



PARTICLE PROJECT REPORT 2008 - 2010

Particulate contribution from traffic in Copenhagen

NERI Technical Report no. 837 2011



NATIONAL ENVIRONMENTAL RESEARCH INSTITUTE
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Data sheet

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Abstract:	This report presents the results from the third particle research project. The project was carried out for the Danish Environmental Protection Agency by NERI during the period from 2008 to 2010. The main aim of the projects was to continue the long term research on levels, trends, chemical composition and sources of particulate air pollution in Denmark. The results show that there is a tendency for a decrease in particulate mass since 2002 and that the number of particles has decreased by a factor of two at H.C. Andersens Boulevard, Copenhagen. It is mainly particles with diameter from 10-40 nm that has decreased primarily due to reduced emissions related to traffic. Moreover, the chemical composition of PM _{2.5} and PM ₁₀ was measured during two monthly field campaigns in 2008 and 2009 at the rural measurement station Lille Valby situated 30 km west of Copenhagen. Source apportionment modelling using COPREM was used to determine the sources of the different chemical components of the particle mass.
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Dansk sammenfatning

I perioden fra 2008-2010 har Danmarks Miljøundersøgelser, Aarhus Universitet (DMU-AU) udført det tredje partikelforskningsprojekt for Miljøstyrelsen. Dette projekt er en forlængelse af to tidligere partikelforskningsprojekter udført henholdsvis i perioden fra 2001-2004 og i perioden 2005-2007.

Det tredje partikelforskningsprojekt bygger på resultaterne fra de to tidligere projekter og lige som i disse tidligere projekter har fokus været på målinger af de fysiske egenskaber (masse, antal, størrelsesfordeling, lysabsorption) for de luftbårne partikler. Målingerne er blevet udført ved den stærkt trafikerede gadestation på H.C. Andersens Boulevard (HCAB), bybaggrundsstationen på H.C. Ørstedes Institut (HCØ) og ved landbaggrundsstationen ved Lille Valby/Risø (LVBY) ca. 6 km nord for Roskilde. Ved at sammenligne resultaterne fra disse tre målestationer, er det muligt at vurdere andelen af luftforureningen fra selve byen og hvor meget der er transporteret ind til byen fra omgivelserne eller via langtransport. Målingerne er foretaget med høj tidsopløsning (30 minutter), så det er muligt at få information om kilderne til luftforureningen ved at studere døgnvariation i de målte koncentrationer og sammenholde disse med variationerne i udledningerne.

Projektet har endvidere omfattet udførelse af to intensive målekampanjer med fokus på bestemmelse af den kemiske sammensætning af de luftbårne partikler ved landbaggrunds-målestationen LVBY. Målekampanjerne blev udført i foråret 2008 og sen vinter/tidligt forår 2009 og indgik som en del af et større fælles europæisk projekt koordineret af det europæiske luftovervågningsprogram EMEP.

Partikelmasse

Målingerne af partikelmasse med TEOM-instrumenter, som blev initieret i det første partikelprojekt (2001-2004), blev fortsat og udbygget i perioden fra 2008-2010, så der nu findes en relativt lang tidsserie for disse målinger. TEOM har den fordel, at instrumentet giver målinger med relativt høj tidsopløsning (halvtimes middelværdier), men til gengæld har metoden den ulempe at en del af partikelmassen "tabes" inde i selve instrumentet grundet fordamning af partiklernes indhold af vand samt semivolatilt forbindelser. TEOM måler derfor en for lav partikelmasse. For at få en bedre forståelse af dette tab er der blevet foretaget grundige sammenligninger mellem målingerne med TEOM og målinger med SM200-instrumenter (24-timers middelværdier), hvor SM200 giver resultater i overensstemmelse med referencemetoden.

Sammenligningen bekræftede, at en betragtelig del af partikelmassen blev tabt i TEOM. I det tidligere partikelforskningsprojekt blev det vurderet, at det var muligt at korrigere for dette tab på årlig basis ved at lægge en konstant masse (omkring $9 \mu\text{g m}^{-3}$) til både $\text{PM}_{2.5}$ og PM_{10} , og uafhængig af målestedet (Wählin 2008). Den nye og udvidede sammenligning baseret på større datasæt viste imidlertid, at tabet af masse afhænger af såvel størrelsesfraktionen ($\text{PM}_{2.5}$ eller PM_{10}) som målestedet (landbaggrund, bybaggrund, gade). Endvidere blev det fundet, at tabet

af masse i TEOM har en sæsonvariation, hvilket kan forklares med sæsonvariationer i den kemiske sammensætning af partiklerne samt de meteorologiske forhold.

Trods den rumlige og tidslige variation i tabets størrelse er det muligt at estimere den korrekte partikelmasse ud fra TEOM ved at korrigerer de målte værdier med en korrektionsfaktor på 1.2-1.7 afhængigt af sted, årstid og størrelsesfraktion. Det er vurderet, at denne metode giver rimelige estimater, når først korrektionsfaktoren er bestemt for den aktuelle årstid og sted. Denne korrektionsmetode svarer til den korrektionsmetode, som anbefales i forbindelse med rapportering under EU-direktivet (2008/50/EF). Estimater af partikelmasse ud fra korrigerede TEOM-målinger skal imidlertid altid udføres med forsigtighed og så vidt muligt forsøge at tage højde for de aktuelle tidslige og rumlige variationer i korrektionsfaktoren. Alle partikelmålinger foretaget med TEOM-instrumenter er præsenteret i denne rapport som ikke-korrigerede tal.

På trods af tabet vurderes det, at målingerne af PM_{2.5} og PM₁₀ med TEOM fortsat kan anvendes til at skønne den generelle udviklingstendens for partikelmassen. PM_{2.5} målt med TEOM ved gademålestationen HCAB er faldet fra omkring 17 µg m⁻³ i 2002 til omkring 13 µg m⁻³ i 2010 (ukorrigerede værdier). I bybaggrund (HCØ) og landbaggrund (LVBY) er der observeret et forholdsvis konstant niveau.

For PM₁₀ målt med TEOM er der målt et fald i perioden fra 2002 til 2010 fra omkring 35 µg m⁻³ i 2002 til omkring 26 µg m⁻³ i 2010 (ukorrigerede værdier) ved gademålestationen HCAB. En del af dette fald skyldes ny asfaltbelægning på H.C. Andersens Boulevard i 2008. Ved bybaggrundsmålestationen blev der ligeledes observeret et fald i PM₁₀ i perioden 2002 til 2010.

Analyser af døgnvariationen i PM_{2.5} og PM₁₀ målt med TEOM viste, at partikelmassen på gadeniveau har en døgnvariation, som følger døgnvariationen i trafikintensiteten i byerne. Dette bekræfter tidligere resultater, og viser at PM_{2.5} og PM₁₀ i nogen grad skyldes den lokale trafik. Den resterende andel af partikelmassen kommer hovedsageligt fra langtransporterede partikler. På basis heraf vurderes det, at reduktionen i partikelforeningen skyldes såvel mindre langtransporteret forurening, såvel som i fald i partikelforureningen fra den lokale trafik.

Partikelantal

Som et resultat af de tre forløbne partikelforskningsprojekter er der nu foretaget målinger af det samlede partikelantal og størrelsesfordelingen af partiklerne (6-700 nm) i perioden fra 2002 til 2010. Resultaterne viser, at årsmiddelværdien for antallet af partikler ved HCAB i 2010 lå på ca. 16.000 partikler cm⁻³, hvilket er ca. en faktor 2 og 4 højere end årsmiddelværdierne målt ved henholdsvis HCØ (ca. 6.800 partikler cm⁻³) og LVBY (3.800 partikler cm⁻³).

På HCAB er antallet af partikler faldet til omkring halvdelen i perioden fra 2002 til 2010. På HCØ og LVBY ses også tendenser til fald i antallet af partikler, men disse fald er mindre end målt på HCAB. På HCØ og LVBY var faldet på henholdsvis omkring 30% og 15%.

Det højere niveau for antallet af partikler på HCAB sammenholdt med HCØ og LVBY skyldes primært udstødning af partikler fra trafikken på HCAB. HCØ og LVBY ligger længere væk fra trafikale kilder, hvilket er årsagen til det lavere partikelantal ved disse målestationer.

DMU-AU vurderer, at faldet i antallet af partikler på HCAB skyldes teknologiske forbedringer af køretøjerne (nyere biler, partikelfiltre, miljøzoner m.m.). Denne vurdering underbygges af resultaterne fra 2 opgørelser af partikelmasseemissionerne fra trafikken, selv om emissioner i partikelmasse og antal er ikke helt sammenligneligt. På Åboulevarden faldt udstødningen af partikler med omkring 40% i perioden fra 2004 til 2008 (Jensen et al., 2010) og partikeludstødningen fra den tunge trafik reduceredes i 2010 med 60% som en kombinationseffekt af miljøzonekravene i 2010 og generelle miljøkrav til busser i København (Jensen et al., 2011).

Døgnvariationen i partikelantal følger døgnvariationen i trafikmønsteret med højt partikelantal i forbindelse med myldretiderne. Den typiske døgnvariation i meteorologien modificerer dog det typiske døgnmønster, således at toppen i morgenmyldretiden er højere end toppen relateret til myldretiden om eftermiddagen. Døgnvariationen i partikelantal viser, at størstedelen af partikelantallet skyldes udledninger relateret til trafikken.

Udviklingen i størrelsesfordelingen er ligeledes undersøgt i forbindelse med projektet. Målingerne ved de tre målestationer viser, at den gennemsnitlige diameter for partiklerne øges fra gadeniveau til landbaggrund. I bybaggrund (HCØ) observeredes en betydelige øgning i 'modediameter' (svarende til maksimum i størrelsesfordelingen) i perioden fra 2002 til 2010 på 67% - fra 30 nm til 50 nm. Tilsvarende udvikling blev ikke observeret på de to øvrige målestationer. Endvidere viste en detaljeret undersøgelse af udviklingstendens for de forskellige fraktioner af partiklerne, at det hovedsageligt er antallet af de mindste partikler fra 6-40 nm i diameter, som er faldet med omkring en faktor 2 i perioden fra 2002 til 2010, mens de større partikelfraktioner er faldet betydeligt mindre. Disse resultater understøtter konklusionen om, at faldet i det samlede antal partikler på gadeniveau skyldes fald i udledningerne af ultrafine partikler (partikler mindre end 100 nm i diameter) fra trafik.

Det anvendte måleudstyr er teknisk kompliceret og er egentligt ikke udviklet til rutinemålinger over lange tidsrum. Det er derfor vanskeligt at opnå måleresultater, som er fuldt repræsentative for alle kalenderårene. Derfor har DMU-AU lavet en grundig analyse for at sikre, at den manglende datarepræsentativitet ikke giver anledning til fejltolkninger af udviklingstendensen. Denne analyse viser, at den manglende datarepræsentativitet på HCAB giver en højere usikkerhed på årsmiddelværdierne for år 2002, 2004, 2005 og 2010. Den højere usikkerhed for disse år påvirker imidlertid ikke konklusionen om niveauet og udviklingstendensen for HCAB.

Lysabsorption og sod

Partiklernes absorption af lys kan anvendes som et indirekte mål for mængden af sod (black carbon, BC), da størstedelen af denne absorption skyldes tilstedeværelsen af sod. Denne har været stort set konstant i landbaggrund (LVBY) i perioden fra 2006 til 2010. I bybaggrund (HCØ) er der observeret et mindre fald i lysabsorptionskoefficienten fra 2007 til

2010. På gadeniveau (HCAB) er der målt en stigning fra 2007-2008, som er de eneste to år, hvor det har været muligt at bestemme en årsmiddelværdi. Denne stigning er uventet og understøttes ikke af andre målinger i en række projekter, hvor der er målt partikelindhold af elementært kulstof (EC, som svarer til sod). Derfor undersøges det pt. om stigningen er reel eller kan skyldes en hidtil ukendt fejl i instrumentet. Målingerne af lysabsorptionskoefficienten viser en tydelig døgnvariation, hvilket indikerer at lysabsorptionen hovedsageligt er relateret til udledninger fra trafik og dermed at hovedparten af byluftens indhold af sod stammer fra udledninger relateret til trafikken. Det kan ikke udelukkes at forurening fra brændeovne udgør en mindre andel især i vinterperioden.

Kemisk sammensætning

For at få en bedre forståelse af den kemiske sammensætning og kilderne til PM_{2.5} og PM₁₀ i danske landbaggrundsområder, blev der i efteråret 2008 (september-oktober) og sent vinter/tidligt forår 2009 (februar-marts) udført to målekampanjer ved LVBY. I alt blev der målt 36 kemiske komponenter omfattende såvel gasser som partikler. Kampanjerne varede omkring en måned hver, hvilket til sammen gør målekampanjerne til den hidtil mest omfattende undersøgelse af den kemiske sammensætning af og kilderne til partikelmasse i Danmark. Målekampanjerne blev udført i forbindelse med en større europæisk målekampagne organiseret af den europæiske samarbejdsorganisation for måling af luftforening, EMEP.

I gennemsnit for de to kampanjer lå PM_{2.5} og PM₁₀ på henholdsvis 13 µgm⁻³ og 17 µgm⁻³. Heraf kan der udfra de kemiske målinger gøres rede for (mass closure) henholdsvis 64% og 73% af PM_{2.5} og PM₁₀ svarende til 9 µgm⁻³ og 14 µgm⁻³ som gennemsnit for PM_{2.5} og PM₁₀ for de to kampanjer. Den ukendte andel af massen (omkring 3-4 µgm⁻³) lå udelukkende i de fine partikler (diameter under 2.5 µm) og vurderes at bestå af vand samt en række grundstoffer (for eksempel oxygen og hydrogen). Vand og disse grundstoffer kan ikke bestemmes via de udførte kemiske analyser, men vand kan udgøre en betragtelig andel af atmosfæriske partikler stigende med den relative fugtighed (RF) (McMurry, 2000). Eks. er vand rapporteret til at udgøre 10% af atmosfæriske partikler ved 50% RF, og 40% ved 70% RF. Disse grundstoffer er bundet til forskellige uorganiske grundstoffer som kalium, silicium, jern og calcium i form af for eksempel sand (SiO₂), calciumcarbonat (CaCO₃) og jernoxid (Fe₂O₃). Andelen af ukendt masse var højest i forbindelse med efterårskampanjen. Luftfugtigheden var høj på dette tidspunkt, hvilket fører til en større andel af vand bundet til de hygroskopiske uorganiske salte, og dermed til en relativt set større andel af ukendt masse.

De uorganiske ioner udgør henholdsvis 32% og 29% af PM_{2.5} og PM₁₀. Disse består hovedsageligt af sekundære uorganiske salte (secondary inorganic aerosols (SIA) bestående af navnlig ammoniumnitrat, ammoniumbisulfat og ammoniumsulfat) dannet i atmosfæren på baggrund af udledninger af SO₂, NO_x og NH₃. Havsalt (Na, Cl, sulfat fra hav, Br, Mg) udgør hovedparten af de resterende uorganiske ioner. Tungmetaller udgør mindre end 1.5% og 3.1% af henholdsvis PM_{2.5} og PM₁₀. Elementært kulstof (sod) og organisk bundet kulstof udgør en anden stor del af partikelmassen; 30% og 23% af henholdsvis PM_{2.5} og PM₁₀. Såvel PM_{2.5} og PM₁₀ var højere i kampanjen om efteråret end i kampanjen sent vin-

ter/tidlig forår. Dette skyldes formentligt variationer i de meteorologiske forhold.

De målte kemiske parametre (36 parametre med daglig opløsning) blev analyseret ved hjælp af DMU-AU's COPREM-model, der anvendes til beregning af kilderne til luftforurening. 12 forskellige kildeprofiler blev anvendt i forbindelse med kildeanalysen:

1. Havsalt (hovedsageligt NaCl)
2. NaNO_3 – "gammelt" havsalt
- 3, 4, 5. Sekundære uorganiske ioner (SIA) bestående af ammoniumnitrat, ammoniumbisulfat og ammoniumsulfat
6. Silikatbjergarter
7. Kalkbjergarter
8. Biomasseafbrænding (brændeovne, skovbrande etc.),
9. Olieforbrænding,
10. Kulforbrænding,
11. Køretøjer (partikler genereret direkte fra trafik)
12. Sekundære organiske partikler (SOA).

COPREM-analysen viste, at den største kilde til PM_{10} i landbaggrund var de sekundære uorganiske ioner, som udgjorde omkring 30% af massen. Samme konklusion blev draget direkte fra den "simplere" direkte analyse af selve måledata. Havsalt, biomasseafbrænding og sekundære organiske partikler (SOA) udgjorde hver omkring 11-15% af PM_{10} . SOA og biomasseafbrænding kan enten dannes lokalt eller de kan blive langtransporteret til LVBY. Partikler fra trafik og afbrænding af olie og kul udgjorde til sammen omkring 14% af PM_{10} .

Analysen af $\text{PM}_{2.5}$ og PM_{10} viste, at der er en væsentlig forskel mellem den kemiske sammensætning af de fine partikler (mindre end $2.5 \mu\text{m}$) og de grove partikler (mellem $2.5 \mu\text{m}$ og $10 \mu\text{m}$). Havsalt og partikler fra silikat-, kalkbjergarter og mineraler samt bidrag relateret til trafik var hovedsageligt associeret med grove partikler. Forbrændingskilderne (olie, kul og biomasse) blev hovedsageligt fundet i de fine partikler, selv om et bidrag til de grove partikler ikke kan udelukkes, for navnlig partikler relateret til afbrænding af olie.

COPREM-beregningerne viste, at SOA primært findes i $\text{PM}_{2.5}$ mens omkring 20% findes i den grove fraktion. Det skal nævnes, at OC som SOA-profilen er baseret på, kun blev målt i PM_{10} , af hensyn til de økonomiske ressourcer i dette projekt. Det vurderes, at disse overvejende er associeret med $\text{PM}_{2.5}$ (Stone et al., 2011).

Resultaterne viste, at den ukendte masse var associeret med $\text{PM}_{2.5}$, og at den kemiske sammensætning for de grove partikler var fuldt bestemt. Dette var uventet da den ukendte masse for en stor andel forventes at være vand bundet til de hygroskopiske dele af partikelmassen, som både findes i de fine og grove partikler.

Det kemiske indhold i PM_{2.5} og grove partikler (fraktionen mellem 2.5 µm og 10 µm) stemmer overens med de forventningerne, der kan opstilles på basis af den atmosfæriske transport af PM_{2.5} og grove partikler.

PM_{2.5} kan transporteres over store afstande (f.eks. Rusland og Kina) og indeholder derfor en stor andel af langtransporteret partikelmasse. Kun en lille andel af de grove partikler kan forventes at være langtransporterede (f.eks. fra Øst- og Sydeuropæiske lande) og indeholder derfor primært partikelmasse af mere lokal og regional oprindelse (f.eks. Sjælland og Nordtyskland). Et eksempel på dette er de sekundære uorganiske partikler, som for en stor del stammer fra kilder uden for Danmark (Ellermann et al., 2010b). Dette er i overensstemmelse med målingerne, som viser, at 80% af den sekundære uorganiske partikelmasse findes i PM_{2.5}.

Fortsatte undersøgelser og anbefalinger

I forbindelse med de tre forløbne partikelforskningsprojekter er der skabt værdifuld ny viden om partikelforureningen i Danmark. På trods af dette, er der imidlertid fortsat huller i vores viden på området. For at reducere disse huller i vores viden vil vi forslå, at forskning fortsættes på følgende områder:

- TEOM er et nyttigt instrument i forbindelse med studier af partikelmasse, hvor høj tidsopløsning er nødvendigt. Imidlertid er det nødvendigt at tage højde for tabet af partikelmasse i instrumentet. I forbindelse med kommende undersøgelser baseret på TEOM vil det være nødvendigt at anvende en korrektionsfaktor, som afhænger af partikelfraktion, årstid og sted for målingerne d.v.s.. om det drejer sig om landbaggrund, bybaggrund eller gadeniveau. Derfor vil det være nødvendigt med fortsatte studier af tabet af partikelmasse i TEOM. For eksempel studier af, hvor stor en andel af tabet, som skyldes ammoniumnitrat.
- På bybaggrundsmålestationen (HCØ) blev der observeret en mindre stigning i partikelantal. Årsagen til denne stigning bør undersøges.
- Undersøgelserne af udviklingstendensen for partikelstørrelsesfordelingen har vist, at denne har ændret sig i løbet af de seneste 10 år. Det anbefales derfor at fortsætte målingerne af størrelsesfordelingen, og at igangsætte undersøgelser af årsagerne til udviklingstendensen. En af de ting, som bør studeres er hvorvidt den øgede anvendelse af brændeovne har spillet en rolle i forbindelse med ændringerne af partikelstørrelsesfordelingen. Endvidere vil der i forbindelse med EU fortsat ske reguleringer af udledningerne af partikler. Fortsatte målinger af partikelstørrelsesfordelingen vil kunne give information om effekten af disse reguleringstiltag.
- De nuværende undersøgelser har desværre ikke givet et klart billede af udviklingstendenserne for sod (BC). For at få bedre viden om sod anbefales, at målinger af sod baseres på direkte målinger af elementært kulstof frem for anvendelse af de indirekte absorptionsmålinger. Denne anbefaling er baseret på, at der skaffes ekstra information, idet metoden måler organisk kulstof samtidig med elementært kulstof. Anbefalingen er også baseret på de mulige problemer med absorptionsmålemetoden.
- Resultaterne fra de to målekampagner viser, at der er store forskelle fra dag til dag i det kemiske indhold af partiklerne, og at der ligeledes

er sæsonvariation i det kemiske indhold. Det er derfor vigtigt at måle det kemiske indhold af partiklerne gennem relativt lange perioder (måned eller mere), og dække de forskellige sæsoner.

- Partikelmassen relateret til forskellige kulstofkomponenter udgør en stor andel af den samlede partikelmasse. I de to målekampaner var det imidlertid kun muligt at bestemme kulstofkomponenterne i PM_{10} og vi måtte anvende en antagelse om fordelingen af kulstofforbindelserne i fine og grove partikler. Dette er et svagt punkt i den nuværende undersøgelse. I forbindelse med kommende målinger af det kemiske indhold i partiklerne bør der derfor måles kulstofkomponenter i både $PM_{2.5}$ og PM_{10} .
- Det organiske indhold udgør en betragtelig andel af partikelmassen. Vi kender imidlertid ikke det kemiske indhold af den organiske partikelmasse, hvilket gør det umuligt at vurdere kilderne til de organiske partikulære forbindelser. Samtidigt er der usikkerhed på selve estimatet af den organiske masse. Det foreslås derfor, at der udføres nye målekampaner med det formål at bestemme de væsentligste organiske kemiske komponenter ved anvendelse af specifikke markører for sekundære organiske partikler, primære biologiske organiske partikler og marine organiske partikler.
- Omkring en tredjedel af $PM_{2.5}$ består af ukendt kemi. Det antages, at en stor del af denne masse udgøres af vand (McMurry, 2000) associeret med de hygroskopiske salte. Det er imidlertid nødvendigt med yderligere eksperimenter for at øge viden om de dele af partikelmassen, som i dag har ukendt kemi.
- Med den nuværende viden vurderes det, at trafik er den væsentligste kilde til sod i byområder. Andre kilder som for eksempel brændeovne og industriel forbrænding, bidrager også til dannelse af sod. Der er imidlertid ikke særlig stor viden om disse kilders bidrag til partikelbåret sod i Danmark. Det er derfor nødvendigt at udføre yderligere målekampaner med det formål at få bedre viden om kilderne til sod.
- En række studier indikerer, at de ultrafine partikler har negativ effekt på human sundhed. Det er derfor nødvendigt at udføre undersøgelser, som kan kortlægge den kemiske sammensætning af de ultrafine partikler, for derved bedre at kunne vurdere sammenhængen mellem partikelforurening og sundhedseffekter.

Udover disse aktiviteter er der generelt interesse for at overvåge udviklingstendens for partikelantal og størrelsesfordeling for derved at kunne vurdere effekten på luftkvaliteten af de tiltag, som bliver implementeret internationalt og nationalt (fx miljøzoner) med henblik på at reducere problemerne med de ultrafine partikler i danske byområder.

1 Introduction

During the last decade the National Environmental Research Institute (NERI) at Aarhus University has carried out detailed physical and chemical measurements in order to characterize atmospheric particles. This work has been carried out within three consecutive projects financed by the Danish Environmental Protection Agency (EPA). The first project ran from 2001-2004 and was reported by Palmgren et al. (2005) and the second project ran from 2005-2007 and was reported by Wählén (2008). This report presents the results of the third particle research project over the time period 2008-2010. The third research project follows up on the results of the two previous projects and hence this report includes selected results from the two previous projects.

All three research projects have focused on detailed measurements designed for determining the microphysical properties of particles mainly in the urban environment. The parameters that have been measured were particle mass, volume, number and size distribution since these parameters are important for the microphysical properties of the particles as well as they affect the associated health effects. The measurements were carried out with high time resolution (typical $\frac{1}{2}$ hourly averages) because this gives the possibility to determine the diurnal variations of the microphysical parameters. This information can again be used to estimate the sources of the particles based on knowledge of the typical diurnal variations of for example traffic emissions. In the previous particle reports, it was found, that a large part of the particulate air pollution in Copenhagen especially at street level was due to traffic emissions.

The measurements have been carried out at three measurement stations Lille Valby (LVBY, rural background), H.C. Ørsted's Institute (HCOE, urban background), and H.C. Andersens Boulevard (HCAB, street station). All three stations are situated in the Copenhagen area and are part of the Danish urban air quality monitoring program LMP. The measurement stations have been selected because they can be used to characterise:

- The particles in ambient air at a rural background site outside Copenhagen. These particles are for a large part long range transported and hence only a minor part of the particles originate from local sources.
- The particles in urban background air in Copenhagen i.e. the particles at some distance from the busy roads.
- The ambient air particles at kerbside in one of the busiest streets in Copenhagen. These particles come to a large part from the traffic in the street, however the long range transported particles may also contribute significantly depending on the exact particle parameter.

A combined analysis of the measurements at all stations provides useful information about the sources of the particles.

In addition to the above mentioned parameters the light absorption of particles has also been studied. The parameter measured is the light ab-

sorption coefficient, which is an indirect measure of the amount of Black Carbon (BC). BC is believed to have negative impacts on health. Diesel driven vehicles are known to emit BC particles, which are transformed after aging processes into particles of mixed composition (Swietlicki et al., 2008). Close to their sources, BC particles appear as externally mixed (pure black carbon particles) and their emissions result in high local concentrations close to the sources.

The microphysical parameters have now been measured since 2001 as continuously as possible within the available resources. It will therefore be possible to determine the long term trends for these parameters. On both national and international level several reduction measures have been implemented in order to reduce the particulate air pollution. Based on the long time series it is now possible to evaluate the impact that these reduction measures have had on the particulate air pollution in Denmark.

In addition to these long-term measurements, two field campaigns, each of one month duration, were carried out in 2008 and 2009 at Lille Valby. The campaigns were funded by the Danish EPA and coordinated within EMEP (European Monitoring and Evaluation Programme) with the aim to obtain better information on the chemical properties of the long range transported particles. The objective of these campaigns was to measure inorganic, organic and elemental composition of particulate matter (PM₁₀ and PM_{2.5}) at the rural background site LVBY with diurnal time resolution. These detailed measurements have subsequently been used to determine the sources of the particles in rural areas in Denmark. This source apportionment was carried out using the CONstrained Physical REceptor Model, COPREM, (Wåhlin, 2003).

The overall aim of this third particle research project has been to continue the research on characterisation of the particulate air pollution in Denmark. In this project special attention has been given to studies of:

- the long term trends of the microphysical particle properties (mass, number size distribution, light absorption).
- the chemical composition and sources of particulate matter in rural areas of Denmark.

2 Methods: Measurements and modelling

Measurements within this project were carried out between 2008 and 2010 at the three different measurement stations LVBY (rural background station at Lille Valby about 30 km west of central Copenhagen), HCOE (urban background station in Copenhagen on top of H. C. Ørsted's Institute), and HCAB (street station downtown Copenhagen at H.C. Andersens Boulevard). From July 2010, the LVBY station was moved to the Risø peninsula which is situated inside the campus of NERI and DTU Risø National Laboratory for Sustainable Energy (Risø). The intention was to take advantage of the synergy with other activities carried out by RISØ and NERI and make a new intensive measurement station for gas and particle monitoring in Denmark. In the following presentation all data observed at LVBY and RISØ will be labelled only as LVBY.

2.1 Physical particle measurements

The measurements of particle mass were carried out on a half-hourly basis and comprise measurements of $PM_{2.5}$ at LVBY, HCOE, and HCAB and PM_{10} at HCOE and HCAB. Tapered Element Oscillating Microbalance (TEOM) instruments were used for these measurements. The TEOM measures mass concentrations by the change in frequency of a filter-connected oscillating unit. The temperature in the sensor unit is adjusted to 50 °C. Due to the high temperature, the volatile compounds of the particles evaporate inside the instruments. The TEOM instruments are therefore known to measure a too low mass concentration compared to reference measurements of particle mass.

Additionally, SM200 instruments are used to measure $PM_{2.5}$ and PM_{10} via a beta attenuation method with a time resolution of 24h. These measurements are carried out as part of the Danish urban air quality monitoring program and are used in the PM monitoring in Denmark. The SM200 instrument is in agreement with reference measurements of particle mass. A comparison between TEOM and SM200 data is presented in this report for evaluating the expected loss of particle mass from the TEOM instruments. However, no correction for this loss of mass has been applied to the TEOM data presented in this report.

DMPS (Differential Mobility Particle Sizer) instruments were used to measure the particle number size distribution from 6 to 700 nm at LVBY, HCOE, and HCAB. These instruments measure also the total particle number and the particle volume can be derived from the results.

Finally the light absorption coefficient σ_a was measured at all three stations using a PSAP (Particle Soot Absorption Photometer). This instrument measures the light absorption coefficient by determining the transmission of light through a filter, which is continuously loaded with particles in ambient air. Black carbon (BC) also called "soot" is known to be the main absorbing component of urban and rural particle samples. BC is therefore to a good approximation proportional to the absorption coefficient and BC can be estimated from the absorption coefficient by

applying a conversion term called *specific* absorption coefficient σ_{spe} to the measured light absorption coefficient σ_a (Johansson, C. and Hansson, H.C. , 2007).

In Tables 2.1 to 2.3, the data coverage for each year and each station is listed for the TEOM, the DMPS, and the PSAP data. It has to be noted that instruments were typically not set up in January during their first year of operation meaning that the first year of operation can by definition not have full data coverage.

Table 2.1. Data coverage (TEOM data) in % between 2001 and 2010 at the three measurement stations LVBY, HCOE, and HCAB.

Year	PM _{2.5} LVBY	PM _{2.5} RISOE	PM _{2.5} HCOE	PM _{2.5} HCAB	PM ₁₀ HCOE	PM ₁₀ HCAB
2001	-	-	-	-	-	19
2002	-	-	-	61	63	73
2003	4	-	30	98	94	98
2004	12	-	96	90	88	85
2005	78	-	92	88	93	97
2006	93	-	83	75	40	95
2007	92	-	98	91	98	38
2008	94	-	80	94	42	52
2009	99	-	96	94	96	89
2010	41	9	92	87	88	55

Table 2.2. Data coverage (DMPS data) in % between 2002 and 2010 at the three measurement stations LVBY, HCOE, and HCAB.

Year	LVBY	HCOE	HCAB
2001	-	25	26
2002	-	39	24
2003	-	27	61
2004	-	60	30
2005	43	73	55
2006	66	87	58
2007	86	74	71
2008	48	46	86
2009	82	45	68
2010	63	50	32

Table 2.3. Data coverage (PSAP data) in % between 2006 and 2010 at the three measurement stations LVBY, HCOE, and HCAB.

Year	LVBY	HCOE	HCAB
2006	30	-	40
2007	89	63	81
2008	94	87	63
2009	95	68	40
2010	76	64	32

2.2 Chemical particle measurements: Intensive Chemistry campaigns 2008-2009

During autumn 2008 and spring 2009 two intensive campaigns were coordinated within the EMEP-network (European Monitoring and Evaluation Programme) with the aim of assigning sources to the background aerosol in Europe. NERI participated in this work and carried out two intensive field campaigns at LVBV during the time periods 17.09.08-16.10.08 (Autumn campaign) and 25.2.09-24.3.09 (Spring campaign). PM₁₀ and PM_{2.5} were measured on diurnal basis directly by SM200 and the particle filter samples were collected for subsequent chemical analysis of the inorganic components in the particle mass. Moreover, low volume samplers (LVS) were installed to collect particle samples for subsequent analysis for elemental and organic carbon (EC, OC), and the organic compounds levoglucosan and mannosan (tracers of wood burning). All these particle samples were collected on diurnal basis. Table 2.4 gives an overview of the collected samples and the chemical analysis.

Table 2.4. Measured parameters at Lille Valby (LVBV), Roskilde, during the autumn and spring campaigns in 2008 and 2009, respectively.

Parameters	Phase	Resolution	Analysis ¹
Elements Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Sr, Zr, Mo, Sn, Sb, Ba, Pb	PM ₁₀ , PM _{2.5}	diurnal	PIXE
PM	PM _{2.5} , PM ₁₀	diurnal	Beta gauge
Ionic species Na ⁺ , Cl ⁻ , NH ₄ ⁺ , SO ₄ ²⁻ , NO ₃ ⁻ , K ⁺ , Mg ²⁺ , Ca ²⁺	PM _{2.5} , PM ₁₀	diurnal	IC
NO_x NO, NO ₂	Gas	30 min	Chemiluminescence
CO	Gas	30 min	photometry
Carbon analysis elemental (EC) and organic carbon (OC)	PM ₁₀	diurnal	thermal/ optical
Organic compounds levoglucosan, mannosan	PM ₁₀	diurnal	HPLC-MS

1. Instruments/methods of analysis are: proton induced X-ray emission (PIXE); ion chromatography (IC), beta gauge particle mass monitor (SM200) and high performance liquid chromatography - mass spectrometry (HPLC-MS). NO_x and CO were measured using monitors based on chemiluminescence and infrared spectroscopy, respectively.

In addition all the standard monitoring of gasses was carried out at LVBV as part of the Danish urban air quality monitoring program. NO_x and CO are of particular interest for the campaign as they act as tracers for the impact of traffic on the air pollution at LVBV.

The main advantage of the intensive campaigns was the simultaneous sampling and analysis of as many chemical compounds as possible within the available resources. The aim was here to enable a much better understanding of the chemical composition and origin of the particles in Denmark. Especially analysis of the carbon content and the tracers levoglucosan and mannosan improve the results from the campaigns since these tracers give information on particulate mass for biomass burning, secondary organic aerosol etc.

Low volume samplers (LVS) were used to sample particles on weekly time resolution. These filters were analyzed for radiocarbon (^{14}C), elemental and organic carbon (EC, OC), and the organic compounds levoglucosan and mannosan. These results will be reported elsewhere. ^{14}C data was organized by Oslo University.

2.3 The COstrained Physical REceptor Model (COPREM) applied to the chemical dataset

The large data set from the intensive chemistry campaigns served as input for source apportionment analysis of $\text{PM}_{2.5}$ and PM_{10} in Danish rural background aerosol.

Various mathematical techniques are available for source apportionment analysis assuming that the original receptor site concentrations can be adequately explained by a linear combination of contributions from various relevant sources with constant source profiles and variable source strengths. Chemical mass balance (CMB) and factor analysis (FA) are two widely used approaches, which are fundamentally different with respect to data input. While CMB requires an a priori knowledge about the sources, which is defined in a set of source profiles, FA requires no knowledge about any sources and mathematically assigns a number of sources, which can describe the data set. We used the Constrained Physical Receptor Model COPREM (Wählin, 2003), which has characteristics from both CMB and FA. COPREM requires an a priori knowledge about the sources, but the weighting of the source profiles is controlled by the analytical uncertainty of the individual measurements. The analyst can fix the individual source profiles like in CMB, or allow for a solution beyond the defined profiles, when less information about the sources is available. In this work, 13 source profiles are used for the source receptor analysis of particulate matter. More details about the source profiles are given in chapter 3.3 and the Appendix.

3 Results and discussion

The following section will present all results obtained within this project including physical and chemical analysis and the receptor analysis by COPREM. The section is structured by the three subsections “Physical particle measurements”, “Chemical composition in PM_{2.5} and PM₁₀ during the intense chemistry field campaigns” and “Source to receptor analysis (COPREM)”.

3.1 Physical particle measurements

In the following sections the PM_{2.5} and PM₁₀ measured by TEOM will be labelled as PM_{2.5}-TEOM and PM₁₀-TEOM to distinguish between the values derived by the SM200 monitors, which will accordingly be labelled as PM_{2.5}-SM200 and PM₁₀-SM200.

The time series of diurnal averages, the annual trends, and the diurnal variations are presented corresponding to the above described parameters of PM_{2.5}-TEOM, PM₁₀-TEOM, particle number, and the light absorption coefficient. Also, the particle number size distributions are discussed in more detail. In addition, special attention is given to a comparison between measurements of PM_{2.5} and PM₁₀ using the TEOM instruments and the SM200 monitors.

3.1.1 PM_{2.5} and PM₁₀ measured with the TEOM and a comparison to SM200 measurements

PM_{2.5}-TEOM was measured continuously at rural background (Lille Valby), urban background (HCØ) and at street level (HCAB) throughout the period from 2005-2010. The TEOM was further used to measure PM₁₀ at HCOE and HCAB. PM₁₀-SM200 was also measured at rural and urban background from 2005-2010 and from 2006 also at street level at HCAB. However, PM_{2.5} was only measured using SM200 from 2007 at HCAB. To investigate the particle mass loss in the TEOM during measurements, the TEOM values for the last three years were compared to data retrieved by SM200 measurements at the same sites. SM200 monitors measure in agreement with the reference method while TEOM instruments measure too low PM values due to evaporation of parts of the particle mass inside the instruments as mentioned above.

Comparison of TEOM with SM200 measurements and conclusions

The previous report from the particle research project “Partikelrapport 2005-2007” (Wåhlin, 2008) presented values of the general levels of PM_{2.5} and PM₁₀ for the Copenhagen area for rural and urban background and at street level for the period from 2005-2007. These values were based on the available measurements of PM_{2.5}-SM200 (only one station) and PM₁₀-SM200 and estimates based on TEOM instruments.

Only a limited amount of data for the real PM_{2.5}-SM200 was therefore available at the time when writing the previous particle project report (Wåhlin, 2008). The general levels of PM_{2.5} were therefore estimated on the basis of the assumption that the loss of PM_{2.5} inside the TEOM instrument as annual average was the same as the loss of PM₁₀ inside the

TEOM and that the losses were the same at rural and urban background and at street level (Wählin, 2008). This assumption was justified by:

- Previous measurements showing that the annual average of the loss of PM₁₀-TEOM was the same in urban background and at street level (Palmgren et al., 2003 ; Wählin, 2008).
- Comparison between the loss of PM₁₀-TEOM at HCØ with the loss of PM_{2.5}-TEOM at HCAB. This comparison showed that there was very low correlation between the losses of PM₁₀-TEOM at HCØ and PM_{2.5}-TEOM at HCAB. However, the average annual losses were about the same size (9-10 µgm⁻³).
- The argument was, that the coarse fraction (particles between 2.5 and 10 µm in diameter) mainly consists of hygroscopic salt particles and mineral non volatile compounds. The loss of PM inside the TEOM instruments is therefore mainly due to evaporation of particles with diameters below 2.5 µm.

The amount of measurements of PM_{2.5} using both SM200 and TEOM has increased significantly since the previous particle project report. Therefore a new determination of the general levels of PM_{2.5} and PM₁₀ for the Copenhagen area for rural and urban background and at street level has been carried out. This time, the conclusions are solely based on measurements. The new results are presented in Table 3.1 together with the results from Wählin (2008).

For PM₁₀ the results from Wählin (2008) for 2005-2007 are in agreement with the measurements for the same period. From 2005-2007 to 2008-2010 there is a decrease in PM₁₀ of 3.8-5.8 µgm⁻³ corresponding to 17% on average. The reasons for the decrease in PM₁₀ are decreases in emissions of PM₁₀, SO₂, NH₄, NO_x etc. At HCAB part of the decrease was most likely due to the new asphalt pavement in 2008 (Ellermann et al., 2010a). The long term trends for PM₁₀ will be analysed in further detail during the next years when longer time series are available.

Table 3.1. Estimates of PM_{2.5} and PM₁₀ based on Wählin (2008) and values of PM_{2.5}-SM200 and PM₁₀-SM200 based on measurements using SM200. The numbers given are averages for the given periods in units of µgm⁻³ at 0°C and 1 atm pressure. PM_{2.5}-SM200 based on measurements using SM200 during 2005-2007 are not given since it was only measured at HCAB during 2007. The large decrease in PM₁₀ at HCAB from 2005-2007 to 2008-2010 is explained by new asphalt on HCAB in 2008 (Ellermann et al., 2010b). The measurement station at Lille Valby was moved 2 km to DMU/Risø during the last half year of 2010.

	Wählin 2008 2005-2007		SM200 2005-2007	SM200 2008-2010	
	PM _{2.5}	PM ₁₀	PM ₁₀	PM _{2.5}	PM ₁₀
Street level (HCAB)	22.7	42.5	39.1	19.5	33.7
Urban Background (HCØ)	20.8	26.6	24.8	13.1	21.0
Rural background (Lille Valby)	20.4		25.3	12.6	19.5

For PM_{2.5} there were only SM200 measurements available from 2007-2010 at HCAB and from 2008-2010 at HCØ and LVBY. It is therefore not possible to obtain measurements representative for the same period as used by Wählin (2008).

At street level at HCAB there is only a 15% difference between the estimates based on TEOM (22.7 $\mu\text{g}\cdot\text{m}^{-3}$) and the averages measured using SM200 (19.5 $\mu\text{g}\cdot\text{m}^{-3}$). The estimates and measurements seem therefore to be in good agreement, when a plausible decrease in $\text{PM}_{2.5}$ from 2005-2007 to 2008-2010 is taken into account.

In rural and urban background the difference between the estimates for 2005-2007 and measurements using SM200 from 2008-2010 are much larger. In absolute terms the difference is about 7.7 $\mu\text{g}\cdot\text{m}^{-3}$ and in relative terms about 40%. It is unlikely that the long term trends or meteorological variations can account for this change. First, because PM_{10} (that includes $\text{PM}_{2.5}$) only decreased by about 3.8 and 5.8 $\mu\text{g}\cdot\text{m}^{-3}$ respectively at the rural and urban background stations. Second, because the secondary inorganic particles account for about 50% of $\text{PM}_{2.5}$ and measurements of the secondary inorganic particles show a much slower decrease (data from the monitoring programme of air quality in Denmark; Ellermann et al., 2010a).

The difference between the previous estimates for 2005-2007 based on TEOM and measurements for 2008-2010 based on SM200 therefore indicate that the assumptions used in Wåhlin (2008) need to be adjusted. Table 3.2 shows average $\text{PM}_{2.5}$ and PM_{10} measured during the period 2008-2010 using both SM200 and TEOM together with the calculated loss (SM200 – TEOM). Only days with simultaneous measurements using SM200 and TEOM are included. The average losses from $\text{PM}_{2.5}$ (3.3-6.8 $\mu\text{g}\cdot\text{m}^{-3}$) are smaller than for PM_{10} (7.1-8.4 $\mu\text{g}\cdot\text{m}^{-3}$). Moreover, the losses from $\text{PM}_{2.5}$ in rural and urban background are lower than the losses measured at street level and for PM_{10} in urban background. More specifically the loss of $\text{PM}_{2.5}$ in urban background is only about half of the loss measured for PM_{10} in urban background.

Table 3.2 includes also the number of diurnal averages available for the comparison of SM200 and TEOM. It is clear that the data coverage is low in some of the cases and this should be taken into account when conclusions are drawn from the data. Despite this uncertainty, it can be concluded that loss of PM inside the TEOM instruments depends on the particle fraction (PM_{10} and $\text{PM}_{2.5}$) and on the measurement site (rural, urban background or street level). Moreover, the previous assumption that TEOM could be corrected for the average loss by addition of a constant factor (Wåhlin, 2008) is not sufficiently accurate.

Table 3.2. Average $\text{PM}_{2.5}$ and PM_{10} determined using SM200 and TEOM at rural background (LVBY), urban background (HCØ) and at street level (HCAB) during the period 2008-2010. In addition, the table gives the number of measurements and the loss of PM in TEOM calculated as (SM200 – TEOM). Finally, the table includes the ratio SM200/TEOM and the correlation coefficient as determined from the regression lines in Figures 1 and 2. Only data from days with simultaneous measurements are used in this analysis.

	$\text{PM}_{2.5}$			PM_{10}	
	Rural background	Urban background	Street level	Urban background	Street level
	Lille Valby	HCØ	HCAB	HCØ	HCAB
Number	384	636	958	775	381
Average SM200, $\mu\text{g}/\text{m}^3$	13.3	12.8	19.5	21.0	32.8
Average TEOM, $\mu\text{g}/\text{m}^3$	8.8	9.5	12.7	12.6	25.7
Loss, $\mu\text{g}/\text{m}^3$	4.5	3.3	6.8	8.4	7.1
Ratio SM200/TEOM	1.5	1.3	1.5	1.7	1.3
Correlation coefficient r^2	0.73	0.61	0.64	0.74	0.71

The measurements of PM_{2.5} and PM₁₀ using SM200 and TEOM are compared directly in Figures 3.1 and 3.2. As shown there is a reasonable correlation between SM200 and TEOM for the different size fractions and different measurement sites. The ratios between SM200 and TEOM fall in the range from 1.3 to 1.7 (Table 3.2). Similar findings have been found in other countries (Casella Stanger and University of Birmingham, 2003; Hauck et al., 2004).

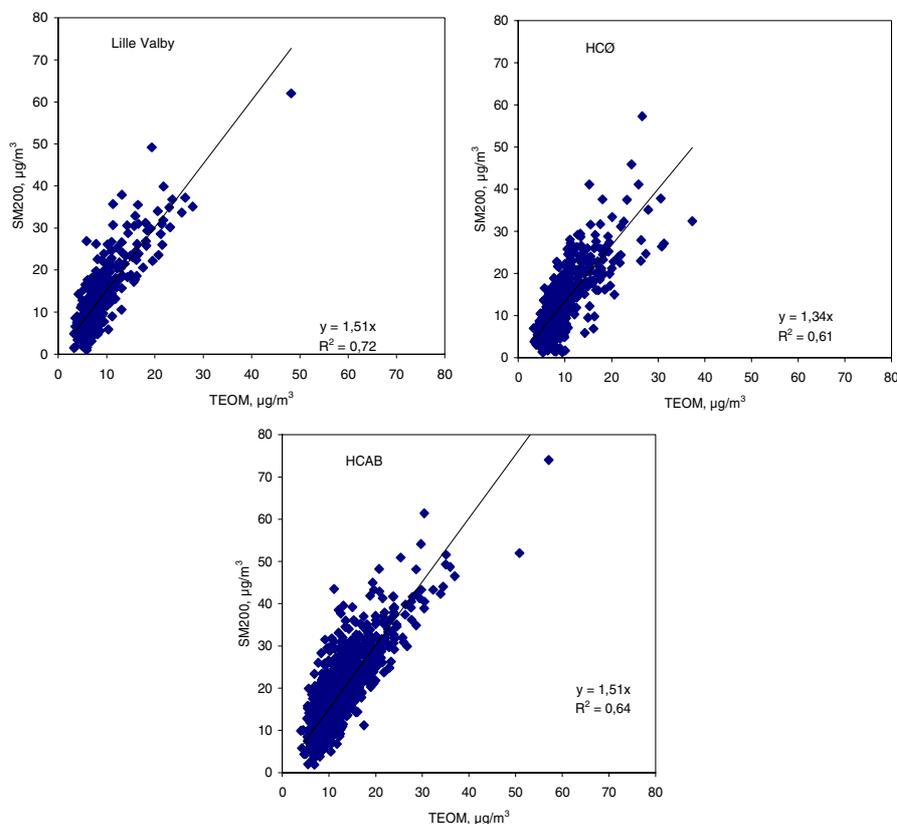


Figure 3.1. Simultaneous measurements of PM_{2.5} using SM200 and TEOM at rural background (LVBY), urban background (HCØ) and at street level (HCAB) during the time period 2008-2010. SM200 measures diurnal averages while TEOM measurements on ½-hour average have been averaged to diurnal averages. The slope is calculated using simple linear regression lines forced through zero.

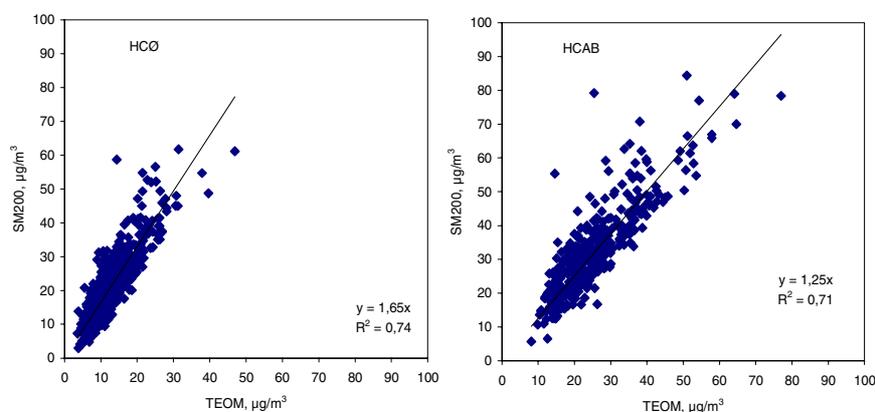


Figure 3.2. Simultaneous measurements of PM₁₀ using SM200 and TEOM at urban background (HCØ) and at street level (HCAB) during the period 2008-2010. SM200 measures diurnal averages while TEOM measurements on ½-hour average have been averaged to diurnal averages. The slope is calculated using simple linear regression lines forced through zero.

More detailed analysis shows that there is a significant temporal variations in the ratio between SM200 and TEOM. The ratio between SM200 and TEOM varies between the years. This can be illustrated by data for PM_{2.5}:

	2008	2009	2010
HCAB	1.65	1.50	1.38
HCOE	1.31	1.18	1.52

A pronounced seasonal variation is found in the data. Figure 3.3 shows the monthly variations of PM_{2.5} measured at HCOE using TEOM and SM200. Also, the TEOM loss and the ratio between SM200 and TEOM is shown in this Figure. It is clearly seen that the loss of mass in TEOM is highest during winter and early spring and lowest during the summer months. Consequently the ratio varies between about 1.6 in winter and about 1.3 in summer for PM_{2.5} at HCOE. A similar seasonal variation was found by Hauck et al. (2004).

Both the temporal and the spatial variations can be explained based on knowledge about the chemical compounds that are lost by evaporation in TEOM. The loss is mainly due to evaporation of ammonium nitrate, ammonium chloride and semi volatile organic compounds (Casella Stanger and University of Birmingham, 2003). This study shows further that the loss depends inversely on the relative humidity and temperature. The seasonal variation and spatial variation may therefore be understood by the following arguments:

- On average, the concentration of ammonium nitrate is highest during winter and early spring (based on data from the Danish air quality programme). Hence the loss will be highest during this period of the year.
- The loss of semi volatile organic compounds may be highest during winter because a relatively higher part of the semi volatile compounds is found in the particle phase relatively to the gas phase.
- Water is another constituent that is lost in TEOM. The amount of water is highest at high relative humidity, and the relative humidity has a seasonal variation with highest values during winter and lowest values during summer.
- The spatial variability can be explained by the spatial variability of the abundance in different compounds that are observed at the different stations and that may evaporate in the TEOM.

In principle the TEOM data should be corrected by a factor according to the above mentioned ratios of 1.2-1.7 and this would be more accurate rather than not to use any correction. This could be done by adding a constant factor or just by using the "standard" correction factor of 1.3 commonly applied. To correct the TEOM data with a correction factor is in line with recommendations for the data reporting under the EU directive (EU 2008/50/EC). However, since there is clear evidence that the correction factor depends on e.g. size fraction, measurement site and season the use of a constant correction factor should be done with precaution and take the temporal and spatial variations into account if possible. No correction factor has been applied to the TEOM data presented in this report.

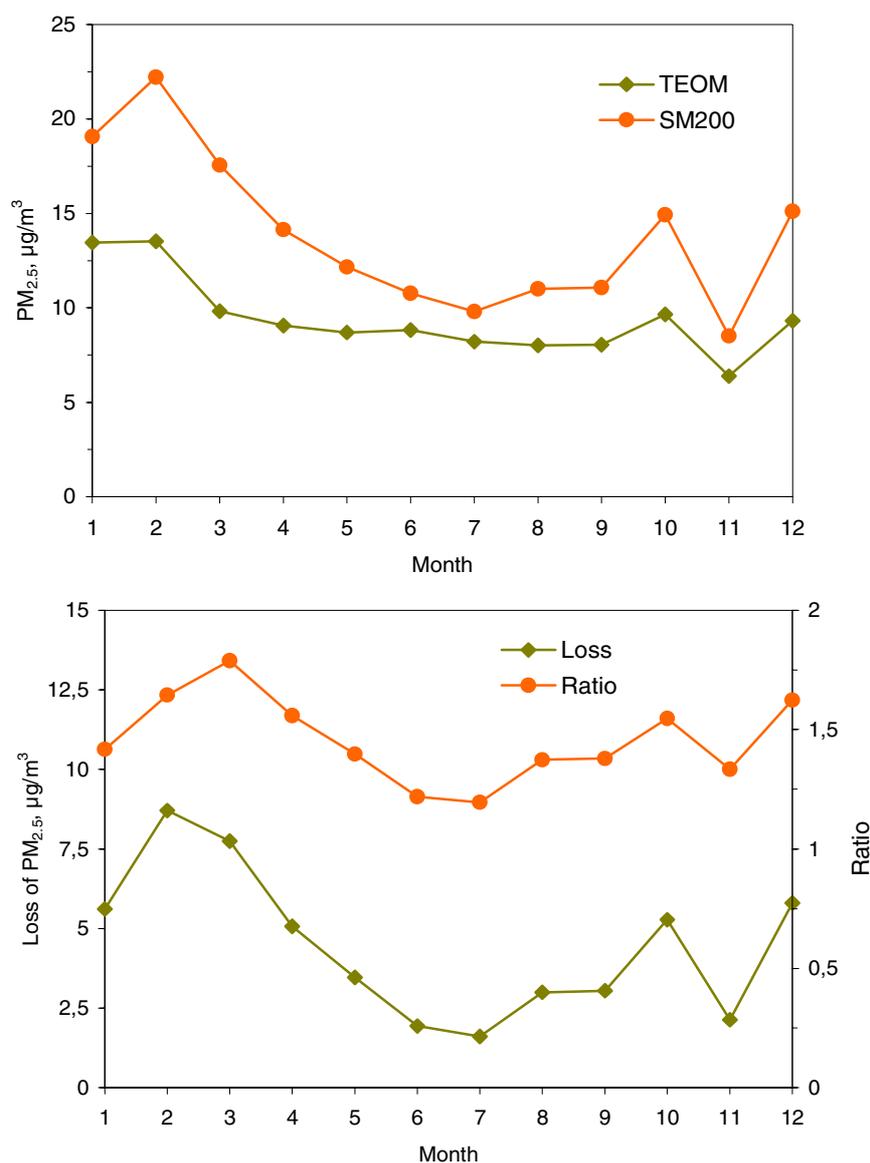


Figure 3.3. Monthly averages of PM_{2.5} in 2010 at HCOE measured using TEOM and SM200 (above). Loss of mass in TEOM (SM200-TEOM) and ratio between SM200 and TEOM (below).

Data from the other Danish measurement stations in rural and urban background and at street level show that PM_{2.5} and PM₁₀ are on the same level as found for the similar type of stations in the Copenhagen area (Table 3.3). The urban background measurements of PM_{2.5} are also in agreement with measurements performed by OPSIS for Copenhagen Airports A/S at background stations at Copenhagen Airport Kastrup. These measurements show average levels of PM_{2.5} of about 12 µg/m³ for the period 2006-2008 (Copenhagen Airport, 2009).

As in the previous particle project report (Wählin, 2008), it can therefore be concluded that the spatial variation of PM_{2.5} and PM₁₀ is small on a regional basis. However, the new analysis based on better and more representative measurements shows that the difference in PM_{2.5} between rural background, urban background and street level is larger than previously found.

Table 3.3. Averaged PM_{2.5}-SM200 and PM₁₀-SM200 measured during the period 2008-2010. Units of $\mu\text{g m}^{-3}$ are given at 0°C and 1 atm pressure. The PM_{2.5} value at Jagtvej represents measurements in 2010 only. n.m. = no measurements in monitoring program.

Street level					
	Copenhagen HCAB	Copenhagen Jagtvej	Odense	Aarhus	Aalborg
PM _{2.5}	19.5	19.1	n.m.	15.8	18.9
PM ₁₀	33.7	31.1	30.6	27.2	n.m.
Urban background					
	Copenhagen		Odense	Aarhus	Aalborg
PM _{2.5}	13.1		n.m.	13.0	18.9
PM ₁₀	21.0		n.m.	n.m.	n.m.
Regional background					
	Lille Valby		Keldsnor		
PM _{2.5}	12.6		n.m.		
PM ₁₀	19.5		19.3		

Annual time series of PM_{2.5}-TEOM and PM₁₀-TEOM

Figure 3.4 shows the diurnal averages of PM_{2.5}-TEOM for the period 2008-2010 at LVBY, HCOE and HCAB.

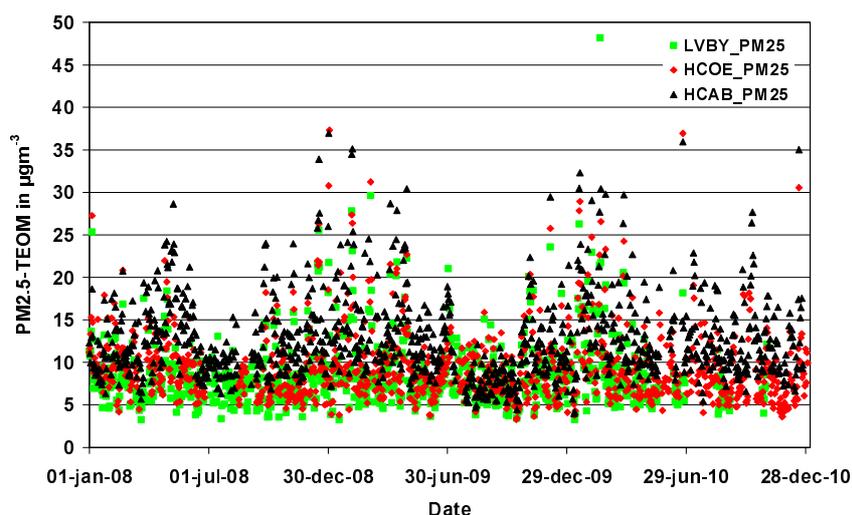


Figure 3.4. Time series of measured diurnal averages of PM_{2.5}-TEOM at LVBY, HCOE, and HCAB during the period 2008–2010.

It is shown, that PM_{2.5}-TEOM is much higher at the street level (HCAB) compared with the urban background (HCOE) and rural background site (LVBY). A seasonal variation is visible as well with higher values in the winter period.

In Figure 3.5, the time series of PM₁₀-TEOM diurnal averages are displayed for the period 2008-2010 at HCOE and HCAB.

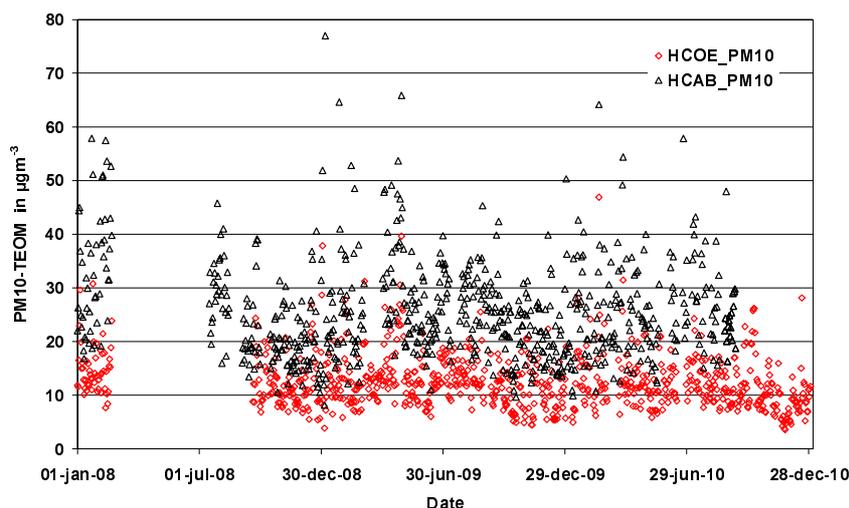


Figure 3.5. Time series of diurnal averages of PM₁₀-TEOM at HCOE and HCAB during the period 2008–2010.

PM₁₀-TEOM appears to be much higher than PM_{2.5}-TEOM, especially at street level. Moreover, the relative difference between kerbside and urban background is more pronounced for PM₁₀ compared with PM_{2.5}. The seasonal variation in PM₁₀ is not as pronounced as for PM_{2.5}, since also high PM values are observed in summer.

Annual trends of PM_{2.5}-TEOM and PM₁₀-TEOM

In Figure 3.6 and Figure 3.7 the annual averages of PM_{2.5}-TEOM and PM₁₀-TEOM from 2002 to 2010 are displayed. Averages were only calculated when the data coverage was at least 50%.

Annual average concentrations of PM_{2.5}-TEOM range from 8.1 µg m⁻³ to 9.4 µg m⁻³ at LVBY, from 9.4 µg m⁻³ to 9.5 µg m⁻³ at HCOE, and from 12.1 µg m⁻³ to 13.3 µg m⁻³ at HCAB during the project period 2008-2010. Annual average concentrations of PM₁₀-TEOM at HCOE range from 12.1 µg m⁻³ to 13.2 µg m⁻³ and at HCAB from 25.5 µg m⁻³ to 25.7 µg m⁻³ during this period. A substantial part of this difference is due to high non-exhaust traffic emissions contributing in the coarse (PM₁₀ – PM_{2.5}) size range.

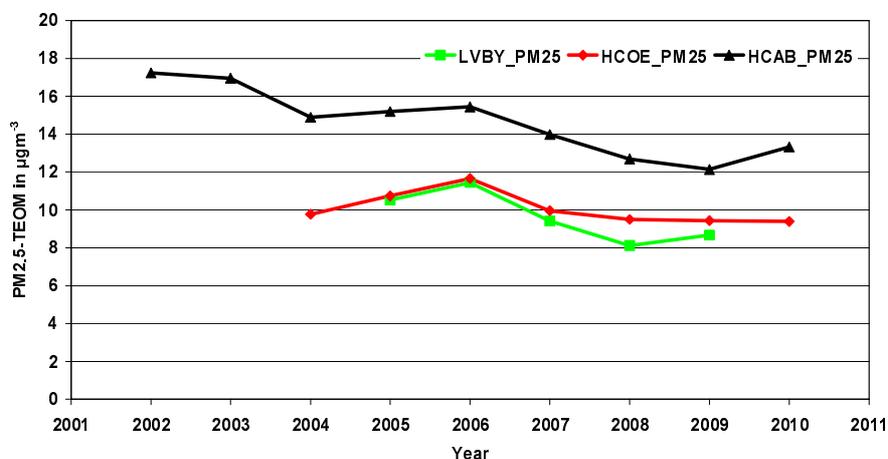


Figure 3.6. Annual averages of PM_{2.5}-TEOM measured at LVBY, HCOE, and HCAB during 2001-2010.

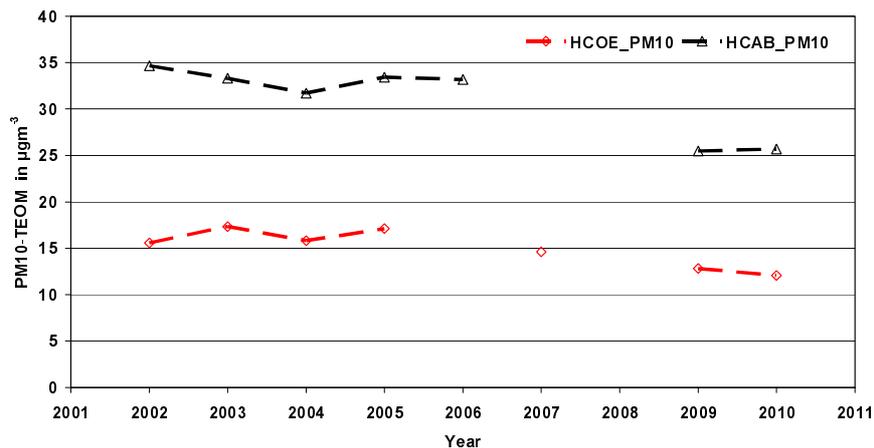


Figure 3.7. Annual averages of PM₁₀-TEOM measured at HCOE and HCAB during 2001-2010.

A general decrease in PM_{2.5}-TEOM is observed at the street level (HCAB), while rural background and urban background sites show more stable values over the time period from 2004-2010. PM_{2.5}-TEOM at background sites is mostly imprinted by long-range transported particulate matter and to some extent by local emissions as e.g. emissions from wood stoves and other combustion sources. Chapter 3.3 will give a deeper analysis of the PM_{2.5} sources.

For PM₁₀-TEOM a decrease is evident at HCOE and HCAB in the time period 2005-2010. Because of low data coverage, values for 2007 and 2008 (HCAB) and 2006 and 2008 (HCOE) are not shown. The periods with missing data are usually not only regarding single values but instead periods lasting several days up to full months, which may falsify the annual averages. Otherwise, we would expect to see a clear stepwise decrease from 2007 to 2009 in PM₁₀-TEOM as the asphalt pavement at HCAB was changed in August 2008 reducing non-exhaust emissions. This observation was supported by SM200 measurements and elemental analysis (Ellermann et al., 2010b).

Diurnal variation of PM_{2.5}-TEOM and PM₁₀-TEOM

The main advantage of TEOM is the high time resolution (½ hour) that allows investigating the diurnal patterns in PM_{2.5} and PM₁₀ in order to identify the emission patterns and relate them to e.g. traffic variations, and to other measurements at high time resolution (CO, NO_x).

Figures 3.8 and 3.9 show the diurnal variation in PM_{2.5}-TEOM and PM₁₀-TEOM for the three years period from 2008 to 2010.

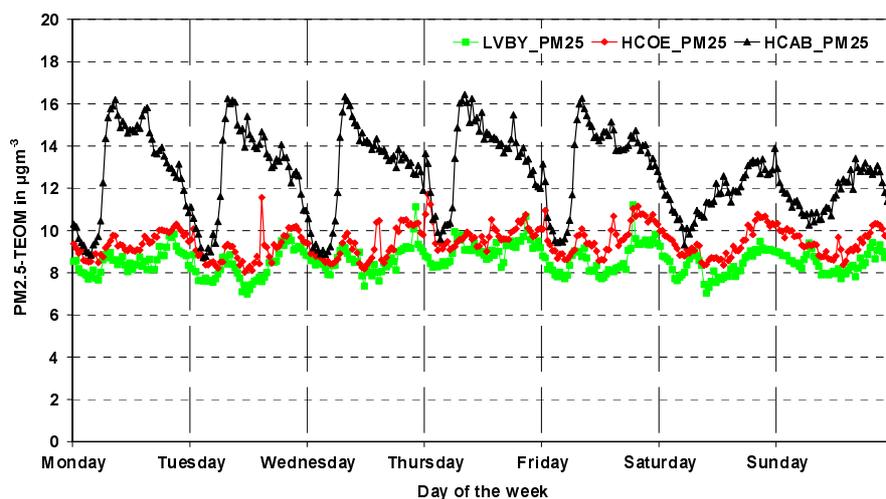


Figure 3.8. Diurnal variation of PM_{2.5}-TEOM measured at LVBY, HCOE and HCAB during the time period 2008-2010.

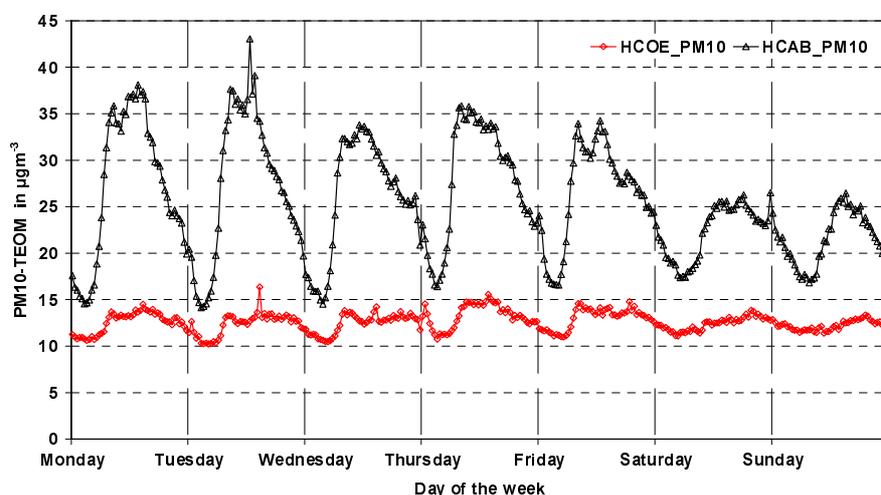


Figure 3.9. Diurnal variation of PM₁₀-TEOM measured at HCOE and HCAB during the time period 2008-2010.

A pronounced diurnal variation is observed for PM_{2.5}-TEOM and PM₁₀-TEOM at street level (HCAB). For PM₁₀-TEOM, values range from 15 $\mu\text{g m}^{-3}$ during night-time hours to about 38 $\mu\text{g m}^{-3}$ at noon. The variation follows the typical diurnal and weekly pattern as observed in traffic densities, which is also reflected for other traffic-related pollutants in Copenhagen (Ketzel et al. 2003). This finding is in agreement with Wählén (2008), who found values of about 20 to 40 $\mu\text{g m}^{-3}$ for the time period from 2005-2007. The diurnal variation is also observed for the PM_{2.5}-TEOM at street level (HCAB), but the difference between night-time and day-time values is much smaller (from about 10 $\mu\text{g m}^{-3}$ during night-time hours to about 16 $\mu\text{g m}^{-3}$ at noon).

At HCOE, the urban background station, the typical diurnal variation is much less pronounced for PM₁₀-TEOM and nearly no typical traffic pattern is observed for PM_{2.5}-TEOM. In principle, the imprinting of urban traffic density is decreasing with an increase of the distance to the traffic and when switching from PM₁₀-TEOM to PM_{2.5}-TEOM.

Table 3.4 presents the differences in annual averages of PM_{2.5}-TEOM and PM₁₀-TEOM for the three different stations LVBY, HCOE, and HCAB.

Table 3.4. Differences in annual averages of PM₁₀-TEOM and PM_{2.5}-TEOM between the different stations at rural background (LVBY), urban background (HCOE), and at street level (HCAB) in the period 2002-2010.

Year	PM ₁₀ -TEOM (HCAB-HCOE) in μgm^{-3}	PM _{2.5} -TEOM (HCAB-HCOE) in μgm^{-3}	PM _{2.5} -TEOM (HCOE-LVBY) in μgm^{-3}
2002	19.1	-	-
2003	16.0	-	-
2004	15.9	5.1	-
2005	16.3	4.5	0.2
2006	-	3.8	0.2
2007	-	4.0	0.6
2008	-	3.2	1.4
2009	12.7	2.7	0.8
2010	13.6	4.0	-

From Table 3.4 it can be concluded, that the PM₁₀-TEOM contribution from the street defined as the difference between PM₁₀-TEOM at HCAB and PM₁₀-TEOM at HCOE has been decreased from about 19.1 μgm^{-3} in 2002 to about 13.6 μgm^{-3} in 2010 (partly due to new asphalt). In comparison, the PM_{2.5}-TEOM contribution from the street defined as the difference between PM_{2.5}-TEOM at HCAB and PM_{2.5}-TEOM at HCOE does not show a significant decrease. Values for PM_{2.5}-TEOM at the urban background (HCOE) and the rural background (LVBY) show quite similar values from 2005-2009 stating that most of PM_{2.5} in the urban background does not have urban sources and can rather more be assigned to long range transport.

3.1.2 Particle number size distributions from 6 to 700 nm measured with the DMPS (Differential Mobility Particle Sizer)

DMPS (Differential Mobility Particle Sizer) instruments were used within this project to measure particle number size distributions in the range between 6 and 700 nm in diameter. Because this projects benefits from two previous studies, which involved the same technique and measurements, some time series are presented involving in addition data from these previous studies, which started in the middle of 2001.

Annual time series of total particle number concentrations

In Figure 3.10 the time series of diurnal averages of total particle number concentrations at LVBY, HCOE, and HCAB are illustrated for the period 2008–2010.

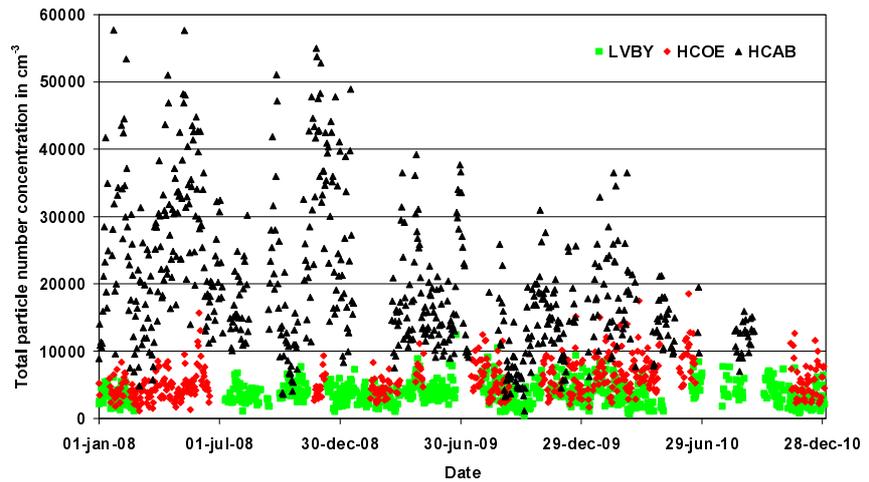


Figure 3.10. Time series of diurnal averages of total particle number concentrations at LVBY, HCOE, and HCAB during the period 2008-2010.

As a general trend, and similar to the PM measurements, number concentrations at the rural background station LVBY are lowest followed by the urban background station HCOE and the street station HCAB with highest total particle number concentrations. Although traffic activities at HCAB follow a very regular pattern, the daily total number of particles between 6 and 700 nm in diameter is highly variable because of the changing meteorological conditions e.g. wind speed, wind direction and the variable contribution from regional transport.

Annual trends of total particle number concentrations

In Figure 3.11 the correlation between total particle number concentrations (integral over the measured size range 6-700 nm) and measured NO_x concentrations at the street level (HCAB) is presented by way of example for the year 2007. This graph illustrates the very good correlation of NO_x and total particle number, which both originate from traffic emissions. This good correlation is further used to correct the annual averages of total particle number in Figure 3.12 as especially at the street level the data coverage was low for some years. The data coverage for NO_x is better than 90% for all years in 2002-2010.

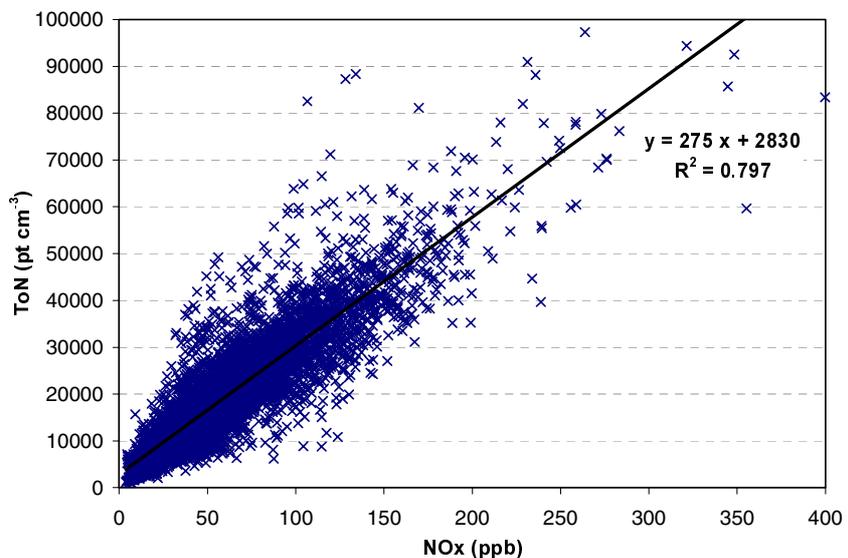


Figure 3.11. Correlation between NO_x (in ppb) and total particle number concentration (in cm⁻³) measured at street level (HCAB) in 2007. Data points are 1 hour mean values.

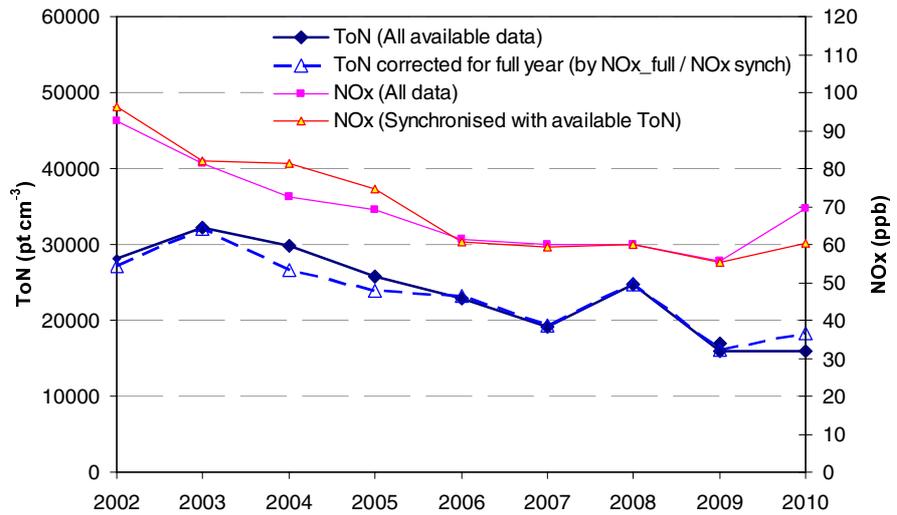


Figure 3.12. Annual averages of total particle number concentration and NO_x concentration at the street level (HCAB). Plotted are the averages for all available data as well as NO_x-data synchronised for those periods, when total particle number was measured.

Figure 3.13 also shows the annual averages of total particle number concentrations at all 3 stations.

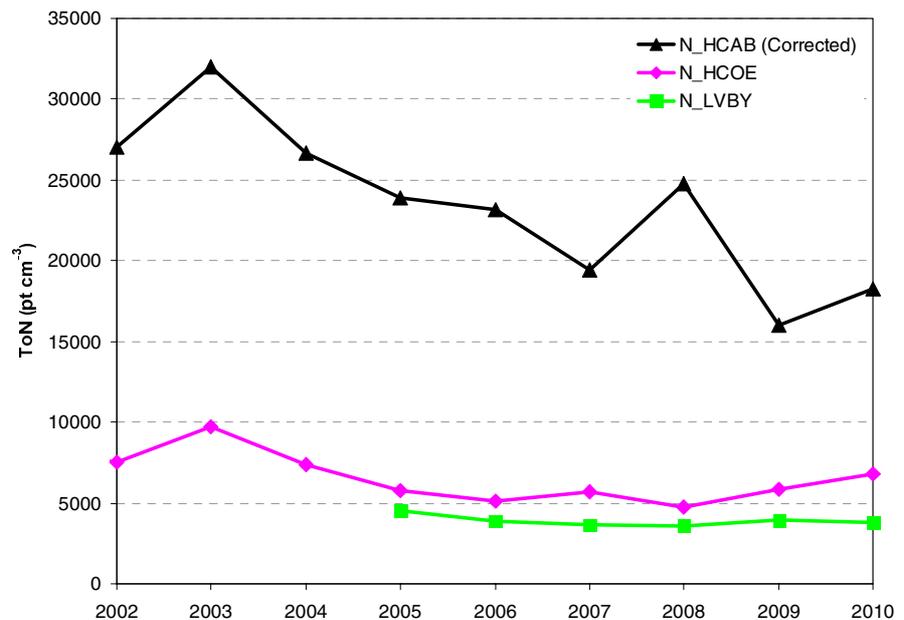


Figure 3.13. Annual averages of total particle number concentrations measured at LVBY, HCOE, and HCAB from 2002-2010.

Since 2005, the total particle number concentration has been almost constant at the rural background site LVBY. At the urban background site HCOE, the total particle number concentration shows a slight decrease as a general trend over the years 2003-2008, however a slight increase for the last two years 2009 and 2010. Moreover, the total particle number concentration shows a clear decreasing trend from 2002 to 2010 at the street station HCAB. For few years (2003, 2008, 2010) an increase has been observed. The numbers in 2009 and 2010 are nearly at the same level and the downward trend seemingly has ceased and it will thus be interesting to follow the future development. It can be concluded, that the general decrease in total particle number concentration at HCAB can be assigned to a vast change in engine exhaust technology and a composi-

tional change in the fuels used. Wåhlin (2009) found similar results for the period 2002 to 2007 where in addition, the influence of the reduced sulphur content in diesel fuels was investigated by looking detailed into the Friday and Saturday night emissions, which mostly represent emissions from diesel driven taxis. It was found that the amount of particles with diameters $D_p < 30$ nm has decreased significantly with the reduced sulphur content in diesel fuels. In addition, nowadays an increasing number of passenger car engines are equipped with diesel particle filters influencing the number emissions of primary particles.

Diurnal variation of total particle number concentrations

In Figure 3.14 the diurnal variation of measured total particle number concentrations at LVBY, HCOE, and HCAB during the time period 2008-2010 is shown.

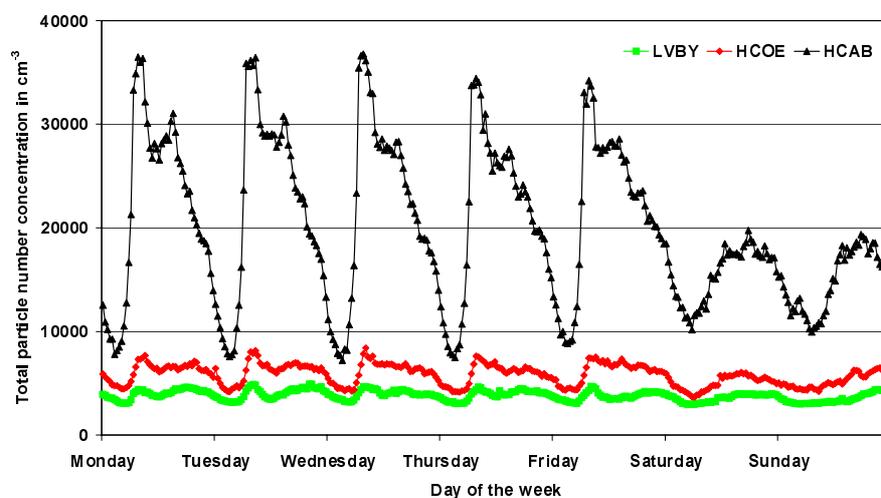


Figure 3.14. Diurnal variation of total particle number concentrations at LVBY, HCOE, and HCAB during the period 2008-2010.

The diurnal pattern in total particle number concentrations follows the traffic density at HCAB and was also observed by Wåhlin (2008). Peak maximum values correspond to about 35000 to 38000 cm^{-3} at HCAB during morning rush hours compared to about 8000 to 9000 cm^{-3} during night-time for weekdays at the street level. In accordance to Figure 12, Wåhlin (2008) measured slightly larger numbers during the previous study from 2005-2007. The diurnal pattern of traffic is also observed at the urban background station HCOE with a much weaker imprinting. Total particle number concentrations at HCOE rise from about 5000 cm^{-3} during night-time up to about 7000 to 8000 cm^{-3} in the morning rush hours during weekdays. Besides traffic emissions, also other sources as e.g. house warming, industrial and wood stove emissions are expected to contribute to concentrations observed at HCOE and HCAB. The rural background at LVBY shows only very small changes in total particle number concentration during the day as the rural background is only slightly affected by traffic activities.

Annual trends of particle number size distributions

In Figure 3.15 annual averages of the particle number size distributions (PNSD) measured from 2002-2010 are presented.

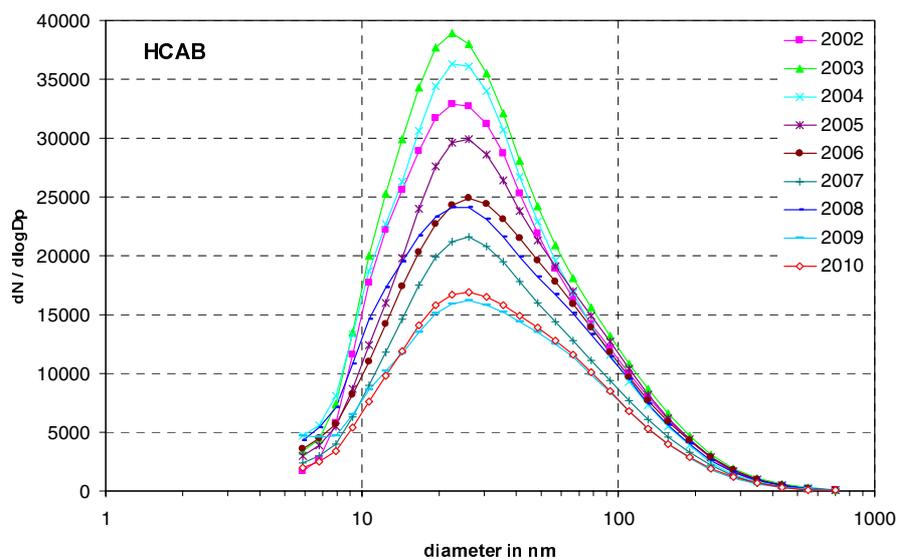
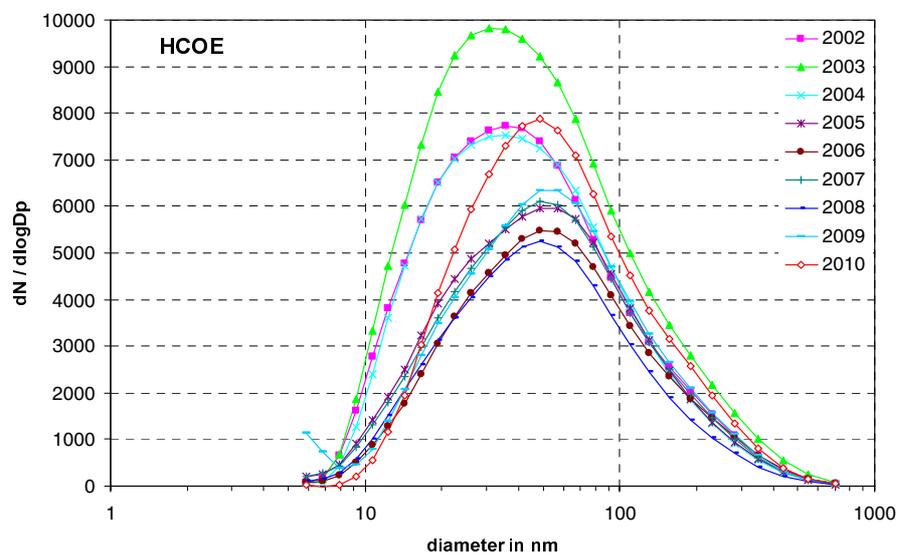
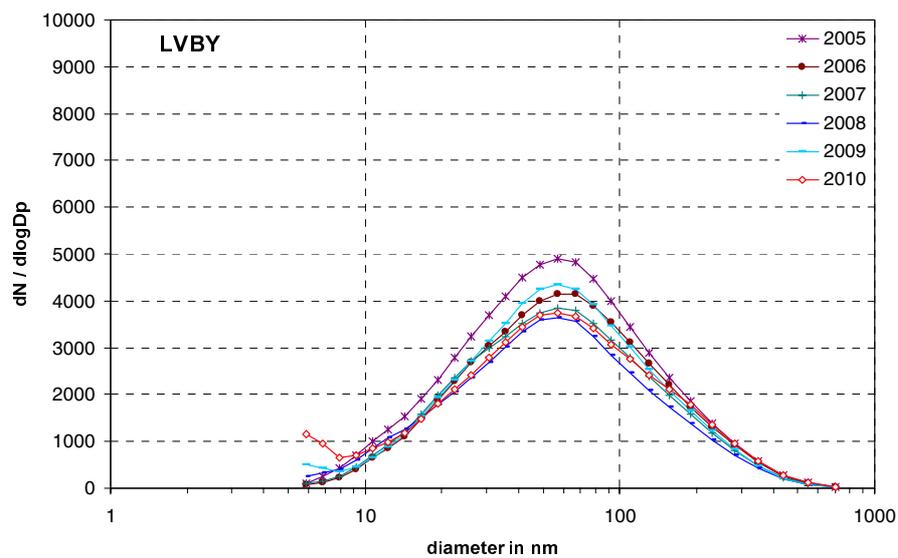


Figure 3.15. Annual averages of particle number size distributions (PNSD) measured at LVBY, HCOE, and HCAB from 2002-2010. Units: particles cm^{-3}

For the rural background (LVBY) a large time stable particle number size distribution is observed throughout the period from 2005 to 2010. The PNSD shows a monomodal structure with count mean diameters at about $D_p = 50\text{-}70$ nm. At the urban background (HCOE) a significant decrease and as well a shift in the maximum diameter (mode) was observed during the period from 2002-2010 from about 30 nm to 50 nm. A discussion of this behaviour will follow below.

At the street level (HCAB), findings that the total particle number concentration has been constantly decreasing from 2002 to 2010, are reflected by a continuous decrease of the peak maximum concentration of the smallest particle mode as part of the bimodal particle number size distribution. This smallest particle mode is located at about $D_p = 20\text{-}30$ nm and the peak maximum concentration has decreased from about $32000\text{-}38000$ cm^{-1} in the first years of the measurement period down to about $16000\text{-}17000$ cm^{-1} in 2009 and 2010. This decrease is most likely due to a change in motor engine exhaust technology and a change in the sulphur content in Danish fuels.

In Figure 3.16, the annual averages of particles in certain size regimes as ($D_p = 6\text{-}40, 40\text{-}110, 110\text{-}700$ nm) are presented additionally. Here, it can be clearly seen, that particle numbers have been decreased in all size regimes at HCAB stating the general trend the smaller the particles, the larger their relative decrease over the years.

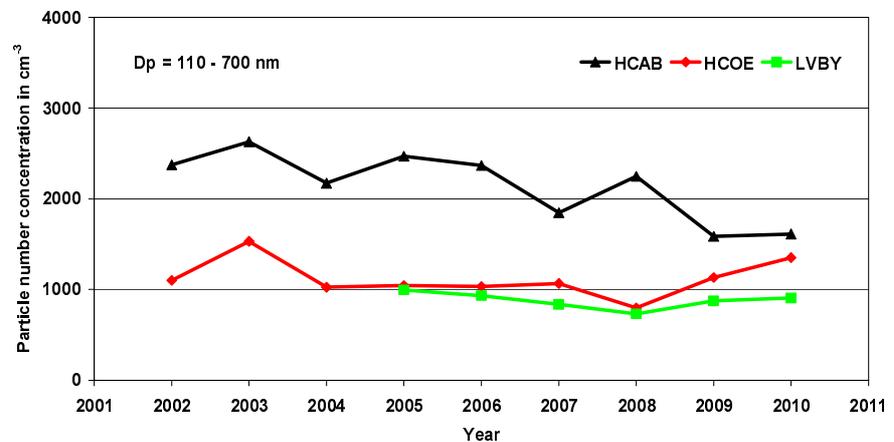
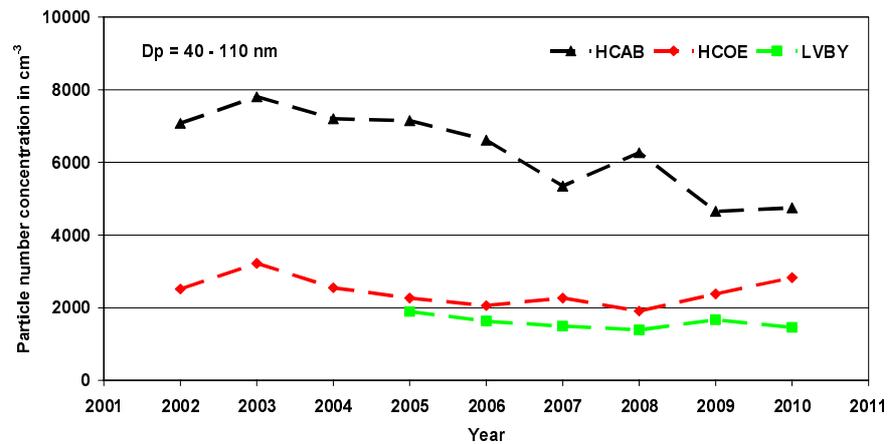
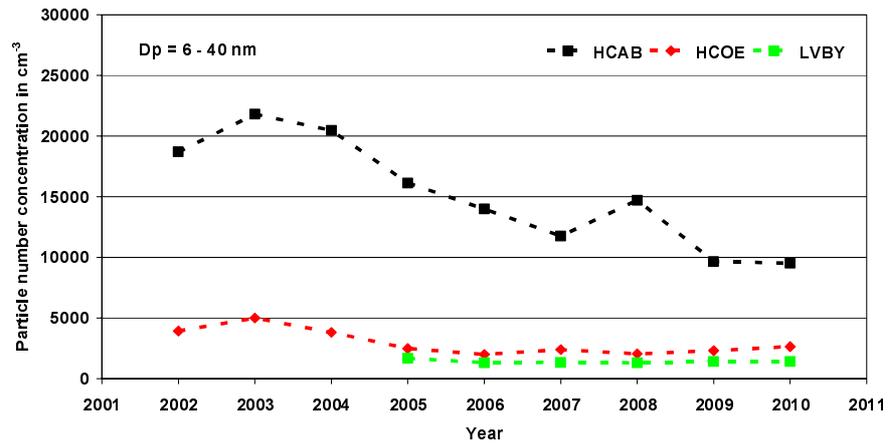


Figure 3.16. Annual averages of particle number concentrations in defined size fractions as $D_p = 6\text{--}40\text{ nm}$, $D_p = 40\text{--}110\text{ nm}$, $D_p = 110\text{--}700\text{ nm}$ measured at LVBY, HCOE, and HCAB from 2002-2010.

At the urban background (HCOE), a different picture is presented with respect to the annual trend. Here, the ultrafine particle mode with count mean diameters of $D_p = 20\text{--}30\text{ nm}$ observed as a consequence of urban traffic emissions has also clearly decreased throughout the measurement period (Figure 3.15 and 3.16), but an opposite tendency is observed for Aitken mode particles with count mean diameters of about $D_p = 50\text{--}70\text{ nm}$ in 2008-2010. This finding could be explained by an increase in the use of wood stoves during this period. This explanation may be the rea-

son why this tendency is not observed at street level (HCAB) because emissions from the street may superpose this effect due to the very high particle number in traffic emissions. For a further illustration of the change in number concentrations in the certain size fractions, Figure 3.17 shows these values for all three stations in 2005 and 2010.

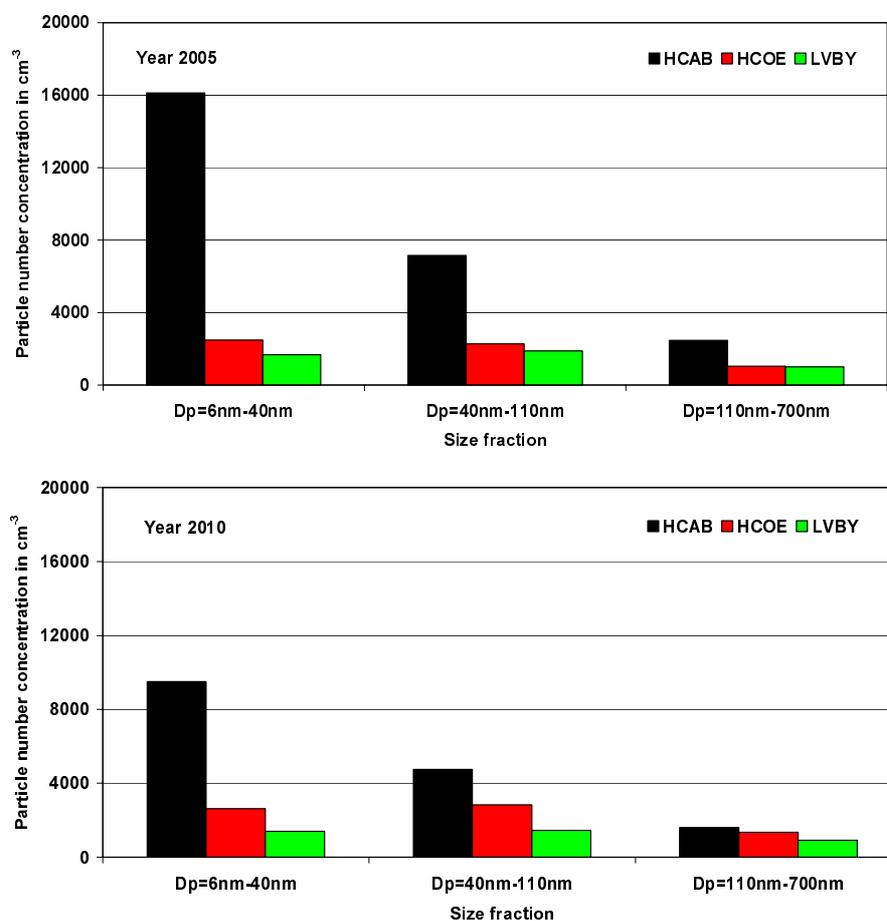


Figure 3.17. Comparison of annual averages of particle number concentrations in three size regimes defined as $D_p = 6\text{--}40\text{ nm}$, $D_p = 40\text{--}110\text{ nm}$, $D_p = 110\text{--}700\text{ nm}$ measured at LVBY, HCOE, and HCAB in 2005 and 2010.

3.1.3 Light absorption coefficients using the PSAP (Particle Soot Absorption Photometer)

The Particle Soot Absorption Photometer (PSAP) was used to measure the light absorption coefficient of the observed aerosol. The light absorption coefficient is proportional to the mass of black carbon (BC), assuming that black carbon is the only absorbing particle component in the sample. Even if this is not absolutely correct, we can assume that black carbon is the dominating absorbing particle component in the samples measured at LVBY, HCOE, and HCAB. By division of the light absorption coefficient with the black carbon *specific* absorption coefficient, the signal can be transformed into a black carbon mass concentration. Here, the *specific* absorption coefficient is estimated as $10\text{ m}^2\text{g}^{-1}$ according to Pitts et al. (1999). This means that a light absorption coefficient of 10 (Mm)^{-1} corresponds to a black carbon mass concentration of $1\text{ }\mu\text{gm}^{-3}$.

Annual time series of the light absorption coefficient

In Figure 3.18 the time series of diurnal averages of the light absorption coefficient are presented for the three stations LVBV, HCOE, and HCAB during the period 2008-2010.

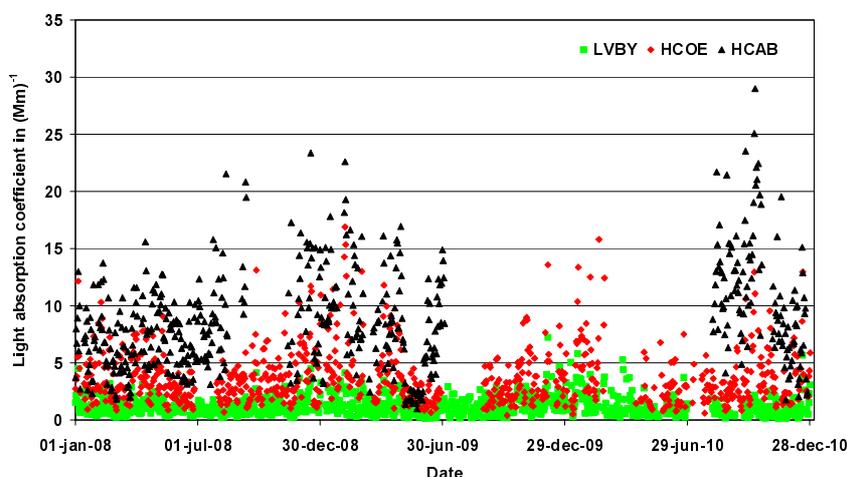


Figure 3.18. Time series of diurnal averages of the light absorption coefficients measured at LVBV, HCOE, and HCAB during the period 2008–2010.

In general, mean values of the light absorption coefficient decrease with the distance to potential sources of black carbon particles. High emissions of BC are expected from urban traffic in Copenhagen, but also from wood stoves in downtown Copenhagen in addition to urban industrial sources (Krecl et al., 2007). For LVBV and HCOE, a trend of seasonal variation shows higher concentrations of black carbon particles during winter compared to summer. This finding is assumed mainly to be due to higher emissions during winter from wood stoves etc. but is also a result of different meteorological conditions. The seasonal variation is less pronounced at HCAB, due to a large data gap in 2009/2010 caused by technical problems and a renewing of the station.

Annual trends of the light absorption coefficient

In Figure 3.19 the annual averages of the light absorption coefficients measured at LVBV, HCOE, and HCAB during the period 2007-2010 are presented. Again, because of low data coverage, average values for 2009 and 2010 at HCAB are left out.

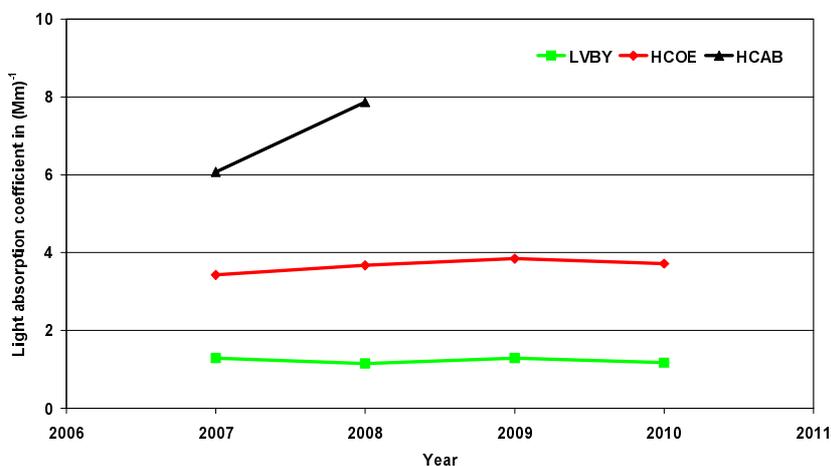


Figure 3.19. Annual averages of the light absorption coefficients measured at LVBV, HCOE, and HCAB during 2006-2010.

For the rural background site LVBY and the urban background site HCOE, the light absorption coefficient has been fairly constant over the time period of the previous four years with values between 1.2–1.3 $(\text{Mm})^{-1}$ (LVBY) and 3.4–3.8 $(\text{Mm})^{-1}$ (HCOE). In contrast, the light absorption coefficient has increased at street level (HCAB) ranging from about 6.1 $(\text{Mm})^{-1}$ in 2007 to about 7.9 $(\text{Mm})^{-1}$ in 2008. This finding does not have an easy explanation. Nevertheless, a general tendency of the BC concentration increase at street level is not found in the years 2009 and 2010 by other projects where e.g. EC (elemental carbon) measurements were carried out in these project during 2009 and 2010. Also, a correlation between the number of particles with diameters between $D_p = 50\text{--}100$ nm, a fraction where primary traffic emitted BC particles are located, cannot be proved. So far, the cause of this phenomenon in 2007 and 2008 remains for the time being unexplained.

Diurnal variation of the light absorption coefficient

In addition to our analysis of $\text{PM}_{2.5}/\text{PM}_{10}$ and particle number size distribution the diurnal variation of the light absorption coefficients was determined and is presented in Figure 3.20 for LVBY, HCOE, and HCAB based on data from the period 2008–2010.

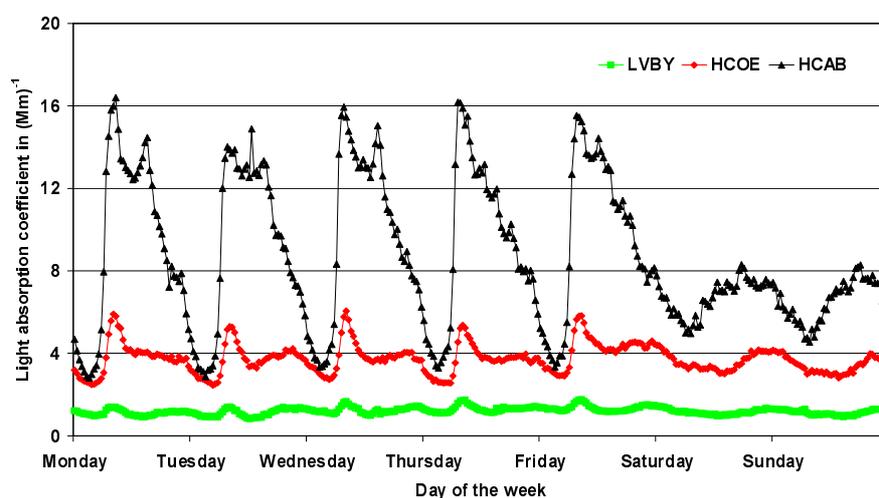


Figure 3.20. Diurnal variation of the light absorption coefficients at LVBY, HCOE, and HCAB during the period 2008–2010.

It is clearly shown, that the light absorption coefficient at the rural background station LVBY does only show a slight increase during the morning rush hours. Black carbon particulate mass at the rural background is assumed to originate from long range transported air masses from other European countries and most likely also from short range transport from emissions on Zealand where the use of local wood stoves might contribute. Thus, the influence of Copenhagen emissions from traffic is expected to be small at LVBY. A much higher imprinting of the daily activities in Copenhagen is observed at the urban background station (HCOE). Here, the light absorption coefficient increases from about 3 $(\text{Mm})^{-1}$ during night-time hours to about 6 $(\text{Mm})^{-1}$ in the morning rush hours during the weekdays. In comparison, similar values are observed at the street level station (HCAB) during night-time hours, but values tend to rise to about 12 to 16 $(\text{Mm})^{-1}$ in the morning rush hours during weekdays. As discussed above, values at HCAB seem to be very high and the results remain at present unexplained. The diurnal pattern corresponds well with

the traffic density observed at a comparable street in Copenhagen (Ketzel et al., 2003).

3.2 Chemical composition in PM_{2.5} and PM₁₀ measured during the intense chemistry field campaigns

Two field campaigns were carried out by NERI at Lille Valby, Roskilde, during autumn 2008 (17.09.2008-16.09.2008) and early spring 2009 (25.02.2009-24.03.2009). The campaigns were part of the European field campaigns organised by EMEP. The aim of the campaigns was to get a more complete picture of the chemical compositions of PM_{2.5} and PM₁₀ and hence the possibility to get a better understanding of the sources as well as the associated health effects of the particles.

Previous Danish studies of the chemical compositions of PM_{2.5} and PM₁₀ have been based on data that were often obtained from different measurement locations and for different fractions of the particles. At a national level the aim of the current study was therefore to improve the experimental data set by analysis of as many as possible of the chemical components of PM_{2.5} and PM₁₀ at the same time and location.

The measured parameters during the Danish part of the EMEP field campaigns are listed in Table 3.5. The main advantages of the campaigns were the co-location of the measurements and that defined particle fractions were measured. Moreover, the campaign included measurements of elemental carbon (EC) and organic compounds (organic carbon (OC), levoglucosan, manosan) in addition to the inorganic measurements. Hence it was possible to obtain a more complete picture of the chemical composition of the particles. The campaign included also measurements of NO_x and CO because they are used as tracers of traffic in the source apportionment modelling (see chapter 3.3).

The results of the field campaigns are listed in Table 3.6 as average concentrations during the two campaigns. The unknown mass is the part that could not be accounted for by the chemical analysis. The unknown mass accounts for 3.7–5.8 µg m⁻³ and is the same in PM_{2.5} and PM₁₀. Hence the unknown mass is related to PM_{2.5}, only, and the chemical composition of the coarse particles (PM₁₀-PM_{2.5}) is fully known. The negative result for the unknown mass of coarse particles during the field campaign in 2008 is only 2% of PM₁₀. Hence the negative mass is small and a result of the uncertainty in the measurements.

The unknown mass is believed partly to be due to water absorbed on the hygroscopic particles. It is mainly the inorganic salts that are hygroscopic. It is very difficult to determine the amount of water on the particles since the water content will change with changes of the relative humidity.

Table 3.5. Measured parameters at Lille Valby, Roskilde during the autumn and spring campaigns in 2008 and 2009, respectively.

Parameters	Phase
Elements	
Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Sr, Zr, Mo, Sn, Sb, Ba, Pb	PM ₁₀ , PM _{2.5}
PM	PM _{2.5} , PM ₁₀
Ionic species	
Na ⁺ , Cl ⁻ , NH ₄ ⁺ , SO ₄ ²⁻ , NO ₃ ⁻ , K ⁺ , Mg ²⁺ , Ca ²⁺	PM _{2.5} , PM ₁₀
NO_x	
NO, NO ₂	gas
CO	gas
Carbon analysis	
elemental (EC) and organic carbon (OC)	PM ₁₀
Organic compounds	
<i>levoglucosan, mannosan</i>	PM ₁₀

Elementary carbon and organic compounds are due to limited resources only measured in PM₁₀. Since these are believed to belong to PM_{2.5} we have assumed that the mass of the elementary carbon and organic compounds were the same in PM₁₀ and PM_{2.5}.

The measurements determine only the mass of carbon in organic compounds (OC). In order to estimate the total mass from the organic compounds (OM), we have here applied a constant conversion factor of 2.1 between OC and OM. This conversion factor is based on literature values (Turpin and Lim 2011). The estimated OM accounts for 3.4-3.7 $\mu\text{g m}^{-3}$ and hence it is one of the larger fractions of the particle mass.

The inorganic ions account for 3.8-4.8 $\mu\text{g m}^{-3}$ and 7.4-7.9 $\mu\text{g m}^{-3}$ of the mass of PM_{2.5} and PM₁₀, respectively. The inorganic ions are mainly secondary inorganic aerosols (SIA; ammoniumnitrate, ammoniumbisulphate and ammoniumsulphate) formed in the atmosphere from emissions of SO₂, NO_x and NH₃. Moreover, sea salt accounts for the remaining part of inorganic ions. Sea salt is mainly found in PM₁₀.

Particles contain also traces of many other chemical components here determined by the presence of more than 20 different elements. The mass of the elements accounts for less than 0.3 $\mu\text{g m}^{-3}$ of PM₁₀ and 0.08 $\mu\text{g m}^{-3}$ of PM_{2.5}. The elements can be grouped into elements related to particles from dust (Al, Si, Fe) and into a group that consist of heavy metals (Ti, V, Cr, Mn, Ni, Cu, Zn, Ga, As, Rb, Sr, Zr).

Figure 3.21 shows the results for PM_{2.5} and PM₁₀. Sea salt and heavy metals have been lumped together in two groups in order to get a better overview. Figure 3.22 shows the similar results for PM_{2.5} and the coarse particle fraction (PM₁₀-PM_{2.5}).

Table 3.6: Results from the measurement campaigns in 2008 and 2009. Coarse particles are the difference between PM₁₀ and PM_{2.5}. The unknown mass is calculated from subtraction of the analysed mass from the measured total particle mass (PM). All in units of $\mu\text{g m}^{-3}$. Negative mass are due to the uncertainty of the measurements.

	PM _{2.5}		PM ₁₀		Coarse particles	
	2008	2009	2008	2009	2008	2009
Total particle mass (PM)	14.6	11.7	17.2	16.1	2.6	4.4
Unknown mass	5.8	3.7	5.4	3.7	-0.4	0.0
Carbon compounds ¹						
Elementary carbon (EC)	0.46	0.36	0.46	0.36	0.00	0.00
Organic mass (OM) ²	3.4	3.7	3.4	3.7	0.0	0.0
Levoglucosane ³	0.060	0.069	0.060	0.069	0.000	0.000
Manosane ³	0.009	0.014	0.009	0.014	0.000	0.000
Elements						
Al	0.03	-0.01	0.11	0.06	0.08	0.07
Si	0.009	0.009	0.107	0.095	0.097	0.086
Ti	0.0001	0.0007	0.0032	0.0033	0.0031	0.0026
V	0.0017	0.0021	0.0023	0.0025	0.0006	0.0003
Cr	0.0003	0.0003	0.0018	0.0008	0.0015	0.0005
Mn	0.0003	-0.0001	0.0024	0.0013	0.0021	0.0014
Fe	0.017	0.008	0.091	0.056	0.074	0.048
Ni	0.0015	0.0012	0.0021	0.0013	0.0006	0.0001
Cu	0.0019	0.0015	0.0050	0.0028	0.0032	0.0013
Zn	0.009	0.007	0.018	0.009	0.009	0.002
Ga			0.00000	0.0001	0.0000	0.0001
As	0.0007	0.0005	0.0008	0.0006	0.0001	0.0001
Se	0.0004	0.0002	0.0005	0.0003	0.0001	0.0002
Pb			0.0004	0.0002	0.0004	0.0002
Sr	0.0001	0.0001	0.0011	0.0010	0.0010	0.0009
Zr	0.0000	-0.0001	0.0003	0.0001	0.0003	0.0001
Mo	0.0002	0.00000	0.00003	0.0000	0.0001	0.0001
Sn	0.0007	-0.0001	0.0018	0.0001	0.0012	0.0002
Sb	0.0001	-0.0002	0.0002	0.0004	0.0001	0.0006
Ba	0.0051	0.0037	0.0067	0.0043	0.0016	0.0006
Pb	0.0039	0.0021	0.0056	0.0027	0.0016	0.0006
Inorganic ions						
NO ₃ ⁻	2.00	1.72	2.91	3.17	0.91	1.45
SO ₄ ²⁻ from combustion ⁵	1.43	0.94	1.62	1.15	0.19	0.21
NH ₄ ⁺	1.01	0.68	1.19	0.95	0.18	0.27
K ⁺	0.08	0.08	0.11	0.12	0.03	0.05
Ca ²⁺	0.04	0.01	0.10	0.11	0.05	0.10
Br	0.001	0.001	0.003	0.002	0.001	0.001
Cl ⁴	0.09	0.14	0.63	1.15	0.55	1.00
Na ⁺	0.07	0.12	0.60	0.93	0.53	0.81
Mg ⁺⁺	0.01	0.02	0.06	0.10	0.05	0.08
SO ₄ ²⁻ from sea salt ⁵	0.02	0.03	0.15	0.24	0.13	0.20

1. The mass of the carbon compounds in PM_{2.5} is estimated from the results of PM₁₀ assuming that all carbon compounds are found in particles with diameter below 2.5 μm .
2. Organic mass is estimated from measurements of organic carbon (OC) multiplied by a factor of 2.1.
3. The mass of levoglucosane and manosane is included in the organic mass.
4. The chlorine mass in PM_{2.5} during the 2009 campaign has been estimated based on the average ratio for Na/Cl measured for the remaining results.
5. The split between sulphate from combustion and sea salt have been calculated by estimate of the sea salt part of sulphate from $0.084 \cdot \text{Na}^+$. A similar procedure is used under EMEP.

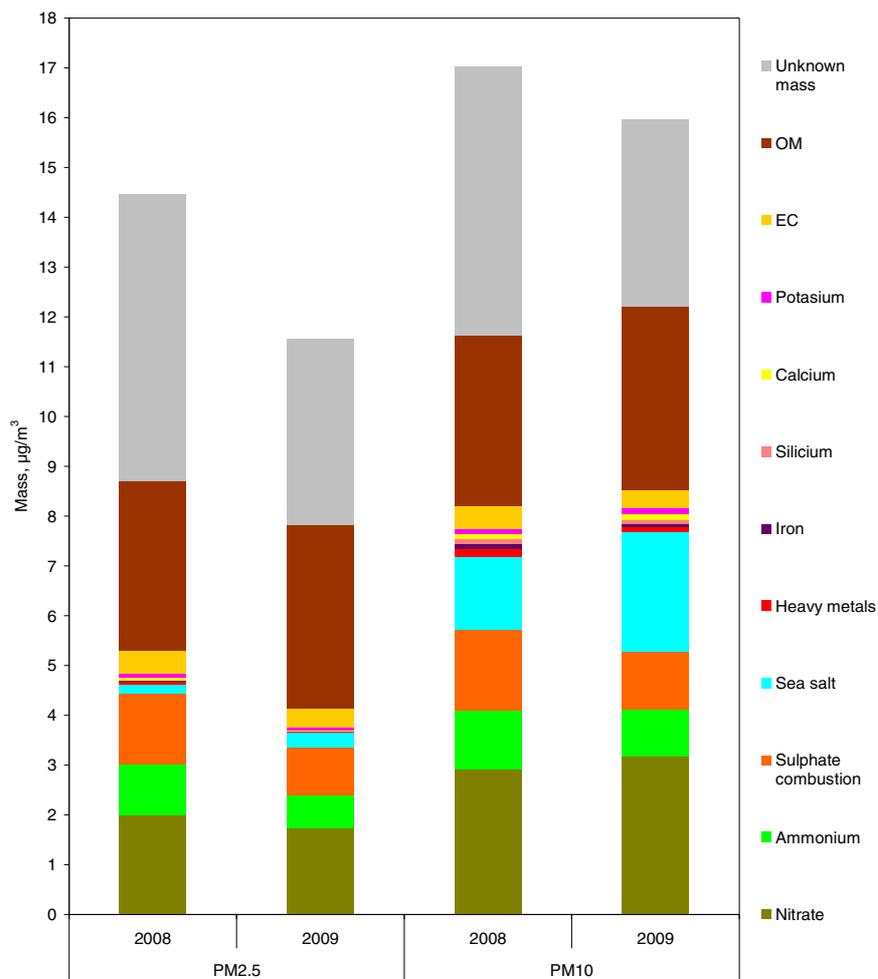


Figure 3.21. The measured chemical composition of PM_{2.5} and PM₁₀ during the autumn campaign in 2008 and spring campaign in 2009. Sea salt consist of sodium, chlorine, magnesium, bromine and sea salt sulphate. The heavy metals consist of Ti, V, Cr, Mn, Ni, Cu, Zn, Ga, As, Rb, Sr, Zr.

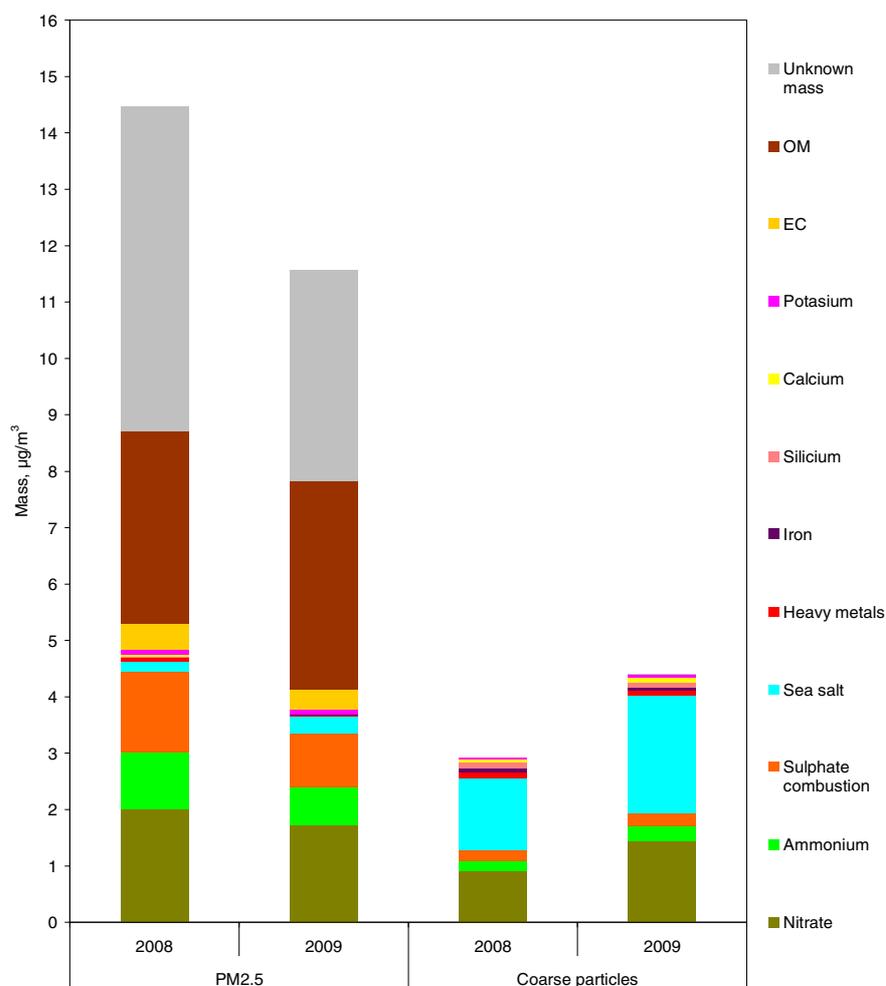


Figure 3.22. The measured chemical composition of PM_{2.5} and for the coarse particles (PM₁₀-PM_{2.5}) during the autumn campaign in 2008 and spring campaign in 2009. Sea salt consists of sodium, chlorine, magnesium, bromine and sea salt sulphate. The heavy metals consist of Ti, V, Cr, Mn, Ni, Cu, Zn, Ga, As, Rb, Sr, Zr.

The amount of secondary inorganic ions (ammonium, nitrate and sulphate) complies well with measurements of the same components using the filter pack sampler in the Danish air quality monitoring programme. The average mass of secondary inorganic ions in PM₁₀ during the two campaigns was 5.5 µg m⁻³ compared with an annual average of 6.7 µg m⁻³ for 2008 for the 5 Danish stations with filter pack measurements (Anholt, Tange, Ulborg, Lindet, Keldsnor). The spatial variations of these compounds are known to be small. The filter pack sampler collects particles with diameters below 15-20 µm depending on the wind speed. However since the main part of the secondary inorganic ions is found in particles with diameters below 2.5 µm it is evident that the filter pack results should only be slightly higher than the results from analysis of PM₁₀.

The two campaigns look similar in many ways. However, there are some noticeable differences. The sulphate and ammonium are 20-35% lower during the early spring campaign compared with autumn. This is most likely due to differences in the Danish emissions of ammonia and/or differences in meteorology. The amount of sea salt is in contrast about 70% higher in 2009 compared to 2008. The reason for this is the difference in precipitation, wind speed and prevailing direction, since sea salt originates from wind generated sea spray, mainly at the Danish West Coast.

Table 3.7 gives an overview of the average results from the two campaigns at the rural station at Lille Valby. 80% and 20% of the total mass were found as fine particles (PM_{2.5}) and coarse particles (PM₁₀-PM_{2.5}), respectively.

The particle mass consist roughly of the following groups:

- Unknown mass. 27-36%. All unknown mass is found in PM_{2.5}.
- Organic mass. 21-27%. All organic mass is estimated to be found in PM_{2.5}.
- Secondary inorganic aerosols (sulphate, ammonium, nitrate). 29-32%. Secondary inorganic aerosols are mainly found in PM_{2.5} (75%).
- Sea salt accounts for 2% of PM_{2.5} and 12% of PM₁₀.
- Elementary carbon. 2-3%. All elementary carbon is estimated to be found in PM_{2.5}.
- Minor part (1-2%) including heavy metal and dust. Dust is mainly found in PM₁₀.

The chemical components originate from various sources and several from more than one source. The later includes among other potassium that can originate from dust and biomass burning. It is not possible to distinguish between the sources based on the measurements alone. That is why we use the source apportionment model COPREM to make a more detailed assignment of the sources of the different chemical components. These results will be presented in the following chapter.

Table 3.7. Average mass for PM_{2.5}, PM₁₀ and the chemical constituents for the measurement campaigns in 2008 and 2009. In addition the percentage of mass from the different chemical constituents and the ratio between PM₁₀ and PM_{2.5}. The unknown mass is calculated from subtraction of the analysed mass from the measured total particle mass (PM). All in units of µg m⁻³. Negative mass are due to the uncertainty of the measurements.

	PM _{2.5}		PM ₁₀		PM _{2.5} /PM ₁₀
	Average campaigns 2008 and 2009		Average campaigns 2008 and 2009		
	µm/m ³	%	µm/m ³	%	%
Particle mass (PM)	13.2	100	16.7	100	79
Unknown mass	4.7	36	4.6	27	104
Elementary carbon (EC) ¹	0.41	3	0.41	2	100
Organic mass (OM) ¹	3.6	27	3.6	21	100
Heavy metals	0.03	0.2	0.13	0.8	25
Potassium	0.08	1	0.12	0.7	68
Calcium	0.03	0.2	0.10	0.6	25
Silicium	0.009	0.1	0.101	0.6	9
Iron	0.01	0.1	0.07	0.4	17
Sea salt	0.25	2	1.94	12	13
Sulphate combustion	1.19	9	1.39	8	86
Ammonium	0.85	6	1.07	6	79
Nitrate	1.86	14	3.04	18	61

1. The mass of the carbon compounds in PM_{2.5} is estimated from the results of PM₁₀ assuming that all carbon compounds are found in particles with diameter below 2.5 µm.

3.3 Source receptor analysis (COPREM)

In order to get a better understanding about the chemical composition and sources to PM_{2.5} and PM₁₀ in the rural background aerosol in Denmark, we conducted intensive field campaigns in the autumn 2008 and spring 2009 at Lille Valby, North of Roskilde. We measured 36 gaseous and particulate phase compounds (Tables 3.5 and 3.6) during 58 days in

two PM fractions. A total of 12 sources were included in the analysis (Table A1). The 12 sources are:

1. *Salt* is a primary marine aerosol dominated by NaCl and derived from an average chemical composition of seawater. Marine aerosol is also a source of organic carbon, which however would require organic tracer compounds, and cannot be evaluated for the present dataset.

2. *NaNO₃* is aged marine aerosol. Chlorine may be protonised upon acidification of the particles by HNO₃ and evaporate as HCl (gas). Following, the counter-ion Na⁺ becomes enriched relative to the primary marine profile, which is accounted for by the construction of the NaNO₃ profile.

3, 4, 5. *Secondary inorganic aerosols (SIA)* is accounted for in the profiles NH₄NO₃, (NH₄)HSO₄ and (NH₄)₂SO₄. These inorganic salts are formed in the atmosphere from emissions of the gaseous precursors SO₂, NO₂, and NH₃.

6. *Rock* is mineral/crustal matter mainly characterized by Al, Si, Ca and Fe of which other tracers may be found in trace amounts (Vianna et al., 2008).

7. *Limestone* is a sedimentary rock largely composed of calcite and aragonite, i.e. the crystal forms of calcium carbonate, CaCO₃.

8. *Biomass burning* includes natural and anthropogenic activities such as wildfires, deforesting, and biomass burning for heating and cooking purposes. Its source profile is based on a PM_{2.5} study of prescribed burning of pine-dominated forest areas (Lee et al., 2005) normalized to PM₁₀ by assuming an insignificant contribution of biomass burning particles to the coarse (PM₁₀-PM_{2.5}) fraction. Levoglucosan has been normalized to OC and included in the profile based on measurements of chemical composition in fresh smoke plumes from boreal wild-land fires in Europe (Saarnio et al, 2010). As for the traffic source, the primary organic carbon will eventually convert into SOA during atmospheric oxidation (see below).

9, 10. *Oil and Coal combustion*. These source profiles are based on fitted profiles from COPREM analyses, where V and Se, respectively, were used as tracers for these sources (Laden et al., 2000; Viana et al., 2008). The resulting profiles are shown in Table A1.

11. *The Vehicle* profile includes combustion and mechanical wear and is based on the SAPPHIRE study in Copenhagen, Denmark, where a street- and an urban background station were used to establish PM_{2.5} and PM₁₀ vehicle profiles (Oliveira et al., 2007). EC and OC have been included in the established profile based on the work of Chan et al. (1999). The concentrations of NO_x and CO are used as tracers for the vehicle profile. The vehicle profile accounts only for the local emissions and not for the long range transported contributions to secondary inorganic aerosols.

12. *Secondary organic aerosols (SOA)* is gas to particle conversion of biogenic and anthropogenic VOC 's and SVOC's, which react with atmospheric oxidants such as O₃, NO₃ and OH, to form low-volatility products. These carbonaceous products are measured as organic carbon (OC)

along with elemental carbon (EC) in a carbon analyzer. In order to convert OC to organic matter (OM), a factor of 2.1 is used as suggested by Turpin and Lim for rural environments (2011). Hence, the O, H, N, S and other atoms that were bound to the organic carbon prior to the carbon analysis, are accounted for. The largest fraction of OC is by far secondary in nature. A recent review by Hallquist et al (2010), suggests that of the 150 Tg particulate C, which is emitted annually worldwide, 134 Tg C is secondary. The remaining part is of primary anthropogenic origin (5 Tg C) and from biomass burning (11 Tg C). Here we define SOA as OM derived from the part of OC, which is not attributed to primary combustion sources. This is not entirely true since *primary biological organic aerosols* (PBOA) such as vira, pollen and bacteria are not accounted for, but it is a best estimate for the present dataset.

Offset is a feature of COPREM, which serves to establish a constant background level of a particular compound in addition to the apportioned variation. These conditions are actually met for CO, for which reason an offset was calculated by COPREM.

3.3.1 Evaluation of intensive chemistry campaigns 2008–2009

The coarse particle fraction, PM₁₀

A total of 58 samples, 37 variables and 12 sources were included in the analysis of the intensive chemistry campaigns (PM₁₀ fraction) using source receptor analysis (Figure 3.23).

COPREM was operated with a constant CO offset because of its high background level, which is a consequence of a relatively slow removal rate of CO. A tentative offset of 100 µg m⁻³ CO was assigned to the source profile (Table A.1), which, however, is not fixed but allows for a solution beyond the specified value. In fact, a value of 161 µg m⁻³ CO was obtained in the COPREM fit to the PM₁₀ data (Table A.2). A PM offset has previously been used to account for unexplained mass in COPREM analyses of datasets absent of carbon, water and secondary organic aerosols. In the present study, an experimental carbon analysis of EC and OC was included in addition to elements and ions (Tables 3.5 and 3.6). We obtained a mass closure of 83% based on the COPREM fit, which is somewhat higher than based on the measurement data itself (77%), since the source apportionment takes into consideration oxygen and other species not measured directly. A significant fraction of the remaining unexplained mass is assumed to be mostly water. However, the OM/OC ratio of 2.1 was not measured directly. Thus, a part of the explained mass could be carbon, if the real OM/OC ratio is higher than the recommended value. Conversely, the unexplained mass (“Mass gap”) may be higher than listed in Tables 3.8 and 3.10.

PM₁₀ averaged 18.4 µg m⁻³ in the two campaigns, which is identical to the 2008 annual average for rural background. SIA from oxidation of NO₂ to HNO₃ and SO₄ to H₂SO₄ make up 30% of the mass, and is by far the largest source to PM₁₀ in Denmark. The second largest (known) sources are marine aerosol (13%) and biomass burning (13%). The latter was 26% higher in the late winter/spring campaign as compared to the warmer autumn campaign. SOA is comparable with Marine aerosol and Biomass burning, by mass. *Rock* and *limestone* are minor sources, while the primary anthropogenic combustion sources *Oil* and *Coal* are comparable by mass (Table 3.8). *Vehicles* constitute a minor source in the rural back-

ground, though it should be noted that a fraction of the vehicular volatile emissions are transferred to the particle-phase following atmospheric oxidation and may add to the particle mass as SOA in this analysis (Robinson et al., 2007). *Marine aerosols, biomass burning* and *SOA* are comparable sources in this study, which make up 11-13% of PM₁₀.

Table 3.8. Source apportionment of the 2008-2009 chemistry campaigns (PM₁₀). Mass gaps show the difference between modeled and measured PM concentrations. Note that this table covers the full campaign.

	PM ₁₀ (μg m ⁻³)	
PM modelled	15.25	
PM measured	18.38	
Salt	1.34	13%
NaNO ₃	1.09	
NH ₄ NO ₃	3.20	30%
(NH ₄) ₂ SO ₄	1.67	
(NH ₄)HSO ₄	0.66	
Rock	0.34	2%
Lime	0.16	1%
Biomass burning	2.34	13%
Oil	1.18	6%
Coal	0.91	5%
Vehicle	0.29	2%
SOA	2.06	11%
Mass gap	3.13	17%

During the two campaigns, 95% of the OC was apportioned to SOA and biomass burning (Table A.2), which is comparable to source apportionment analyses of rural PM_{2.5} in Germany, Hungary and France, where OC from fossil fuel combustion accounted for 3-8% (Genlencser et al., 2007). A more accurate apportionment of SOA and biomass burning, however, calls for an inclusion of SOA markers, e.g. monoterpenes and isoprene oxidation products (Hu et al., 2008, Yttri et al., 2011).

Table 3.9: Fossil carbon in the intensive chemistry campaigns 2008-2009 (PM₁₀)

PM ₁₀ (μg m ⁻³)	COPREM analysis	¹⁴ C analysis
TC (fossil)	0.44 (19%)	0.49 (23%)

PM₁₀ was sampled with weekly time resolution in parallel with the daily filters. Each of those 8 weekly filters were analyzed for radio-carbon (¹⁴C) for determination of “old carbon”, that is from fossil carbon, and modern carbon from e.g. biomass burning and natural SOA. The ¹⁴C analysis and the carbon apportionment by COPREM are in good agreement and differ by 10% (Table 3.9).

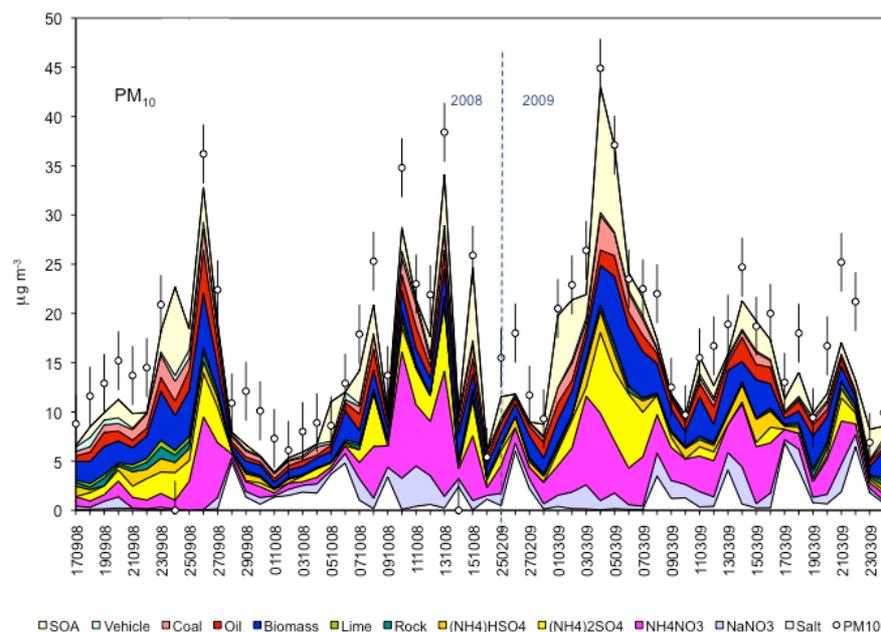


Figure 3.23. Source apportionment of the 2008-2009 chemistry campaigns (PM_{10}).

The fine particle fraction, $PM_{2.5}$

$PM_{2.5}$ was sampled in parallel with PM_{10} during the intensive chemistry campaigns 2008-2009. The parameters were similar to those measured in the PM_{10} fraction, except for carbon analyses, levoglucosan and mannan. In order to build comparable $PM_{2.5}$ profiles for SOA and biomass burning, the PM_{10} measurements of EC, OC, levoglucosan and mannan were directly included in the $PM_{2.5}$ dataset. EC and OC may thus be too high in this case, though studies in e.g. Sweden, Switzerland and Austria support $PM_{2.5}/PM_{10}$ ratios of (OC+EC) close to unity (Querol et al., 2004). Also, the concentrations of the biomass burning tracers may be too high, which is compensated for by loosening the constraints in the source profile (see Table A.1 and section 3.2.). The inorganic source profiles are identical to those of PM_{10} , but a dedicated $PM_{2.5}$ vehicle profile was obtained from the SAPHIRE study in Copenhagen (Oliveira et al., 2007). The biomass burning profile is obtained from a dedicated $PM_{2.5}$ study of a prescribed burning episode (Lee et al., 2005), where levoglucosan has been included and normalized to OC based on the study of Saarnio et al. (2010). Oil and coal profiles were derived from PM_{10} COPREM analyses and normalized to $PM_{2.5}$ by assuming an insignificant contribution to the coarse fraction

Table 3.10. Source apportionment of intensive chemistry campaigns 2008-2009 (PM_{2.5} and PM₁₀). The comparison does not include the period from 03.03.09-08.03.09 in the spring cam-paign, for which reason the values differ slightly from those in Table 3.8. Mass gaps show the difference between modeled and measured PM concentrations.

	PM ₁₀ (µg m ⁻³)		PM _{2.5} (µg m ⁻³)		PM _{2.5} /PM ₁₀
PM modelled	13.78		8.91		58%
PM measured	16.65		13.15		78%
Salt	1.42	15%	0.09	2%	12%
NaNO ₃	1.07		0.22		
NH ₄ NO ₃	2.88	28%	2.20	28%	80%
(NH ₄) ₂ SO ₄	1.28		1.20		
(NH ₄)HSO ₄	0.60		0.40		
Rock	0.34	2%	0.02	0.2%	6%
Lime	0.16	1%	0.01	0.1%	8%
Biomass	1.87	11%	1.27	10%	68%
Oil	1.15	7%	0.64	5%	56%
Coal	0.81	5%	0.68	5%	84%
Vehicle	0.29	2%	0.09	0.7%	31%
SOA	1.92	11%	2.10	16%	109%
Mass gap	3.28	19%	4.43	33%	165%

PM_{2.5} averaged 13.2 µg m⁻³ in the intensive chemistry campaigns. Under the assumption that all OC was confined to the fine fraction, we obtained a mass closure of 67% based on the COPREM fit (Figure 3.24). Note that the period from 03.03.09-08.03.09 in the second campaign was omitted from the PM_{2.5} dataset and the comparison of PM_{2.5}/PM₁₀, for which reason the values in Tables 3.8 and 3.10 differ somewhat.

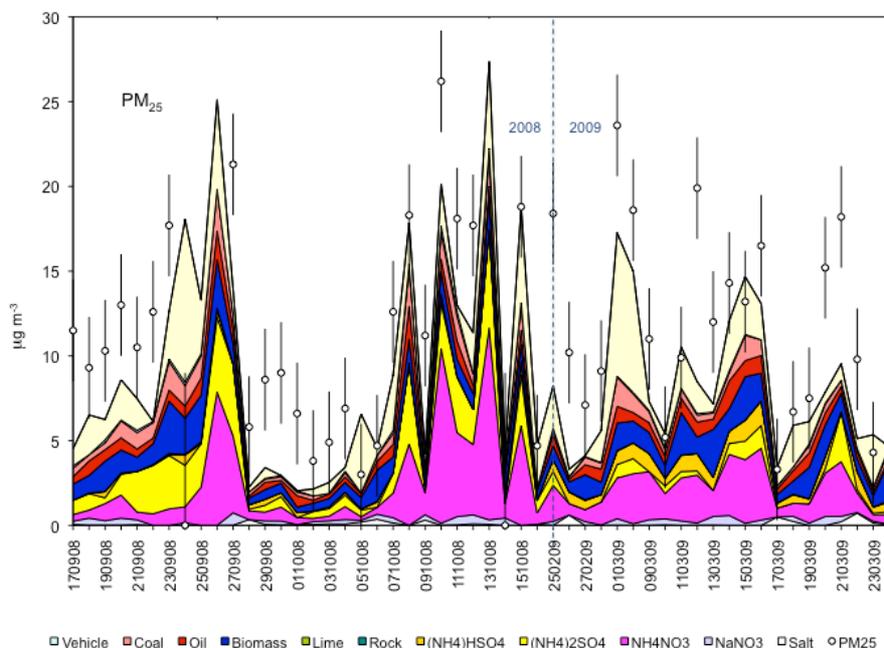


Figure 3.24. Source apportionment of the intensive chemistry campaigns 2008-2009 (PM_{2.5}).

The distribution of the individual sources between the particle size fractions is derived from the PM₁₀ and PM_{2.5} source apportionment analyses (Table 3.10). Although marine aerosols are released in a broad size range, the PM_{2.5} fraction contributes only to a minor extent by mass. Organic

marine aerosols could be an important source in this context. However, appropriate tracers for marine organic aerosols were not sampled in this study. SIA is preferentially apportioned in the fine fraction with 20% confined to particles with aerodynamic diameters above 2.5 μm . As for marine aerosols, rock and lime are associated with coarse particles. The PM_{10} fraction dominates the vehicle source, which also includes wear of tires and brakes. Combustion particles are predominantly in the fine fraction, as expected, except for the oil combustion particles, which probably reflects the uncertainty of the analysis. Inconsistencies of the COPREM analyses were the apportionment of more SOA and unexplained mass/mass gap in the $\text{PM}_{2.5}$ fraction relative to PM_{10} . While the uncertainty of the analysis may impact both results, the apportionment of SOA was based on OC from the PM_{10} filter samples, and the assumption that all OC was confined to the fine fraction. With this in mind, we conclude that SOA is most largely confined to $\text{PM}_{2.5}$.

The apportionment is based on two campaigns of 4 weeks duration, each, which covered the autumn and late winter/early spring. In particular, PM, EC, sulfate, ammonium and unknown mass (mostly water) in the $\text{PM}_{2.5}$ fraction differed largely between the campaigns. The results illustrate the necessity of including season-representative data in the apportionment analysis, and calls for an additional summer campaign. The latter could e.g. clarify whether biomass burning and use of fossil fuel are smaller on an annual average, than concluded from the present data. Furthermore, carbon analysis and organic tracer compounds should be included, especially in the $\text{PM}_{2.5}$ fraction, to reduce the uncertainty in the profiles SOA, marine aerosol and to establish a new profile of primary biological organic particles, which is believed to account for a significant fraction of OM (Yttri et al., 2011).

4 Conclusions and Outlook

During the years 2008-2010 NERI has carried out the third particle research project for the Danish Environmental Protection Agency. As in the two previous projects, detailed measurements of physical particle parameters (mass, number, size distribution, absorption) have been measured with high time resolution at the street station at H.C. Andersens Boulevard (HCAB), the urban background station at H.C. Ørsteds Institute (HCOE) and the rural background station at Lille Valby/Risø (LVBY). Moreover, two intensive measurements campaigns with focus on the chemistry of the particles were carried out at LVBY during autumn 2008 and late winter/early spring in 2009. The main conclusions from this work are summarised below together with an outlook for future scientific investigations suggested on the basis of the results from the present particle project.

Particle mass

The measurements of particle mass using TEOM instruments ($\frac{1}{2}$ hourly time resolution) were continued during 2008-2010 and compared to measurements of particle mass using SM200 instruments (24h time resolution) that are in agreement with the reference method. This comparison confirmed that a considerable fraction of particulate matter evaporates in the TEOM during measurement. In the previous particle research project it was found that it was possible on an annual basis to correct for the loss of mass by addition of a constant value of about $9 \mu\text{g m}^{-3}$ for both $\text{PM}_{2.5}$ and PM_{10} (Wählén 2008). However, the new and extended comparison based on the larger data set showed that the loss of mass depends on the size fraction ($\text{PM}_{2.5}$ or PM_{10}) and on the type of location (rural background, urban background, street, etc.). Moreover, the loss of mass in TEOM has a temporal variation, which is reasonable when considering the change in chemical composition during the year, the seasonal and long term variation of atmospheric processes and emissions. Despite the spatial and temporal variations of the loss of mass in TEOM we suggest to correct for the loss of particle mass inside TEOM by multiplication with a site specific constant correction factor in the range from 1.2-1.7. This method is believed to give reasonable estimates for the annual averages, when the correction factor has been measured. The correction factor depends on the size fraction, the measurement site and on the season. This correction method is in line with the correction method recommended for the data reporting under the EU directive (EU 2008/50/EC). However, use of a constant correction factor should be done with precaution and take the temporal and spatial variations into account.

Nevertheless, $\text{PM}_{2.5}$ and PM_{10} measured using TEOM can still be used to evaluate the general long term trends for PM if the uncertainty due to evaporation is kept in mind. With respect to $\text{PM}_{2.5}$ measured with TEOM, the amount of particulate matter has decreased from about $17 \mu\text{g m}^{-3}$ in 2002 to about $13 \mu\text{g m}^{-3}$ at the street station HCAB. At the urban background (HCOE) and rural background (LVBY) a fairly stable level of $\text{PM}_{2.5}$ has been.

For PM_{10} measured using TEOM, a decreasing trend has been observed at the street station (HCAB) from 2002-2010. Parts of this trend can be attributed to the new asphalt surface at H. C. Andersens Boulevard, which was renewed in 2008. At the urban background (HCOE) a decrease in PM_{10} is also observed.

Analysis of the diurnal variations of $PM_{2.5}$ and PM_{10} using TEOM showed that PM at street level has a diurnal variation that follows the traffic intensity of the city. This confirms previous findings that $PM_{2.5}$ and PM_{10} to some extent are due to local traffic generated emissions. The remaining part of PM is mainly due to long range transported PM. Hence, the decreases of both PM_{10} and $PM_{2.5}$ are believed to be due to reductions in both long range transport of particles and reductions in local traffic generated particles.

Particle number

Due to the three consecutive particle projects we have now measurements of total particle number concentrations and size distributions (6-700 nm) in the period from 2002 to 2010. The annual average total particle number (6-700 nm) in 2010 was about 16 000 particles cm^{-3} on the street station HCAB. This was about a factor of 2 and 4 higher than measured at the urban background station HCOE (about 6 800 particles cm^{-3}) and rural background station LVBY (about 3 800 particles cm^{-3}).

At HCAB the number of particles has decreased by a factor of about 2 during the period 2002-2010. At the urban background station (HCOE) and rural background station (LVBY) we also observed a reduction in particle number though the decrease is smaller than at HCAB. The decreases were only 30% and 15% at HCOE and LVBY, respectively. The main reason for the large decrease at HCAB is believed to be improvements of the vehicle fleet (newer vehicles, particle filters etc.), decrease of sulphur content in diesel and possibly the introduction of environmental zones in Copenhagen. During the last two years a slight increase in particle number was observed at HCOE. At present it is not known whether or not this is a persistent trend. The reason for the slight increase is not known either, but might partly be due to a larger amount of wood stoves operated in Copenhagen.

The diurnal variation of the particle number has been determined on the basis of the $\frac{1}{2}$ hourly measurements. At the street station the diurnal variation follows the traffic pattern with high particle number during rush hours. The typical diurnal variations in the meteorology modify this pattern so that the peak during morning rush hours is higher than during afternoon.

The development in the particle number size distribution has also been studied in detail. The measurements of the size distribution at the three stations show that the average diameter of the particles increases from street level over urban background to rural background. At HCOE a significant shift in mode diameter (corresponds to the maximum in the size distribution) was observed during the period from 2002-2010 from about 30 nm to 50 nm. A similar shift was not observed for the other two stations. Moreover, analysis of the long term development of different size regimes showed that it were mainly the smallest particles with diameters from 6-40 nm that decreased during the period from 2002-2010. All these

findings support that the decrease in the total particle number concentration at street level is due to reductions of the ultrafine particle emissions from traffic.

The instruments for measurements of particle numbers are not developed to carry out routine measurements. They are therefore technically difficult to operate and hence there are large gaps in the measurements for the years 2002, 2004, 2005 and 2010. NERI has therefore corrected the annual averages for these years by comparison with NO_x. The gaps in the measurements lead to increased uncertainties for the annual averages despite these corrections. However, this does not change the overall conclusion that there has been a reduction of about 50% in the particle number at HCAB.

Light absorption and black carbon

The light absorption coefficient, which is an indirect measure of the black carbon (BC) mass concentration, has been fairly constant during 2006–2010 at the rural background (LVBY). A slight increase in light absorption coefficient has been observed at the urban background site (HCOE) from 2007–2010. At the street level (HCAB) an increase in the light absorption coefficient has been observed between 2007 and 2008. This increase is not supported by other measurements carried out in different projects investigating the elemental carbon (EC) concentration at HCAB. It is currently investigated whether the increase is real or due to some unknown failure of the instrument. Nevertheless, measurements of the light absorption coefficient at the urban background and especially at the street level show a high diurnal variation indicating that traffic emissions are one of the main sources for light absorbing particulate material that is mostly due to EC. Minor contributions may also originate from wood stoves especially during winter time.

Chemical composition

In order to get a better understanding of the chemical composition and sources to PM_{2.5} and PM₁₀ in Danish rural background areas, we conducted two intensive field campaigns in the autumn 2008 and late winter/early spring 2009 at Lille Valby, north of Roskilde. We measured 36 gaseous and particulate phase compounds during 58 days in two PM fractions, which makes this study the most comprehensive Danish source apportionment study to date. These campaigns were carried out as part of the European field campaigns initiated by EMEP.

Mass closures (the percentage of mass with known chemistry) based on the measured data were 64% and 73% for PM_{2.5} and PM₁₀, respectively, which average to 13 µg m⁻³ and 17 µg m⁻³ for the two campaigns. The unknown mass was confined to the fine fraction and expected to be mostly water, and to a minor part oxygen and other elements bound in inorganic species like K, Si, Fe and Ca. Moreover, the unknown mass (the mass of unknown chemistry) was highest in the humid autumn campaign supporting that a large part of the unknown mass was water. The inorganic ions account for 32% and 29% of PM_{2.5} and PM₁₀, respectively. These are mainly secondary inorganic aerosols (SIA; ammoniumnitrate, ammoniumbisulphate and ammoniumsulphate) formed in the atmosphere from emissions of SO₂, NO_x and NH₃. Sea salt (Na, C, sea salt sulphate, Br, Mg) accounts for the main part of the remaining inorganic

ions. Heavy metals account for less than 1.5% of $PM_{2.5}$ and 3.1% of PM_{10} . Elemental and organic carbon account for 30% and 23% of $PM_{2.5}$ and PM_{10} , respectively. Both average $PM_{2.5}$ and PM_{10} were higher during the autumn campaign than during the late winter/early spring campaign. This difference is most likely due to variations in the meteorological conditions.

The measured chemical parameters (36 parameters of daily resolution) were analyzed using the COPREM source receptor model. 12 different source profiles were used in the source receptor analysis:

1. Sea salt (mainly NaCl)
2. $NaNO_3$ -aged sea salt
- 3, 4, 5 Secondary inorganic aerosols (SIA) consisting of ammonium nitrate, ammonium bisulphate and ammonium sulphate
6. Rock
7. Lime stone
8. Biomass burning (wood stoves, natural fires etc.),
9. Oil combustion,
10. Coal combustion,
11. Vehicle (directly traffic generated particles)
12. Secondary organic aerosols (SOA).

In accordance with the initial data analysis, the largest source to the PM_{10} rural background aerosol was SIA accounting for 30% of the mass. SIA is mainly long range transported to LVBY. Sea salt, combustion particles from biomass burning and SOA were almost equal sources contributing 11-13% to PM_{10} . SOA and biomass burning particles may be formed either locally or may be long range transported. Particles from vehicles and combustion of oil and coal added up to 13%.

The analysis of the chemical content of $PM_{2.5}$ and PM_{10} shows that there is a marked difference between the chemical content in $PM_{2.5}$ and the coarse particles (between 2.5 μm and 10 μm). Sea salt as well as the crustal material/minerals was largely associated with coarse particles. Vehicular emissions were of little importance and mainly found in the coarse fraction. SIA is mainly associated with $PM_{2.5}$ although about 20% of SIA are found in the coarse particles. The combustion sources: oil, coal and biomass burning are mainly found in the $PM_{2.5}$ fraction, though a contribution to the coarse particles cannot be neglected, especially the oil combustion source. SOA was only measured in PM_{10} , but it is assumed that SOA is mainly associated with $PM_{2.5}$.

Interestingly, it was found that the unknown mass was associated with the $PM_{2.5}$ and that the chemistry of the coarse particles was fully known. This was somewhat unexpected since the unknown mass is mainly believed to be water associated with the hygroscopic parts of PM and the hygroscopic parts of PM are both associated with fine and coarse particles.

The chemical content of PM_{2.5} and coarse particles was in agreement with the fact that the transport time of particles in PM_{2.5} is considerably longer than that of the coarse particles. Hence PM_{2.5} can consist of material that to a large extent is long range transported (e.g. distances as Russia and China) and coarse particles are expected to consist of material that is of more local and regional origin (e.g. Zealand and Northern Germany). As an example model calculations have shown that SIA to a large extent originates from outside Denmark (Ellermann et al., 2010b) in agreement with the fact that 80% of SIA is found in the PM_{2.5} fraction.

Recommendations and outlook

Although valuable new knowledge has been obtained within the current project there are still gaps in the understanding of the physics and chemistry of airborne particles in Denmark. In order to reduce these gaps we have the following suggestions for continued research in this area:

- TEOM is a useful instrument to use for studies of particle mass concentrations with high time resolution. However care has to be taken due to the evaporation of mass inside the instrument. For future investigations a correction factor for the TEOM, which is dependent on season and type of aerosol (regional background, urban background, curbside, etc.) could be introduced and obtained on the base of diurnal measurements with the SM200 to retrieve quantitative results with high time resolution. Moreover, work has to be done in order to quantify how much of the evaporated mass is assigned to evaporation of ammonium nitrate.
- An increase in particle number was observed at the urban background station during the last years. The reasons behind this increase have to be determined.
- This report presents interesting measurements that show the long term trend for the particle number size distributions. It is therefore recommended to continue the measurements of the size distribution and to further investigate the reason behind these changes in the particle number size distribution. One possibility is that increased use of wood stoves have a significant influence on the changes of particle size, but this has to be further studied. Moreover, future EU regulations on the particle number emissions of individual vehicles will also have impact on the size distribution. The trends of the particle size distribution have to be measured during the next years in order to evaluate the impact of these regulations on air quality.
- For an indication of trends of black carbon mass concentrations, we recommend in future work to use direct methods as for example EC/OC analysis on sampled filter probes. This recommendation is based on the additional information that is gained with this method and also based on problems that are encountered with the absorption measurements.
- The variation of specific species and unknown mass between the two chemistry campaigns illustrates the importance of longer campaigns, which are representative for various seasons.
- The mass from various carbon compounds was responsible for a large part of the particle mass. In the two campaigns we only measured this mass in PM₁₀ and had to make assumptions on the partitioning of this

mass between fine and coarse particles. This was a weak point in this study. For future studies on the chemistry of particles it is necessary to measure the partitioning of the carbon compounds between fine and coarse particles.

- The organic matter made up a substantial part of the mass, however we do not know the chemistry of the organic compounds. This makes the sources unclear and makes the estimate of the organic mass uncertain. We therefore suggest to carry out measurements attempting a full carbon speciation and inclusion of specific organic markers for SOA, primary biological organic aerosols and marine organic aerosols.
- About a third of the mass is still with unknown chemistry. It is reasonable to assume that water makes up a large part of this mass. However, experiments have to be carried out in order to increase knowledge on the unknown mass.
- Traffic is believed to be the main source of black carbon. However, other sources such as wood stoves or industrial combustion in the city may be responsible for the variations of black carbon. For further explanations of the individual sources of urban black carbon mass, we recommend to carry out field studies within limited time periods including extensive investigations of the chemical composition of PM_{2.5} as also EC/OC analysis. Source to receptor modelling can be applied to such datasets and enlighten the knowledge of individual black carbon sources in Denmark.
- Finally, the ultrafine particles are expected to have large impact on human health. Studies of the chemistry of these ultrafine particles are therefore needed.

In addition to these gap filling activities it is in general important to monitor the trends of the particle number and size distribution in order to be able to evaluate the impact on air quality of the measures taken to reduce the problem with ultrafine particles in Danish urban areas.

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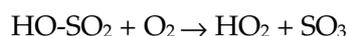
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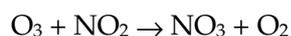
Appendix

Secondary inorganic aerosol (SIA) is accounted for in the profiles NH_4NO_3 , $(\text{NH}_4)\text{HSO}_4$ and $(\text{NH}_4)_2\text{SO}_4$, of which gas-particle conversion of HNO_3 and H_2SO_4 accounts for a major fraction of the rural background aerosol. These acids may be formed during oxidation of the precursor gasses, i.e. for sulfuric acid:

$\text{SO}_2 + \text{OH} + \text{M} \rightarrow \text{HO-SO}_2 + \text{M}$, where M is a third body molecule, that removes excess energy from the reaction.



$\text{SO}_3 + \text{H}_2\text{O} + \text{M} \rightarrow \text{H}_2\text{SO}_4 + \text{M}$, the low vapor pressure of sulfuric acid will cause it to nucleate or adsorb to e.g. aerosols.



$\text{NO}_3 + h\nu \rightarrow \text{NO}_2 + \text{O}$, where $h\nu$ is the photon energy. The reactions with NO_3 and N_2O_5 are only relevant in the absence of sunlight.

$\text{N}_2\text{O}_5 + \text{H}_2\text{O}_{(s)} \rightarrow 2 \text{HNO}_3$, the reaction with water in solution (s) implies that the formation of nitric acid takes place on e.g. preexisting aerosols or water droplets.

$\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$, which describes formation of nitric acid in the presence of sunlight.

Although SO_2 and NO_2 compete for OH in the formation of H_2SO_4 and HNO_3 , the reaction rate of the latter is much higher due to a higher rate constant (Atkinson et al., 2004) and higher ambient NO_2 concentrations. With respect to growth of particles, H_2SO_4 reacts with NH_3 to form $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 in an irreversible process, whereas HNO_3 reacts with NH_3 to form semivolatile NH_4NO_3 (Renner and Wolke, 2010).

Table A.1. Source profile for PM₁₀. Source profiles are listed as (column) vectors, of which parameters that are allowed to change beyond the profile are shown in bold.

	Offset	Salt	NaNO ₃	NH ₄ NO ₃	(NH ₄) ₂ SO ₄	(NH ₄)HSO ₄	Rock	Lime	Biomass	Oil	Coal	Vehicle	SOA
PM10	0	1.00	1.44	1.000	1.000	1.000	1.000	1.000	1.00	1.1756	0.9078	1.00	2.1
Al	0	1.54E-05	1.54E-05	0	0	0	0.081	0	1.55E-04	0	0	4.22E-03	0
Si	0	6.14E-07	6.14E-07	0	0	0	0.277	0	1.26E-04	0	0	0	0
S	0	2.72E-02	2.72E-02	0	0.242	0.278	0.001	0	7.26E-04	0	0	6.19E-03	0
Cl	0	5.83E-01	0	0	0	0	0	0	2.85E-03	0	0	0	0
K	0	1.17E-02	1.17E-02	0	0	0	0.026	0	3.86E-03	0	0	2.64E-04	0
Ca	0	1.23E-02	1.23E-02	0	0	0	0.036	0.400	0	0	0	0	0
Ti	0	0.00E+00	0	0	0	0	0.004	0	2.70E-06	0	0	4.39E-04	0
V	0	9.21E-09	9.21E-09	0	0	0	0	0	0	0.0024	0	3.57E-05	0
Cr	0	0	0	0	0	0	0	0	0	0	0.0002	6.51E-04	0
Mn	0	3.07E-08	3.07E-08	0	0	0	0.001	0	7.44E-06	0	0.0005	6.13E-04	0
Fe	0	6.14E-08	6.14E-08	0	0	0	0.050	0	5.54E-05	0	0	1.07E-01	0
Ni	0	3.07E-09	3.07E-09	0	0	0	0	0	0	0.0015	0.0002	8.18E-05	0
Cu	0	3.07E-08	3.07E-08	0	0	0	0	0	6.76E-06	0	0.0010	9.41E-03	0
Zn	0	1.54E-07	1.54E-07	0	0	0	0	0	1.08E-04	0	0.0145	2.30E-03	0
Ga	0	0	0	0	0	0	0	0	0	0	0	0	0
As	0	3.07E-07	3.07E-07	0	0	0	0	0	1.35E-06	0	0.0001	0	0
Se	0	1.23E-07	1.23E-07	0	0	0	0	0	6.76E-07	0	0.0004	0	0
Br	0	2.00E-03	2.00E-03	0	0	0	0	0	9.53E-05	0	0.0012	1.10E-05	0
Rb	0	3.70E-06	3.70E-06	0	0	0	0	0	2.84E-05	0	0	8.85E-06	0
Sr	0	2.40E-04	2.40E-04	0	0	0	0	0	1.35E-06	0	0	2.27E-05	0
Zr	0	0	0	0	0	0	0	0	0	0	0	6.22E-04	0
Mo	0	1.54E-08	1.54E-08	0	0	0	0	0	0	0	0	5.44E-04	0
Sn	0	0	0	0	0	0	0	0	0	0	0	8.95E-04	0
Sb	0	0	0	0	0	0	0	0	0	0	0	2.00E-03	0
Ba	0	1.54E-06	1.54E-06	0	0	0	0	0	0	0	0	1.94E-03	0
Pb	0	1.23E-07	1.23E-07	0	0	0	0	0	6.76E-07	0	0.0043	9.09E-04	0
Cl-	0	5.83E-01	0	0	0	0	0	0	2.85E-03	0	0	0	0
N-NO ₃ ⁻	0	0	2.30E-01	0.175	0	0	0	0	2.98E-03	0	0	0	0
S-SO ₄ ⁻	0	2.72E-02	2.72E-02	0	0.242	0.278	0	0	1.66E-03	0	0	0	0
Na ⁺	0	3.24E-01	3.24E-01	0	0	0	0	0	1.08E-04	0	0	0	0
N-NH ₄ ⁺	0	0	0	0.175	0.212	0.122	0	0	7.24E-04	0	0	0	0
K ⁺	0	1.17E-02	1.17E-02	0	0	0	0.026	0	4.39E-03	0	0	2.64E-04	0
Mg ⁺⁺	0	3.91E-02	3.91E-02	0	0	0	0	0	6.76E-07	0	0	0	0
Ca ⁺⁺	0	1.23E-02	1.23E-02	0	0	0	0.036	0.400	4.06E-06	0	0	0	0
NO _x	0	0	0	0	0	0	0	0	0	8.3233	0	1.04E+01	0
CO	100	0	0	0	0	0	0	0	0	24.0153	9.6753	4.68E+01	0
EC	0	0	0	0	0	0	0	0	2.65E-02	0.1409	0.0759	4.28E-01	0
OC	0	0	0	0	0	0	0	0	4.07E-01	0	0	3.55E-01	1
Levoglucosan	0	0	0	0	0	0	0	0	1.12E-02	0	0	0	0
Mannosan	0	0	0	0	0	0	0	0	0	0	0	0	0

Table A.2. COPREM fitted profiles of PM₁₀ during the intensive chemistry campaigns. The sources' (columns) contributions to the individual parameters can be derived from the numbers in a particular row, e.g. OC from vehicles makeup 5% (=0.103/(0.954+0.103+0.979)).

	Offset	Salt	NaNO ₃	NH ₄ NO ₃	(NH ₄) ₂ SO ₄	(NH ₄)HSO ₄	Rock	Lime	Biomass	Oil	Coal	Vehicle	SOA
PM10	0	1.345	1.095	3.200	1.66825	0.663	0.342	0.158	2.342	1.185	0.908	0.289	2.055
Al	0	2.07E-05	1.17E-05	0	0	0	0.0715	0	0.000363	0	0	0.00122	0
Si	0	8.26E-07	4.68E-07	0	0	0	0.0947	0	0.000295	0	0	0	0
S	0	0.0365	0.0207	0	0.404	0.184	0.000178	0	0.00170	0	0	0.00179	0
Cl	0	0.784	0	0	0	0	0.000164	0	0.00668	0	0	0	0
K	0	0.0157	0.00889	0	0	0	0.00885	0	0.100756	0	0	7.64E-05	0
Ca	0	0.0165	0.00936	0	0	0	0.0124	0.0632	0	0	0	0	0
Ti	0	0	0	0	0	0	0.00318	0	6.34E-06	0	0	0.000127	0
V	0	1.24E-08	7.02E-09	0	0	0	5.13E-05	0	0	0.00244	0	1.03E-05	0
Cr	0	0	0	0	0	0	6.84E-05	0	0	0.000378	0.000235	0.0001889	0
Mn	0	4.13E-08	2.34E-08	0	0	0	0.00135	0	1.74E-05	0	0.000470	0.000177	0
Fe	0	8.26E-08	4.68E-08	0	0	0	0.0460	0	0.000129	0	0	0.0310	0
Ni	0	4.13E-09	2.34E-09	0	0	0	3.42E-05	0	0	0.00148	0.000206	2.36E-05	0
Cu	0	4.13E-08	2.34E-08	0	0	0	2.39E-05	0	1.58E-05	0	0.00105	0.0027	0
Zn	0	2.07E-07	1.17E-07	0	0	0	2.73E-05	0	0.000254	0	0.0145	0.000664	0
Ga	0	0	0	0	0	0	5.13E-07	0	0	0	0	0	0
As	0	4.13E-07	2.34E-07	0	0	0	1.71E-06	0	3.17E-06	0.000558	0.000103	0	0
Se	0	1.65E-07	9.37E-08	0	0	0	3.08E-07	0	1.58E-06	0	0.000389	0	0
Br	0	7.862E-04	2.833E-04	0	0	0	8.54E-07	0	0.000223	0	0.00115	3.18E-06	0
Rb	0	0	2.82E-06	0	0	0	0.000245	0	6.65E-05	0	0	2.56E-06	0
Sr	0	3.237E-04	1.828E-04	0	0	0	5.13E-05	0.000434	3.17E-06	0	0	6.56E-06	0
Zr	0	0	0	0	0	0	7.52E-05	0	0	0	0	0.000180	0
Mo	0	2.07E-08	1.17E-08	0	0	0	6.84E-07	0	0	0	0	0.000157	0
Sn	0	0	0	0	0	0	1.37E-05	0	0	0	0	0.000259	0
Sb	0	0	0	0	0	0	3.42E-05	0	0	0	0	0.000579	0
Ba	0	2.07E-06	1.17E-06	0	0	0	8.54E-05	0	0	0	0	0.000561	0
Pb	0	1.65E-07	9.37E-08	0	0	0	2.05E-06	0	1.58E-06	0	0.00432	0.000263	0
Cl-	0	0.784066	0	0	0	0	0	0	0.00668	0	0	0	0
N-NO3-	0	0	0.175417	0.560124	0	0	0	0	0.00697	0	0	0	0
S-SO4--	0	0.0365181	0.0206879	0	0.404273	0.184414	0	0	0.00388	0	0	0	0
Na+	0	0.436248	0.24714	0	0	0	0	0	0.000253	0	0	0	0
N-NH4+	0	0	0	0.560	0.354	0.0806	0	0	0.00169	0	0	0	0
K+	0	0.0156978	0.008893	0	0	0	0.0088526	0	0.0889647	0	0	7.64E-05	0
Mg++	0	0.0525848	0.0297899	0	0	0	0	0	1.58E-06	0	0	0	0
Ca++	0	0.016524	0.00936106	0	0	0	0.0124073	0.0632965	9.50E-06	0	0	0	0
NOx	0	0	0	0	0	0	0	0	0	8.389	0	3.019	0
CO	161.109	0	0	0	0	0	0	0	36.045	24.205	9.675	13.515	0
EC	0	0	0	0	0	0	0	0	0.0621	0.142	0.0759	0.124	0
OC	0	0	0	0	0	0	0	0	0.954	0	0	0.103	0.979
LEVO	0	0	0	0	0	0	0	0	0.0638	0	0	0	0
MANO	0	0	0	0	0	0	0	0	0.0114	0	0	0	0

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PARTICLE PROJECT REPORT 2008 - 2010

Particulate contribution from traffic in Copenhagen

This report presents the results from the third particle research project. The project was carried out for the Danish Environmental Protection Agency by NERI during the period from 2008 to 2010. The main aim of the projects was to continue the long term research on levels, trends, chemical composition and sources of particulate air pollution in Denmark. The results show that there is a tendency for a decrease in particulate mass since 2002 and that the number of particles has decreased by a factor of two at H. C. Andersens Boulevard, Copenhagen. It is mainly particles with diameter from 10-40 nm that has decreased primarily due to reduced emissions related to traffic. Moreover, the chemical composition of PM_{2.5} and PM₁₀ was measured during two monthly field campaigns in 2008 and 2009 at the rural measurement station Lille Valby situated 30 km west of Copenhagen. Source apportionment modelling using COPREM was used to determine the sources of the different chemical components of the particle mass.