$ and TEOM-PM_{10} mass concentrations are shown in Figure 2.1 for the regional background site (RISØ). The data series for the measurement period from 2014 to 2016 is displayed.

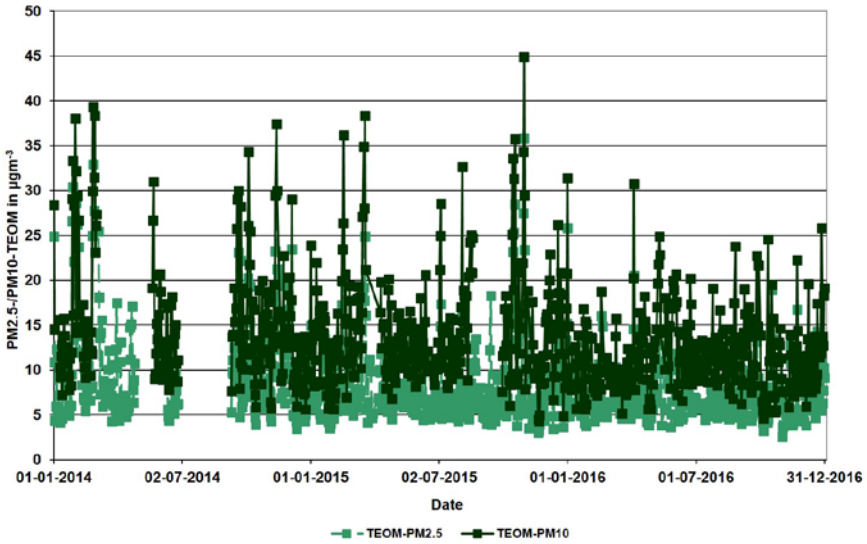


Figure 2.1. Time series of TEOM-$PM_{2.5}$ and TEOM-PM_{10} daily averages at the regional background station (RISØ) in 2014, 2015 and 2016.

In general it was found that the mass concentrations of TEOM-PM_{10} at the regional background site are higher compared to TEOM-$PM_{2.5}$ at the corresponding site. At the regional background station, $PM_{2.5}$ as well as PM_{10} are highly influenced by atmospheric transport from other regional or even hemispheric sites. Contributions from the region nearby are typically very minor and can only have larger contributions during seasonal periods. E.g. the harvesting on the countryside can have a seasonal contribution mainly to PM_{10} for selected days in the year. However, some contribution to PM_{10} and $PM_{2.5}$ may also originate from non-exhaust emissions caused by traffic, as a major road is located in a distance of about 1 km from the site. Additionally, emissions from wood stoves can contribute especially to $PM_{2.5}$ values during periods with residential heating. A detailed analysis of wood stove emissions was conducted in a previous project (Nøjgaard et al., 2015a) and later in Section 4.

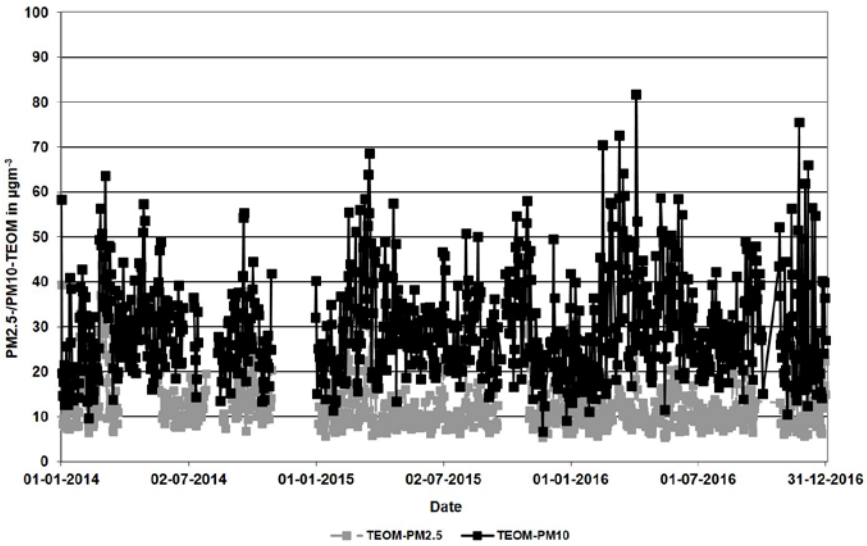


Figure 2.2. Time series of TEOM-$PM_{2.5}$ and TEOM-PM_{10} daily averages at the urban curbside station (HCAB) in 2014, 2015 and 2016.

Daily averages of the measured TEOM-$PM_{2.5}$ and TEOM-PM_{10} mass concentrations at the urban curbside site (HCAB) are shown in Figure 2.2 for the entire project period from 2014 – 2016.

From Figure 2.2 it can be concluded that mass concentrations related to TEOM-PM_{10} are much higher compared to TEOM-$PM_{2.5}$ for the urban curbside station at HCAB. This finding is not surprising as non-exhaust emissions like break dust, tire wear dust or resuspended dust from the road can highly contribute to TEOM-PM_{10} but only to a minor extent to TEOM-$PM_{2.5}$ (Nøjgaard et al., 2015b). Also, road salting does contribute to PM at the urban curbside site HCAB during the winter periods (Massling et al., 2011).

Both TEOM-$PM_{2.5}$ and TEOM-PM_{10} at HCAB are highly impacted by regional and hemispheric transport of particulate matter originating from Denmark and other countries. In general, the contribution from this source is expected to be as high as at the regional background site RISØ where these contributions are assumed to be the major contributor to the observed values. The regional background aerosol is expected to be composed of a mixture of inorganic and organic matter and to a lower extent by elemental carbon (Nøjgaard et al., 2013).

Comparing average values for the actual project period from 2014 to 2016 with the average values from the previous project period from 2011 to 2013, the following facts have to be stated. At the regional background site RISØ, TEOM-$PM_{2.5}$ concentrations averaged to about 8.2 $\mu g/m^3$ and about 8.4 $\mu g/m^3$ for the actual and previous project period, respectively. In comparison, TEOM-$PM_{2.5}$ concentrations at the urban curbside HCAB average to about 11.9 $\mu g/m^3$ and about 12.9 $\mu g/m^3$ for the actual and previous project period, respectively. Correspondingly, TEOM-PM_{10} concentrations measured at the regional background station RISØ averaged to about 13.5 $\mu g/m^3$ and about 12.9 $\mu g/m^3$ for the actual and previous project period. At the urban curbside, the measurements resulted in about 29.6 $\mu g/m^3$ and in about 30.0 $\mu g/m^3$ for TEOM-PM_{10} concentrations for the actual and previous project period, respectively.

2.1.2 TEOM measurements – Yearly trends

TEOM-$PM_{2.5}$ and TEOM-PM_{10} has been measured from 2001/2002 and ongoing at the different measurement sites in and around Copenhagen. For TEOM-$PM_{2.5}$ a data series is available for the entire time period at the regional background station RISØ and the urban curbside station HCAB. Measurements at the urban background station HCØ are only available up to 2010, where these measurements were closed down. In Figure 2.3 the time series of the annual averages of $PM_{2.5}$-TEOM are displayed between 2002 (HCAB) / 2003 (HCØ and RISØ) and 2016 for all three sites. Please note that the present regional background site at RISØ replaced the previous regional background site at Lille Valby (LVBY) in summer 2010.

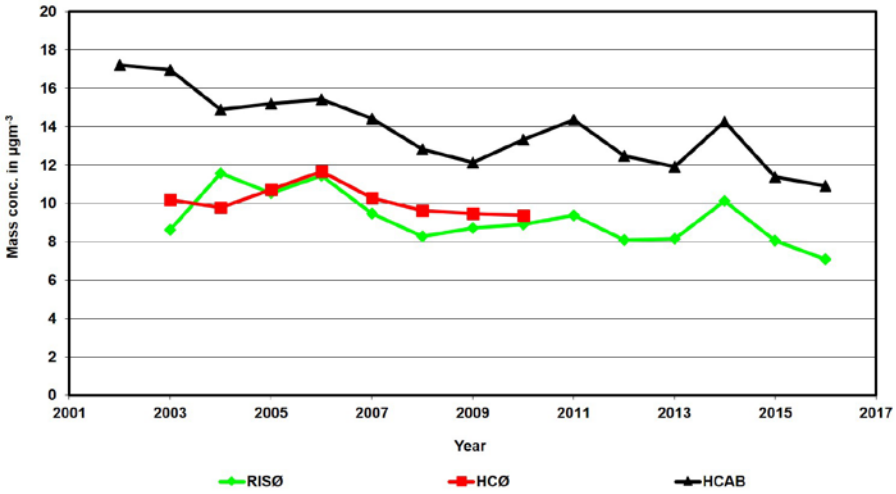


Figure 2.3. Yearly trend of TEOM-$PM_{2.5}$ at the regional background station RISØ, urban background station (HCØ) and urban curbside station (HCAB) measured from 2002 - 2016.

As a general finding a slight decrease of the annual averages of $PM_{2.5}$-TEOM is observed at all three stations, the regional background site RISØ, the urban background site HCØ, and the urban curbside site HCAB over the period from 2002 to 2016. This decrease is most evident at HCAB, which is surprising, as the number of cars evidently has increased over the last 15 years increasing the contribution of non-exhaust emissions. On the other hand, a large fraction in $PM_{2.5}$-TEOM is originated from exhaust emissions, which have been constantly decreased as new technologies (e.g. particle filters for after treatment) and regulations on fuel composition (banning of sulfur in the fossil fuels) have been Europe wide introduced.

Values for TEOM-$PM_{2.5}$ at the urban background station HCØ were only measured up to 2010 and appear to be very close to those measured at the regional background station LVBY. This fact gives evidence that urban sources only contribute little to $PM_{2.5}$ in the urban background and that most of this mass can be assigned to long-range transported air masses.

The general decreasing trend in $PM_{2.5}$ reflects the situation in Europe, where both precursors to particle formation and particle emissions are constantly decreasing. This fact leads to substantially lower ambient mass concentrations and thus resulting exposure levels for the public even at the urban and regional background sites (Nøjgaard et al., 2015a).

In Figure 2.4 the annual averages of TEOM-PM_{10} are displayed for the regional background site RISØ, the urban background site HCØ and the urban curbside site HCAB. For HCAB and HCØ the data series started in 2001 and 2002 and for RISØ the data series started in 2011. Measurements at HCØ were only carried out up to the year 2010.

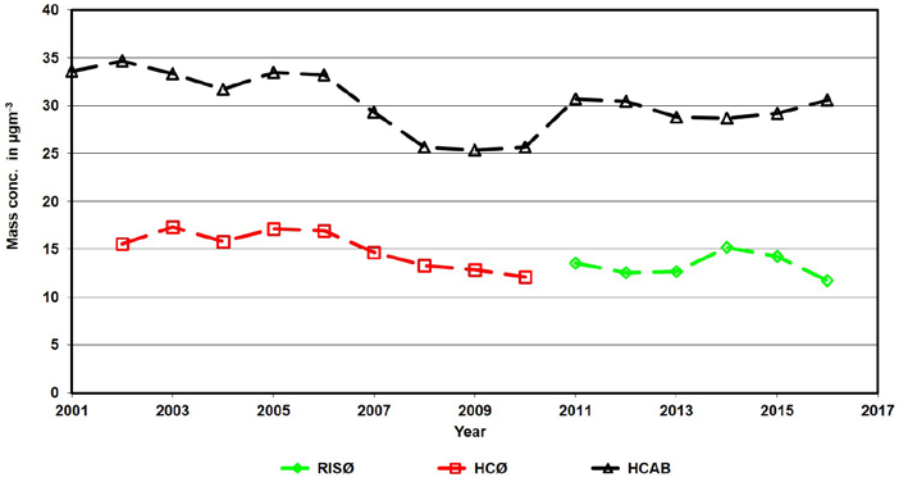


Figure 2.4. Yearly trend of TEOM-PM_{10} at the regional background station RISØ, urban background station HCØ and urban curbside station HCAB measured from 2001 – 2016.

For TEOM-PM_{10} a slight decrease in aerosol mass is observed at the urban curbside station HCAB when considering the whole measurement period from 2001 to 2016. From 2008 to 2010 the PM_{10} level is lower than the rest of the observations. This coincides with the asphalt pavement at HCAB has been renewed in 2008, which resulted in a significant decrease of particulate mass levels at the station for the upcoming years. This observation was also reported by Ellermann et al. (2010) who carried out SM200 particle mass measurements in combination with elemental analysis.

At the urban background station HCØ the decreasing trend is also noticeable, but measurements were only carried out up to 2010, which means that further trends cannot be evaluated. At the regional background station RISØ measurements of TEOM-PM_{10} were initiated in 2011 and thus a trend cannot be concluded while values seem to be more or less stable over the last five years.

The overall slightly decreasing trend in TEOM-PM_{10} can be partly explained by the argument mentioned above reflecting the situation in Europe where aerosol precursors and particle emissions have continuously decreased over the last one to two decades.

2.2 Particle number size distribution measurements

To measure the particle number size distribution in the sub micrometer size regime a DMPS instrument (Differential Mobility Particle Sizer) / SMPS instrument (Scanning Mobility Particle Sizer) was used within this project. The DMPS instrument measures the size distribution in the range from 6 to 700 nm in diameter. Measurements were carried out in and around Copenhagen at the regional background station RISØ, the urban background station HCØ and at the urban curbside station HCAB. The SMPS instrument measures the size distribution in the range from 10 to 480 nm in diameter. Measurements were carried out at the semi-urban background station in Hvidovre (HVID). Measurements in HVID were initiated the first time in autumn 2015. As previous projects do exist where these measurements were carried out at the various stations, some time

series are presented from the year 2002 and ongoing in some of the presented investigations. From the measurements, also the total particle number and the number observed in specific size regimes can be deducted.

Table 2.2 lists the data coverage of DMPS / SMPS measurements that was observed in the last three years from 2014 to 2016.

Table 2.2. Data coverage for the DMPS / SMPS measurements for the years 2014 to 2016 at the regional background site RISØ, the semi-urban background site HVID, the urban background site HCØ and the urban curbside site (HCAB).

	Regional background	Semi-urban background	Urban background	Urban curbside
2014	84%	-	73%	84%
2015	72%	23%	66%	65%
2016	77%	82%	40%	43%

The data of the particle number size distributions were obtained with a half hourly time resolution. In the following section the data will be discussed in detail.

2.3 Particle number size distribution – yearly means

In Figure 2.5, the yearly averaged particle number size distributions at the regional background station RISØ, the semi-urban background station HVID, the urban background station HCØ and the urban curbside station HCAB are displayed for the time period of the previous three years from 2014 to 2016. Please note that the present regional background site at RISØ replaced the previous regional background site at Lille Valby (LVBY) in summer 2010. As stated previously, measurements at HVID were initiated in autumn 2015.

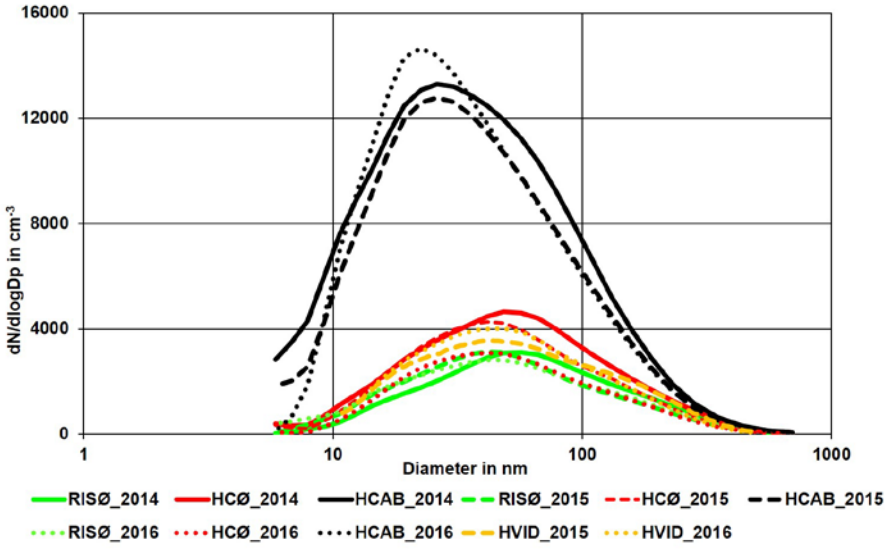


Figure 2.5. Yearly averaged particle number size distributions at regional background station RISØ, semi-urban background station HVID, urban background station HCØ and urban curbside station HCAB in 2014, 2015 and 2016.

The results illustrate that the particle number size distributions decrease with distance to major sources of aerosol particles. This explains that the largest numbers are observed at HCAB, where smaller particles especially particles smaller than 100 nm in diameter originate from traffic exhaust emissions of traffic activities as a major source. For larger particles, non-exhaust emissions as break ware, tire ware or resuspended dust from the road can have substantial contributions. At the urban background, these particles do occur, but dilution processes are resulting in much more lower numbers in the specific size ranges. Similarly, we do expect this effect at the semi-urban background while the dilution effect is here more progressed. For the regional background at RISØ one can clearly see that a decrease in the particle number size distribution is observed compared to the semi-urban background at HVID and the urban background at HCØ. Only for 2016 the particle number size distribution at HCØ and RISØ look very similar which most likely is due to the relatively low data coverage at HCØ having in mind that most of the displayed data originate from spring and autumn leaving out those periods as summer (nucleation induced by higher photooxidation capacity) and winter (accumulation by inversion periods) which appear with higher particle number values. At RISØ we expect regional and long-range transported aerosols to contribute to a large extent to the particle number in the sub micrometer size range. This means that particles observed at this station will simultaneously also contribute at HVID, HCØ and HCAB, but the relative contribution of these particles is lower at HVID and HCØ and especially much lower at HCAB.

The processed aerosol at the regional, semi-urban and urban background sites results in a nearly monomodal particle number size distribution with mean diameters of about 40 - 60 nm at RISØ, HVID and HCØ. As a general difference the particle number size distributions at HCAB appears somewhat bimodal as an additional peak can be observed at around 20 nm as also stated in a previous report (Nøjgaard et al., 2015). The large number of small particles at the urban curbside station is a result of the presence of ultrafine particles originating from vehicle exhaust emissions at HCAB. These particles are either directly emitted as unburned fuel particulates or they are freshly nucleated based on the emissions of volatile organic compounds.

For a more detailed analysis, the particle number concentrations at RISØ, HCØ and HCAB were determined in specific size regimes, in this case particles with diameters of Dp_{F1} = 6–40 nm, Dp_{F2} = 40–110 nm, and Dp_{F3} = 110–700 nm. The results of this grouping are presented in Figure 2.6 for the regional background site RISØ, the urban background site HCØ and the urban curbside site HCAB for the years 2014 to 2016.

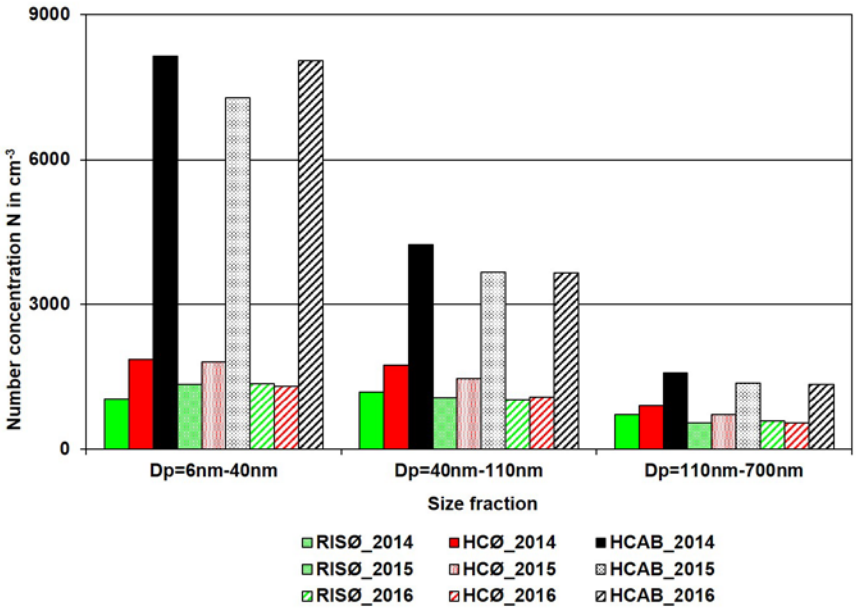


Figure 2.6. Yearly averaged particle number concentrations in specific size regimes Dp_{F1} = 6–40 nm, Dp_{F2} = 40–110 nm, and Dp_{F3} = 110–700 nm at regional background station RISØ, the urban background station HCØ and the urban curbside station HCAB in 2014, 2015 and 2016.

A closer look into the number concentrations observed in the specific size regimes does reflect that the largest fraction in particle number is observed in the smallest size regime Dp_{F1} = 6–40 nm at the urban curbside station HCAB. This size regime is highly influenced by vehicle exhaust emissions while the influence to the following size regime Dp_{F2} = 40–110 nm is much lower, but still noticeable. In the largest size regime Dp_{F3} = 110–700 nm, there is still an increased concentration of particles observed compared to regional, semi-urban and urban sites which is predominantly due to vehicular non-exhaust emissions at the curbside station. Reductions of emissions are regulated in the European legislation and resulted in e.g. after exhaust treatment of vehicles and do explain yearly trends. For this reason, more solid statements should be made based on longer time series of yearly averages. Thus, the next section has been prepared to look into long time trends. The particle number observed in the specific three size regimes has been almost stable for the urban background and the regional background sites RISØ and HCØ, respectively.

2.4 Particle number fractions – yearly trends

Yearly averages of the total particle number at the three measurement stations RISØ, HCØ and HCAB for the time period from 2002 to 2016 are presented in Figure 2.7. The total particle number corresponds to the sub micrometer size range from Dp = 6 – 700 nm.

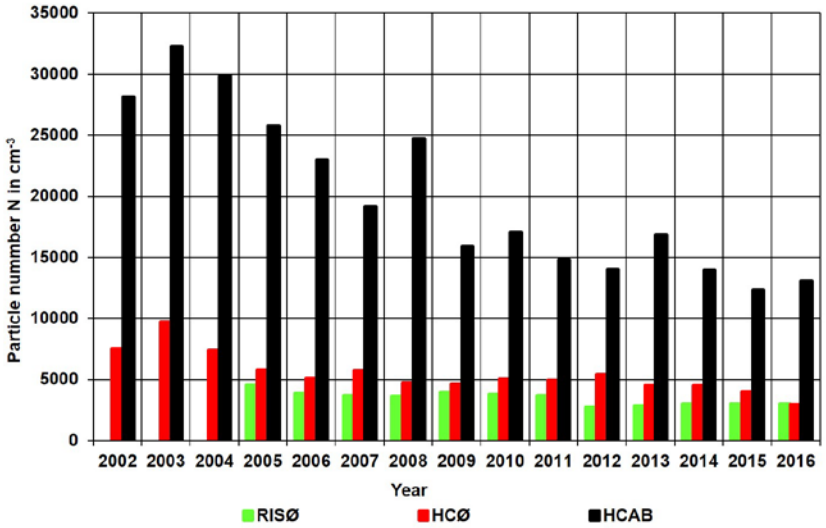


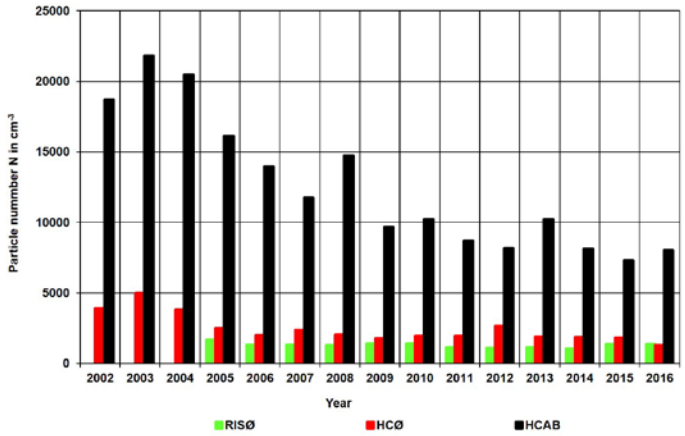
Figure 2.7. Yearly trend of total particle number concentrations (Dp = 6 – 700 nm) at the regional background site RISØ, the urban background site HCØ and the urban curbside site HCAB from 2002 to 2016.

As a general finding it has been observed that the total sub micrometer number concentration has been constantly decreased throughout the entire measurement period from 2002 to 2016. This statement is evident for all measurement sites, the urban curbside station HCAB, the urban background station HCØ, and the regional background station RISØ. Measurements at HCAB and HCØ started in 2002 while measurements at RISØ were initiated in 2005. The decrease in total particle number at RISØ is not very significant, but still noticeable. At HCØ, this change is more obvious but mostly for the first years between 2002 and 2006 compared to the subsequent period. A clear and obvious change in total particle number is observed for the urban curbside station HCAB where the strongest decrease is observed from 2002 to 2009. In the following years only a slight decrease in total particle number is observed here. This decrease is most likely due to a change in motor engine exhaust technology and also to a change in the sulfur content in Danish fuels. Wåhlin (2009) investigated the compositional change in Danish fuels as he looked in detail into the Friday and Saturday night emissions, which mostly represent emissions from diesel driven taxis.

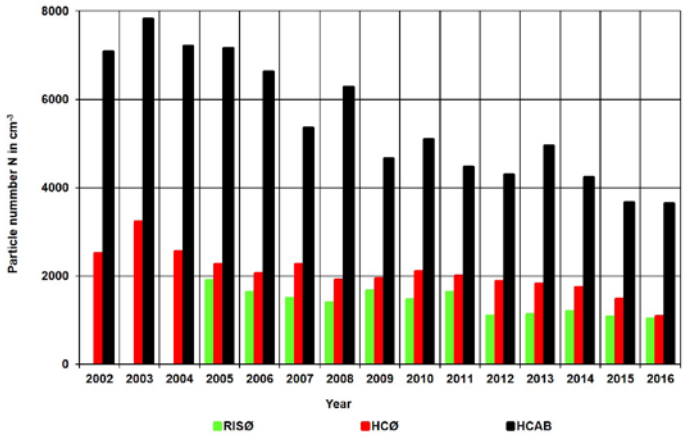
In contrast it has to be mentioned that the traffic density at HCAB has been constantly increasing during the years of the measurement period. The slight decrease in particle number at HCØ is due to a reduction in regional particle mass concentration, which is also observed at HCØ, but also the reduction in traffic related particle mass concentration as observed at HCAB. That is the freshly emitted traffic particles reach the HCØ station after some minutes to hours of aging time. Changes at RISØ are most likely due to a general reduction in particle emissions in Europe as the regional background site is highly impacted by regional and long-range transported aerosols.

For a further analysis, the particle number concentrations were determined in the above discussed specific size regimes, namely particles with diameters of Dp_{F1} = 6–40 nm, Dp_{F2} = 40–110 nm, and Dp_{F3} = 110–700 nm at all three stations. The results are presented in Figure 2.8 covering the whole measurement period from 2002 to 2016.

Dp_{R1} = 6–40 nm



Dp_{R2} = 40–110 nm



Dp_{R3} = 110–700 nm

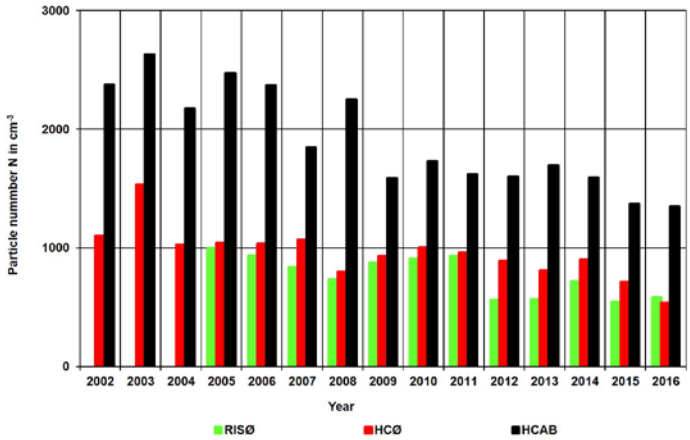


Figure 2.8. Yearly trend of averaged number concentrations in Dp_{F1} = 6–40 nm (upper figure), Dp_{F2} = 40–110 nm (middle figure), and Dp_{F3} = 110–700 nm (lower figure) at RISØ, HCØ and HCAB from 2002 to 2016.

A detailed look into the number concentrations in the three specific size regimes does show that values are elevated for urban curbside at HCAB compared to urban and regional background sites at HCØ and RISØ, respectively.

Number concentrations of particles in the lowest size regime (DP_{F1}= 6 - 40 nm) are about four times higher at the urban curbside compared to the urban background. This factor is even higher for the regional background site RISØ. This statement is valid over the whole measurement period from 2002 to 2016.

In the middle size regime (DP_{F2} = 40 - 110 nm) the values are still twice as high at the urban curbside compared with the urban background, explaining that even for this size the particle traffic emissions seem to highly contribute in the near distance to a major road.

Traffic emissions contribute less to the largest size regime (DP_{F3} = 110 - 700 nm) than the smaller size regimes apparent from Figure 2.8. There is a high impact of regionally and long-range transported particles in DP_{F3}. But still it can be concluded that exhaust and non-exhaust emissions from vehicle traffic play some significant role as HCAB appears to be highest in number concentration with values about twice as high compared to HCØ or RISØ.

The largest reduction in particle number concentrations over the whole measurement period has appeared in the smallest size regime regime (DP_{F1}= 6 - 40 nm) at HCAB followed by the middle size regime (DP_{F2} = 40 - 110 nm) at HCAB. At HCØ these reductions are also noticeable.

Average values for the period 2002 – 2004 at HCAB were about 20,320 cm^{-3} for the smallest, 7,360 cm^{-3} for the middle and 2,390 cm^{-3} for the largest size regimes and compare to 7,820 cm^{-3} for the smallest, 3,840 cm^{-3} for the middle and 1,440 $cm^{-3}$for the largest size regimes in the actual period from 2014 – 2016.

The corresponding average values observed at the urban background station HCØ in 2002 - 2004 are 4,240 cm^{-3} for the smallest, 2,760 cm^{-3} for the middle and 1,220 cm^{-3} for the largest size regimes compared to 1,660 cm^{-3} for the smallest, 1,430 cm^{-3} for the middle and 720 cm^{-3} for the largest size regimes for the actual time period from 2013 – 2015.

2.5 EC in $PM_{2.5}$ in urban background

The blackish or brownish substance soot formed during incomplete combustion (Andrea and Gelencsér, 2006) is typically measured by exploiting its light absorbing properties as Black Carbon (BC) or its chemically inertness as elemental carbon (EC). In this section we will use EC as a measure of soot. While soot may actually contain significant amounts of organic carbon from combustion of some sources, EC is operationally defined as carbon, which in this case is only combusted in the presence of oxygen at temperatures higher than 500˚C (Cavalli et al., 2010). EC and organic carbon (OC) have been monitored routinely at RISØ and HCAB from 2009/2010. Monitoring of EC was extended to the urban background site HCØ in September 2014 and the suburban site HVID at Fjelstedvej in Hvidovre in October 2015.

2.6 Ambient concentrations in rural and urban background

Samples for chemical analysis were collected at the rural site RISØ and urban background HCØ. Both sites are part of the Danish Air Quality Monitoring Program (NOVANA LMP) and equipped with a number of filter samplers and analytical instruments. Low Volume Samplers (LVS)

equipped with a $PM_{2.5}$ inlet collected atmospheric aerosols on quartz fiber filters on both measurement sites. The quartz fiber filters were weighed to find the $PM_{2.5}$ mass concentration. Punches of the filters were analyzed for EC by a Thermal/Optical Carbon Analyzer (Sunset Laboratory, Oregon USA) according to the EUSAAR 2 protocol (Cavalli et al., 2010). A filterpack sampler and a SM200 PM monitor equipped with PM_{10} inlet collected atmospheric aerosols on cellulose filters for analysis of chemical elements using inductively Coupled Plasma Mass Spectrometry (ICP-MS). At urban background, only, Volatile Organic Compounds (VOC) were collected from ambient samples on adsorbent tubes packed with the adsorbent Carbopack X. Adsorbent tubes were desorbed and analyzed using Thermal Desorption Gas Chromatography Mass Spectrometry (TD-GC-MS) for selected C_5-C_9 organic species, including benzene. Samples of $PM_{2.5}$, EC, elements and benzene analysis were collected with a time resolution of 24 hours.

The annual mean concentration in 2015 was 0.22 µg/m³ at the rural site RISØ and 0.37 µg/m³ in urban background, which equals an urban increment of 0.15 µg/m³ (67%). In 2016, the measured concentrations averaged 0.26 µg/m³ and 0.33 µg/m³, respectively, equal to an urban increment of only 0.07 µg/m³ (26%). Suburban EC averaged 0.44 µg/m³. That is an increment of 70% from rural conditions. Based on two years of data, EC averaged 0.24 µg/m³ and 0.35 µg/m³ at the rural site RISØ and urban background, respectively. The increment was higher on weekdays (0.12 µg/m³) compared to weekends (0.08 µg/m³) in agreement with the reduction in traffic on Saturdays (-30%) and Sundays (-60%) (Ketzel, 2016).

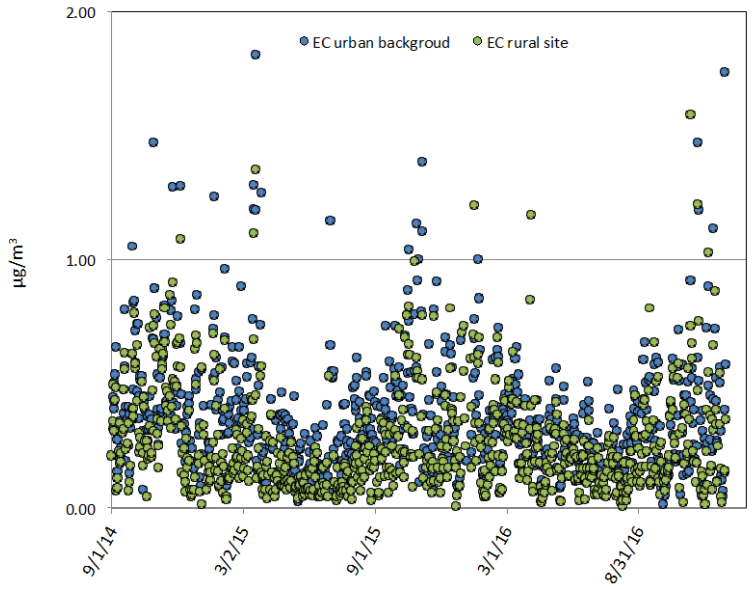


Figure 2.9. EC in $PM_{2.5}$ at the rural site Risø and urban background HCØ

Rural and urban background concentrations covariated and showed highest concentrations during winter and lowest concentrations during summer (Figure 2.9).

2.7 EC increment in urban background

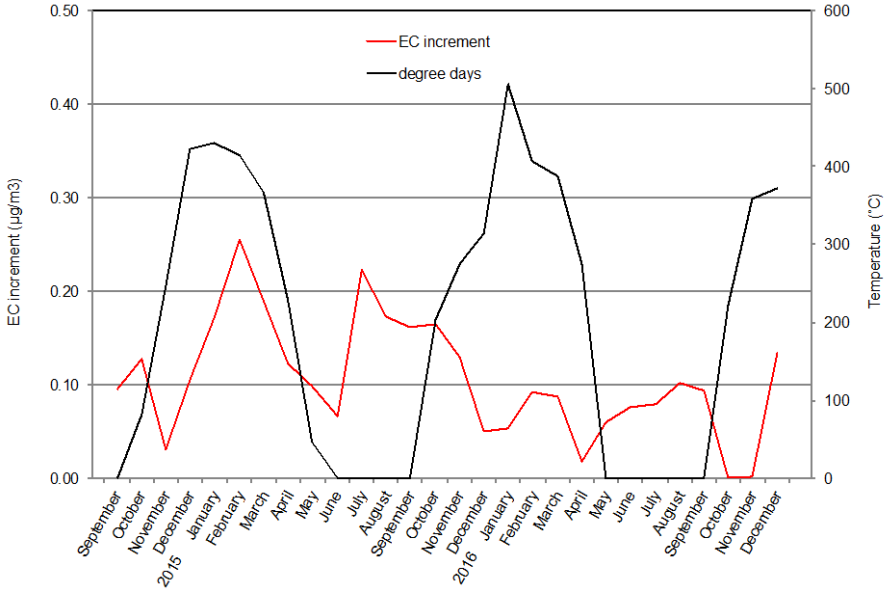


Figure 2.10. Degree days and monthly increments in EC at the urban background HCØ relatively to the rural site are shown for comparison. The latter is provided by Technological Institute (in Danish: Teknologisk Institut) and shows differences between actual daily temperature and 17 ˚C added up to monthly numbers

The urban increment in EC was highest in 2015 and apparently not inversely correlated with absolute temperature (Table 2.3). Traffic is expected to contribute significantly to the urban increment of EC, but constantly throughout the year (Vejdirektoratet, 2006). The EC increment was plotted against time along with degree days (Figure 2.10).

Table 2.3. Urban background concentrations and increments relative to the rural site RISØ and average ambient temperature (Copenhagen Airport) for the years 2015 – 2016.

	EC concentration (µg/m^3)	**EC increment** (µg/m^3)	**Temperature** (˚C)
January	0.44	0.11	1.8
February	0.39	0.17	2.4
March	0.47	0.14	4.4
April	0.26	0.07	7.4
May	0.24	0.08	12.2
June	0.22	0.07	15.5
July	0.27	0.15	17.3
August	0.31	0.14	17.7
September	0.37	0.13	15.6
October	0.42	0.08	9.8
November	0.40	0.07	6.2
December	0.38	0.09	5.7
Annual average	**0.35** (0.08)	**0.11** (0.04)	**9.6** (5.6)

Degree days are calculated by Teknologisk Institut and used to estimate the need for residential heating. Degree days states the differences between actual daily temperature and 17 ˚C added up to monthly numbers. Whereas the increment in EC and degree days appeared to correlate in December-March 2015, no such behavior was observed in 2016. On the other hand, increments in EC are observed during Summer/Autumn 2015 and 2016. However, at this point more data is needed to conclude on observed increments.

In Figure 2.11, relatively large positive and negative increments are observed on single days, whereas the general EC increment is positive.

In the Particle Project 2011-2013 urban EC was apportioned to mainly traffic and RWC. Only 20% could be attributed to emissions from ship traffic, coal and oil (Nøjgaard et al., 2015a). In this project we will further investigate the residential wood combustion (RWC) source contribution to ambient particulate matter in urban background over 2 years of daily time resolution.

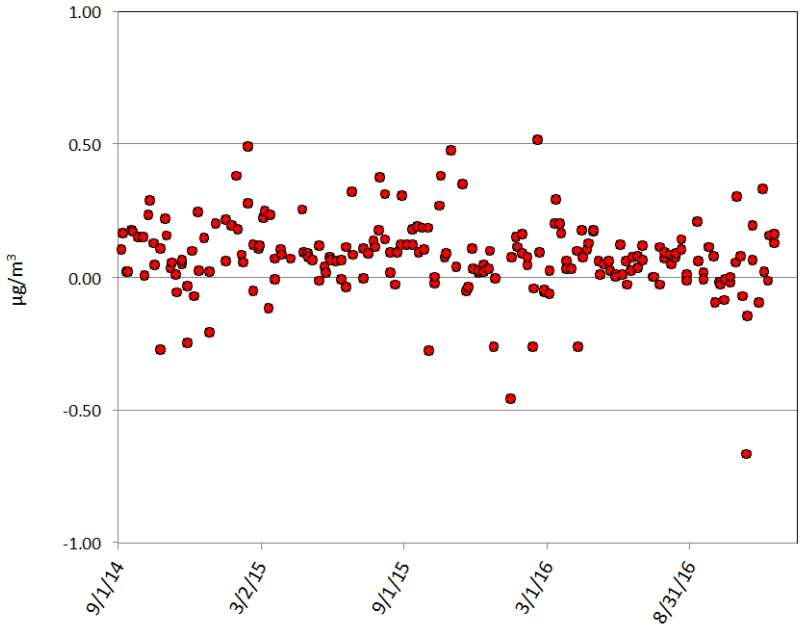


Figure 2.11. Increment of urban EC in $PM_{2.5}$, i.e. the difference between urban background and rural EC for daily samples.

3 Markers for residential wood combustion (RWC) in $PM_{2.5}$

3.1 Source apportionment of rural background in the previous Particle Projects

Sources to *rural* PM were evaluated in the P*article Project 2008-2010* (Massling et al., 2011) 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). Particulate matter from RWC and Traffic was considered to be entirely in the $PM_{2.5}$ fraction of which RWC accounted for 1.27 µg/m^3 and *Vehicular Traffic* only 0.09 µg/m^3 annually.

Also sources to $PM_{2.5}$ in *urban background* were evaluated in the preceding Particle Project from 2011-2013, where RWC and traffic amounted to 0.88 µg/m^3 and 0.26 µg/m^3, respectively (Nøjgaard et al., 2015). Although the difference between urban background and rural site partly explains the difference in vehicular traffic, the difference is also partly attributed to the analytical and modeled error. Sources to EC based on two measurement campaigns from 14.11 - 14.12 2011 and 28.06 - 28.07 2012 were mainly RWC (0.13 µg EC/m^3 – 36%) and traffic emissions (0.16 µg EC/m^3 – 44%). The remaining 20% were attributed to ship emissions (0.04 µg/m^3), coal (0.03 µg/m^3) and oil (0.002 µg/m^3).

In the present project we will evaluate the RWC source based on a continuum of measurements in urban background from 01.09 2014 - 31.08 2016. This approach more accurately apportions the RWC source and its variation in time based on 668 daily samples in a 2-year time period. On the other hand, it will only give little information on other sources. That is, traffic and other sources will be lumped together in one factor, and RWC as another factor.

3.2 Sampling at urban and rural sites 2014 - 2016

While the two previous Particle Projects used receptor modeling and specific markers for biomass burning, traffic and other sources in only two campaigns of totally 8 weeks duration, the present Particle Project uses EC of daily time resolution as a marker from September 2014 - ultimo 2016 in rural environment and urban background. RWC is not a single chemical species, but comprise gasses, VOC's and a number of particulate species including EC and a vast amount of organic compounds. Except during spatially and time limited case studies (Olsen et al., 2010), RWC can only be quantified indirectly by use of markers for wood combustion. By definition, the particle mass directly emitted from the wood stove is called Primary Biomass Burning Aerosol (PBBA). During their lifetime VOC's from wood combustion are processed in the atmosphere and partly transformed into additional particle mass, called Secondary Organic Aerosols (SOA). While SOA from wood combustion is extremely difficult to isolate and quantify, PBBA can be quantified by use of marker species.

The markers for traffic and wood combustion were used for calculation of PBBA in 3 steps:

1) Identification of a suitable marker for PBBA and subtraction of its contribution from other sources.
2) Evaluation of $PM_{2.5}$ to marker concentrations from a literature study.
3) Calculation of equivalent PBBA from marker concentrations.

3.3 Markers for Residential Wood Combustion

RWC covers biomass combustion for heating purposes using primarily woodstoves, and some fireplaces and automatic boilers including pellet burners using wood logs, briquettes and pellets as fuel. In Denmark, 750.000 wood stoves (Miljøstyrelsen, 2016) account for 99% of the stoves in terms of activity and pollution, the remaining part being fireplaces. Wood stoves account for 54% of the residential biomass combustion activity in terms of TJ, but 76% of the $PM_{2.5}$ emission (Kindbom et al., 2015), whereas 46% of the activity and 22% of the $PM_{2.5}$ emission from residential wood combustion is ascribed to biomass-fueled boilers. Biomass is also combusted during wild fires and prescribed burning of agricultural residues and forests. In Denmark, burning of agricultural fields is not permitted, but farmers have a dispensation in some cases. Bonfires and campfires are frequently lit and typically in the outdoor season, when woodstoves are only rarely used for residential heating, and massively during Saint Johns Eve. Combustion for energy or heat production occurs in residential houses as well as in power plants and Combined Heat and Power Plants (CHP). In 2015, 14% of the Danish production of electricity was based on biomass, which is expected to increase in the future, also for heat production (Energinet Danmark, 2016).

The combustion process in wood stoves is incomplete, which results in emission of gaseous and particulate compounds associated with RWC. The abundance and share of emitted species are available for different types of ovens and fuels in the literature. Emitted species include specific markers such as the sugar anhydrides levoglucosan and mannosan (Nøjgaard et al, 2014), but also markers emitted during incomplete combustion from a number of sources, e.g. benzene, Polycyclic Aromatic Hydrocarbons (PAH), and elemental carbon (EC). Benzene and EC are volatile and particulate species, respectively, and PAHs cover several species distributed in both phases. While the costs of analyzing specific markers are expensive and only sampled during shorter campaigns, benzene, PAH and EC are sampled and analyzed on routine basis in the Danish Air Quality Monitoring Programme (Ellermann et al., 2016).

In this Project we focus on EC and benzene, which are available in daily concentration at the rural site Risø as EC and in urban background as EC and benzene. Both markers show a strong seasonal profile with summer minima and winter maxima (Figure 3.1). During summertime the markers show only little variation in concentrations and is believed to originate from mainly traffic, and a small contribution from campfires, prescribed agricultural burning, as well as long range transported air pollution from mainly wild fires, but also wood combustion in other countries. In the colder seasons the EC marker concentrations are more scattered than those of benzene.

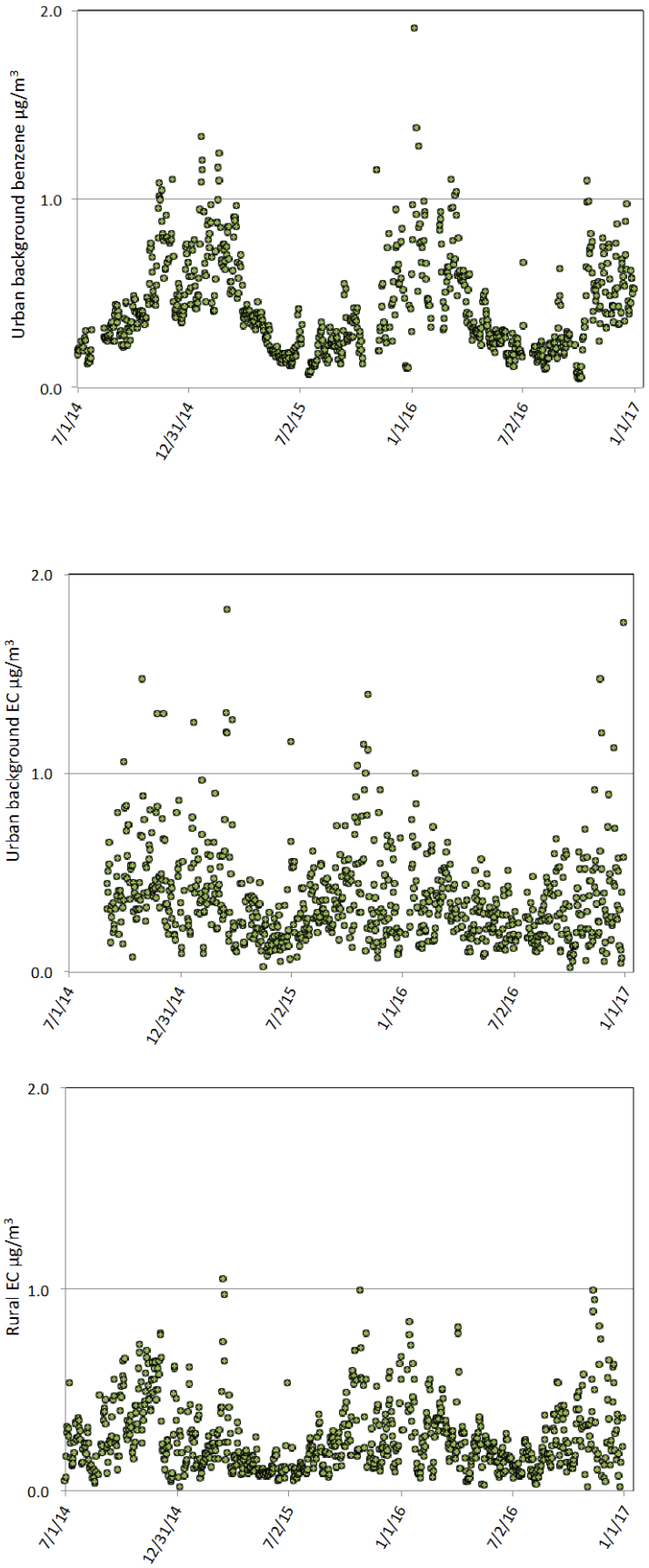


Figure 3.1. EC and benzene in urban background HCØ and at the rural site RISØ.

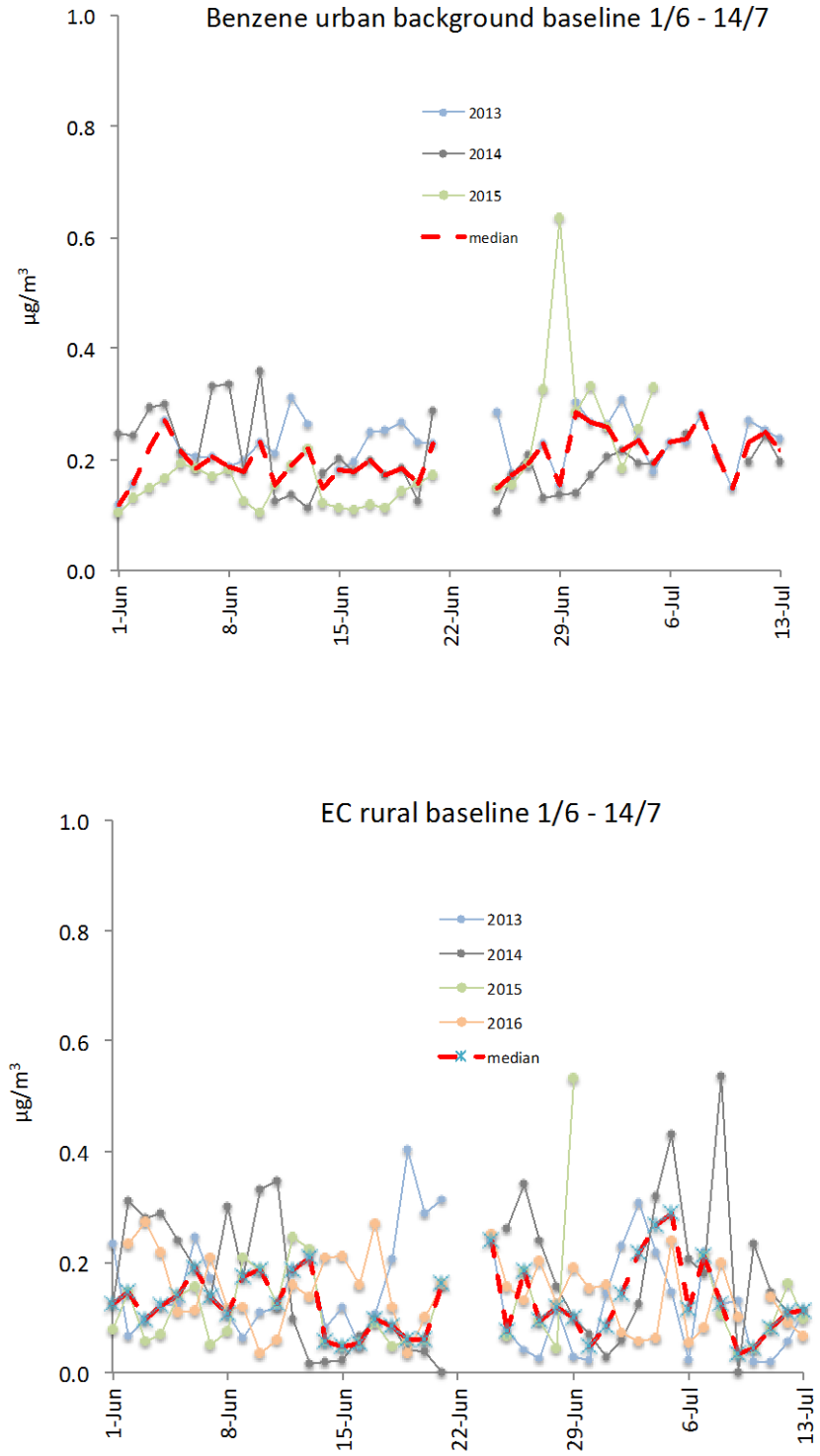


Figure 3.2. Rural and urban background baseline concentrations of EC and benzene, respectively (excluding 22-24 June). Median of 2013-2016 is shown in red.

A possible explanation is that more sources contribute to ambient EC than those of benzene. In fact, benzene is mainly emitted by gasoline cars, which are typically private vehicles, whereas EC is mainly emitted by diesel cars (Winther, 1999). The fleet of diesel vehicles is more diverse than the fleet of gasoline vehicles and comprise private cars, taxies as well as

vans and trucks with large differences in emission factors and driving patterns which are not necessarily homogenously distributed over time.

Emission inventories suggest that the major sources to EC and benzene are traffic and biomass combustion, while the contributions from industry and heat and power production are much smaller. For benzene, other sources than traffic and processes related to handling of fuel are considered negligible. The traffic contribution to EC and benzene were deduced in two different ways based on summertime concentrations.

The traffic source was based on summer concentrations of the markers during 1 June- 14 July (excluding 22-24 June encompassing St. Johns Eve), where biomass combustion is assumed to be minimal and yet excluding the summer holyday traffic, which may different from the rest of the years (Trafikstyrelsen, 2006). Two approaches served to identify the traffic source:

A: A relationship between the summer and winter concentration of levoglucosan was established in the Particle Project 2011-2013 (Nøjgaard et al., 2015a), where summer concentrations of levoglucosan averaged 10% of the winter concentrations. EC and benzene are assumed to follow the same relationship as levoglucosan, hence the following set of equations can be formulated:

$$\text{Equation 3.1 } EC_{PBBA\ summer} = 0.10 \times EC_{PBBA\ winter}$$

$$\text{Equation 3.2 } EC_{PBBA} = EC_{ambient} - EC_{other\ sources}$$

EC_{PBBA} is the primary contribution to EC from wood stoves, and $EC_{ambient}$ is the total EC concentration measured irrespective of which sources contributed. $EC_{other\ sources}$ equals other sources that wood stoves, primarily traffic. The EC concentrations averaged 0.38 during winter and 0.15 $\mu g/m^3$ during summer, respectively. In this context, summer and winter corresponded to the periods in Equation 3.1 was derived. The traffic contribution is assumed to be constant over the year (Vejdirektoratet, 2006), excluding the summer holydays 15/7 - 15/8 (Figure 3.2), and Christmas holydays 20/12 - 2/1. Thus, the contribution to EC from other than wood stoves can be derived by solving 3 equations with 3 unknowns.

$$\text{Equation 3.2a } EC_{PBBA\ winter} = 0.38 - EC_{other\ sources}$$

$$\text{Equation 3.2b } EC_{PBBA\ summer} = 0.15 - EC_{other\ sources}$$

$$0.1 \times (0.38 - EC_{other\ sources}) = 0.15 - EC_{other\ sources}$$

$$EC_{other\ sources} = 0.12\ \mu g/m^3$$

Thus, the sources to EC excluding wood stoves average 0.12 $\mu g/m^3$, which includes mainly traffic but also emissions from combined heat and power plants, industry and shipping. Benzene can be calculated using the same procedure.

$$Benzene_{baseline} = 0.14\ \mu g/m^3$$

B: Visual inspection of the marker concentrations is another approach to derive the contributions to EC and benzene from other sources than residential wood combustion. In the lower end of the concentration scale during the summer, the data points will distribute themselves around con-

centrations corresponding to contribution from other sources than residential wood combustion. Due to variations in meteorological parameters, e.g. wind speed and wind direction, and variations in traffic, the contribution from other sources will display some variation. Concentrations exceeding other sources during summer may arise from wild fires or wood combustion including bonfires and barbeque as well as abnormal traffic and fluctuating industrial emissions. Thus, a straight line with zero slope assigned to several of the lower concentrations should correspond to the contributions from other sources than residential wood combustion.

$$EC_{\text{other source}} = 0.12\ \mu g/m^3$$

$$\text{Benzene}_{\text{other sources}} = 0.16\ \mu g/m^3$$

The minor differences in the contribution from other sources than residential wood combustion using two different approaches, justify the assumption that the contributions from PBBA and other sources can be separated. In order to take year-year variations into account, and to minimize subjective interpretations, the equations 3.1-3.2 are solved for each year and both markers.

The baseline corrected marker concentrations were converted into PBBA by multiplication with conversion factors obtained from laboratory studies of wood stove emissions under controlled conditions. A conversion factor for EC of 6.2 was averaged from 5 studies involving hardwood (3) and softwood (2) (McDonald et al., 2000; Fine et al., 2004; Smidl et al., 2008.

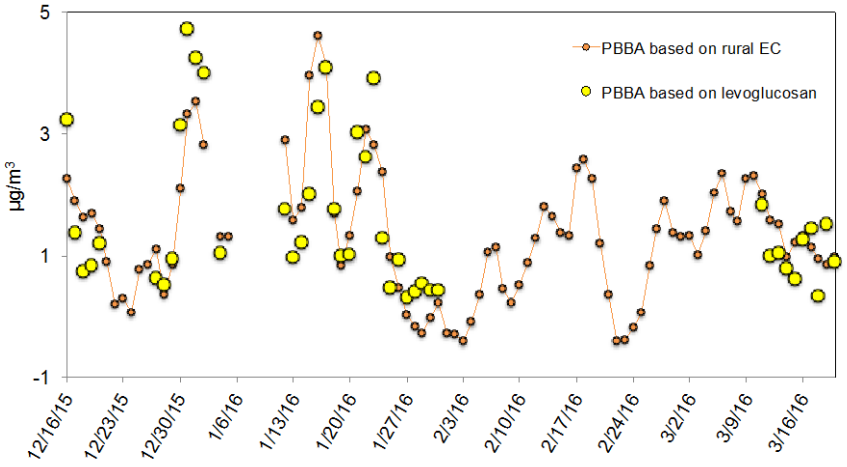


Figure 3.3. Comparison of rural PBBA calculated from markers of wood combustion: EC (red) and levoglucosan (yellow), respectively (R^2 = 0.67).

Similarly, a conversion factor for benzene of 3.7 was averaged from studies based on softwood (2) and hardwood (1) (McDonald et al., 2000; Tissari et al., 2007; Pettersson et al., 2011). A conversion factor for levoglucosan of 9.4 was based on equal amounts of softwood and hardwood, i.e. oak, beech, spruce and larch (Smidl et al., 2008). Levoglucosan is a specific and unique marker of wood combustion, which origins from pyrolysis of cellulose in high yields (Simoneit et al., 1999. Although levoglucosan is a unique marker for cellulose based biomass combustion, it is subject to decay during atmospheric degradation by reaction with the OH radical (Hennigan et al., 2010; Hoffmann et al., 2010). In addition to its non-inert

character, levoglucosan is formed in different yields depending on combustion conditions, type of fuel (hardwood vs. softwood) and oven (reference). However, levoglucosan can be analyzed from stored filter samples and is suitable for determination of short-range transported emissions of RWC during wintertime, where atmospheric degradation is at its minimum.

Benzene and EC were tested against levoglucosan as markers for wood combustion by conversion to PBBA. For this purpose, filter samples were collected at the rural site, RISØ (n=43) and urban background, HCØ (n=14) in 2015 and 2016. PBBA calculated from EC (corrected for traffic and other sources) generally agreed well with PBBA calculated from levoglucosan, which indicates that EC is a suitable marker for RWC in rural (R^2 = 0.67), and urban background (R^2 = 0.68).

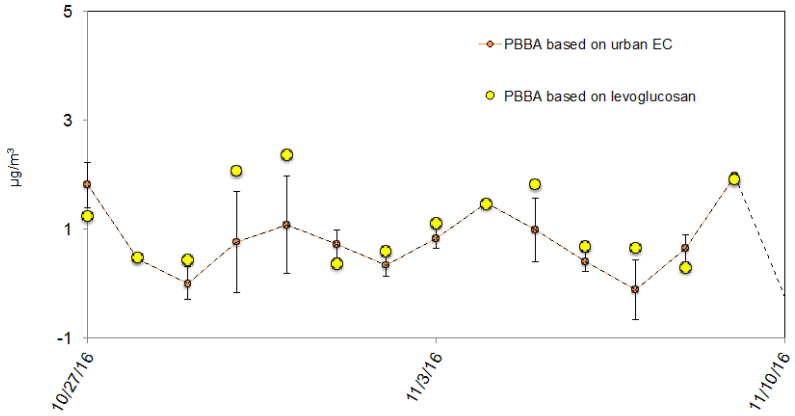


Figure 3.4. Comparison of urban PBBA calculated from markers of wood combustion: EC (red) and levoglucosan (yellow), respectively (R^2 = 0.67).

The method uncertainty is reflected in occasionally negative concentrations during the summertime, and quantitatively in the numerical difference between PBBA calculated from levoglucosan and EC. The standard deviation of PBBA was calculated using Equation 3.3 assuming that the true PBBA can be derived from the levoglucosan samples at the rural site and in urban background.

$$\text{Equation 3.3} \qquad s = \sqrt{\frac{1}{n} \times \sum_{i=1}^{n} (x - \mu)^2}$$

By use of Equation 3.3 a standard deviation of 0.72 µg/m³ is obtained, which is an expression for the agreement between EC and levoglucosan as markers for biomass combustion, implicit that both markers are subject to error.

3.4 Reconstructed PBBA particle concentration in urban and rural background 2014 - 2016

EC was selected as marker for reconstruction of PPBA in rural and urban background. Although benzene has a longer record in urban background, comparison of PBBA from these two markers reveal the presence of false high PBBA based on benzene, for which reason it was decided to proceed with EC based PBBA, only.

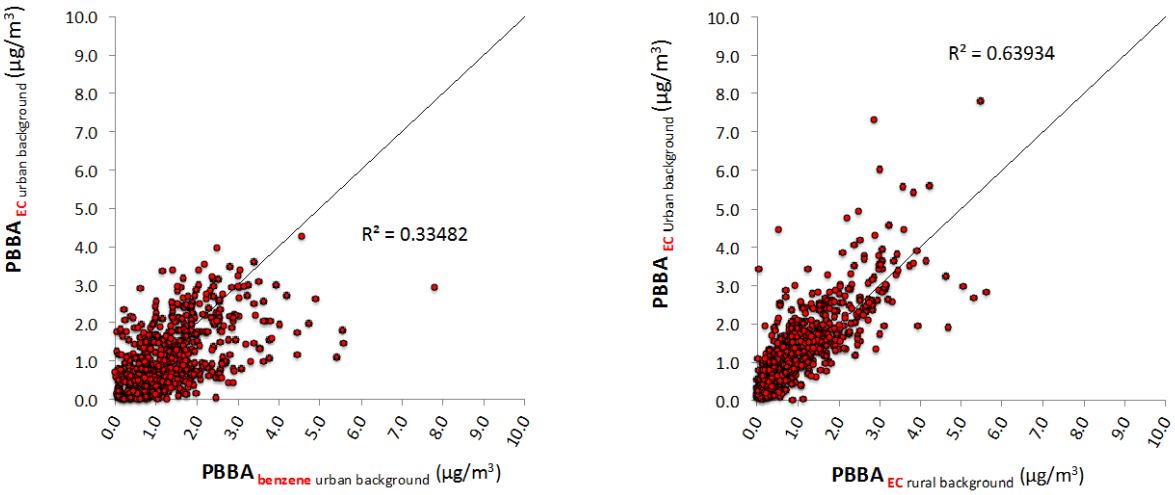


Figure 3.5. Left: Correlation plot of EC based PBBA and benzene based PBBA, which shows benzene based PBBA not matched by those of EC. Right: Correlation plot of EC based PBBA in rural and urban background showing good agreement (R2 = 0.69).

PBBA based on EC correlated well at the rural site and in urban background (R^2 = 0.69) (Figure 3.5), though rural PBBA (1.0 µg/m³) were lower than urban background PBBA (1.2 µg/m³). A scatter plot of PBBA based on urban benzene and EC revealed occasionally higher concentrations of PBBA based on benzene. Furthermore, PBBA based on benzene correlated poorly with PBBA based on levoglucosan (not shown).

Long range transport of benzene and EC from highly polluted source areas may result in falsely high PBBA concentrations. Figure 3.6 illustrates the origin of air masses with PBBA concentrations higher than 3 µg/m³ in selected periods during the autumn/winter months 2013 - 2015/2016. Northern/Eastern Europe and the Baltic countries are clearly overrepresented, which introduces the risk of false high PBBA calculated concentrations. However, elements associated with long-range transported pollution (Cu, Ni, Zn, Se, V) did not correlate with markers of wood combustion.

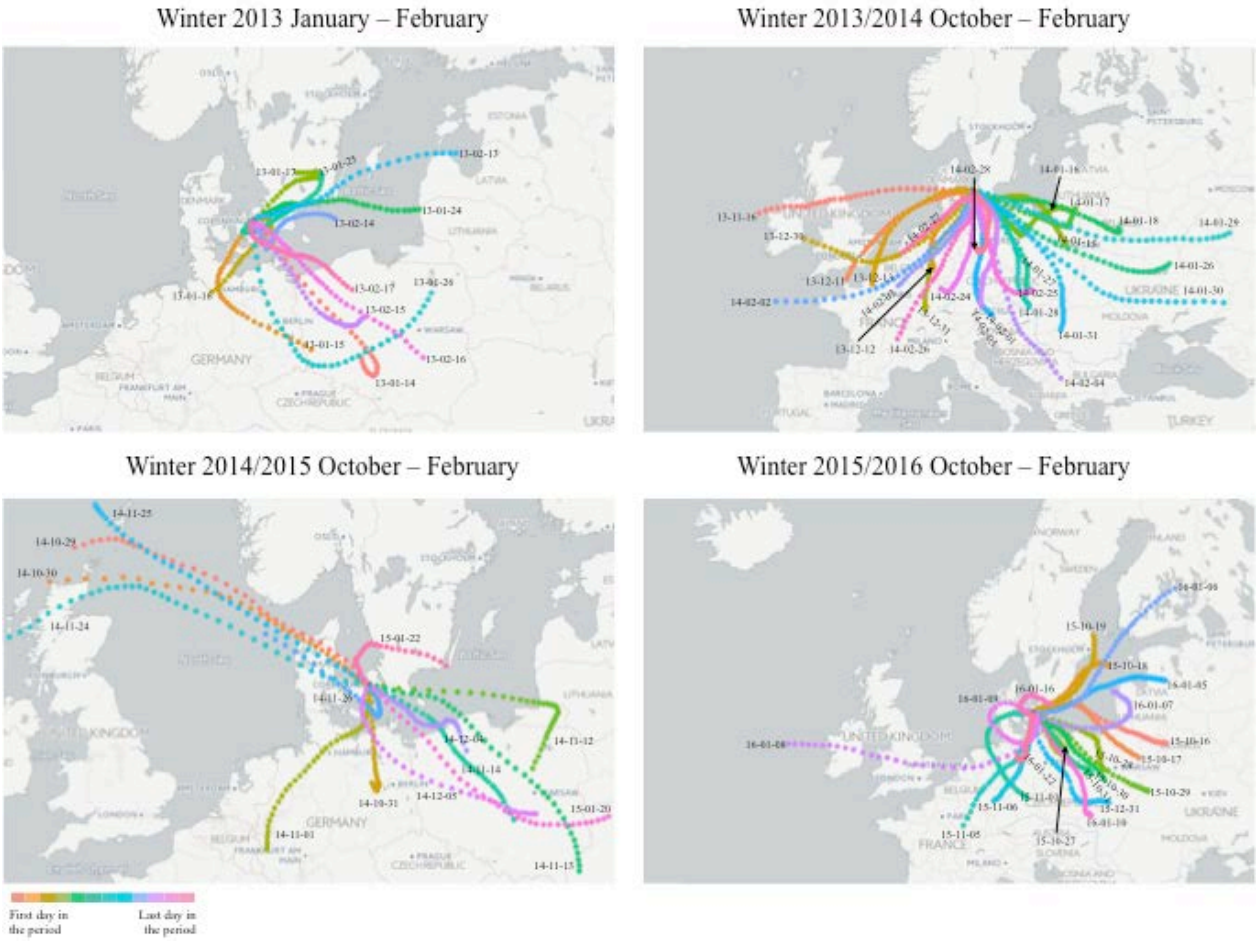


Figure 3.5. Back trajectories from the rural site RISØ calculated 36 hours back in time from the dates shown in the legends. Upper left: Figure includes only the two first months of 2013. Other Figures: the autumn/winter months October - February.

Figure 3.7 illustrates the monthly variation in PBBA at the rural site RISØ and urban background HCØ from September 2014. As the ambient temperature decrease from September to a minimum in January/February, PBBA increases from a non-zero starting point during the summer indicating biomass burning from other sources as evidenced by previous measurements of levoglucosan (Nøjgaard et al., 2015a). For both 2014 and 2015, the highest concentrations were observed at the onset in autumn (October - November), and not when the temperature was lowest around January - February. In order to investigate if a particular wind direction or origin of air mass dominates these observations, back trajectories were calculated for the highest concentrations of PBBA in August - October 2014. However, cleaner air masses from North were encountered as frequently as air masses from East. Part of PBBA observed during the summer and early autumn is believed to be caused by forest fires on the northern hemisphere, which may be particular frequent until late summer (San-Miguel-Ayanz et al., 2016). Still, forest fires probably cannot explain high PBBA concentrations in September-October, and furthermore the urban background PBBA is higher than at the rural site, which evidences local sources (Figure 3.7). Wood burning in September-October could arise from actual use of wood stoves during the transition time where central heating is turned off and the stove is lid once or twice a day, until central heating is eventually turned on and becomes the sole source of heat, until it becomes very cold. However, this is an untested hypothesis.

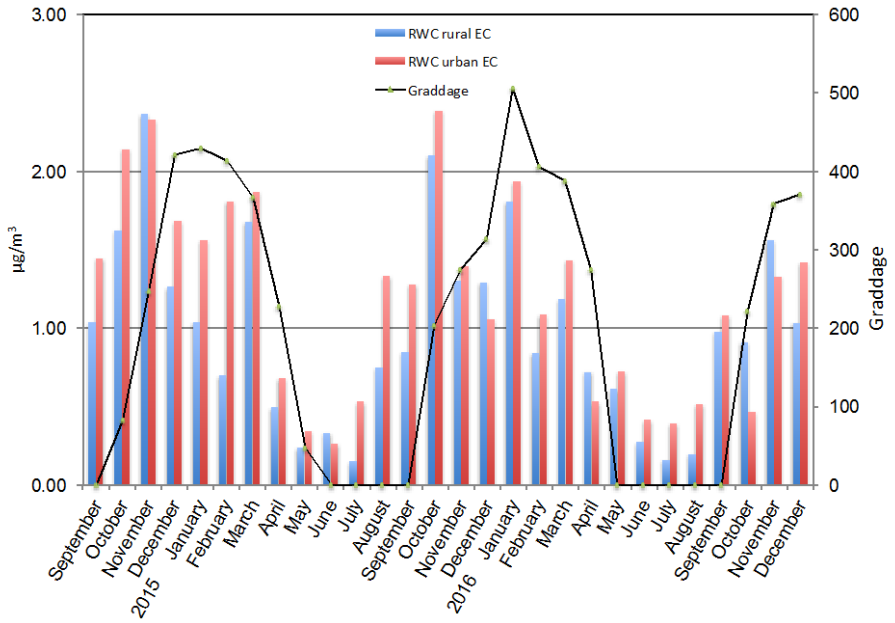


Figure 3.7. Monthly concentrations of PBBA at the rural site (blue bar) and urban background (red bar) September 2014 - August 2016. Degree days are shown for comparison.

Urban background concentrations of PBBA exceeded those at the rural site in 19 of 24 months (Figure 3.7. The increment in PBBA from rural to urban background averaged 23% from 2015 - 2016, but varied from +1.1 µg/m³ in February 2015 to -0.44 µg/m³ in October 2016. Higher concentrations of PBBA were measured at the suburban site in Hvidovre. In 2016 PBBA averaged 0.83 µg/m³ at Risø, 0.93 µg/m³ in urban background and 1.7 µg/m³ at the suburban site in Hvidovre, which is in accordance with the longer time series. Implications are 12% higher PBBA in urban background relative to the rural site, and 102% higher PBBA in the suburb relative to the rural site. The results are within the range of previous annual concentration estimates of 0.5 - 2 µg/m³ (Nøjgaard et al., 2015a, Olesen et al., 2010)

Table 3.1. PBBA in rural and urban background from October to March in 2013/2014, 2014/2015, 2015/2016 and from September 2014 to August 2016. The share of EC apportioned to Biomass Burning is listed in brackets. Degree days are shown in brackets in the first column.

		Rural environment (µg/m³)	Urban background (µg/m³)	Suburban site (µg/m³)
2013/2014		2.00	-	-
2014/2015	(327)	1.47 (66% EC)	1.92 (63% EC)	-
2015/2016	(349)	1.41 (66% EC)	1.52 (56% EC)	2.70 (70% EC)
2016	(211)	0.83 (53% EC)	0.93 (44% EC)	1.68 (58% EC)
2015-2016	(103)	0.87 (54% EC)	1.07 (48% EC)	-

By application of EC as a marker, we thus find that the Danish population is exposed to about 1 µg/m³ of PBBA in the rural environment North of Roskilde, whereas the population in the denser urban background of Copenhagen is exposed to 23% higher concentrations from 01.01.2015 - 31.12.2016. A direct comparison with the suburban site HVID is not possible in the same period, since the station was inaugurated by October

2015. However, in 2016 the annual increment from rural to suburban site was 102% as compared to only 12% increment from rural to urban background (Table 3.1). It is noteworthy, that the rural to suburban increments are comparable for the calendar year 2016 and the colder period from October 2015 to March 2016, where the use of wood stoves for residential heating is more common. A possible explanation is frequent activities involving bon fires and prolonged use of wood stoves from April - September.

PBBA decreased from 2013/2014 to 2015/2016 in both rural and urban background and could not be explained by corresponding changes in average temperature. Also evident from Table 3.1 is that the urban increment from 2014-2016 of 24% is mainly driven by the situation in 2014/2015. During the 2-year period from 2015-2016 biomass burning accounted for 48% of EC in urban background, and even higher: 54% at the rural site RISØ.

3.5 Timely variation of PBBA

A conservative estimate of PBBA in the Greater Copenhagen area was calculated as the mean PBBA of rural and urban background during 01.01.2015 - 31.12.2016 (Figure 3.8). As expected from Figure 3.5, rural and urban background PBBA show good agreement. Hence, the standard deviations of the Greater Copenhagen PBBA based on the rural and urban PBBA were generally small (Figure 3.8).

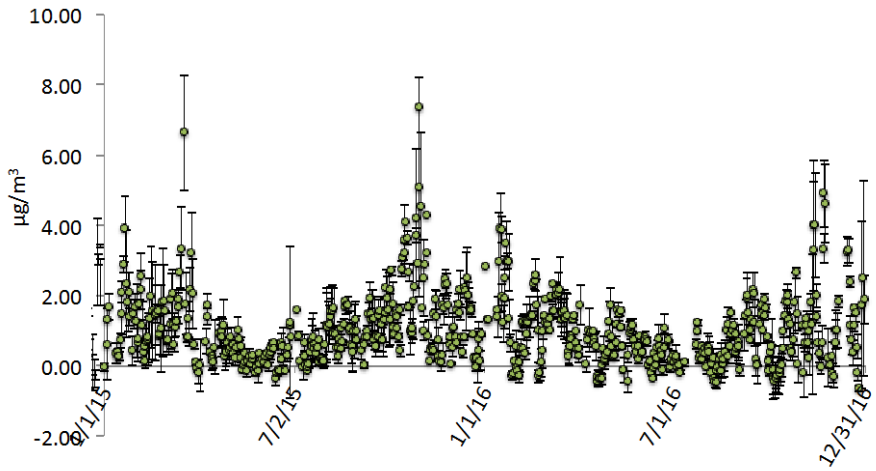


Figure 3.8. Estimate of PBBA (µg/m^3) in the greater Copenhagen area in 2015-2016 (+/- 1 standard deviation.

First, the time series in Figure 3.8 illustrates the characteristic variation showing high winter concentrations and low, (though not zero) summer concentrations of PBBA. Negative concentrations reflect the error of the method (section 4.3). Second, several episodes during the coldest months in January and February demonstrate low PBBA concentrations comparable to summer concentrations of PBBA. Third, rural and urban background concentrations of PBBA are highly correlated, but occasionally differ substantially illustrated by the one-standard deviation-bars in Figure 3.8.

Ambient submicron aerosols were sampled in the rural environment in parallel with daily EC samples using the online Aerosol Chemical Speciation Monitor (ACSM). In addition to major inorganic particulate species, the ACSM analyses the non-refractory particulate organic fraction of ambient aerosols, defined as species, which evaporates at 600 ˚C (Figure 3.9). Thus, soot-carbon and extremely-low-volatility organic species were not analyzed. However, the ACSM is capable of analyzing the wood burning tracer levoglucosan in 10 min time resolution by measuring molecular fragments $C_2H_4O_2^+$ and $C_3H_5O_2^+$ from levoglucosan.

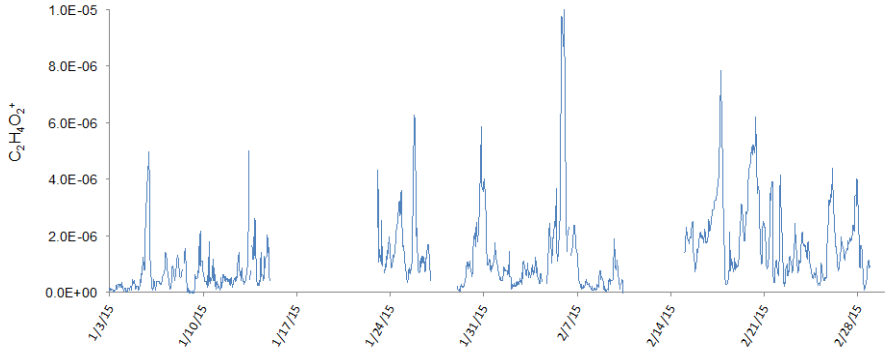


Figure 3.9. Hourly time resolution of the levoglucosan marker ion $C_2H_4O_2^+$ (µg/m^3) at the rural site RISØ from 01.01.2015 - 28.02.2015. Missing data is shown as gaps in the time series.

Time plots of the levoglucosan fragment $C_2H_4O_2^+$ reveal the large concentration differences, the importance of meteorology and transient nature of wood combustion, including during a single day of importance for evaluating human exposure. As an example, two months of monitoring the levoglucosan fragment $C_2H_4O_2^+$ at the rural site at Risø is plotted in Figure 3.9. High concentrations are encountered on all weekdays at all hours.

References

Andrea, M.O, Gelencsér, A., 2006. Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols. Atmospheric Chemistry and Physics 6, 3131–3148.

Cavalli, F., Viana, M., Yttri, K.E., Genberg, J., Putaud, J.-P., 2010. Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol. Atmospheric Measurement Techniques 3, 79–89.

Danmarks Statistik, 2016. http://www.dst.dk/da/Statistik/Analyser/-visanalyse?cid=27322

Ellermann, T., Wåhlin, P., Nordstrøm, C., Ketzel, M. (2010) Vejbelægningens indflydelse på partikelforureningen (PM10) på stærkt trafikerede gadestrækninger i Danmark, Paper presented at Trafikdage 2010, University of Aalborg; Aalborg, Denmark, August 2010, Paper available at: http://www.trafikdage.dk/papers_2010/380_ThomasEllermann.pdf

Ellermann, T., Nygaard, J., Nøjgaard, J.K., Nordstrøm, C., Brandt, J., Christensen, J., Ketzel, M., Massling, A. & Jensen, S.S., 2016. The Danish Air Quality Monitoring Programme. Annual Summary for 2015. Aarhus University, DCE – Danish Centre for Environment and Energy, 65 pp. Scientific Report from DCE – Danish Centre for Environment and Energy No. 201. dce2.au.dk/pub/SR201.pdf

Energinet Danmark, 2016.http://www.energinet.dk/DA/KLIMA-OG-MILJOE/Miljoerapportering/Sider/Braendsler.aspx

Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2004. Chemical Characterization of Fine Particle Emissions from the Wood Stove Combustion of Prevalent United States Tree Species. Environmental Engineering Science 21, 6, 705-721.

Glasius, M., Hansen, A.M.K., Claeys-Maenhaut, M., Henzing, J.S., Jedynska, J.D., Kasper-Giebl, A., Kristensen, K., Martinsson, J., Maenhaut, W., Nøjgaard, J.K., Spindler, G., Stenström, K.E., Swietlicki, E., Szidat, S., Simpson, D., Yttri, K.E., 2017. Composition and sources of carbonaceous aerosols in Northern Europe during winter. Submitted.

Hennigan, C.J., Sullivan, A.P., Collett Jr., J.L., Robinson, A.L., 2010. Levoglucosan stability in biomass burning particles exposed to hydroxyl radicals. Geophysical Research 37, L09806.

Hoffmann, D., Tilgner, A., Ilnuma, Y., Herrmann, H., 2010. Atmospheric Stability of Levoglucosan: A Detailed Laboratory and Modeling Study. Environmental Science & Technology 44, 694–699.

Janssen, N.A.H., Hoek, G., Simic-Lawson, M., Fischer, P., van Bree, L., ten Brink, H., Keuken, M., Atkinson, R.W., Anderson, H.R., Brunekreef, B., Cassee, F.R., 2011. Black Carbon as an Additional Indicator of the Adverse Health Effects of Airborne Particles Compared with PM10 and PM2.5. Environmental Health Perspectives 119, 12, 1691-1699.

Ketzel, M., 2016. Personal communication.

Kindbom, K., Skårman, T., Nielsen, O.-K., Winther, M., Saarinen, K., Lappi, M., Lamberg, H, Kolka Jo□nsson, P.V., 2015. Improved emission inventories of SLCP - Background analysis. Göteborg 2015, ISSN 0908-6692. TemaNord 2015:523

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.

Miljøstyrelsen, 2016. http://mst.dk/virksomhed-myndighed/luft/luftforurening-fra-braendeovne-og-braendekedler/

McDonald, J.D., Zielinska, B., Fujita, E.M., Sagebiel, J.C., Chow, J.C., Watson, J.G., 2000. Fine Particle and Gaseous Emission Rates from Residential Wood Combustion. Environmental Science & Technology 34, 2080-2091.

Nøjgaard, J. K., Massling, A., Ellermann, T. (2013) Status for Partikelprojektet 2011 – 2013, Aarhus University, DCE – Danish Centre for Environment and Energy, T10 p.

Nøjgaard, J. K., Massling, A., Christensen, J. H., Nordstrøm, C., & Ellermann, T., 2015a. The Particle Project 2011-2013, Aarhus University, DCE – Danish Centre for Environment and Energy, Scientific Report from DCE, No. 156, 55 p.

Nøjgaard, J. K., Massling, A., Ellermann, T., 2015b. Status for Partikelprojektet 2014-2016, Aarhus University, DCE – Danish Centre for Environment and Energy, 13 p.

Olesen, H. R., Wåhlin, P. & Illerup, J.B. 2010: Brændefyrings bidrag til luftforurening. Nogle resultater fra projektet WOODUSE. Danmarks Miljøundersøgelser, Aarhus Universitet. 71s. Faglig rapport fra DMU nr. 779. http://ww.dmu.dk/Pub/FR779.pdf.

Palmgren, F., Glasius, M., Wåhlin, P., Ketzel, M., Berkowicz, R., Jensen, S.S., Winther, M., Illerup, J.B., Andersen, M.S., Hertel, O., Vinzents, P.S., Møller, P., Sørensen, M., Knudsen, L.E., Schibye, B., Andersen, Z.J., Hermansen, M., Scheike, T., Stage, M., Bisgaard, H., Loft, S., Lohse, C., Jensen, K.A., Kofoed-Sørensen, V. & Clausen, P.A., 2005: Luftforurening med partikler i Danmark, Miljøstyrelsen, Miljøprojekt 1021, 84 p.

Pettersson, E., Boman, C., Westerholm, R., Boström, D., Nordin, A., 2011. Stove Performance and Emission Characteristics in Residential Wood Log and Pellet Combustion, Part 2: Wood Stove. Energy Fuels 2011, 25, 315–323.

Puxbaum, H., Caseiro, A., Sanchez-Ochoa, A., Kasper-Giebl, A., Claeys, M., Gelencser, A., Legrand, M., Preunkert, S., Pio, C., 2007. Levoglucosan

levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosol background. Journal of Geophysical Research 112, D23S05

Schmidl, C., Marr, I.L., Caseiro, A., Kotianova, P., Berner, A., Bauer, H., Kasper-Giebl, A., Puxbaum, H., 2008. Chemical characterisation of fine particle emissions from wood stove combustion of common woods growing in mid-European Alpine regions. Atmospheric Environment 42, 126–141.

Jesu□s San-Miguel-Ayanz, Tracy Durrant, Roberto Boca, Giorgio Liberta□, Francesco Boccacci, Margherita Di Leo, Jorge Lo□pez Pe□rez, Ernst Schulte, 2016. Forest Fires in Europe, Middle East and North Africa 2015. EUR 28158 EN. doi:10.2788/914

Simoneit, B.R.T., Schauer, J.J., Nolte, C.G., Oros, D.R., Elias, V.O., Fraser, M.P., Rogge□, W.F., Cass, G.R., 1999. Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. Atmospheric Environment 33,173-182.

Tissari, J., Hytönen, K., Lyyränen, J., Jokiniemi, J., 2007. A novel field measurement method for determining fine particle and gas emissions from residential wood combustion. Atmospheric Environment 41, 8330–8344.

Vejdirektoratet, 2006. Trafiktællinger Planlægning, udførelse og efterbehandling - Vejledning. Vejdirektoratet, Vej og Tafikområdet. Rapport nr. 315. ISSN 1600-4396, ISBN 87-7923-877- 7

Winther, M. (1999): Analyse af emissioner fra vejtrafikken. Sammenligning af emissionsfaktorer og beregningsmetoder i forskellige modeller. Danmarks Miljø- undersøgelser. 120 s. - Faglig rapport fra DMU, nr. 265

Wåhlin, P., 2003. COPREM—A multivariate receptor model with a physical approach. Atmospheric Environment 37, 4861-4867.

Wåhlin, P. 2008: Partikelprojektet 2005-2007. Danmarks Miljøundersøgelser, Aarhus Universitet. 31s. – Faglig rapport fra DMU nr. 688. http://www.dmu.dk/Pub/FR688.pdf.

Wåhlin, P. (2009) Measured reduction of curbside ultrafine particle number concentrations in Copenhagen, Atmos Environ, 43, 3645 – 3647.

THE PARTICLE PROJECT 2014-2016

The Particle Project 2014-2016 continues the record of particle mass and number measurements on urban and rural locations. Monitoring of Elemental Carbon (EC) has been extended from the rural site RISØ and the urban curbside station HCAB to furthermore include the urban background site HCØ and the suburban site HVID. In addition to traffic, wood combustion is known to be a major source of EC. The Particle Project 2014 - 2016 demonstrates how EC can be used as a marker of wood combustion to quantitatively evaluate primary wood combustion particle concentrations since autumn 2014 at HCØ and RISØ, and from October 2015 at HVID.

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