



THE PARTICLE PROJECT 2017-2018

Scientific Report from DCE - Danish Centre for Environment and Energy

No. 285

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Data sheet

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| Abstract: | The Particle Project 2017-2018 continues the record of particle mass and number measurements on urban and rural locations. Monitoring of Elemental Carbon (EC) has been extended from rural location and curbside station in Copenhagen (2009/2010) to include an urban background site (2014) and a suburban site (2015). EC has traffic and wood combustion as major sources, which is also the case for the volatile compound benzene. The Particle Project 2017 - 2018 evaluates trends in Primary Biomass Burning Particles (PBBA) from Residential Wood Combustion (RWC) based on EC and benzene measurements from late 2009 – 2017 at rural and suburban locations, and urban background. Trends in PBBA from RWC based on measurements are compared with trends in modelled emissions based on emission inventories. |
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Abbreviations and definitions

| | |
|-------------------|---|
| AARHG | Urban curbside measurement site in Aarhus. |
| BC | Black carbon, which is roughly equivalent to elemental carbon. |
| °C | Degrees Celsius. |
| DMPS | Differential Mobility Particle Sizer. |
| CX | Carbon species with x carbon atoms. |
| Dp | Particle diameter. |
| EC | Elemental carbon, roughly equivalent to black carbon (BC). |
| Degree days | Degree days are provided by the Technological Institute and Danish Meteorological Institute (in Danish: Graddage) and shows the differences between actual daily temperature and 17 °C added up to monthly numbers. |
| HCAB | Urban curbside measurement site in Copenhagen. |
| HCØ | Urban background measurement site at H.C. Ørsted Institute in Copenhagen. |
| HVID | Suburban measurement site at Fjelstedvej in Hvidovre. |
| LVS | Low Volume Sampler for atmospheric particles. |
| MS | Mass spectrometry, a technique for quantification of chemical species. |
| OC | Organic carbon, only the mass of carbon itself. |
| PM | Particle mass 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 burning 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. |
| SMPS | Scanning Mobility Particle Sizer. |
| SOA | Secondary Organic Aerosols, i.e. particulate species formed during atmospheric oxidation of VOCs, including VOCs from residential wood combustion. |
| TD-GC-MS | Thermal Desorption Gas Chromatography Mass Spectrometry. |
| TEOM | Tapered Element Oscillating Microbalance. |
| VOC | Volatile Organic Compounds. |

Preface

This report, Partikelprojektet 2017, is divided into two sections. Measurements presents the measurements of 2017 and recent time series at selected monitoring stations, which are not entirely covered by the National Air Quality Program, NOVANA LMP (Ellermann et al., 2017). Particle number concentration, their size distribution and particle mass concentration are physical parameters for particle size classes PM_{10} , $PM_{2.5}$ and PM_1 , i.e. particles with diameter less than or equal to 10, 2.5 and 1 μm , respectively. Chemical parameters include Organic Carbon (OC) and Elemental Carbon (EC) in $PM_{2.5}$, and benzene as a volatile compound. In the second section, Primary Particles from Biomass Burning (PBBA) are calculated based on EC and benzene, which serve as markers for residential wood combustion (RWC). PBBA are calculated from 2010 - 2017 for the monitoring station RISØ north of Roskilde, representing the rural atmosphere, and HCØ in urban background of Copenhagen. The time series is shorter for PBBA at the suburban site HVID, where the marker EC was not sampled until the end of 2015. Finally, the trends of PBBA in different environments are discussed and compared to modelled emissions.

Sammenfatning

I Partikelprojektet 2017 analyseres måletidsserier af PM_{2.5} og PM₁₀, dvs. massekoncentrationer af partikler med diametre mindre end hhv. 2.5 og 10 µm. PM_{2.5} og PM₁₀ måles med Tapered Element Oscillating Microbalance (TEOM) på gadestationerne HCAB og AARHG i hhv. København og Aarhus. Partikelantal og størrelsesfordeling måles endvidere på den landlige målestation RISØ, HCØ, der er bybaggrund i København, målestationen HVID i forstaden Hvidovre samt på en trafikeret gade HCAB. Elementært kulstof, EC, måles endvidere i PM_{2.5} på RISØ, HVID, HCAB og HCØ. På sidstnævnte station måles også det flygtige organiske stof benzen i luften.

Anden del af rapporten omhandler partikelforurening fra brændeovne. Ud fra tidligere benzen og sodmålinger er partikelforureningen fra brændeovne beregnet for perioden slut-2009 til 2017 på RISØ, HCØ og HVID.

Regionale og langtransporterede partikler antages at bidrage i udtalt grad til partikelantallet i PM₁, dvs. partikler med diameter mindre end 1 µm. Den relative forekomst af disse partikler forventes at være størst i landlig baggrund, dvs. på RISØ. Langtransporterede partikler bidrager imidlertid på alle typer målestationer, også målestationer tættere på lokale kilder. Andelen af langtransporterede partikler er dog mindre på HVID, HCØ og især HCAB, hvor partikelforureningen fra brændeovne i fyringssæsonen, og trafikken især på HCAB bidrager med lokale forbrændingspartikler. Regionale og langtransporterede partikler vil have opholdt sig lang tid i atmosfæren og undergået en række fysiske og kemiske reaktioner, der fører til en ensartet størrelsesfordeling. Partikelantalskoncentrationen udviser således én top på 40 nm eller større på RISØ, HVID og HCØ. HCAB adskiller sig fra de andre målestationer ved en størrelsesfordeling, hvor partikelantalskoncentrationen har en ekstra top ved 20 nm. Denne størrelse partikler er tidligere identificeret som emissioner fra biludstødning. Toppen kunne dog ikke verificeres i 2017, da der ikke er data til rådighed i netop dette måleområde pga. problemer med måleudstyr. I denne rapport er der undersøgt størrelsesfordelingerne 41-550 nm (oprindelige måleinstrumenter) og 41 - 478 nm (nye måleinstrumenter). Partikelantalskoncentrationerne på HCAB, RISØ, HVID og RISØ har været omtrent konstante fra 2016 - 2017. Mindre forskelle skyldes sandsynligvis meteorologiske forskelle. Over en 10-årsperiode er der observeret faldende partikelantalskoncentrationer på alle målestationer. Partikelantalskoncentrationen var højere i forstaden HVID end i bybaggrund på HCØ i 2017. Forskellen skyldes sandsynligvis en tættere trafikal infrastruktur omkring målestationen HVID samt flere brændeovne i området, der især påvirker målingerne i den koldere del af året. Tilsvarende findes det, at Partikelantalskoncentrationen på HCØ er højere end på RISØ, samt at partikel antalskoncentrationen på HCAB overstiger HCØ og HVID.

Partikelmassekonzentrationer blev målt med TEOM. PM_{2.5} på HCAB fortsatte den generelle trend siden 2002 med at aftage til 10 µg/m³ i 2017. Modsat blev der observeret en stigning i PM₁₀ på både RISØ (12 µg/m³) og HCAB (26 µg/m³) i 2017. En ny tidsserie blev påbegyndt på AARHG (15 µg/m³) i 2017.

EC-målinger i bybaggrund blev påbegyndt september 2014. I 2017 udgjorde EC årsmidlerne 0,27 µg/m³ på RISØ og 0,33 µg/m³ - >33 µg/m³ på HCØ. Højere koncentrationer blev målt på HVID (0,39 µg/m³), og endnu højere blev

målt på HCAB ($1,16 \mu\text{g}/\text{m}^3$). EC vedblev i 2017 med at aftage, hvor en nedadgående trend har været observeret på HCAB siden 2010 og på HVID siden 2015, hvor målingerne blev påbegyndt. Kun små ændringer blev observeret på RISØ og HCØ.

Benzen-målinger i bybaggrund blev igangsat på HCØ i 2009. Her har benzen siden 2010 ($0,75 \mu\text{g}/\text{m}^3$) aftaget med 52% til 2017 ($0,49 \mu\text{g}/\text{m}^3$). På HCAB er benzen aftaget med 52% fra 2010 ($1,33 \mu\text{g}/\text{m}^3$) til 2017 ($0,64 \mu\text{g}/\text{m}^3$).

Benzen og EC er i denne rapport anvendt som markører for biomasseafbrænding til at beregne koncentrationen af primære partikler fra brændeovne, forkortet PBBA, i perioden 2010 – 2017. Til dette er anvendt en teknik, som blev introduceret i det forgangne Partikelprojekt 2014 - 2016. PBBA er beregnet i daglig tidsopløsning og som årsmidler for den landlige station RISØ, bybaggrund på HCØ og forstad HVID. Den længste tidsserie fra 2010 – 2017 er beregnet for den landlige station på baggrund af EC samt bybaggrund baseret på benzen. Idet målinger af markører er en forudsætning for beregningen af PBBA, er den korteste tidsserie for HVID, hvor måling af EC først blev startet op i slutningen af 2015. Idet to markører er til rådighed på HCØ, kan uafhængige beregninger af PBBA sammenlignes fra 2015. Begge beregninger viser, at PBBA aftager i perioden, hvor begge markører er målt. Generelt aftog PBBA på alle stationer i perioden 2010-2017, og de højeste målinger blev observeret på HVID.

PBBA-årsmidler var sammenlignelige på det landlige site og bybaggrund, dog var sidstnævnte højest i perioden 2015-2017, hvor markøren EC blev målt på begge stationer. Denne forskel aftog dog fra 2015 (40%) til 2017 (5%). PBBA-årsmidlerne var højest i 2010 og 2011 og er siden aftaget. Det vil sige, som et årgennemsnit på de to lokaliteter indeholdt luften $1,6-2,5 \mu\text{g}/\text{m}^3$ primære partikler, der overvejende kommer fra brændeovne. Koncentrationerne er højere i fyringssæsonen og tilsvarende lavere om sommeren. PBBA blev beregnet over to kalenderår for vintersæsonen (december, januar, februar). PBBA i bybaggrund aftog fra $4,0 \mu\text{g}/\text{m}^3$ i 2010/2011 til $2,7 \mu\text{g}/\text{m}^3$ i 2016/2017. En tilsvarende trend blev beregnet for RISØ, nemlig $3,9 \mu\text{g}/\text{m}^3$ i 2010/2011, hvilket aftog til $2,5 \mu\text{g}/\text{m}^3$. Højere koncentrationer blev beregnet på HVID ($3,3 \mu\text{g}/\text{m}^3$) i 2016/2017. Resultaterne indikerer, at eksponering for primære partikler fra brændeovne kan være højere i forstæderne end i bybaggrund. Desuden kan eksponeringen i bybaggrund være højere end det landlige miljø. Tidsserier af PBBA-årsmidler udviser en nedadgående trend til at begynde med, samt en let stigning fra 2016-2017. En sammenligning af PBBA med Black Carbon (BC) "sod" fra brændeovne, som er modelleret ud fra emissionsopgørelser viste, at førstnævnte aftog mere end det modellerede i perioden 2010 – 2017. Begge metoder viste et fald i produkterne til at begynde med.

Summary

The Particle Project 2017 presents time series of particle mass concentrations smaller than 2.5 μm ($\text{PM}_{2.5}$) and particles smaller than 10 μm (PM_{10}) at the rural site RISØ and curbside stations in Aarhus (AARHG) and Copenhagen (HCAB) using TEOM. Particle size distributions are furthermore analyzed at the rural site (RISØ), in urban background (HCØ), street station (HCAB) and at the suburban site (HVID). Also presented are analysis of Elemental Carbon (EC) in particles at RISØ, HVID and HCØ, and at the latter monitoring station also benzene, which is a Volatile Organic Compound (VOC). 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 late 2009 to end of 2017.

Regional and long-range transported aerosols are expected to contribute to a large extent to the particle number in the submicrometer size range. On a relative base the highest contribution of such aerosols are found at rural background sites as e.g. RISØ in Denmark. As a consequence, long-range transported aerosols also contribute to other sites which are located with smaller distances to local sources. For Denmark, this means that the relative contribution of such aerosols decreases when considering the suburban site at HVID, the urban background site HCØ and finally the urban curbside site HCAB. The processed aerosol at the rural, suburban and urban background sites results in a nearly mono modal particle number size distribution with mean diameters of about 40 nm and larger at RISØ, HVID and HCØ. As a general difference the particle number size distributions at HCAB appears somewhat bimodal as an additional peak was observed at around 20 nm from vehicle exhaust emissions during previous projects. This finding cannot be concluded for the year 2017 as no data is available for the smallest size range at HCAB for this specific year. As a general finding it has been observed that the total submicrometer number concentration as discussed in this report in the size range between 41 and 550 (old instruments) and 41 and 478 nm (new instruments) has been nearly constant between the years 2016 and 2017. Smaller differences are most likely due to meteorological variations. A trend of decreasing concentrations can be found at all stations when considering time periods of the order of a decade. Obviously higher particle number concentrations were observed at the suburban background station HVID compared to the urban background station HCØ. A reason might be the location of HVID surrounded within a residential area with potentially high wood stove emissions during wintertime and surrounded by a number of high-trafficked highways.

$\text{PM}_{2.5}$ measured by TEOM at HCAB continued to decrease in 2017 (10 $\mu\text{g}/\text{m}^3$) in agreement with the overall trend since 2002. PM_{10} as measured by TEOM, however, increased at RISØ (12 $\mu\text{g}/\text{m}^3$) and HCAB (26 $\mu\text{g}/\text{m}^3$) in 2017. A new time series for PM_{10} was initiated at AARHG in 2017 (15 $\mu\text{g}/\text{m}^3$).

Measurements of EC in urban background was initiated in September 2014. In 2017, EC averaged 0.27 $\mu\text{g}/\text{m}^3$ at RISØ and 0.33 $\mu\text{g}/\text{m}^3$ at HCØ. Higher concentrations were measured at the suburban station HVID (0.39 $\mu\text{g}/\text{m}^3$) and even higher at HCAB (1.16 $\mu\text{g}/\text{m}^3$). EC concentrations are thus showing

an overall decreasing trend at HCAB since 2010, and at HVID since measurements were initiated in 2015, whereas little changes are observed at rural and urban background.

Measurements of benzene in urban background was initiated in end 2009. Benzene has decreased by 52% from 2010 (1.33 $\mu\text{g}/\text{m}^3$) to 2017 (0.64 $\mu\text{g}/\text{m}^3$) at HCAB. In urban background, benzene has decreased by 35% from 0.75 $\mu\text{g}/\text{m}^3$ to 0.49 $\mu\text{g}/\text{m}^3$ in the same period.

Benzene and EC was utilized to calculate Primary Biomass Burning Aerosols (PBBA) from residential wood combustion (RWC) for the period 2010 – 2017. The applied technique was introduced in the previous Particle Project 2014-2016. Daily and annual concentrations of PBBA were calculated for the rural site RISØ, urban background HCØ and suburban site HVID. The longest time series from 2010-2017 are found for RISØ based on the marker EC, and urban background based on benzene. Since the availability of the marker is a prerequisite of calculating PBBA, the shortest time series is at HVID, where measurements of EC were not initiated until late 2015. At HCØ, both benzene (from 2010) and EC (from late 2014) measurements are available, which provided two independent measures of PBBA. Generally, PBBA concentrations decrease from 2010-2017 at all sites. The highest concentrations were calculated at the suburban station.

Annual averages of PBBA at the rural site and urban background are generally showing comparable concentrations and trends. PBBA concentrations in urban background exceeded those at the rural site during 2015 – 2017, where the same marker was measured at both sites. However, this increment has decreased from 40% in 2015 to 5% in 2017.

Annual averages of PBBA were highest in 2010 and 2011. That is, as an annual average at these sites, ambient air contained 1.6 - 2.5 $\mu\text{g}/\text{m}^3$ primary particles in the $\text{PM}_{2.5}$ fraction originating from biomass burning of which residential wood combustion is believed to be the major contributor. In the winter season, these concentrations were higher and conversely lower during summer.

PBBA concentrations were also calculated season wise during winter (December, January, and February) in two calendar years. Urban background PBBA decreased from 4.0 $\mu\text{g}/\text{m}^3$ in 2010/2011 to 2.7 $\mu\text{g}/\text{m}^3$ in 2016/2017. A comparable trend was calculated for the rural site, i.e. 3.9 $\mu\text{g}/\text{m}^3$ in 2010/2011 decreasing to 2.5 $\mu\text{g}/\text{m}^3$. At the suburban site 3.3 $\mu\text{g}/\text{m}^3$ was calculated for 2016/2017. These results indicate that exposure to primary particles from residential wood combustion may be higher in the suburbs than rural and urban background. Furthermore, the exposure may be higher in urban background than at rural locations.

Time series of annual average PBBA concentrations shows an initially decreasing trend, which has increased slightly in 2017. By comparison with a product of RWC modelled from emission inventories, measured concentrations decreased more than modelled ones. Both techniques showed an initial decrease in pollutants from RWC from 2010.

1. Measurement

1.1 Particle number

To measure the particle number size distribution in the submicrometer size regime, custom built DMPS instruments (Differential Mobility Particle Sizer) were used from 2001/2002 and ongoing during several Particle Projects. Measurements of the particle number size distribution in the range from 6 to 700 nm in diameter were carried out in and around Copenhagen at the regional background station RISØ (previously Lille Valby), the urban background station HCØ and the urban curbside station HCAB. From 2017 and ongoing the instruments at HCAB and RISØ were replaced with commercial instruments delivered by TSI (Model 3938). These are SMPS instruments (Scanning Mobility Particle Sizer) and measure in the size range between 11 and 478 nm. At HCØ, one of the original DMPS instruments is still in use and from the end of 2015 and ongoing an additional SMPS instrument delivered by TSI (Model 3938) is operated at the suburban station HVID in Hvidovre.

For future comparison data in the size range from 11 to 550 nm will be discussed for the old instruments and data in the size range from 11 and 478 nm will be discussed for the new instruments as only in this way a comparison of historical and new data is possible. A slightly larger size range up to 550 nm (old instruments) compared to 478 nm (new instruments) does nearly have no effect on the number comparison as numbers for particles larger than 500 nm are typically very small for atmospheric measurements.

In addition, some problems with respect to data for particles smaller than 41 nm in diameter for the new instruments were discovered. These problems are still under investigation and for this reason only data from 41 nm and larger will be included in this specific report. The problems might be linked to the inlets used for the instruments or the instruments themselves.

Also, slight changes of the presented number concentrations of new instruments might occur in the future as preliminary calibration factors for the instrument flows and their inlets are applied to the data that might slightly change when investigations are finalized. Final data will therefore be presented in future reports.

Table 1.1. Data coverage for DMPS/SMPS measurements at the rural site RISØ, suburban site HVID, urban background site HCØ and urban curbside HCAB.

| | Rural (RISØ) | Suburban (HVID) | Urban background (HCØ) | Urban curbside (HCAB) |
|------|--------------|-----------------|------------------------|-----------------------|
| 2017 | 72% | 75% | 38% | 74% |

The data of the particle number size distributions were obtained with 30 minutes time resolution. Data at HCØ were obtained with one of the original DMPS instruments, and that data coverage is affected by constant service and repair of the instrument. Data acquisition at HCAB and RISØ started in February 2017 as new instruments first had to be delivered and tested. In addition, a workshop with the instruments located at Risø, taking the HVID and HCAB system to Risø for data comparison was carried out during the summer 2017 to identify the malfunctioning of the new instruments, or their respective inlets, in the size range between 11 and 41 nm. For this reason, instruments

had to be relocated for intercomparison and could not be operated in the routine air quality monitoring program for a number of weeks.

1.1.1 Particle number size distribution

In Figure 1.1, the average of the annually mean particle number size distributions at regional background (RISØ), suburban station (HVID), urban background (HCØ) and urban curbside (HCAB) are shown for 2017 together with data from 2011 to 2013 (not available at HVID) and from 2014 - 2016 (only 1 year and three months available at HVID), representing previous particle project periods. Particle number size distributions were obtained in the size range from 6 to 700 nm as the old DMPS systems were applied during these projects. For a clear comparison, only the size range 11 - 550 nm and in this special case 41 - 550 nm is shown, so that data can be compared for the years when new instruments were applied in the project. Particle number size distributions were obtained from 11 - 478 nm when the new SMPS systems were applied in this project, but because of the problems mentioned earlier at RISØ, HVID and HCAB, only data between 41 and 478 nm are considered for 2015-2017 (HVID), and 2017 (RISØ and HCAB).

In general, a decay in particle numbers has been observed at all three stations, i.e. HCAB, HCØ, and RISØ considering the last two Particle Project periods from 2011 - 2013 and 2014 - 2016. At the suburban station HVID, no data is available from 2011 to 2013 and as the measurements were initiated in 2015, the average for 2014 to 2016 only includes about 15 months of data. For this reason, no trend can be observed and discussed at this location.

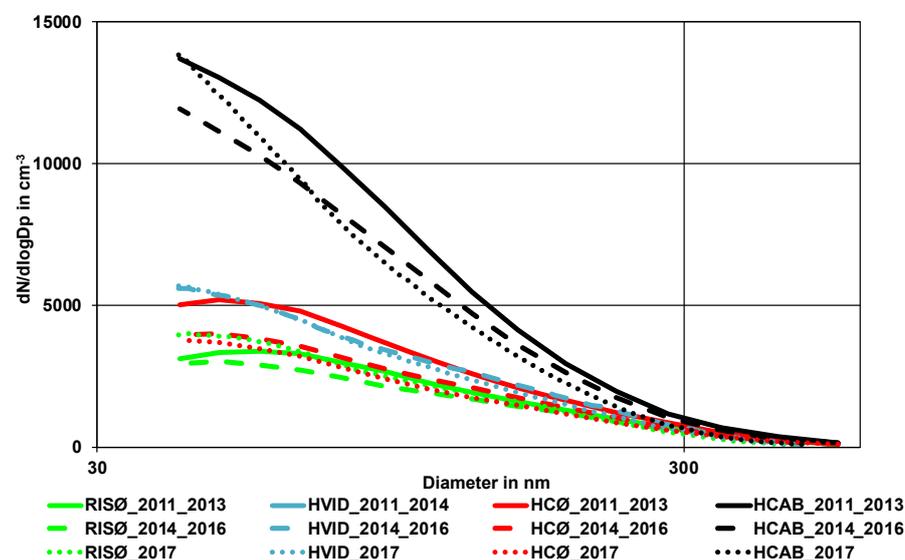


Figure 1.1. Average of annual means of particle number size distributions at regional background (RISØ), suburban background (HVID), urban background (HCØ) and urban curbside (HCAB) during 2011 - 2013 and 2014 - 2016 (previous particle projects) compared to annual means of particle number size distributions (particle diameter $D_p = 41 - 550$ nm for old instruments and $D_p = 41 - 478$ nm, new instruments) at RISØ, HVID, HCØ and HCAB in 2017 (current particle project)

A slight increase in particle number can be observed for smaller particle fractions at RISØ and HCAB in 2017. Whether this trend is real or an artefact introduced with the setup of new instruments and their respective inlets has to be investigated further in future data analysis, and when more data is available. Also, such differences can be caused by meteorological variations that occur from one year to the next year. For this reason data have to be investigated over a series of many years to draw conclusions and analyse real trends.

As a general trend it has been observed that the particle number size distributions decrease with distance to major sources of aerosol particles. This is the case as the polluted air gets diluted with fresh air during aging processes resulting in a general decrease of particle numbers in the respective air mass. Also, the mean diameters are increasing for aerosols observed with larger distance to major sources (Nøjgaard et al., 2015). It is expected that local sources in urban areas mostly contribute to ultrafine particles being smaller than 100 nm in diameter and in this way particle size distributions close to major sources are characterized by in general smaller mean diameters.

At HVID it is also obvious that the particle number size distribution looks quite similar for the period 2014 to 2016 compared to 2017. Having in mind that the period 2014 to 2016 only includes three months of 2015 and the year 2016 (as mentioned earlier) it can be concluded that the particle number size distribution in 2015 and 2016 has been nearly unchanged at the suburban background HVID. Note that the particle number size distribution at HCØ appears with smaller numbers when comparing it to HVID for the same years. One explanation is that HVID is located within a residential area which may have larger emissions based on wood stoves in wintertime and in addition it is also located in the vicinity of a number of highly busy roads and highways resulting in a site as polluted as HCØ located in the middle of Copenhagen with respect to submicrometer aerosol.

The largest number of small particles is expected at the urban curbside station HCAB also in 2017. This large number is a result of ultrafine particles originating from vehicle exhaust emissions close to trafficked roads.

1.1.2 Particle number fractions

For a more detailed analysis, particle number concentrations were determined in specific size regimes, in this case particles with diameters of $D_{pF1} = 41 - 110$ nm and $D_{pF2} = 110 - 550$ nm for old instruments and $D_{pF1} = 41 - 110$ nm and $D_{pF2} = 110 - 478$ nm for new instruments at all four stations. In Figure 1.2 averages of the annual means for the years 2011 to 2013 and 2014 to 2016 are calculated. At HVID, no data is available prior to late 2015. In addition, data for the year 2017 are added as annual means for all four stations. The results of this grouping are presented in Figure 1.2 for RISØ, HVID, HCØ and HCAB.

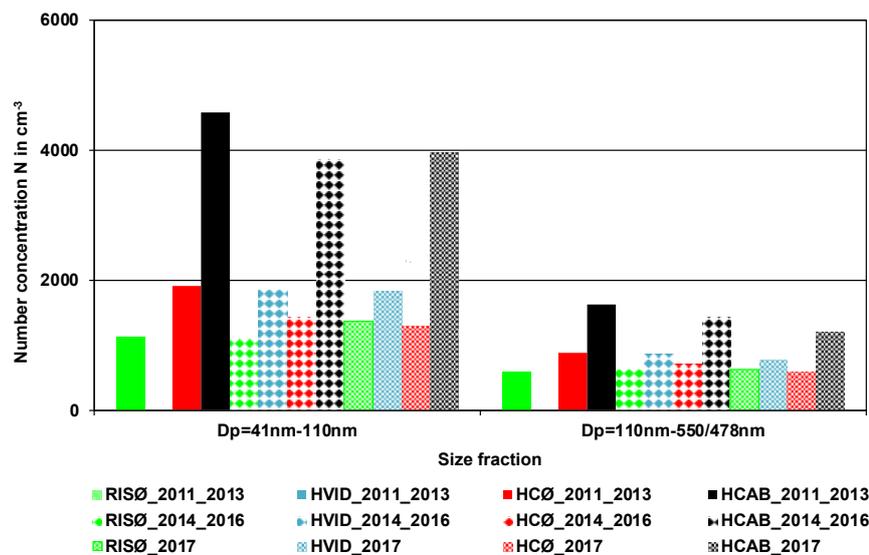


Figure 1.2. Average of annual means of particle number concentrations in specific size regimes DpF1 = 41 – 110 nm and DpF2 = 110 – 550 nm (old instruments) and DpF1 = 41 – 110 nm and DpF2 = 110 – 478 nm (new instruments) at regional background (RISØ), sub-urban background (HVID), urban background (HCØ) and urban curbside (HCAB) during 2011 - 2013 and 2014 - 2016 (previous particle projects) compared to annual means of particle number concentrations in specific size regimes DpF1 and DpF2 at RISØ, HVID, HCØ and HCAB for the year 2017 (current particle project).

For HCAB, the largest particle number is typically found in the smallest size regime from 11 to 41 nm (Wåhlin, 2009), which is not presented here. However, a tendency for decreasing particle number can be observed at HCAB for the largest size regime when comparing the last 7 years. For the middle size regime, a decrease is observed between 2011 – 2013 and 2014 - 2016 data. In 2017, a slight increase is observed. A general decrease in particle number is in accordance to the European trend of avoiding particulate emissions especially from road traffic where new environmental regulations and cleaner technologies are continuously introduced. This tendency can also be observed at the urban background station HCØ when looking at the trends comparing 2011 - 2013, 2014 - 2016 and finally 2017.

Measurements at HVID do not reflect this trend which is most likely due to the short time period that is under investigation. Nevertheless, it can be concluded that HVID is showing larger numbers compared to HCØ especially in the middle size regime. This might be the case because of the location having in mind that HVID is surrounded by a residential area and many trafficked roads and highways. As mentioned above, emissions from the residential area can especially in wintertime significantly contribute to particle number because of the application of wood stoves.

In general, particle number size distributions cannot be obtained with higher certainty than 10% in number even if highest calibration procedures are applied. This makes clear that differences between urban background and sub-urban background must not be significantly different especially for the larger particle size fraction where more long-range transported aerosols are observed and results are expected to be similar.

Measurements at RISØ do show a small decay in number when considering trends over more than a decade. The small magnitude of this trend is expected as the background aerosol is affected by general emissions in Europe and worldwide based on anthropogenic activities as well as on natural processes resulting in relatively stable values over time. For the middle size regime, numbers at RISØ are increasing a little in 2017, which again can be a natural variation based on meteorological factors that can highly impact on the particle numbers observed for a single year.

1.2 Particle mass concentration using TEOM

Particulate matter (PM) is often based on gravimetric measurements for a specified size range, e.g. smaller than 2.5 micrometre (PM_{2.5}) or less than 10 micrometre (PM₁₀). In addition to gravimetric measurements, PM is measured using a TEOM (Tapered-Element Oscillating Microbalance) instrument at urban curbside HCAB (PM₁₀ and PM_{2.5}), Aarhus curbside (PM₁₀) and at the rural station RISØ (PM₁₀). Time resolution is 30 minutes (Table 1.2 and 1.3), which enables near real time reporting of data to the public. During sampling the collected particles are heated to 50°C. Consequently, semivolatile particulate species may evaporate. Examples are Secondary Organic Aerosols (SOA) and in particular ammonium nitrate, NH₄NO₃. Evaporative loss will depend on chemical composition of the aerosols. The European Commission has accepted that measurements of PM using TEOM could be applied with a default correction factor of 1.3. However, the correction factor depends e.g. on the specific measurement site and seasonality. Correction of TEOM measurements of PM using a correction factor of 1.3 does therefore have considerable uncertainty.

Table 1.2. 2017 annual statistics for PM₁₀ measured by TEOM. The values are based on 30 minutes averages.

| Unit: µg/m ³ | Data coverage | Average | Average x 1.3 |
|-------------------------|---------------|---------|---------------|
| Street | | | |
| HCAB | 98% | 26 | 34 |
| AARHG | 91% | 15 | 19 |
| Rural | | | |
| RISØ | 90% | 12 | 15 |
| Limit value | | | 40 |

Table 1.3. 2017 annual statistics for PM_{2.5} measured by TEOM. The values are based on 30 minutes averages

| Unit: µg/m ³ | Data coverage | Average | Average x 1.3 |
|-------------------------------------|---------------|---------|---------------|
| Street | | | |
| HCAB | 99% | 10 | 13 |
| 2015 Limit value (2020 in brackets) | | | 25 (20) |

The time series of TEOM PM_{2.5} at RISO was discontinued in 2017, leaving HCAB the sole monitoring station left with PM_{2.5} measurements by TEOM. At the same time, measurements of PM₁₀ by TEOM were initiated at a curbside station in Aarhus (AARHG) in 2017. Thus, PM₁₀ is measured by TEOM at the curbside stations AARHG and HCAB, and at the rural site RISØ from 2017.

In 2017 PM_{2.5} continues to decrease at HCAB, whereas PM₁₀ increases at RISØ and HCAB (Figures 1.3 and 1.4).

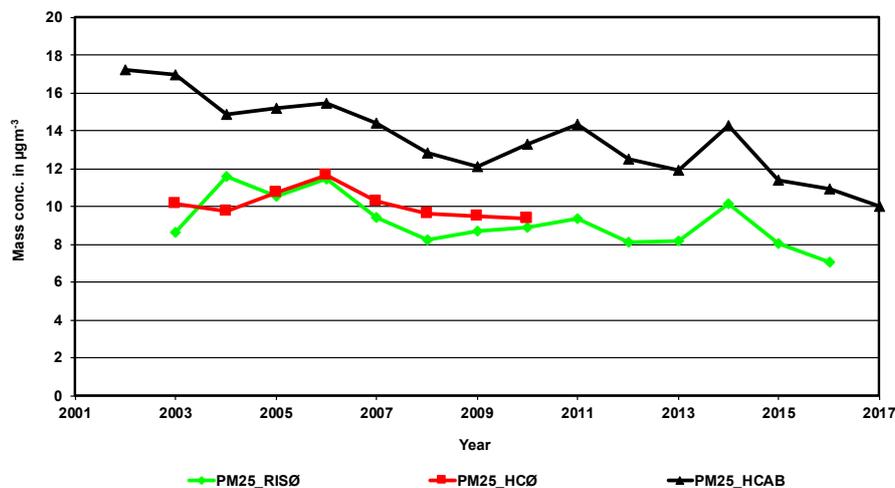


Figure 1.3. Trend in annual means of TEOM PM_{2.5} at rural site (RISØ), urban background (HCØ) and urban curbside (HCAB) during 2002 – 2017.

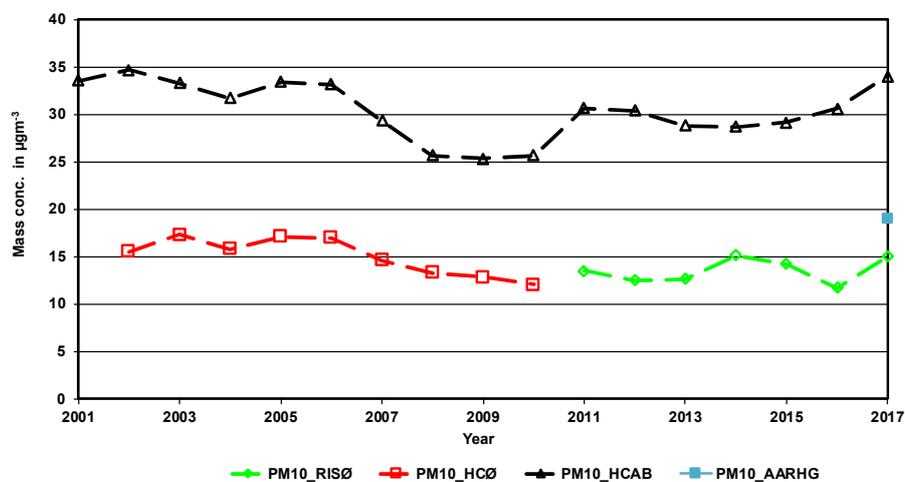


Figure 1.4. Trend in annual means of TEOM PM₁₀ at rural site (RISØ), urban background (HCOE) and urban curbside (HCAB) during 2002 – 2017.

1.3 Elemental carbon (EC) mass concentration

Soot, the blackish or brownish substance formed during incomplete combustion (Andrea and Gelencsér, 2006) is typically measured by exploiting its light absorbing properties as Black Carbon (BC) or its chemical inertness as elemental carbon (EC). EC has been measured using the European standard thermal optical protocol EUSAAR2 (Cavalli et al., 2010).

EC is operationally defined based on a Thermal Optical technique as carbon which is only combusted in the presence of oxygen at temperatures higher than 500°C (Birch and Cary, 1996; Cavalli et al., 2010).

Low Volume Samplers (LVS) located at urban curbside (HCAB) and urban background (HCØ) in addition to rural (RISØ) and suburban (HVID) locations were equipped with PM_{2.5} inlets. Atmospheric aerosols were collected on quartz fiber filters with 24 hour time resolution. Quartz fiber filters were weighed to measure PM_{2.5} mass concentration, and 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).

EC and organic carbon (OC) have been monitored routinely at RISØ and HCAB from 2009/2010 and onwards. Monitoring of EC was extended to urban background in Copenhagen by September 2014, and to a suburban location at Fjelstedvej in Hvidovre by October 2015.

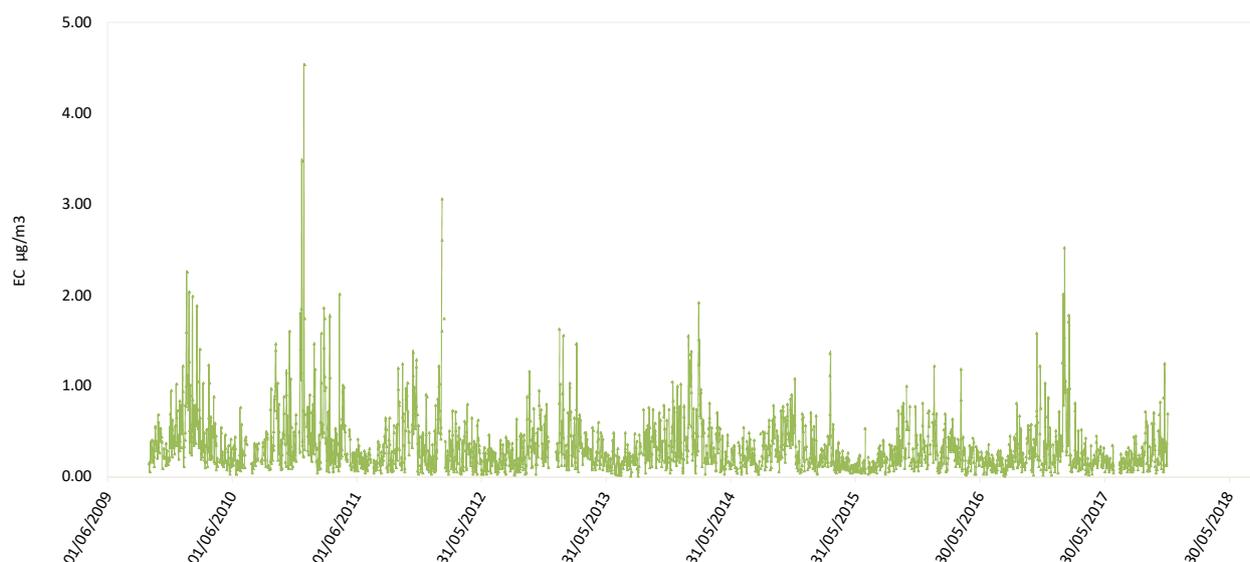


Figure 1.5. Trend in annual EC concentrations at the rural site RISØ.

Figure 1.5 shows more than 7 years of EC measurements at RISØ. The annual variation is mainly caused by wood stove emissions (Section 2). Concentrations down to 0.1 - 0.2 µg/m³ are observed during the summer, whereas average winter concentrations are typically around 0.5 µg/m³. Peak concentrations at 2 - 5 µg/m³ are occasionally observed. Ambient EC concentrations are lowest in rural areas and highest at urban curbside (Figure 1.6). In 2017, annual averages were: rural EC: 0.27 µg/m³ < urban background EC: 0.33 µg/m³ < suburban EC: 0.39 µg/m³ < urban curbside EC: 1.16 µg/m³.

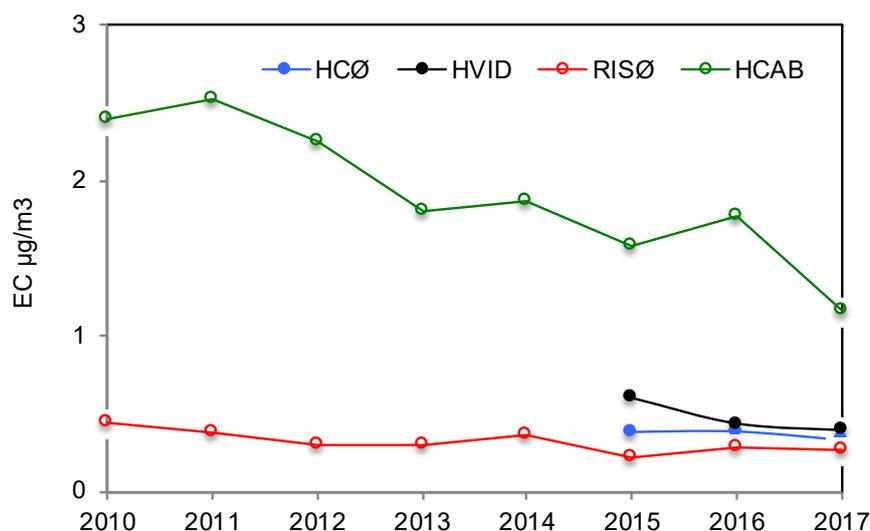


Figure 1.6. Trend in annual EC concentrations at urban background (HCØ), suburban (HVID) and rural locations (RISØ) and urban curbside (HCAB).

EC has shown a pronounced reduction of 51% at HCAB in the period 2010 – 2017, predominantly due to a reduction in traffic emissions as the share of particle filters within the fleet of diesel vehicles increases with more stringent emissions standards for newer vehicles. Although EC decreased by 39% at the rural site RISØ, this corresponds to a much smaller absolute concentration (Figure 1.6). That is, local traffic is a major source of EC. HCØ appears to follow the same trend as the rural site, though only based on 3 years of data. In 2017, HCØ ($0.33 \mu\text{g}/\text{m}^3$) and HVID ($0.39 \mu\text{g}/\text{m}^3$) experienced EC concentrations 29 and 50% higher than at RISØ. For HCØ the increment from rural locations was 31% ($0.10 \mu\text{g}/\text{m}^3$) on weekdays and 21% ($0.07 \mu\text{g}/\text{m}^3$) in the weekends, which reflects the impact of traffic in urban background.

1.4 Benzene mass concentration

Volatile Organic Compounds (VOC) were collected at HCØ 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 C5-C9 organic species, including benzene. Samples were collected with a time resolution of 24 hours. A reduced set of VOCs: Benzene, Toluene, Ethylbenzene, and isomers of Xylene are sampled at the curbside stations HCAB and Jagtvej in Copenhagen. These VOCs are collected in weekly time resolution using passive sampling, and subsequently extracted and analyzed by Gas Chromatography MS (GC-MS).

Benzene has been monitored routinely in urban background since 2010 (Figure 1.7), and on curbside stations since 2001. Concentrations down to $0.1 - 0.2 \mu\text{g}/\text{m}^3$ are observed during summer, whereas winter concentrations are typical $1 - 2 \mu\text{g}/\text{m}^3$. Peak concentrations of $2 - 4 \mu\text{g}/\text{m}^3$ are occasionally observed. Benzene shows the same variation in time as EC, which is repeated every year (Figure 1.7).

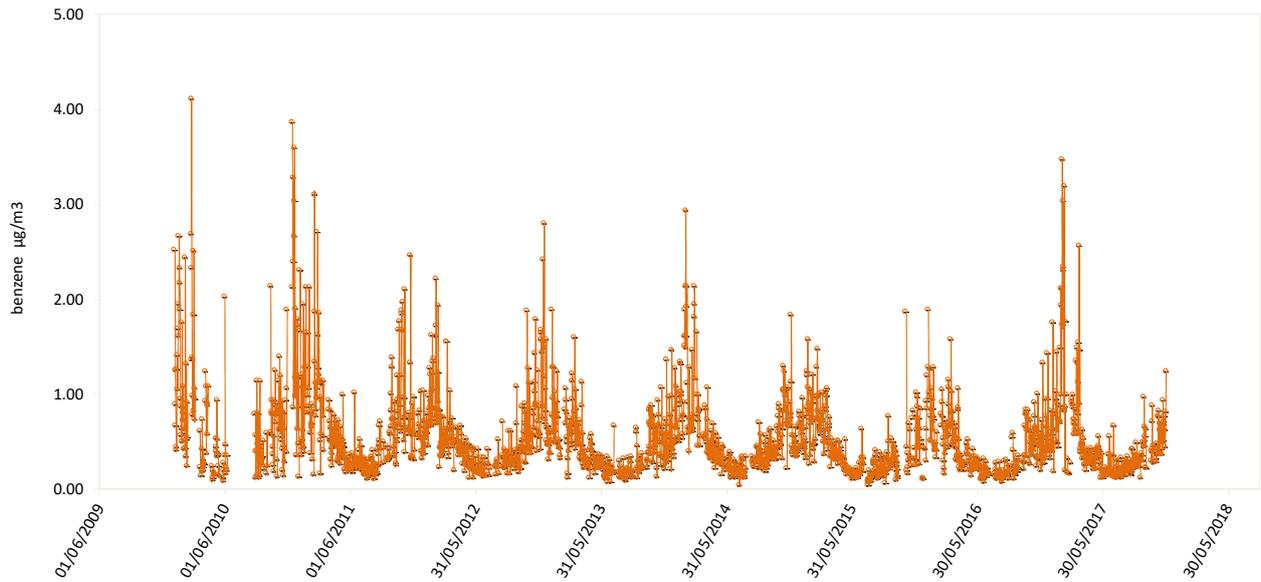


Figure 1.7. Trend in diurnal benzene concentrations at urban background in the period 01.01.2010 – 31.12.2017.

Benzene has decreased by 52% from 2010 (1.33 $\mu\text{g}/\text{m}^3$) to 2017 (0.64 $\mu\text{g}/\text{m}^3$) at HCAB. As for EC, the reduction is predominantly due to improved catalytic removal of VOCs from tailpipe emissions of gasoline fueled vehicles in Europe (Winter, 2018). In urban background, benzene has decreased by 35% from 0.75 $\mu\text{g}/\text{m}^3$ to 0.49 $\mu\text{g}/\text{m}^3$ during the same period. That is, long-range transport of traffic emissions has also decreased.

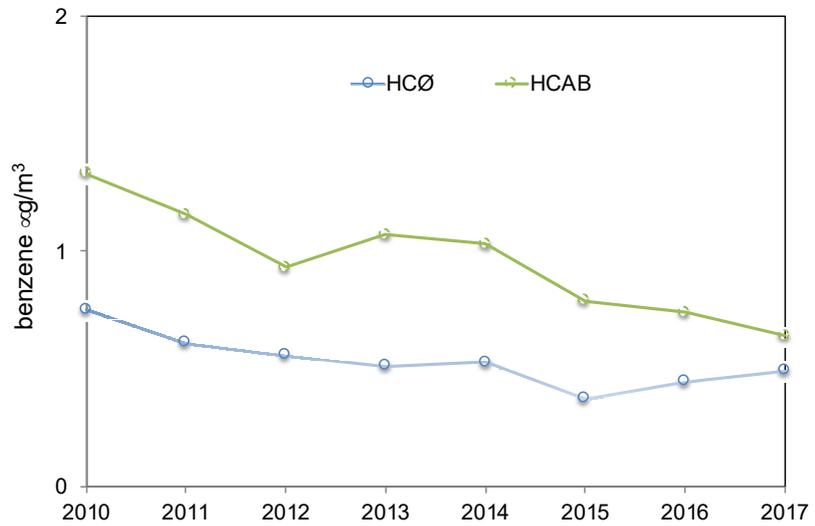


Figure 1.8. Trend in annual benzene concentrations at urban background (HCØ) and urban curbside (HCAB).

2. Residential Wood Combustion

2.1 Marker for residential wood combustion

Major sources of EC and benzene include traffic emissions and residential wood combustion (RWC). Residential heating using wood stoves leads to incomplete combustion, and thereby emission of a number of gaseous pollutants including VOCs such as benzene, and particles containing salts, organic compounds and EC. Benzene and EC are thus markers of biomass burning.

In the literature, abundances and shares of benzene and EC are available for different types of wood stoves and fuels (wood) applied in laboratory studies and field studies. The shares of these markers relative to particle mass are subject to variation, for which reason a number of studies should be averaged to find shares representative for real-life conditions. Markers can be specific for wood combustion, e.g. the sugar anhydrides levoglucosan and mannosan are produced during combustion of cellulose, which is found in wood (Nøjgaard et al., 2015). Other markers are less specific, and they are emitted during incomplete combustion from a number of sources, e.g. benzene and EC.

While the costs of analysing specific markers such as levoglucosan are expensive and therefore typically applied in shorter campaigns, benzene and EC are sampled and analysed on a routine basis in the Danish Air Quality Monitoring Program (Ellermann et al., 2017).

In the Particle Project 2014-2016 we introduced a technique to calculate primary biomass burning aerosols (PBBA) from RWC based on benzene and EC (Nøjgaard et al., 2017), which is briefly presented in section 2.2.

2.2 Calculation of PBBA based on benzene and EC

Pollution from residential wood combustion is not a single chemical compound, but comprise gasses, VOCs and particles containing a number of organic compounds and salts in addition to EC. Apart from spatially and time limited case studies, contribution from 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 Bio-mass Burning Aerosol (PBBA). As the wood smoke ages in the atmosphere, VOCs reacts with e.g. ozone and radicals in the atmosphere and is partly transformed into additional particle mass, which by definition is called Secondary Organic Aerosols (SOA). While SOA from wood combustion is extremely difficult to isolate and quantify, PBBA can be quantified by use of markers, such as levoglucosan. In the following, it is described how the less specific markers benzene and EC are utilized to calculate PBBA. The contribution to SOA is neglected. However, this issue is briefly discussed in section 2.4.

Benzene and EC were used as markers for traffic and wood combustion to calculate PBBA in 3 steps:

- 1) The contribution of other sources than RWC to the markers (EC or benzene) is subtracted. In brief, a baseline concentration with minimum impact from residential wood combustion is calculated from marker concentrations at the specific measurement site during the actual year investigated from 1 June – 15 July. 23-24 June are excluded. Table 2.1 illustrates the trend in EC and benzene baselines, which decrease during 2010 – 2017. It is therefore important to correct a particular concentration of a marker with the baseline from the actual year. Furthermore, since the baseline is mainly impacted by traffic the average is down weighed by 30% on Saturdays and 60% on Sundays (Nøjgaard et al., 2017). Moreover, 17% of the average marker concentration in this period is assumed to origin from biomass burning as evidenced by campaign measurements using the specific tracer levoglucosan (Nøjgaard et al., 2017). A baseline is thus calculated for each year at each measurement site and corrected for traffic on weekdays, and weekends, taking summer biomass burning into account.

Table 2.1. Annual site-specific baseline concentrations for EC and benzene ($\mu\text{g}/\text{m}^3$) calculated from 1 June – 15 July, excluding 23-24 June and subtraction of a summer specific contribution from biomass burning. Blank fields = data not available.

| Date | Urban back-ground | HCØ | Suburban (HVID) | Rural (Risø) |
|---------------|-------------------|------|-----------------|--------------|
| 01.06.-.15.07 | Benzene | EC | EC | EC |
| 2010 | 0.16 | | | 0.17 |
| 2011 | 0.16 | | | 0.15 |
| 2012 | 0.16 | | | 0.14 |
| 2013 | 0.14 | | | 0.10 |
| 2014 | 0.17 | | | 0.13 |
| 2015 | 0.14 | 0.15 | | 0.08 |
| 2016 | 0.15 | 0.16 | 0.14 | 0.11 |
| 2017 | 0.13 | 0.14 | 0.14 | 0.09 |

- 2) Identification of $\text{PM}_{2.5}$ -to-marker ratios from source apportionment databases, e.g. from *US EPA's Speciate* or *JRC's Specieurope*. A conversion factor for EC of 6.2 was averaged from 5 studies involving hardwood (3) and softwood (2). Similarly, a conversion factor for benzene of 3.7 was averaged from studies based on softwood (2) and hardwood (1).
- 3) Calculation of equivalent PBBA from marker concentrations by subtraction of the baseline and multiplication with the conversion factors.
- 4) Validation by a specific marker for biomass burning.
A campaign of four weeks was conducted to sample ambient particles and compare PBBA based on benzene, EC and levoglucosan. Benzene and levoglucosan was sampled at urban background, whereas EC was sampled at urban background and the rural site RISØ, in order to test variation between EC derived PBBA at the two sites, which are located 30 km apart (Nøjgaard et al., 2017).

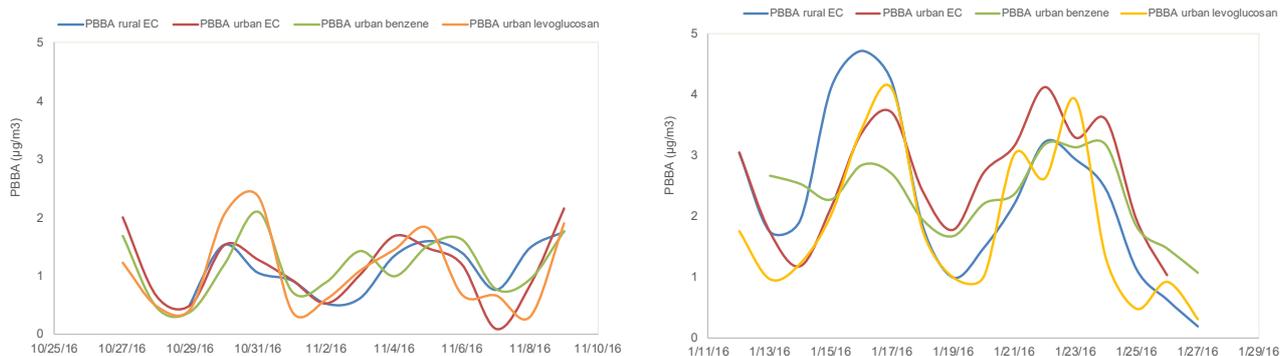


Figure 2.1. Comparison of PBBA ($\mu\text{g}/\text{m}^3$) based on rural EC, urban background EC, urban background benzene and urban background levoglucosan

Apparent from Figure 2.1, PBBA based on EC, benzene and levoglucosan in urban background covariate during the 2×2 campaign weeks, though absolute PBBA concentrations are not identical. Also, PBBA based on EC at the rural site covariates with PBBA based on EC at urban background.

Covariation indicates that benzene and EC are suitable markers for biomass burning, as is the case for levoglucosan, provided the contributions from traffic are corrected for. A more quantitative evaluation requires a more complex setup, since the yield of levoglucosan from bio-mass burning is subject to uncertainty it-self.

The covariation of PBBA based on EC at both stations indicates, that RWC is not only confined to local variation, but can be comparable over a broader scale.

2.3 Time series of Residential Wood Combustion

Parallel time series of PBBA concentrations based on EC and benzene at urban background are available only from 01.09.2014 – 31.12.2017 and are plotted in Figure 2.2 and Figure 2.3.

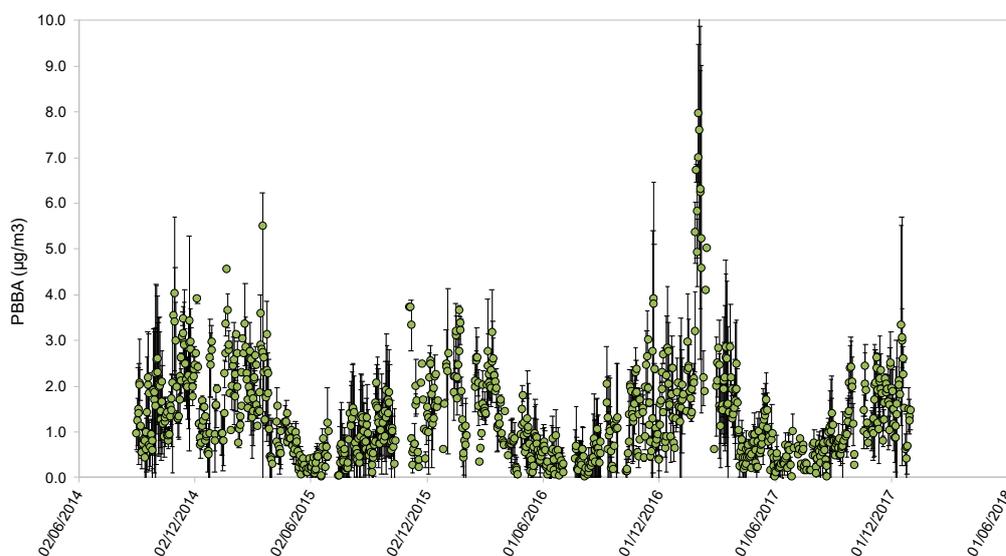


Figure 2.2. Time series of PBBA concentrations based on benzene and EC at urban background. Error bars show the standard deviations of the average PBBA concentrations based on benzene and EC. A scatter plot of the same data is shown in Figure 2.3.

PBBA based on EC and benzene at urban background generally agree well. However, occasionally larger differences are evident from the error bars in Figure 2.2, which illustrate standard deviations between duplicate measurements. Larger differences are also evident on the scatter plots in Figure 2.3. Interestingly, the correlation is stronger between PBBA based on EC at rural and urban background. However, absolute PBBA concentrations are lower at rural compared to urban locations.

It is noted that summer concentrations are not zero, which was demonstrated by use of specific markers for biomass burning in a previous report (Nøjgaard et al., 2015). Summer concentrations originate from anthropogenic as well as natural activities, e.g. camp fires, barbecuing and wildfires. There is a significant variation in PBBA concentrations over the year, even within the heating season (Figure 2.2). The variation in PBBA concentrations is partly related to meteorological parameters.

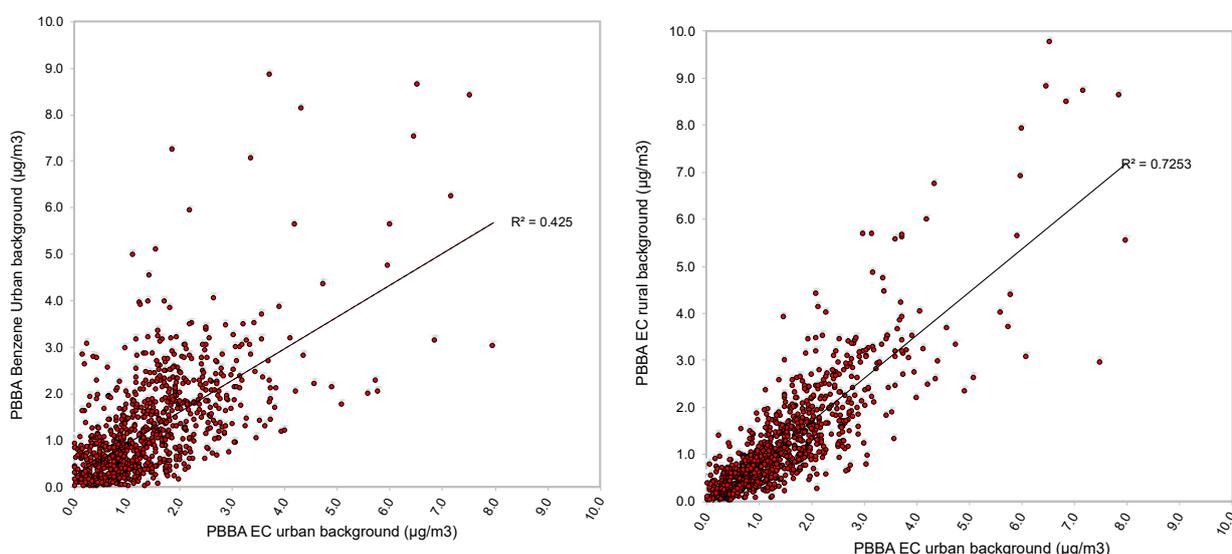


Figure 2.3. Scatter plots of PBBA based on rural EC vs. urban EC (left-hand side), and PBBA based on urban benzene vs. urban background EC (right-hand side). Time series of the latter is shown in Figure 2.2.

The trends in PBBA concentration from 2010 – 2017 are shown for rural, sub-urb and urban background in Table 2.2. At rural and urban background, PBBA based on EC peaks at 2.4 – 2.5 $\mu\text{g}/\text{m}^3$ in 2010 and show the lowest PBBA concentration in 2016 of 1.0 $\mu\text{g}/\text{m}^3$. Some variation is observed at urban background, where PBBA concentrations show some variation depending on the choice of marker, which is used for calculation of PBBA. Suburban concentrations of PBBA are the highest by far. Increments show that suburban PBBA are 36-79% higher than rural PBBA concentrations (Table 2.2). In comparison, the rural-to-urban background increments were 16% in 2016 and only 5% in 2017. Increments at the suburb location and at urban background has continued to decrease since the measurements were initiated in late 2014.

Table 2.2. Annual site-specific PBBA concentrations ($\mu\text{g}/\text{m}^3$) based on EC and benzene. Relative increments in PBBA from rural to urban background based on the marker EC and in the same way for rural to suburb location are shown in hard brackets [%]. Blank fields = data not available.

| Date/ Site | Urban background (HCØ) | | Suburb (HVID) | Rural (RISØ) |
|------------|---|--|--|--|
| | PBBA, benzene ($\mu\text{g}/\text{m}^3$) | PBBA, EC ($\mu\text{g}/\text{m}^3$) | PBBA, EC ($\mu\text{g}/\text{m}^3$) | PBBA, EC ($\mu\text{g}/\text{m}^3$) |
| 2010 | 2.5 | | | 2.4 |
| 2011 | 1.6 | | | 2.0 |
| 2012 | 1.4 | | | 1.5 |
| 2013 | 1.1 | | | 1.3 |
| 2014 | 1.5 | | | 1.5 |
| 2015 | 1.1 | 1.39 [40 %] | | 1.0 |
| 2016 | 1.0 | 1.17 [16 %] | 1.81 [79%] | 1.0 |
| 2017 | 1.4 | 1.29 [5 %] | 1.67 [36%] | 1.2 |

PBBA concentrations at the rural site and urban background covariate within 21%. Apparent from Table 2.2, concentrations of PBBA has decreased over the years 2010 – 2017 with a few disruptions in 2014 and 2017.

A perhaps more meaningful way to illustrate the variation in residential wood combustion is by calculating PBBA concentrations season wise, e.g. during winter (December, January, February) or heating season which may cover September to April. In both cases, a season covers two calendar years. In the following, winter is the choice of season due to its simplicity. Table 2.3 covers the winter seasons (December, January, February), where wood combustion is typically abundant. Winter averages of PBBA were $4 \mu\text{g}/\text{m}^3$ during the cold winters 2009/2010 and 2010/2011. During the more recent winters, PBBA concentrations between $1\text{-}3 \mu\text{g}/\text{m}^3$ have been measured at rural and urban background.

Table 2.2. Site-specific PBBA concentrations ($\mu\text{g}/\text{m}^3$) based on EC and benzene during the winter (December, January, February) season. Meteorological data is from Roskilde airport provided by Danish Meteorological Institute, www.dmi.dk. Blank fields = data not available

| Date/ Site | Urban background (HCØ) | | Suburb (HVID) | Rural (RISØ) | Average temperature ($^{\circ}\text{C}$) | Degree days |
|------------|---|--|--|--|---|-------------|
| | PBBA, benzene ($\mu\text{g}/\text{m}^3$) | PBBA, EC ($\mu\text{g}/\text{m}^3$) | PBBA, EC ($\mu\text{g}/\text{m}^3$) | PBBA, EC ($\mu\text{g}/\text{m}^3$) | | |
| 2009/2010 | | | | 4.1 | -1.5 | |
| 2010/2011 | 4.0 | | | 3.9 | -1.9 | 1514 |
| 2011/2012 | 2.2 | | | 2.1 | 1.5 | 1514 |
| 2012/2013 | 2.4 | | | 2.1 | -0.5 | 1577 |
| 2013/2014 | 2.7 | | | 2.5 | 3.2 | 1246 |
| 2014/2015 | 2.0 | 1.8 | | 1.2 | 2.3 | 1326 |
| 2015/2016 | 2.0 | 1.6 | 2.4 | 1.5 | 2.8 | 1295 |
| 2016/2017 | 2.7 | 2.4 | 3.3 | 2.5 | 2.2 | 1328 |

The colder winters 2009/2010 and 2010/2011 were officially white Christmases with more than 90% of the country covered by snow on Christmas Eve. The colder temperatures resulted in higher concentrations of PBBA during these winters. The following winters 2011/2012, 2012/2013 and 2013/2014 were warmer and consequently lower concentrations of PBBA were measured at the rural site and in urban background. Up to 2014, similar concentrations of PBBA were measured at both sites, only rural concentrations being slightly

smaller. From the winter 2014/2015 this difference became larger, and during the most recent years, urban background is found more polluted with respect to PBBA than the rural site, possibly due to a higher population density in the suburbs with wood stoves as secondary heating. Suburbs west of Copenhagen are thus likely to affect urban background levels of PBBA during predominant westerly winds.

Fuel consumption and emissions from residential heating, which include wood stoves appliances, are discussed in a recent emission inventor report from DCE (Nielsen et al., 2018a). From 1990 – 2016, the total fuel consumption in this sector has decreased by 8%, whereas consumption of wood has increased more than 4 times. Wood consumption as fuel showed a local maximum in 2010 and a slightly lower consumption in the years 2011-2014. In 2015-2016, the consumptions increased to a level slightly above the 2010 level (Nielsen et al., 2018a). About 50% of the fuel consumption in this sector was wood in 2016 with the remaining fuels being gas oil (e.g. oil for residential heating) and natural gas. Even though RWC is a major source of e.g. CH₄, and wood as a fuel has increased more than 4 times, the CH₄ emission has decreased by 10% since 1990, and about 30% from 2010 to 2016, because the emission factors have decreased as a result of improved stove combustion performances. EC and benzene emission factors have also decreased. Based on published time series for CH₄ emission from residential plants and trends in individual emission factors, a slowly decreasing trend was calculated for BC (Nielsen et al., 2018a; Nielsen et al., 2018b), albeit with a temporary minimum in 2014 (Figure 2.4). This drop in emissions would also be expected for PBBA concentrations based on EC and benzene measurements. On the contrary, PBBA calculated from EC and benzene increases slightly from 1.3 µg/m³ (2013) to 1.5 µg/m³ (2014) at the rural location (Table 2.2 and Figure 2.4). Apart from the inconsistency in 2014, the PBBA based on measured benzene and EC appeared to decrease more than observed for emissions of BC as a measure of modelled PBBA (Figure 2.4).

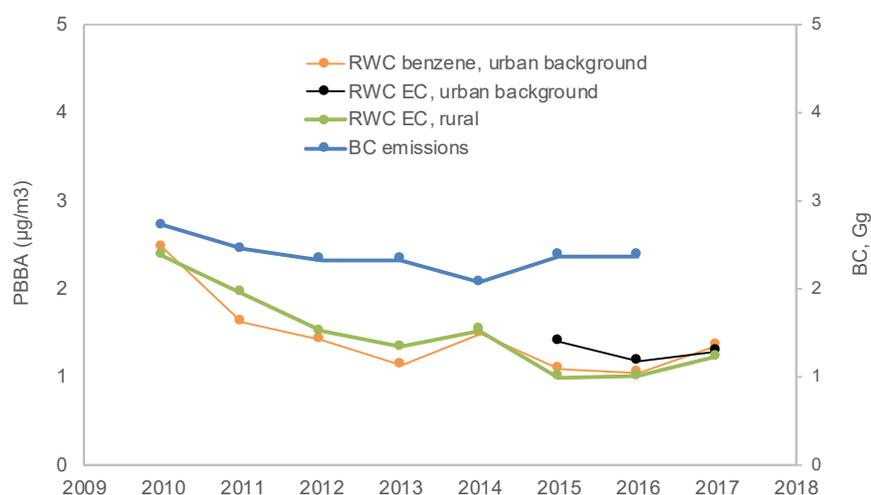


Figure 2.4. Time series of PBBA concentrations (µg/m³) based on EC and benzene (Table 2.2) and BC emissions from residential wood combustion (Nielsen et al., 2018b) during 2010-2017. Note that BC emissions and PBBA have different units. Modelled BC emissions is a fraction of PBBA, only, but should be proportional to PBBA.

2.4 Evaluation of calculated Residential Wood Combustion

Calculation of PBBA concentrations based on EC and benzene, assumes that other contributing sources such as traffic can be subtracted from ambient measurements. By establishing a baseline from summer data prior to the summer holidays in July, where RWC is limited and corrected for (section 2.2) traffic can be subtracted from ambient concentrations. However, the baseline is an average concentration, which is corrected for weekends, but for example not wind direction and variation in traffic intensity other than those already accounted for, e.g. weekdays, Saturday and Sunday.

Negative PBBA concentrations may occur under conditions where baseline concentrations of a marker exceed ambient concentrations of the same marker, in particular during summer. Furthermore, PBBA concentrations will be underestimated when the traffic contribution to a marker is lower than the baseline concentration. Conversely PBBA will be overestimated when the traffic contribution to a marker is higher than the baseline concentration.

Comparison of PBBA concentrations based on the specific wood combustion marker levoglucosan and the markers benzene and EC applied in this report demonstrate the capability of the method (section 2.1).

The approach works well, when traffic and wood combustion are the dominant sources to EC and benzene, and this is typically the case for most countries (Nielsen, 2018c). However, it is plausible that massive episodes of long-range transport in the heating season add to the levels of EC and benzene from sources other than residential wood combustion, which would overestimate PBBA. Time series of PBBA concentrations and typical markers for long-range transport were therefore investigated. Co-variation of these species with EC and benzene could indicate long-range transport episodes (Viana et al., 2008). Two episodes were identified around 1 February and 1 March 2014, where lead (Pb), zinc (Zn), cadmium (Cd), arsenic (As) covaried with EC and benzene (not shown).

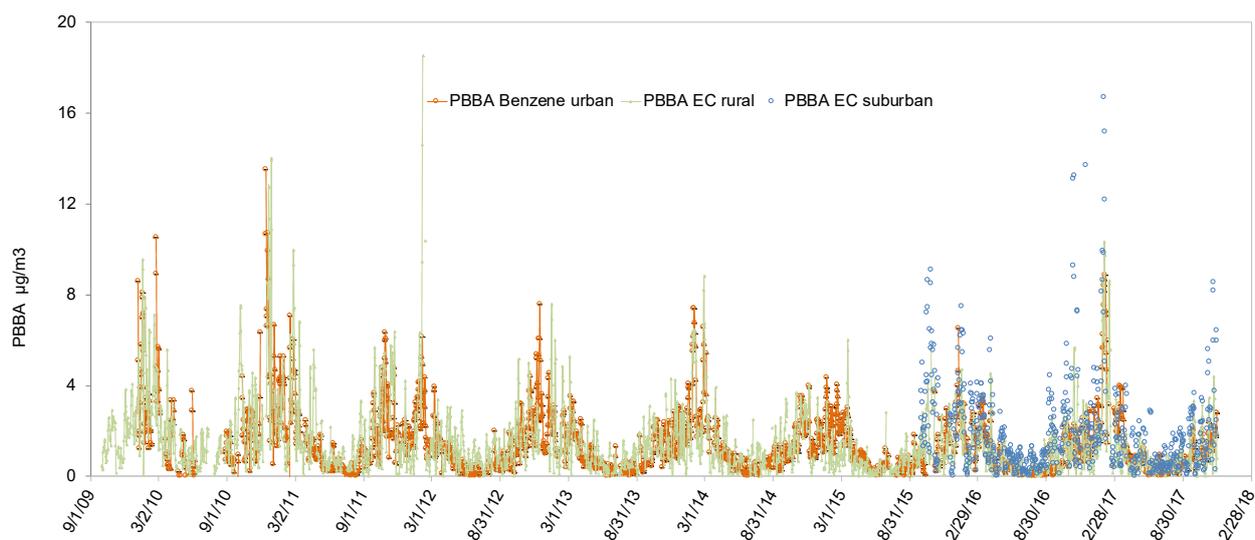


Figure 2.5. PBBA concentration ($\mu\text{g}/\text{m}^3$) based on benzene and EC at rural, suburb and urban back-ground locations in the period from September 2009 to December 2017.

A series of back-trajectories were analysed using HYSPLIT (Rolph et al., 2017; Stein et al., 2015) to identify the origins of air masses around 1 February and 1 March 2014. All days potentially impacted by long-range transport episodes were characterized by northerly winds. Origins of air masses were the North Atlantic Ocean/Southern Greenland, Iceland, Norway, Sweden and Finland, and not Southern Europe as expected. Correlation of Pb with EC ($R^2 = 0.48$) and benzene ($R^2 = 0.68$) also indicated long-range transport in the spring 2014. For comparison, no correlations between these species were observed in Autumn/Winter 2014 nor as expected during the entire 2015 ($R^2 < 0.2$). Long-range transport is therefore likely to explain part of the discrepancy between modelled BC emissions from residential wood combustion and calculated PBBA concentrations based on measured EC and benzene in 2014. However, zeroing the entire PBBA concentrations in January, February and March 2014 did not explain the drop in calculated BC emissions in Figure 2.4. The reason for this discrepancy is therefore assumed to result from the difference in methodology: modelled BC emissions from residential wood combustion includes national emissions, only, whereas calculated RCW concentrations are based on ambient measurements of the markers EC and benzene, which also includes residential wood combustion from surrounding countries.

Camp and bon fires in addition to wild fires and burning of fields will additionally contribute to ambient benzene and EC and thereby PBBA in Tables 2.2 and 2.3. However, it will mainly affect the summer/autumn season, but not winter PBBA concentrations in Table 2.3. Power plants and Combined Heat and Power Plants (CHP) use biomass as fuel. In 2015, 14% of the Danish production of electricity was based on biomass (Energinet Danmark, 2016). However, these plants are equipped with cleaning technology in contrast to residential wood stoves, and they should effectively remove EC and benzene among other emissions. However, the share of biomass for fuel in power plants and CHP is expected to increase in the future (Energinet Danmark, 2016), for which reason emissions from these plants should be subject for future attention.

As mentioned in section 2.1 the PBBA concentrations calculated in this report cover primary particles from wood combustion, PBBA, only. Part of the VOC and semivolatile VOC emitted from residential wood combustion will be transformed to secondary particles, SOA, during atmospheric oxidation. The total concentration of particles from residential wood combustion is therefore higher after hours to days of oxidation in the atmosphere. Some studies claim that secondary particles can account for as much as the primary particles themselves (Heringa et al., 2011), while even higher yields cannot be excluded. This field is subject for research these years, and at present the processes of SOA formation from RWC is poorly understood. For this reason, only the primary particles are considered in this report.

2.5 Conclusion on Residential Wood Combustion

Annual averages of PBBA at the rural site and urban background are generally showing comparable concentrations and trends. PBBA concentrations in urban background exceeded those at the rural site. However, this increment has decreased from 40% in 2015 to 5% in 2017.

Annual averages of PBBA were highest in 2010 and 2011. In the winter season, these concentrations were higher and conversely lower during summer.

Urban background PBBA decreased from 4.0 $\mu\text{g}/\text{m}^3$ in 2010/2011 to 2.7 $\mu\text{g}/\text{m}^3$ in 2016/2017. A comparable trend was calculated for the rural site, i.e. 3.9 $\mu\text{g}/\text{m}^3$ in 2010/2011 decreasing to 2.5 $\mu\text{g}/\text{m}^3$. At the suburban site 3.3 $\mu\text{g}/\text{m}^3$ was calculated for 2016/2017. These results indicate that exposure to primary particles from residential wood combustion may be higher in the suburbs than rural and urban background. Furthermore, the exposure may be higher in urban background than at rural locations.

Time series of annual average PBBA concentrations shows an initially decreasing trend, which has increased slightly in 2017. By comparison with a product of RWC modelled from emission inventories, measured concentrations decreased more than modelled ones. Both techniques showed an initial decrease in pollutants from RWC from 2010.

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THE PARTICLE PROJECT 2017-2018

The Particle Project 2017-2018 continues the record of particle mass and number measurements on urban and rural locations. Monitoring of Elemental Carbon (EC) has been extended from rural location and curbside station in Copenhagen (2009/2010) to include an urban background site (2014) and a suburban site (2015). EC has traffic and wood combustion as major sources, which is also the case for the volatile compound benzene. The Particle Project 2017-2018 evaluates trends in Primary Biomass Burning Particles (PBBA) from Residential Wood Combustion (RWC) based on EC and benzene measurements from late 2009-2017 at rural and suburban locations, and urban background. Trends in PBBA from RWC based on measurements are compared with trends in modelled emissions based on emission inventories.

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