THE DANISH AIR QUALITY MONITORING PROGRAMME

Annual Summary for 2011

Scientific Report from DCE – Danish Centre for Environment and Energy No. 37 2012

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Data sheet

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Abstract: The air quality in Danish cities has been monitored continuously since 1982 within the Danish Air Quality Monitoring network. The aim is to follow the concentration levels of toxic pollutants in the urban atmosphere and to provide the necessary knowledge to assess the trends, to perform source apportionment, and to understand the governing processes that determine the level of air pollution in Denmark. In 2011 the air quality was measured in four Danish cities and at two background sites. In addition model calculations were carried out to supplement the measurements. At one street station (H.C. Andersens Boulevard) in Copenhagen NO_2 was found in concentrations above EU limit values while NO_2 levels in Odense, Aarhus and Aalborg were below the limit value. Model calculations indicate exceedances of NO_2 limit values at several streets in Copenhagen. Annual averages of PM_{10} and $PM_{2.5}$ were below limit values at all stations. However, concentrations levels in Copenhagen exceeded the daily limit value for PM_{10}. Winter salting of roads was one of the main reasons for this exceedance. The concentrations for most pollutants have been strongly decreasing during the last decades, however, only a slight decrease has been observed for NO_2 and O_3.

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Contents

Summary and Conclusion

This report presents the result from the Danish Air Quality Monitoring Programme in 2011. The monitoring programme is carried out by the DCE - Danish Centre for Environment and Energy (DCE) at Aarhus University. The core part of this programme consists of continuous measurements at nine monitoring stations; seven stations situated in the four largest cities and two stations located in background areas. These measurements are supplemented with model calculations using DCE's air quality models.

The aim of the program is to monitor air pollutants relevant to human health in accordance with the EU air quality directives. The programme includes measurements of sulphur dioxide (SO_2), nitrogen oxides (NO_x/NO_2), particulate mass (PM_{10} and $PM_{2.5}$), particle number, benzene (C_6H_6), toluene (C_7H_8), carbon monoxide (CO), ozone (O_3), lead (Pb), arsenic (As), cadmium (Cd), mercury (Hg), nickel (Ni), and polycyclic aromatic hydrocarbons (PAH). In 2009 the programme was expanded with measurements of a number of volatile organic compounds (VOC's) that are precursors for formation of ozone. The measurements and model calculations are used to evaluate the Danish air quality in relation to limit values as well as to follow trends. Further, the program serves as basis for determination of sources of the air pollutants, basis for evaluation of the impact of regulations of emissions and as basis for various research projects related to air quality.

In 2011 there have been the following major changes in the monitoring programme compared to 2010:

- Activities concerning measurements of heavy metals were reduced in 2010 because a new analysis technique (ICP-MS) was used for analysis of heavy metals. In 2011 and 2012 this analysis technique has been improved and DCE are now able to analyse for more than 20 heavy metals in the particle samples compared to only four compounds in 2010. This report presents results from measurements of 10 selected heavy metals in 2011.
- This year presents results of daily sodium concentrations for the street stations. These measurements are carried out in order to be able to determine the contribution from salting of roads and sea salt. These results has been used to evaluate the impact of salt on the exceedance of the daily limit value for PM_{10}.
- Finally, the report presents results from measurements of the chemical composition the main constituents of $PM_{2.5}$ at H.C. Andersens Boulevard (Copenhagen/1103) and Risø.

PM_{10} were at all the stations below both the annual limit value (40 $\mu g/m^3$). The daily limit value for PM_{10} (50 $\mu g/m^3$ must not be exceeded more than 35 days annually) were exceeded at both street stations in Copenhagen, while no exceedances were observed in the two other cities where PM_{10} are measured (Aarhus and Odense). The two exceedances in Copenhagen fall under article 20 and 21 of the Air Quality Directive as they can be attributed to natural sources (sea salt) and winter-salting.

Section 7.4 of this report contains information on the deductions made primarily based on measurements of sodium.

$PM_{2.5}$ was lower than the annual limit value (25 µg/m^3) valid from 2015. The number of particles in ambient air was about 14000 particles per cm^3 at the street station H.C. Andersens Boulevard. This is considerably higher than in urban and rural background. A significant reduction in particle number has been observed since 2002.

The sodium content in PM_{10} on street stations were about 1.5 µg/m^3 corresponding to an estimated annual salt content (NaCl) of about 4.0 µg/m^3. High diurnal values of salt were observed during periods with winter salting of roads.

The annual limit value for NO_2 (40 µg/m^3 in 2011) was exceeded at one street station in Copenhagen (H.C. Andersens Boulevard), whereas no exceedances were observed in Odense, Aalborg and Aarhus. The NO_2 concentrations decreased from 2010 to 2011 at part of the stations while no changes was observed at the remaining part. At H.C Andersens Boulevard (Copenhagen/1103) there were still elevated concentrations of NO_2. These are believed to be a temporary effect due to local construction work at nearby sites to the measurement station that causes increased emissions from non-road machinery used for the construction work and from re-directed and/or congested traffic. These are under further investigation.

Model calculations at selected streets in Copenhagen and Aalborg indicate that the limit value was exceeded at several streets in Copenhagen but not at any streets in Aalborg in 2011. In general, modelling confirmed that the street station at H.C. Andersens Boulevard (1103) in Copenhagen represents one of the most polluted streets in Copenhagen, whereas the traffic station in Aalborg (6153) represents a site with a pollution load at the average level for the 31 selected streets in Aalborg.

The ozone levels were in 2011 almost the same as in 2010 at all rural and urban background stations and no clear trend was thus observed. The information threshold at 180 µg/m^3 was not exceeded in 2011. The target value for the max 8 hours ozone concentration on 120 µg/m^3 was not exceeded, but the long-term objective for this target was exceeded at all non-traffic stations.

The report presents results for volatile organic compounds (VOC) measured at the urban background in Copenhagen. VOC's can act as ozone precursors, although the formation of ozone in Denmark is in general small due to moderate solar radiation. The ozone pollution in Denmark is to a large extent the result of long distance transport of pollutants from other European countries south of Denmark.

The levels of SO_2 and heavy metals have decreased for more than two decades and are now far below the limit values. The limit values for benzene and CO are not exceeded and the levels have decreased for the last decade.

Measurements of particle bound PAH concentrations were performed at H.C. Andersens Boulevard, Copenhagen. The average concentration of

benzo[a]pyrene was 0.21 ng/m^3. The target value for benzo[a] pyrene (1 ng/m^3) was not exceeded in 2011.

For the first time this report presents results from determination of the chemical content in $PM_{2.5}$. The annual average concentrations of NH_4^+, Na^+, K^+, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-} are very similar at the street station at H.C. Andersens Boulevard and at the rural station at Risø. The main difference between the two stations are for elemental carbon (EC), organic matter (OM) and Ca^{2+} where the concentrations are higher at the street station compared to the rural background station. This is mainly due to emissions of these compounds from the traffic in Copenhagen.

Actual data, annual and multi-annual summaries are available at the website of DCE
(http://www.dmu.dk/International/Air).

Danish summary - Dansk resumé

Rapporten præsenterer resultater for 2011 fra Overvågningsprogrammet for luftkvalitet i danske byer. Programmet, som udføres af DCE - Nationalt Center for Miljø og Energi (DCE) ved Aarhus Universitet, er baseret på målinger ved ni målestationer placeret i de fire største danske byer samt ved to baggrundsmålestationer udenfor byerne. Disse målinger kombineres med anvendelse af modelberegninger udført med DCE's luftkvalitetsmodeller.

Formålet med programmet er at overvåge luftforurening af betydning for sundhed i overensstemmelse med EU's luftkvalitetsdirektiver. I henhold til disse og øvrige danske behov måles koncentrationer af svovldioxid (SO_2), nitrogenoxider (NO_x/NO_2), partikelmasse (PM_{10} og $PM_{2.5}$), partikel antal, benzen (C_6H_6) og toluen (C_7H_8), carbonmonoxid (CO), ozon (O_3), udvalgte tungmetaller (fx bly (Pb), arsen (As), cadmium (Cd), kviksølv (Hg), nikkel (Ni)) og polyaromatiske kulbrinter (PAH) samt udvalgte flygtige kulbrinter (VOC), der kan føre til dannelse af ozon. Målingerne og modelberegningerne anvendes til at vurdere om EU's grænseværdier for luftkvalitet er overholdt. Rapporten beskriver endvidere udviklingen i koncentrationerne. Samtidig tjener resultaterne som grundlag for vurdering af kilderne til luftforureningen, vurdering af effekt af reduktionstiltag og som grundlag for en række videnskabelige undersøgelser fx vurdering af små partiklers effekt på sundheden.

Der er fastsat grænse- og målværdier for flere af de målte stoffer. Grænseværdierne skal være overholdt fra 2005, 2010 eller 2015 alt efter, hvilke stoffer der drejer sig om. En detaljeret beskrivelse af gældende mål- og grænseværdier og deres gennemførelse findes i en bekendtgørelse fra Miljøministeriet (Miljøministeriet 2010). Bekendtgørelsen er baseret på det 4. datterdirektiv om tungmetaller og PAH (EC 2005) samt det nye luftkvalitetsdirektiv vedtaget i 2008 (EC 2008). En af de væsentligste ændringer i det nye direktiv i forhold til de tre første datterdirektiver (1999, 2000 og 2002) er, at der stilles krav om målinger af de fine partikler ($PM_{2.5}$), og at der er indført en grænseværdi for $PM_{2.5}$, som skal overholdes i 2015.

I 2011 er der blevet lavet en række ændringer i måleprogrammet, dels som følge af den seneste revision af måleprogrammet og dels som følge af forbedrede analysemuligheder. De vigtigste ændringer er:

- Målinger af tungmetaller blev i 2010 midlertidigt reduceret, fordi der blev taget en ny analyseteknik (ICP-MS) i brug ved analyserne for tungmetaller, hvilket medførte, at der kun blev analyseret for de fire tungmetaller, som er omfattet af direktiverne. I 2011 og 2012 er analyseteknikken blevet forbedret således, at der for 2011 er blevet analyseret for mere end 20 tungmetaller i de indsamlede partikelprøver. I denne rapport præsenteres resultaterne for ti udvalgte tungmetaller.
- Rapporten præsenterer resultater fra analyse af indholdet af natrium i PM_{10}. Disse resultater er blevet anvendt til at vurdere indflydelsen fra hav- og vejsalt på overskridelsen af den daglige grænseværdi for PM_{10}.

- Endelig præsenterer rapporten for første gang resultater fra måling af de vigtigste kemiske komponenter i $PM_{2.5}$ ved gademålestationen på H.C. Andersens Boulevard (Copenhagen/1103) og landbaggrundsmålestationen ved Risø.

De væsentligste konklusioner fra overvågningsprogrammet i 2011 er følgende:

- I 2011 blev grænseværdien for NO_2 overskredet på en (H.C. Andersens Boulevard) af de to gademålestationer i København. I Odense, Aarhus og Aalborg var der ingen overskridelser. Koncentrationerne af NO_2 faldt på visse af målestationerne fra 2010 til 2011, mens der på de øvrige målestationer var stort set uændrede koncentrationer. På gademålestationen ved H.C. Andersens Boulevard er der fortsat en midlertidig forhøjet koncentration af NO_2. Den forhøjede koncentration vurderes at være resultat af en midlertidig påvirkning fra flere større byggerier og vejarbejder nær ved målestationen. Disse medfører større udledninger fra anvendelse af entreprenørmaskiner og højere udledninger, som følge af omlægning af trafikken.
- Modelberegninger indikerer, at grænseværdien i 2011 var overskredet på en række gadestrækninger i København, men ikke på udvalgte gadestrækninger i Aalborg. Modelberegningerne viste endvidere, at gademålestationen ved H.C. Andersens Boulevard (1103) i København repræsenterer en af de mest forurenede gader i København, mens gademålestationen i Aalborg (6153) repræsenterer et middelniveau set i forhold til de 31 udvalgte gader i Aalborg.
- I 2011 var der ingen målestationer, hvor årsmiddelværdierne for luftens indhold af partikler mindre end 10 µm (PM_{10}) overskred grænseværdien for den årlige middelværdi for PM_{10}. Til gengæld blev den daglige middelværdi for PM_{10} (50 $\mu g/m^3$ må ikke overskrides mere end 35 gange årligt) overskredet ved de to gademålestationer i København. Overskridelsen skyldtes bidrag til PM_{10} fra havsalt og vinter saltning af vejene, hvilket falder ind under luftkvalitetsdirektivets artikel 20 og 21 (EC, 2008). Når bidrag fra hav- og vejsalt fratrækkes PM_{10} er antallet af dage med PM_{10} over 50 $\mu g/m^3$ på 33 og 31 for henholdsvis H.C. Andersens Boulevard og Jagtvej. Den daglige grænseværdi for PM_{10} blev ikke overskredet i de to øvrige byer, hvor der måles PM_{10} (Aarhus og Odense).
- Indholdet af partikler mindre end 2.5 µm ($PM_{2.5}$) overskred ikke de kommende grænseværdier, som skal overholdes fra 2015.
- Antallet af partikler mellem 6 og 700 nm var omkring 14.000 partikler per cm^3 på gademålestationen H.C. Andersens Boulevard, mens det var betydeligt mindre i by- og landbaggrund. Antallet af partikler er faldet betydeligt siden 2002.
- Indholdet af natrium i PM_{10} på gademålestationerne var omkring 1,5 $\mu g/m^3$ svarende til et estimeret saltindhold (NaCl) på omkring 4,0 $\mu g/m^3$. Høje døgnmiddelværdier for saltindholdet i PM_{10} som følge af navnlig vejsalt var anledning til at den daglige grænseværdi for PM_{10} blev overskredet på de to gademålestationer i København.
- Der er ikke fastsat egentlige grænseværdier for ozon (O_3), men kun "målværdier" og "langsigtede mål" (hensigtsværdier). Der var i 2011 ingen overskridelser af målværdierne for beskyttelse af sundhed.

mens de langsigtede mål blev overskredet på alle bybaggrunds- og landstationerne. Tærsklen for information af befolkningen om høje ozonniveauer (timemiddel 180 µg/m^3) blev ikke overskredet i 2011.

- De øvrige målte stoffer findes i koncentrationer under grænseværdierne, og for flere stoffer (fx svovldioxid og bly) er koncentrationerne faldet betydeligt siden målingernes start.
- Målinger af partikelbundet PAH blev fortaget på H.C. Andersens Boulevard i København. Middelværdien for benz[a]pyren var 0,21 ng/m^3. Målværdien på 1 ng/m^3 var således ikke overskredet i 2010.
- For tredje år præsenterer rapporten resultater for måling af udvalgte flygtige organiske kulbrinter (VOC) i bybaggrund i København. Disse VOC bidrager til den kemiske dannelse af ozon i Europa. I Danmark skyldes størstedelen af ozon langtransport af luftforurening fra centrale og sydlige dele af Europa.
- For første gang præsenteres resultater for bestemmelse af det kemiske indhold i $PM_{2.5}$ ved gademålestationen ved H. C. Andersens Boulevard og ved landbagrundsmålestation på Risø. De årlige gennemsnits koncentrationer for NH_4^+, Na^+, K^+, Mg^{2+}, Cl^-, NO_3^- og SO_4^{2-} er stort set ens på de to stationer, hvilket skylde,s at de for en stor del stammer fra partikler transporteret til målestationer langvejs fra. De væsentligste forskelle mellem de to målestationer ses for elementært carbon (EC), organiske forbindelser (OM) og Ca^{2+}, hvor koncentrationerne er højere på gadestationen som følge af udledninger relateret til trafikken i København.

1 Introduction

The Danish Air Quality Monitoring Programme (LMP) originates back to 1981. Today the programme is part of the National Monitoring Programme for the aquatic and terrestrial environment (NOVANA). The program consists of an urban monitoring network with stations in the four largest Danish cities and two background stations in rural areas (figure 2.1) which is supplemented by model calculations. The results are used for assessment of the air pollution in Denmark with special focus on Danish urban areas. The programme is carried out in co-operation between the DCE - National Centre for Environment and Energi (DCE), the Danish Environmental Protection Agency, and the Municipalities of Copenhagen, Aarhus, Aalborg and Odense. DCE is responsible for operating and maintaining the programme. Statistical parameters and actual data are accessible at the website: http://www.dmu.dk/-International/Air. Selected actual data are also available at tele-text, Danish National Television. In addition, this report presents results from model calculations of air quality in Denmark carried out as supplement to the measurements.

The monitoring programme is carried out in accordance with the Danish Statutory Order No. 851 of 30 June 2010 from the Ministry of Environment (Miljøministeriet 2010) that implements the EU directives on air quality in Denmark. The EU legislation consisted previously of the framework directive (EC 1996), giving general rules for network design and limit value strategies, and a number of daughter directives giving limit values, target values, alert thresholds, reference methods and monitoring strategies for specific pollutants. Four daughter directives for NO_2, SO_2, particulate matter (PM_{10}) and Pb (EC, 1999), CO and benzene (EC, 2000), O_3 (EC, 2002) and As, Cd, Ni, Hg and PAH (EC, 2005) had been adopted. In 2008 a new directive (EC, 2008) replaced the framework directive and the three first daughter directives. This new directive is now implemented through the Danish statutory order (Miljøministeriet 2010). One of the major changes in the new directive is that monitoring of $PM_{2.5}$ is now part of the measurement programme.

One of the main objectives for the monitoring programme is to assess the air quality in relation to various air quality criteria (i.e. limit values, margin of tolerance, target values, long term objectives and alert thresholds) of which the limit values are the legally most important. The Danish quality criteria's are identical with those laid down in the EU directives described above. The limit values had to be attained in 2005 or here from 2010.

The program was revised in 2010. Due to this revision of the monitoring program there is a number of changes in the monitoring program and in this year's report. The main changes are the following:

- The two Danish monitoring programs (the background monitoring programme aimed at assessing the atmospheric depositions to nature and the air quality programme measurements related to human health) were integrated into one program with two annual reports. The first one with focus on air quality and human health and the se-

cond one with focus on air quality and environment. The material previously presented in this report on air quality and vegetation has therefore been moved to the second report.

- The rural monitoring station at Lille Valby was moved about two km west in June 2010 and is now situated at Risø close to DCE.
- The program concerning measurements of heavy metals has been reduced since the concentrations are low compared to limit values. Moreover, a new analysis technique (ICP-MS) has been used for analysis of heavy metals. In 2011 the new technique was not fully implemented and only few heavy metals (As, Cd, Ni, Pb, Hg) could be reported for 2010. However, the technique was improved in 2012 and this year's report includes results for eleven heavy metals.
- As a new thing this report presents results for PM_{10} that has been corrected for the content of sodium chloride from sea salt and winter salting of roads.
- Finally, the report presents results from measurements of the chemical composition of $PM_{2.5}$ measured in rural background at Risø and at the street station at H.C. Andersens Boulevard, Copenhagen

In the following chapters the results from measurements and model calculations for 2011 are presented and compared to limit and threshold values. Please refer to the EU Directives for a detailed description of the exact definitions of the limit values, margin of tolerance, target values and alert thresholds.

2 Measurements and model calculations

2.1 Measurements

The measuring strategy is in short to place one or more pairs of stations in each of the four largest Danish cities. In each city one of the stations is located close (at the sidewalk) to a street lane with a high traffic density. The other is located within a few hundred meters from the street station, and is placed so that it is representative for the urban background pollution; meaning that it is placed so that it is not influenced by pollutants from a single or a few streets or other nearby sources. In most cases the background stations are placed on rooftops. In addition, two rural stations monitor the pollution outside city areas. The rural station at Lille Valby was in the middle of 2010 moved about 2 km west to Risø and is now situated close to DCE. Further information about the program and results is found at the website: http://www.dmu.dk/International/Air.

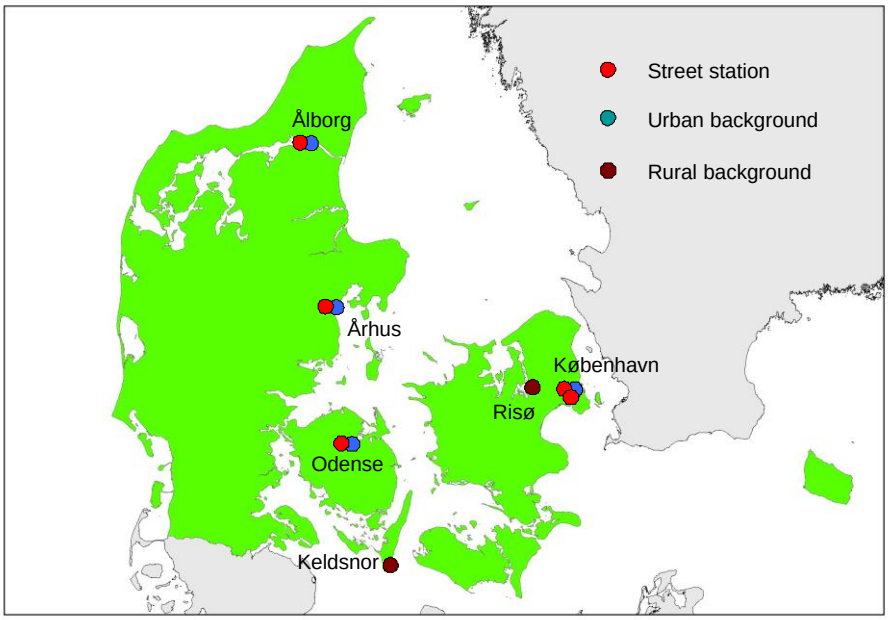


Figure 2.1 Main stations used for monitoring of air quality in relation to health.

Table 2.1. Main stations used for monitoring of air quality in relation to health in 2011

Name	Street/location	Type
Copenhagen/1257	Jagtvej	Street
Copenhagen/1259	H.C. Ørsted Institute (HCØ)	Urban background
Copenhagen/1103	H.C. Andersens Boulevard (HCAB)	Street
Århus/6153	Banegårdsgade	Street
Århus/6159	Valdemarsgade	Urban Background
Odense/9155	Albanigade	Street
Odense/9159	Town hall in Odense	Urban background
Aalborg/8151	Vesterbro	Street
Aalborg/8158	Østerbro	Urban background
Lille Valby/Risø	-	Rural
Keldsnor/9055	-	Rural

The following compounds were measured in 2011:

- Nitrogen oxides (NO, NO_2 and NO_x (= NO + NO_2)) and particle mass (PM_{10} and $PM_{2.5}$) were measured at all stations. PM was measured by means of β-absorption as 24 h averages.
- Elements (heavy metals) in PM were measured at Copenhagen/1103, Copenhagen/1257, Copenhagen/1259, Århus/6153, Århus/6159 and Lille Valby/Risø.
- Additionally PM_{10} was measured at Copenhagen/1103 and Copenhagen/1259 by means of TEOM that measures with high time resolution. $PM_{2.5}$ was also measured at Copenhagen/1103, Copenhagen/1259 and Lille Valby/Risø by means of TEOM. Part of these measurements was carried out in a research project funded separately by the Danish EPA.
- Particle number was measured at Copenhagen/1103, Copenhagen/1259 and Lille Valby/Risø in cooperation with particle research funded separately by the Danish EPA.
- Ozone (O_3) was measured at all urban background and rural stations, and at the street stations Copenhagen/1257 and Copenhagen/1103
- Carbon monoxide (CO) was measured at all street stations as well as at the urban background station, Copenhagen/1259 and the rural site Lille Valby /Risø.
- Benzene and Toluene were measured at Copenhagen/1103 and Copenhagen/1257 using passive sampling on a weekly basis.
- PAH were measured at Copenhagen/1103.
- SO_2 was measured at Aalborg/8151 and at Copenhagen/1103. The main purpose was to monitor episodic high concentrations.
- Elemental carbon (EC) and organic carbon (OC) were measured at Copenhagen/1103 and Lille Valby/Risø.
- The meteorological parameters - temperature, wind speed and direction, relative humidity and global radiation - were measured at all urban background stations.

The pollutants are described in more detail in Appendix 1.

Measurements of gasses (NO, NOx, NO_2, O_3, CO, SO_2) and particle number were recorded as ½-hour averages. Particle mass (PM_{10} and $PM_{2.5}$) were measured both as 24 hour averages using beta measurements and at ½-hour averages using TEOM (only part of particle mass). Elements in the particles as well as PAH were measured as 24 hour averages. EC and OC were measured as 24 hour averages. Benzene and Toluene were measured weekly by passive sampling. Besides this volatile organic compounds were sampled at 24 hour averages.

2.2 Model calculations

In monitoring programme the measurements at the permanent measurement stations are supplemented with model calculations using the Thor modelling system (Brandt et al., 2000). This is an integrated model system, capable of performing model calculations at regional scale to urban background scale and further down to individual street canyons in cities – on both sides of the streets (thor.dmu.dk). At present, the system includes global meteorological analyzed data from National Centres for Environmental Prediction, United States, which is used as input to the meteorological model MM5v3 (Grell et al., 1995). The meteorological data for 2011 from MM5v3 is subsequently used to drive the air pollution models, including the Danish Eulerian Hemispheric Model, DEHM (Christensen, 1997; Brandt et al., 2011), the Urban Background Model, UBM (Berkowicz, 2000b) and the Operational Street Pollution Model, OSPM (Berkowicz 2000a). DEHM is providing air pollution input data for UBM which again is providing air pollution input data to OSPM. Further details about the integrated THOR system can be found in Brandt et al. (2001 and 2003).

Model calculations of air quality on national scale is carried out using DEHM (version 5.0), which is an Eulerian model where emissions, atmospheric transport, chemical reactions, and dry- and wet depositions of air pollutants are calculated in a 3D grid covering the northern hemisphere with a resolution of 150 km x 150 km. The model includes a two-way nesting capability, which makes it possible to obtain higher resolution over limited areas. Three nested domains are used in LMP, where the first nest is covering Europe with a resolution of 50 km x 50 km. The second nest is covering Northern Europe with a resolution of 16.7 km x 16.7 km. The calculations of air quality in Denmark are carried out in a third nest with a horizontal resolution of 5.6 km x 5.6 km. In the vertical direction the model is divided into 29 layers covering the lowest 15 km of the atmosphere. Of these the lowest layers are relatively thin (20 m) while the upper layers are relatively thick (2000 m). The model includes a comprehensive chemical scheme designed for calculation of the chemical reactions in the lower part of the atmosphere. The emission inventories used in DEHM have a geographical resolution of 1 km x 1 km for Denmark transformed into the 5.5 km x 5.5 km resolution domain and 17 km x 17 km for the remaining part of Europe. The emissions are based on Danish national emission inventories for the year 2010 made by DCE (dce.au.dk) and international emission inventories for the year 2009 collected and distributed by EMEP (www.emep.int).

The Urban Background Model, UBM, calculates the urban background air pollution based on emission inventories with a spatial resolution of 1 km x 1 km and based on input data from DEHM concerning the regional background. UBM is suitable for calculations of urban background concentrations when the dominating sources are areal sources like road traffic. The model includes a simple scheme for calculation of the dispersion and transport of the air pollutants and a simple chemical model accounting for the photochemical reactions of NOx and ozone. The model is described in detail in Berkowicz (2000b). The emissions used in the UBM model are based on the newly developed SPREAD model that spatially distributes national emissions from 2008 from all sectors on a 1 km x 1 km grid for Denmark (Plejdrup & Gyldenkærne 2011). Previous assess-

ments have only included road traffic emissions also on a 1 km x 1 km grid for Denmark but using a bottom up approach based on traffic levels on the road network and emission factors from the emission module of the OSPM model.

Finally, the street canyon model OSPM (http://ospm.dmu.dk/) is used to calculate the air pollution at 2 m height at the sidewalks of selected streets. Meteorological data from the meteorological model MM5v3 and air pollution concentrations from UBM are used as input to the model. The model includes emissions from traffic, simple chemical reactions describing the reactions of air pollutants in the street canyons and the dispersion of the air pollution in the street canyon (due to meteorological conditions and turbulence induced by traffic).

The traffic emission data used as input for the calculations with OSPM have been substantially updated for this year's report by detailed information (average daily traffic, vehicle distribution) for the selected streets obtained from the municipalities of Copenhagen and Aalborg based on a project on evaluation of the effects of environmental zones (Jensen at al. 2011). Emission factors are based on the latest version of the COPERT IV model applied for 2011 conditions taking account of the effect of the environmental zones by means of a detailed analysis of the vehicle composition using video number plate analysis linked to the National Auto Registry at a street in Copenhagen, for details see Jensen at al. (2011). The input data for the OSPM model on traffic volume and street configurations for the selected urban streets are generated using the AirGIS system (Jensen et al., 2001; http://airgis.dmu.dk).

The model calculations for 2011 for Copenhagen and Aalborg have been carried out using the full model calculation system based on the THOR system, including DEHM, UBM, and OSPM. The calculations were carried out in order to determine the NO_2 concentration in 138 streets in Copenhagen and 31 streets in Aalborg.

3 Nitrogen oxides

The nitrogen oxides (NO, NO_2, NO_x) are measured at eleven monitoring sites using gas monitors based on chemiluminescence. The concentrations are measured continuously throughout the year with a time resolution on minute scale that is aggregated to hourly averages for this reporting.

3.1 Annual statistics

The annual statistics for 2011 for nitrogen dioxide and nitrogen oxides are shown in Table 3.1 and 3.2. There was only exceedance of the annual limit value (EC, 2008) at H.C. Andersens Boulevard (Copenhagen/1103). There were no exceedances of the hourly limit value on 200 µg/m^3 that must not be exceeded more than 18 times a calendar year (see 19th highest hourly concentration in Table 3.1). In 2011 there was no information to the public due to exceedance of the information threshold for NO_2 (three hours average must not exceed 400 µg/m^3).

Table 3.1. Nitrogen dioxide (NO_2) in 2011. All parameters are based on hourly averages.

Unit: µg/m^3	Number	Average	Median	98. percentile	19. highest
Traffic:					
Copenhagen/1257	8165	40	36	100	132
Copenhagen/1103	7818	54*)	50	126	160
Aarhus/6153	8093	39	35	94	134
Odense/9155	7984	25	19	86	113
Aalborg/8151	7963	31	25	84	111
Urban Background:					
Copenhagen/1259	7940	18	15	52	74
Aarhus/6159	8089	20	17	62	84
Odense/9159	7250	16	13	47	72
Aalborg/8158	7926	13	10	45	69
Rural:					
Risø	7469	9	7	34	52
Keldsnor/9055	7852	10	7	38	62
Limit valuem2010	>7455	40			200

*) Limit value exceeded

Table 3.2. Nitrogen oxides (NO_x=NO+NO_2) in 2011. All parameters are based on hourly averages.

Unit: µg/m^3 (as NO_2)	Number	Average	Median	98. percentile	19. highest
Traffic:					
Copenhagen/1257	8165	87	67	303	479
Copenhagen/1103	7818	136	112	415	643
Aarhus/6153	8093	83	66	281	470
Odense/9155	7984	55	31	274	457
Aalborg/8151	7963	80	56	292	502
Urban Background:					
Copenhagen/1259	7940	22	16	75	139
Aarhus/6159	8089	30	20	132	282
Odense/9159	7250	20	15	77	163
Aalborg/8158	7926	19	12	78	205
Rural:					
Risø	7469	11	8	45	82
Keldsnor/9055	7852	12	8	50	96

3.2 Trends

The long term trends for NO_2 and NO_x are shown in Figure 3.1. For NO_x there are clear down ward trends at all stations. The decreases in the concentrations of nitrogen oxides are due to the national and international regulations of the emissions. The large emission reductions in the cities are achieved by improvement of the vehicles and obligatory use of catalytic converters.

The long term trend for nitrogen dioxide decreases much slower than observed for NO_x. This is mainly due to an increase in the share of diesel cars where up to about half of the emissions of NO_x consist of NO_2. In comparison gasoline cars emits nearly all NO_x as NO. This increase of the direct emissions of NO_2 slows down the decrease of the concentrations of NO_2 compared to NO_x.

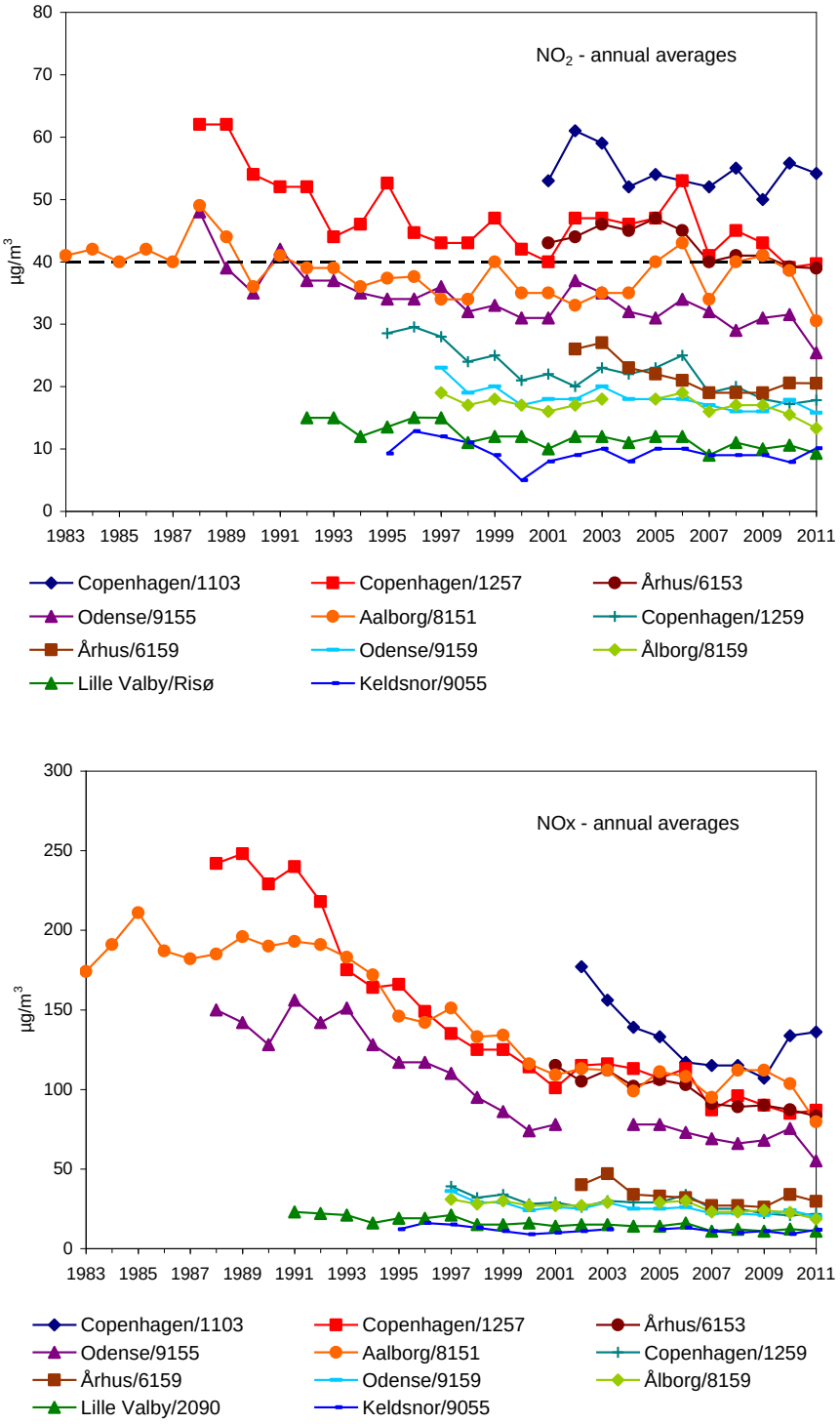


Figure 3.1 The graphs show the time series for the annual average values of NO_2 and NOx. The dashed line on the upper graph show the limit value that entered into force in 2010. Previous results from Copenhagen/1103 can be found at the homepage of Copenhagen Environmental Protection Agency (www.Miljoe.kk.dk)

Both NO_2 and NO_x was higher in 2010 and 2011 compared to 2009 at the street station H.C. Andersens Boulevard (Copenhagen/1103). At all other stations the levels in 2010 and 2011 were equal to or slightly lower that observed in 2009. The increase observed at H. C. Andersens Boulevard in 2010 and 2011 is believed to be a temporary effect of ongoing local construction work at nearby sites. More details about this can be found in Ellermann et al., 2012.

3.3 Results from model calculations

Model calculations of NO_2 and NOx have been performed for selected streets in Copenhagen (capital) and Aalborg (fourth largest city) as well as in a resolution of 5.6 km x 5.6 km for the entire country.

The selected streets represent busy streets and are mainly street canyons. Concentrations are elevated in this type of streets due to the high emissions and restricted dispersion conditions. 99 streets were selected in Copenhagen and 31 in Aalborg. Average Daily Traffic (ADT) was between 6,400 and 67,600 vehicles/day in Copenhagen and between 2,700 and 28,500 vehicles/day in Aalborg. Based on information from Copenhagen and Aalborg municipalities the ADT and vehicle distribution on all streets have been updated compared to last year's report.

Model calculations have been carried out in order to determine the annual concentrations of NO_2 to be able to compare with limit values. The air quality limit value for the annual mean is 40 $\mu g/m^3$ in 2010. The number of exceedances is also given. An exceedance is registered if the calculated concentration is higher than 40.5 $\mu g/m^3$ as the limit value is given as an integer.

An interlinked modelling approach has been applied. The Danish Eulerian Hemispheric Model (DEHM) calculates regional background concentrations, the Urban Background Model (UBM) calculates the urban background concentrations based on DEHM data, and the Operational Street Pollution Model (OSPM) calculates street concentrations based on UBM data. The model assumptions and calculations presented below for Copenhagen for 2011 are identical with the model assumptions and results in the report about impact assessment of different measures for more stringent Low Emission Zones as presented in Jensen at al. (2012).

Calculations with the full model chain of DEHM-UBM-OSPM have been compared to measured NO_2 concentrations in 2010 for all fixed street monitoring stations in Denmark. The model system predicts annual NO_2 concentrations within -1% for Jagtvej (Copenhagen), -10% for H.C. Andersens Boulevard (Copenhagen), -22% for Vesterbro (Aalborg) and -8% for Banegårdsgade (Aarhus) and +12% for Albanigade (Odense) (Jensen et al. 2011).

A recent validation study of the OSPM has been carried out for 10 selected streets in Copenhagen that is a subdivision of all selected streets. Passive measurements of NO_2 were carried out from October 24 to November 28, 2011. The results showed good agreement between

measured and modelled concentrations after updating of input data to the OSPM model (Ellermann et al. 2012).

3.3.1 Model calculations for Copenhagen

The annual mean concentrations of NO_2 for Copenhagen in 2011 are shown in Figure 3.2 (histogram) and Figure 3.3 (map).

In 2011 the limit value for the annual mean concentration was exceeded in 17 out of the 99 selected streets in Copenhagen (Figure 3.2). In 2010 the number of streets exceeding the limit value was 29 out of 138. The share of streets with exceedances are about the same in 2010 (21%) and 2011 (17%) although the considered streets have been reduced from 138 to 99.

In 2010 the street of "Sydhavnsgade" had the highest calculated concentration and the concentration was considerably higher than the rest of the streets. Sydhavnsgade was one of the 10 selected streets for the validation study of OSPM (Ellermann et al. 2012). Measurements showed much lower concentrations for this street than modelled and review of the assumed ADT showed that ADT were considered to be too high when compared to traffic data for nearby streets. Sydhavnsgade is one of the streets that are not represented by a traffic counting station and therefore it has been taken out of the annual assessment.

The number of streets exceeding the limit value is very sensitive to small changes in concentrations and uncertainties in the assumptions taken in the emission estimation and model calculations as can be seen from Figure 3.2 since small changes will lead to either more or less exceedances.

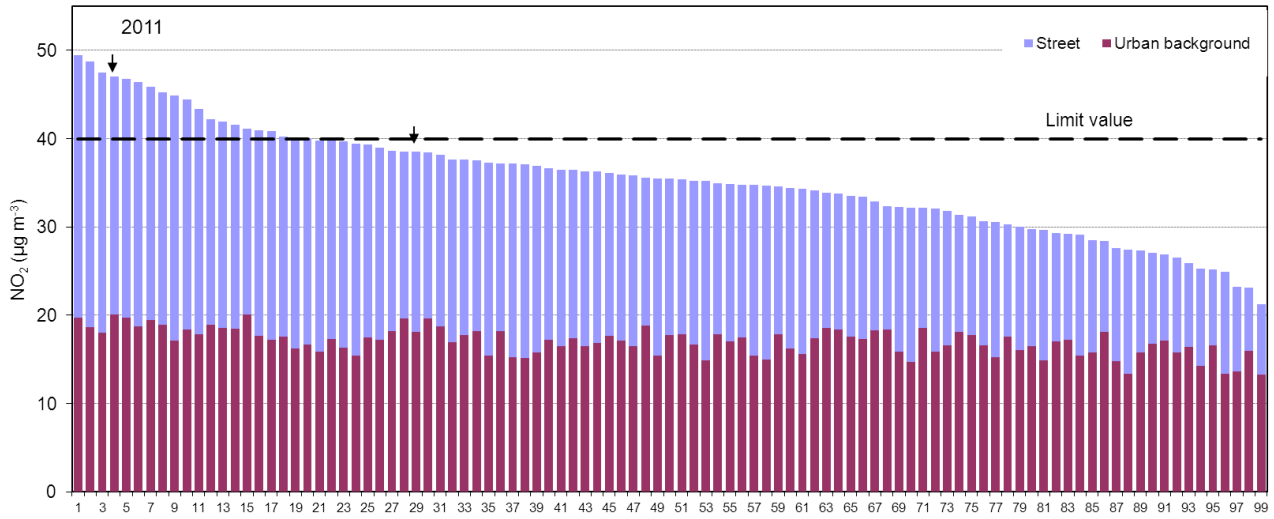


Figure 3.2 Annual mean concentrations of NO_2 in 2011 for 99 streets in Copenhagen. The contribution from traffic in the street canyons is based on the street canyon model OSPM. The urban background (dark red colour) is obtained from calculations with the urban background model UBM with input from the regional scale model DEHM. The value for a street is for the kerb side with the highest annual mean concentration. The names of the streets can be seen in Table 3.3. Arrows indicate the street segments with measurement stations.

The streets where the limit value were exceeded all have daily traffic intensity in the range of 12,500 to 67,500 vehicles per day. However, it is not only the traffic intensity alone which determines the concentration of NO_2. Also the width of the streets, the height of the surrounding

buildings, openings in the building façade, the share of heavy-duty vehicles and orientation of the street have large impact on the concentration of NO_2 in a street.

The names of the 99 streets are given in Table 3.3 and the locations of the streets together with the annual NO_2 concentration levels are shown in Figure 3.3. It is seen that the exceedances are concentrated in the central part of the city and at the main arterial roads from H.C. Andersens Boulevard to Ågade, and also Nørre Søgade to Øster Søgade.

Table 3.3. Number and names for the streets that are shown in Figure 3.2 and 3.4. The streets are numbered (1-138) according to NO_2 levels in 2011 (1 = highest, 138 = lowest). The numbers in parenthesis refer to different segments of the same street that has more than one model calculation. * indicate the street segments with measurement stations.

Number	Street name	Number	Street name	Number	Street name
1	H.C. Andersens Boulevard (2)	34	Nordre Fasanvej (3)	67	Jagtvej (2)
2	Gyldenløvesgade	35	Søndre Fasanvej (2)	68	Øster Voldgade (2)
3	Ågade	36	Tagensvej (3)	69	Roskildevej (1)
4*	H.C. Andersens Boulevard (1)	37	Frederikssundsvej (8)	70	Frederiksborgvej (1)
5	Bernstorffsgade (2)	38	Folehaven (1)	71	Strandvænget (2)
6	Nørre Søgade	39	Toftegårds Allé (1)	72	Slotherrensvej (2)
7	H.C. Andersens Boulevard (3)	40	Østerbrogade (1)	73	Rebildvej
8	Nørre Voldgade (2)	41	Tagensvej (1)	74	Hillerødgade (3)
9	Lyngbyvej (2)	42	Enghavevej	75	Halmetgade
10	Øster Søgade	43	Vesterbrogade (3)	76	Folke Bernadottes Allé
11	Fredensgade	44	Gammel Kongevej (1)	77	Slotherrensvej (1)
12	Hammerichgade	45	Falkoner Allé (2)	78	Vesterfælledvej
13	Åboulevard (1)	46	Hulgårdsvej (2)	79	Peter Bangs Vej (1)
14	Åboulevard (3)	47	Amager Boulevard	80	Tuborgvej (1)
15	Stormgade	48	Nørre Farimagsgade	81	Ålholmvej (2)
16	Scandiagade	49	Gl. Køge Landevej (1)	82	Artillerivej
17	Tagensvej (2)	50	Nørrebrogade	83	Dag Hammarskjølds Allé
18	Vesterbrogade (1)	51	H.C. Ørsteds Vej (2)	84	Frederikssundsvej (2)
19	Tuborgvej (2)	52	Amagerfælledvej	85	Ålholmvej (1)
20	Østerbrogade (4)	53	Frederikssundsvej (5)	86	Hillerødgade (1)
21	Jyllingevej (1)	54	Jagtvej (3)	87	Englandsvej (1)
22	Tomsgårdsvej (2)	55	Godthåbsvej (3)	88	Amagerbrogade (3)
23	Amagerbrogade (2)	56	Bülowsvej (2)	89	Peter Bangs Vej (2)
24	P Knudsens Gade (2)	57	Grøndals Parkvej	90	Blegdamsvej
25	Øster Voldgade (1)	58	Amagerbrogade (1)	91	Godthåbsvej (2)
26	Frederikssundsvej (3)	59	Tagensvej (4)	92	Strandvejen (2)
27	Frederikssundsvej (1)	60	Nordre Fasanvej (1)	93	Røde Mellemvej (1)
28	Bernstorffsgade (1)	61	Strandvejen (1)	94	Vigerslevvej (2)
29*	Jagtvej (1)	62	Toldbodgade	95	Bellahøjvej
30	Vester Voldgade	63	Ingerslevsgade	96	Gl. Køge Landevej (2)
31	Gothersgade (1)	64	Vester Farimagsgade	97	Røde Mellemvej (2)
32	Torvegade	65	Istedgade	98	Frederiksborgvej (2)
33	Bredgade	66	Kalvebod Brygge	99	Englandsvej (2)

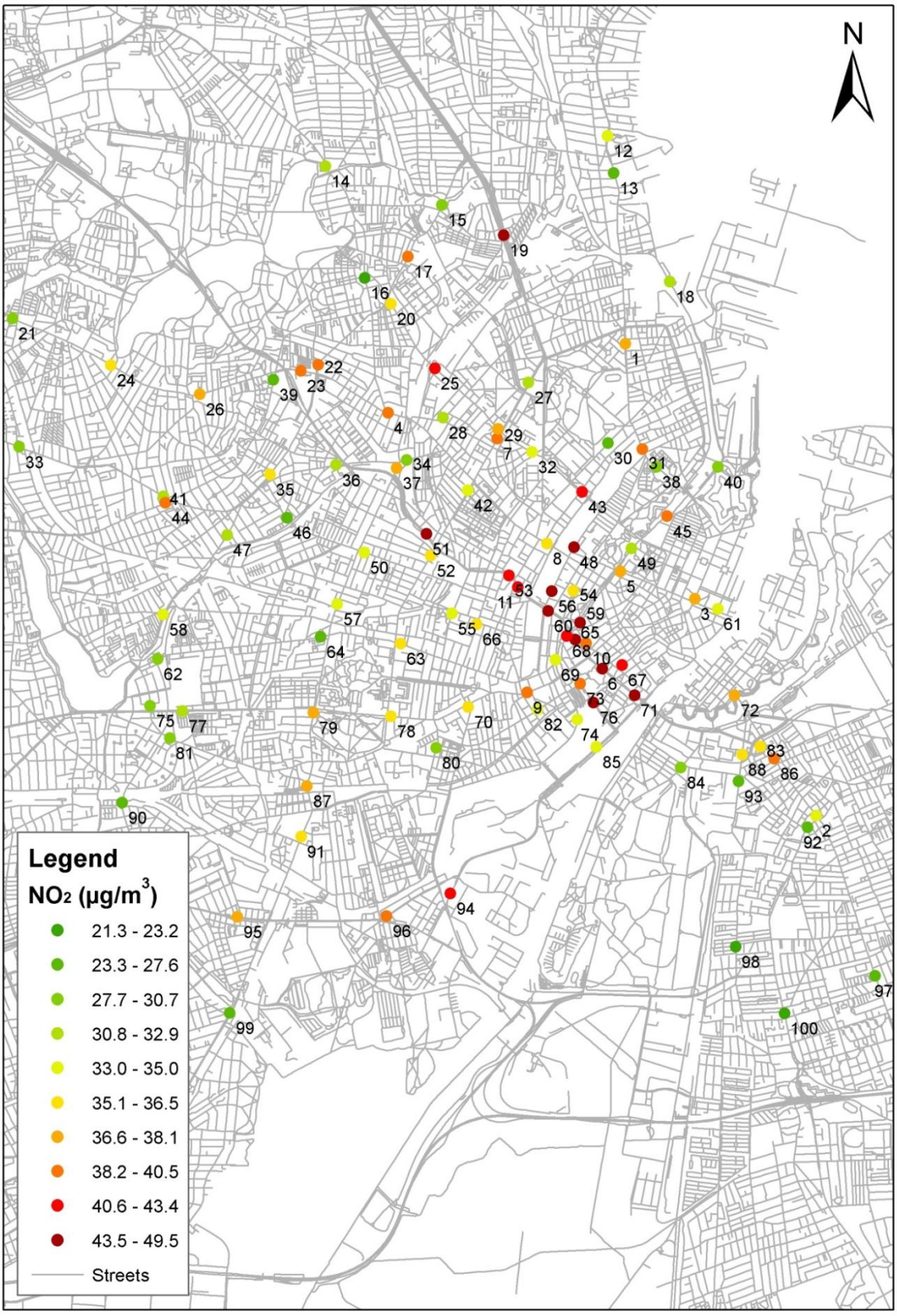


Figure 3.3 Map showing the locations of the selected streets in Copenhagen and the annual mean concentrations of NO_2 for 2011. The contribution from traffic in the street canyons is based on the street canyon model OSPM. The urban background is obtained from calculations with the urban background model UBM with input from the regional scale model DEHM. The value for a street is for the kerb side with the highest annual mean concentration. The names and numbers for the streets are shown in Table 3.3.

3.3.2 Model calculations for Aalborg

For Aalborg the model calculations show in general a reduction in the NO_2 concentrations compared with 2010 for the same reasons given for Copenhagen in the previous section. The average NO_2 concentration is about 4 µg/m^3 lower in 2011 compared to 2010 due to the general turnover of the vehicle fleet where older cars are replaced with new cars with lover emissions.

According to the model calculations the limit value for the annual mean concentration in 2010 was not exceeded at any of the 31 selected streets which was also the case in 2010 (Figure 3.4 and Figure 3.5). The order of the streets has changed slightly due to updated traffic data.

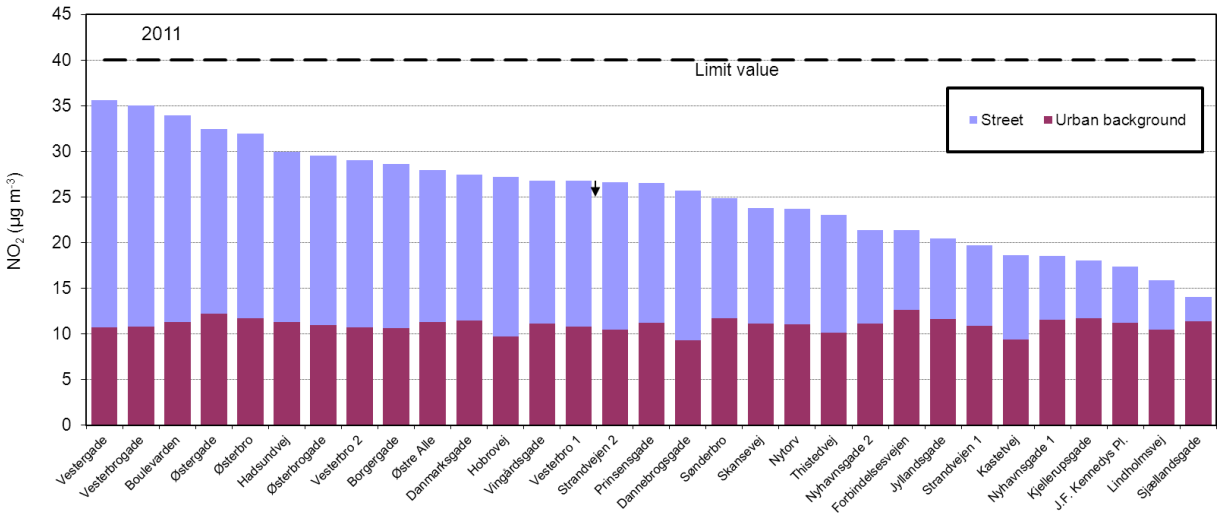


Figure 3.4. Annual mean concentrations of NO_2 in 2011 for 31 streets in Aalborg. The contribution from traffic in the street canyons is based on the street canyon model OSPM. The urban background (dark red colour) is obtained from calculations with the urban background model UBM with input from the regional scale model DEHM. The value for a street is for the kerb side with the highest annual mean concentration. Arrow indicate street segment with measurement station.

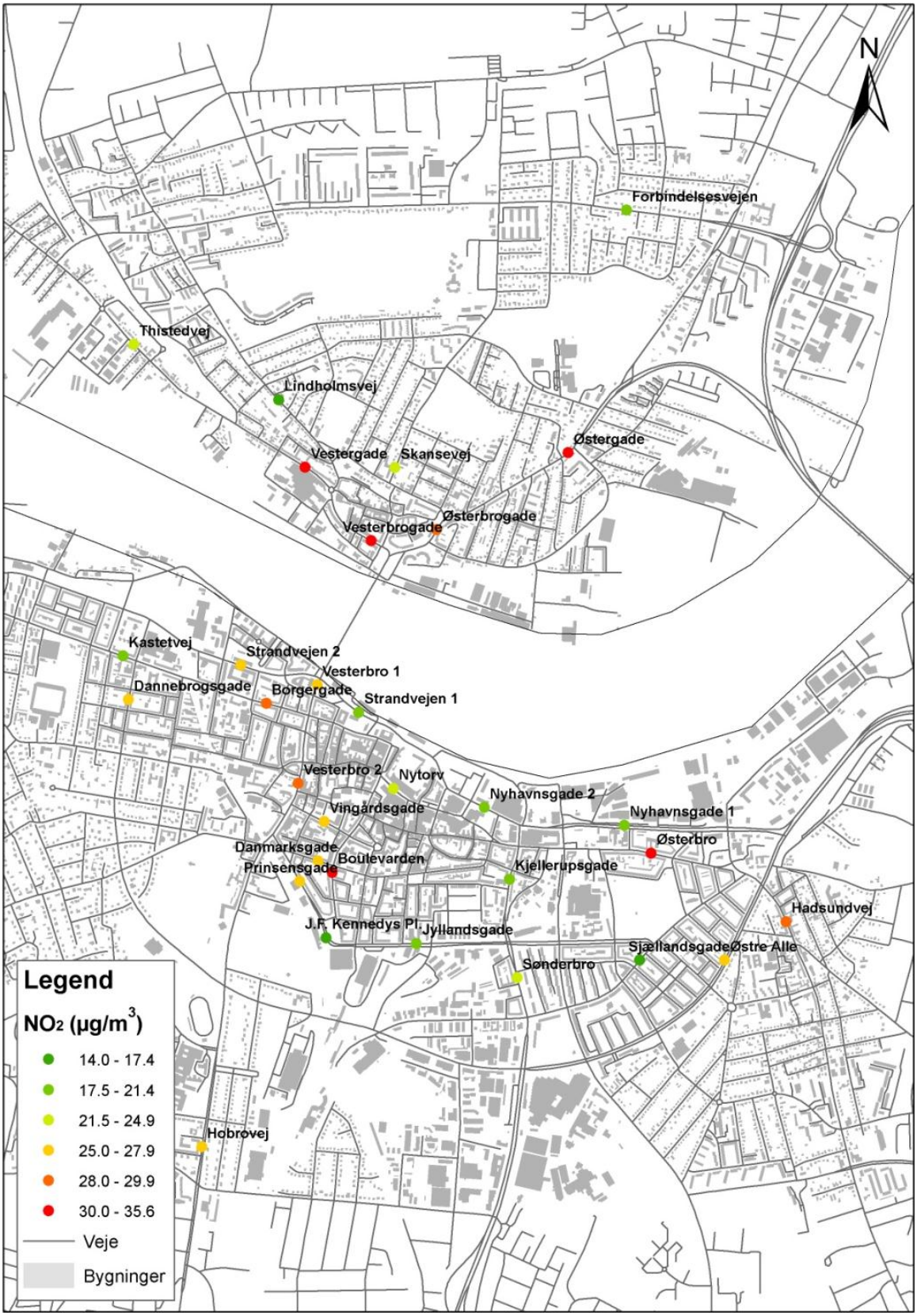


Figure 3.5. Map showing the location of the selected streets in Aalborg and the annual mean concentrations of NO_2 for 2011. The contribution from traffic in the street canyons is based on the street canyon model OSPM. The urban background is obtained from calculations with the urban background model UBM with input from the regional scale model DEHM. The value for a street is for the kerb side with the highest annual mean concentration. Vesterbro 1 is the street segment with the measurement station.

4 Ozone

Ozone is measured at seven monitoring sites using gas monitors based on ultraviolet photometry. The concentrations are measured continuously throughout the year with a time resolution on minute scale that is aggregated to hourly averages for this reporting.

4.1 Annual statistics

The annual statistics for 2011 for ozone are shown in Table 4.1. The maximum 8 hours daily mean value must not exceed 120 µg/m^3 more than 25 days per calendar year averaged over three years (EC, 2008). This target value was not exceeded for 2009-2011 at any of the stations. The long term objective (maximum 8 hours daily mean value must not exceed 120 µg/m^3; Table 4.1 column 5) were exceeded at four of the stations. However, the long term objective has not entered into force.

In 2011 there were no informations to the public due to exceedance of the information (hourly average 180 µg/m^3) or alert (hourly average 240 µg/m^3) thresholds for ozone.

Table 4.1. *O*zone (O_3) in 2011. All parameters are based on one-hour average values. The eight hour values are calculated as a moving average based on hourly measurements. Days above target value is the number of days where the maximum running eight hour average exceeds 120 µg/m^3.

Unit: µg/m^3	**Number of results**	**Average**	**Median**	**Max.**	**Days above target value**	**Max.**
				8 hours	**8 hours**	**1 hour**
Urban Background:						
Copenhagen/1259	7628	56	57	131	8	147
Århus/6159	7951	48	49	117	0	133
Odense/9159	6798	57	58	127	6	137
Aalborg/8158	7704	57	59	125	4	169
Rural						
Risø	7511	61	62	138	12	147
Keldsnor/9055	7634	50	48	115	3	140
Traffic						
Copenhagen/1103	7566	35	33	101	0	119
Target value[1]	>7154	-	-	-	25	-
Long term objective	>7154	-	-	120	-	-
Information threshold	-	-	-	-	-	180

[1.] As average over 3 years

4.2 Trends

The long term trends of ozone are shown in Figure 4.1. The annual averages of ozone have been nearly constant since 1992. The Danish and European reductions of the precursors to ozone formation (NOx, volatile organic compounds) have therefore not been sufficient to reduce the ozone concentration. However, the reductions of the precursors have decreased the maximum concentrations of ozone. This is illustrated by the decrease in the maximum eight hour average concentrations.

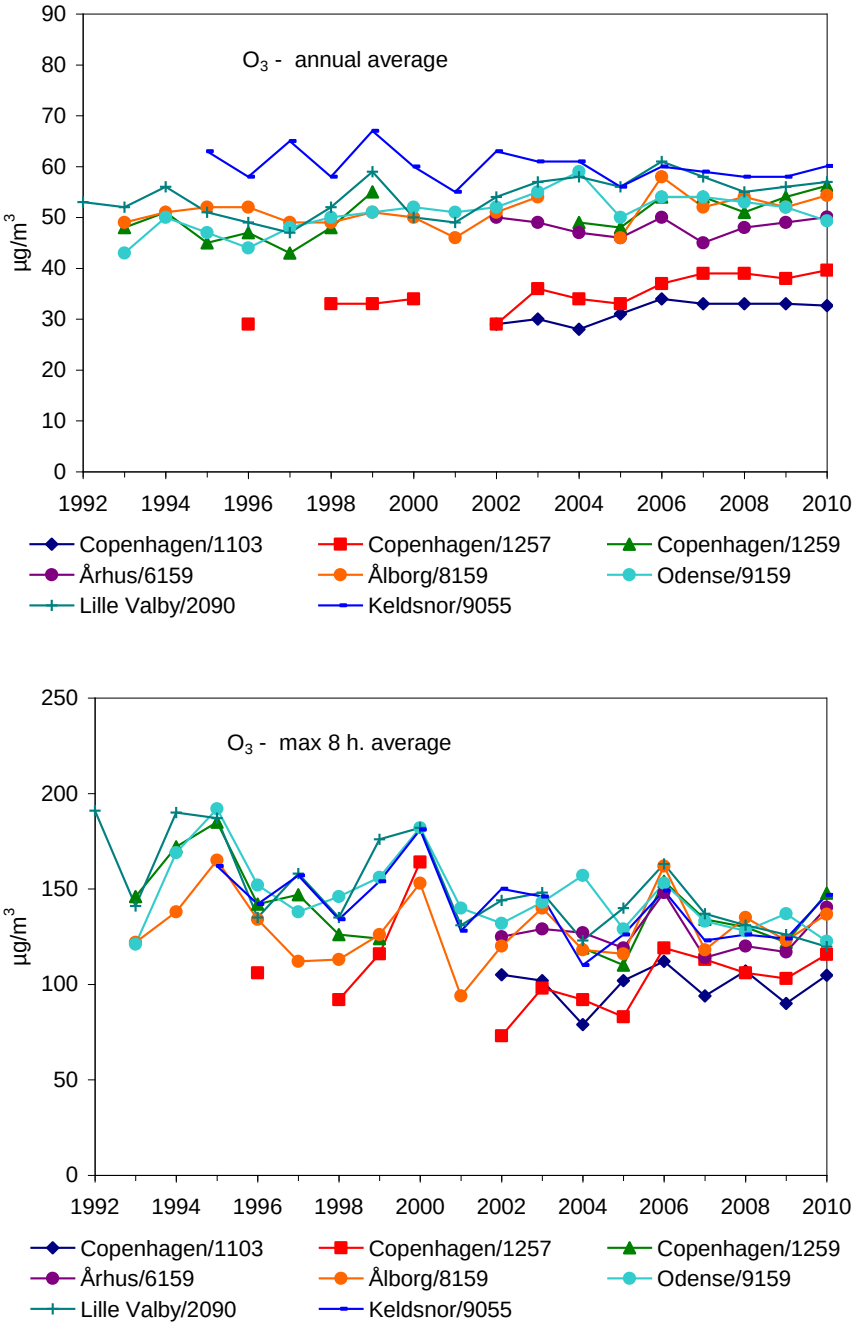


Figure 4.1 Annual average values and the max. 8 hour average value. The latter is calculated as hourly 8 hour running averages according to the provisions in the EU Directive (EC, 2008). Previous results from Copenhagen/1103 can be found at the Website of the Copenhagen Environmental Protection Agency (www. Miljoe.kk.dk).

4.3 Results from model calculations

The annual mean concentration of ozone is fairly constant throughout Denmark (Figure 4.2). This is because the main production of ozone takes part in the southern part of Europe and ozone is subsequently long range transported to Denmark. At the coasts the concentrations are slightly higher than over the remaining land areas, because ozone is deposited faster over land than over sea. In the cities the concentrations are lower than the average, because ozone is degraded by nitrogen oxide emitted from mainly traffic in the cities.

The target value for protection of human health is that the running 8 hour means concentration of ozone must not exceed 120 $\mu g/m^3$ more than 25 times during a calendar year. The long term objectives are that the running 8 hour mean concentration of ozone must not exceed 120 $\mu g/m^3$. The target value and long term objective are given in the EU Directive (EC, 2008). Results from the model calculations for 2011 show that the maximum daily 8 hour mean value of 120 $\mu g/m^3$ was only exceeded up to 5 days during 2011 (Figure 4.3). Similar results were obtained for 2009 and 20010 and hence the target value was not exceeded. However, the long term objective was exceeded at several places in Denmark; mainly in the coastal areas (Figure 4.4).

According to the directive (EC, 2008) the public has to be informed if the one hour average concentration exceeds the information threshold at 180 $\mu g/m^3$. Based on measurements this threshold was exceeded not exceeded in 2011. The model calculations show similarly that the one hour mean concentration did not exceed 180 $\mu g/m^3$ in 2011 (Figure 4.5). The model results are 10-20% lower than the measurements. The reason for this discrepancy is most likely that the model does not include emissions of ozone precursors from wild fires. Large wild fires are known to increase episodic ozone concentrations.

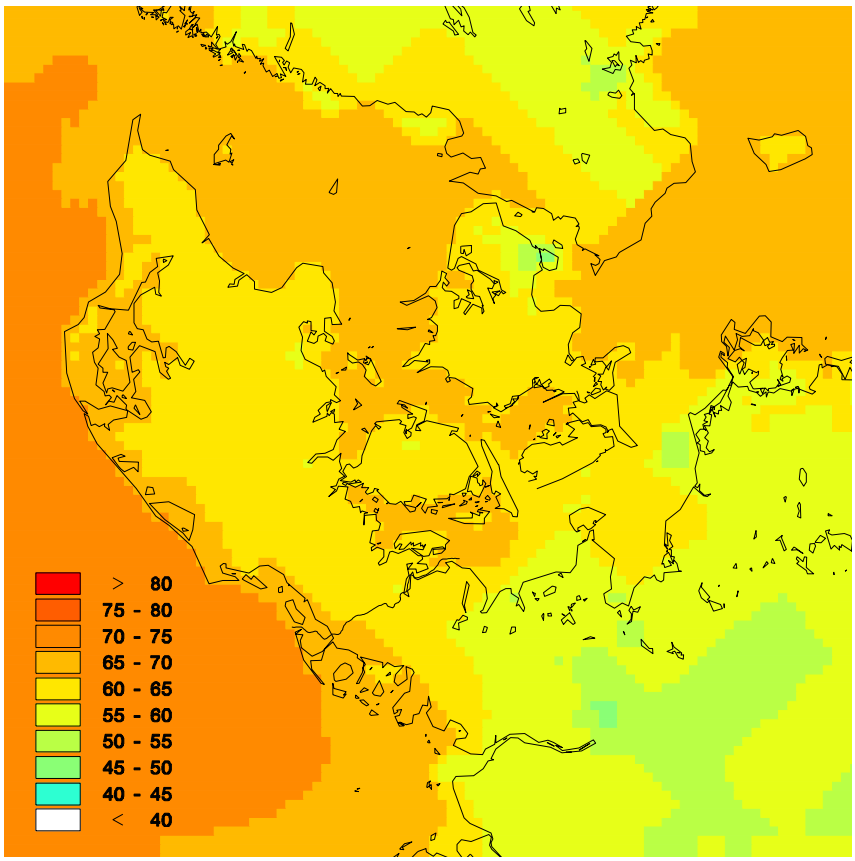


Figure 4.2. Annual mean concentrations of O_3 (µg/m^3) for 2011 calculated using DEHM. The figure shows the average concentrations for the 6 km x 6 km grit cells used in the model**.**

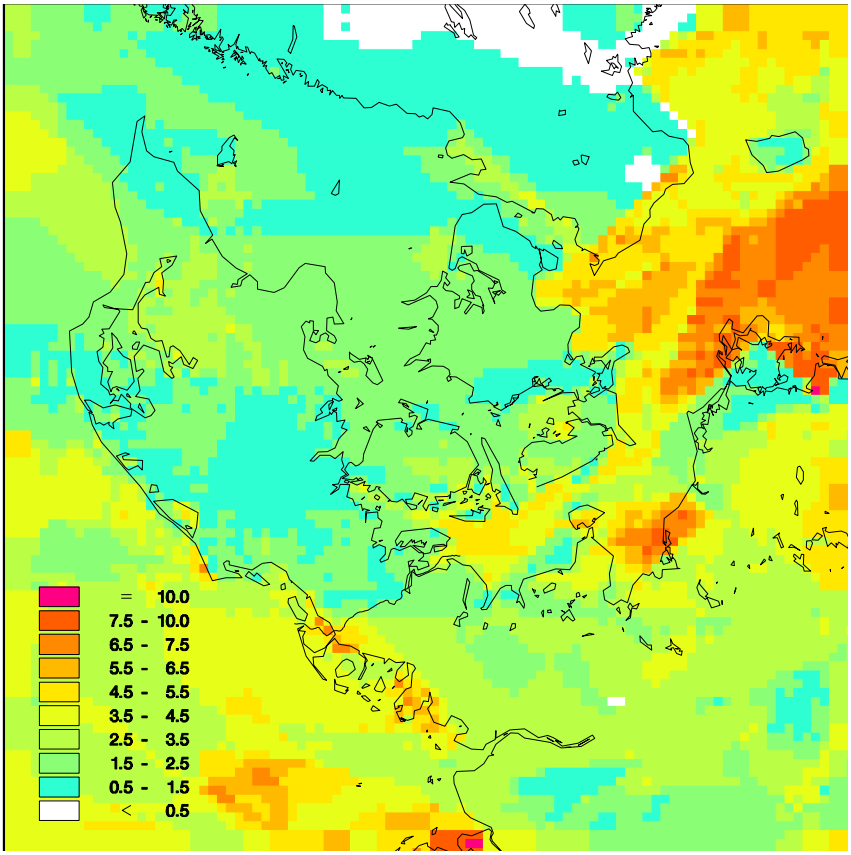


Figure 4.3. Number of exceedances of 120 µg/m^3 for 8-hour running mean concentrations of ozone in 2011. The calculations were carried out using DEHM.

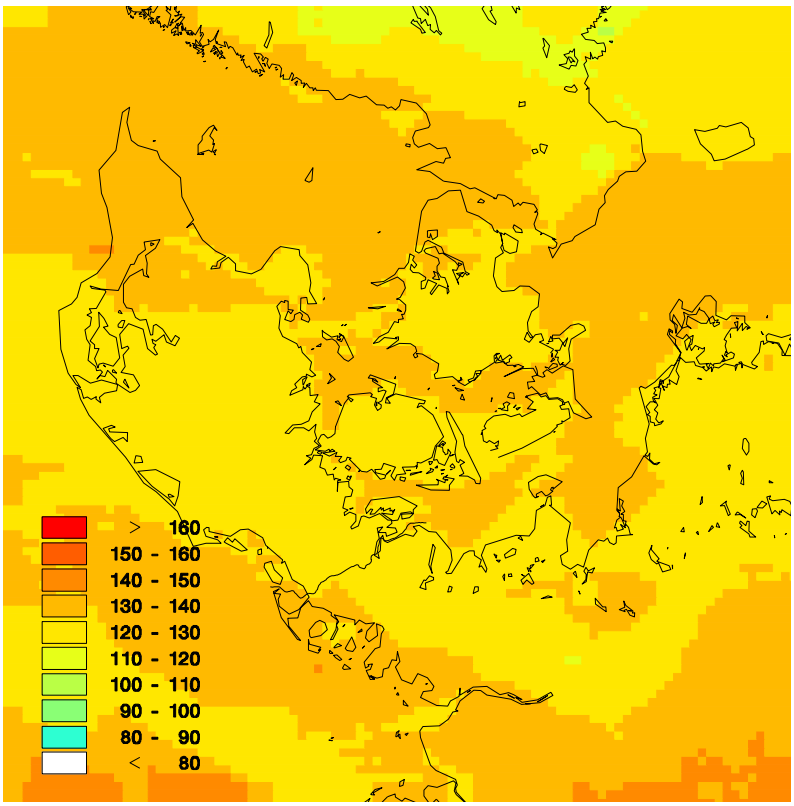


Figure 4.4. Maximum 8 hour running mean concentration (µg/m^3) of ozone in 2011 calculated using DEHM.

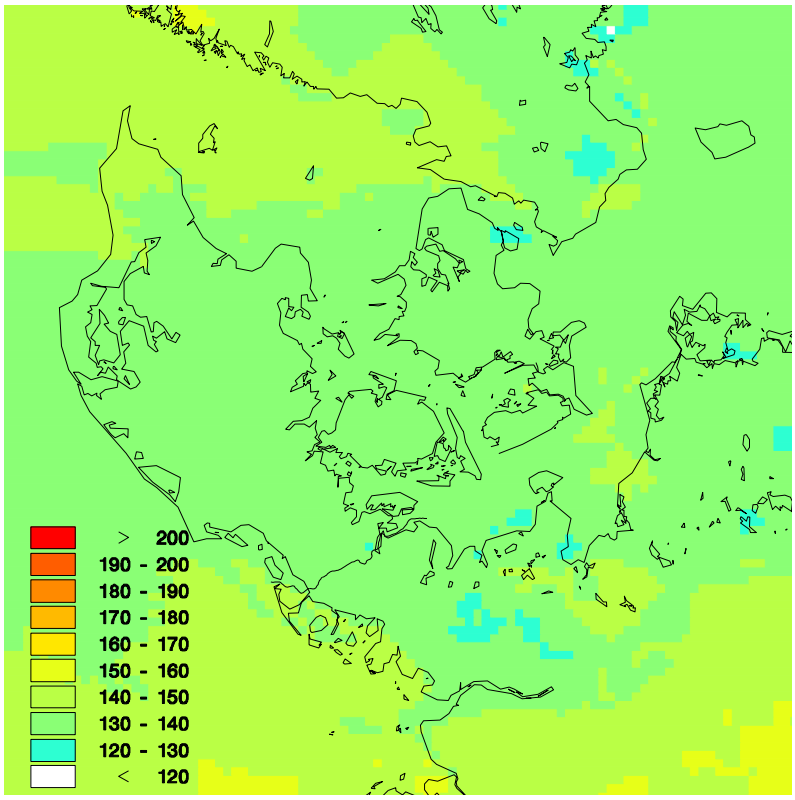


Figure 4.5. Maximum one hour mean concentration of ozone (µg/m^3) in 2011 calculated using DEHM.

5 Carbon monoxide

Carbon monoxide is measured at the four traffic oriented monitoring sites and at urban background in Copenhagen using gas monitors based on non-dispersive infrared spectroscopy. The concentrations are measured continuously throughout the year with a time resolution on minute scale that is aggregated to hourly averages for this reporting.

5.1 Annual statistics

The annual statistics for 2011 for carbon monoxide are shown in Table 5.1. The limit value for carbon monoxide is based on the maximum daily eight hour average concentration that must not exceed 10.000 µg/m^3 (EC, 2008). This limit value was not exceeded at any of the stations.

Table 5.1. Annual statistics for carbon monoxide (CO) in 2011. All parameters are based on hourly average. The 8-hour values are calculated as a moving average based on hourly results.

Unit: µg/m^3	Number	Average	Median	98-percentile	99.9-percentile	Max. 8-hours	Max hour
Traffic:							
Copenhagen/1103	7661	450	416	978	1107	1352	2214
Århus/6153	8245	293	258	679	764	918	1388
Odense/9155	8020	340	263	1068	1252	1580	3100
Aalborg/8151	7978	375	326	893	999	1232	1967
Urban Background:							
Copenhagen/1259	7855	220	207	432	469	557	890
Rural							
Risø	7735	200	185	431	471	525	795
EU Limit value	-	-	-	-	-	10 000	-
WHO Guideline values (WHO, 2000)	-	-	-	-	-	10 000	30 000

5.2 Trends

The long term trends for carbon monoxide are shown in Figure 5.1. During the last two decades there has been a large decrease of both the annual concentrations and of the maximum daily eight hour average concentrations. The reductions are due to national and international regulation of the emissions among others by requirement of catalytic converters on all vehicles.

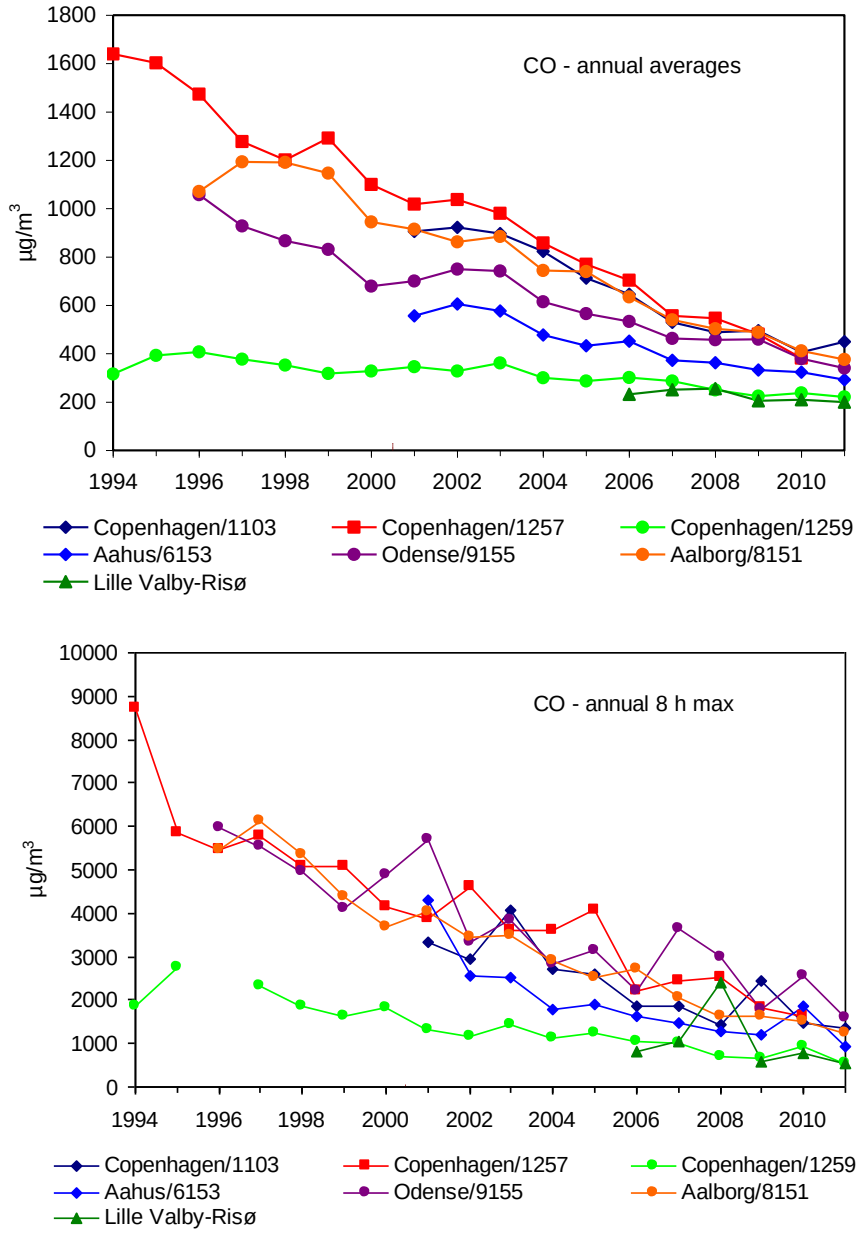


Figure 5.1. Annual average values and highest 8-hour value calculated based on an hourly moving average. Previous results from Copenhagen/1103 can be found at the website of the Copenhagen Environmental Protection Agency (www.Miljoe.kk.dk).

6 Benzene and Toluene

Benzene and toluene are measured at two kerb-side stations in Copenhagen, Jagtvej/1257 and H.C. Andersens Boulevard/1103, using a passive sampling method with weekly averages. Moreover, benzene, toluene and 15 other ozone precursors are measured in urban background (H.C. Ørsteds Institute/1259) as daily averages (Chapter 12).

6.1 Annual statistics

Table 6.1. Annual statistics for benzene in 2011 based on weekly average concentrations at 1 atm. and 293 K.

Concentration µg/m^3	Number of results	Average	Max weekly average
Copenhagen/1103	51	1.2	2.6
Copenhagen/1257	51	1.2	2.8
Limit value		5	

The limit value is based on EU Directive 2008/50/EC (EC, 2008).

Table 6.2. Annual statistics for toluene in 2011 based on weekly average concentrations at 1 atm. and 293 K. The Maximum weekly average is the maximum value for the weekly measurements (WHO, 2000).

Concentration µg/m^3	Number of results	Average	Max weekly average
Copenhagen/1103	51	3.4	7.2
Copenhagen/1257	51	3.6	8.2
Guideline value	-	-	260

The guideline value is established by WHO (WHO, 2000).

The annual averages of benzene and toluene in urban background/1259 were 0.64 µg/m^3 and 1.61 µg/m^3, respectively as described in Chapter 12.

6.2 Trends

Benzene has decreased from approximately 6 µg/m³ on Jagtvej (Copenhagen/1257) in 1998 to a value below the lower assessment threshold (EC, 2008) of 2 µg/m³. In 2011 the annual averages were 1.2 µg/m³ at both kerbside stations in Copenhagen (1103 and 1257). Toluene shows a similar trend, which indicates that benzene and toluene is mainly emitted from traffic. Annually averages for toluene were 3.4 and 3.6 µg/m³, respectively. The main reasons for the significant decreases of benzene and toluene up to 2008 are believed to be reductions of the emissions from gasoline-fuelled traffic due to increased use of catalysts and higher ratio of diesel cars. Only small changes are observed for both compounds from 2008 to 2011.

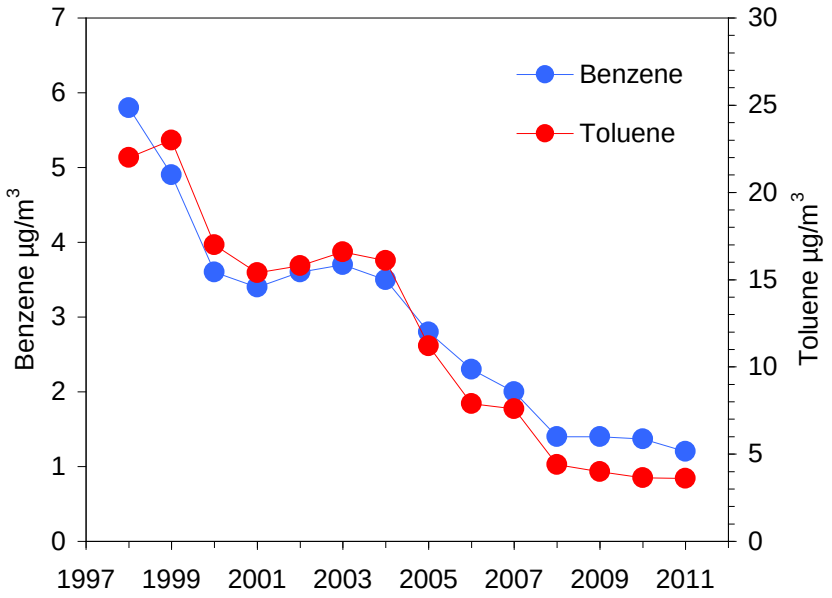


Figure 6.1. Annual average concentrations of benzene and toluene on the kerbside station Jagtvej, Copenhagen/1257.

7 Particles (TSP, PM_{10} and $PM_{2.5}$, particle number)

The SM200 sampler manufactured by OPSIS, Sweden, has been used in Denmark to measure PM_{10} in accordance with the EU Directive (EC, 1999, 2008). Measurements with this instrument have now been extended to include $PM_{2.5}$. The sampler provides the possibility for online diurnal measurements of PM in combination with sampling of PM on filters. The filters can later be used for chemical analysis. The online measurements of PM are determined immediately after the diurnal sampling period by means of absorption of β-rays in the particles. This option provides the possibility of presenting "on-line" results via the internet.

Results indicate that the β-ray results from the SM200 sampler comply better with the reference method for PM_{10} given in the EU Directive, than the results from weighing of the filters (Harrison, 2006). For this reason we have decided from 2006 and onwards to report results from the β-method. Previously, results from weighing of the filters were reported.

The results from the two methods differ slightly. From 2002 to 2005, where comprehensive data sets are available, it is shown that the β-method in average yields results that are 1.08 times the weighing for the yearly average and 1.09 times the weighing for the 36th highest concentration.

Measurements of particle numbers have been carried out since 2002 in cooperation between the monitoring programme and research projects financed by the Danish Environmental Protection Agency. The measurements have been carried out using a Differential mobility particle sizer (DMPS) that counts particle with mobility diameter between 6 and 700 nm.

7.1 Annual statistics

At all stations PM_{10} and/or $PM_{2.5}$ were collected continuously on filters on diurnal basis for subsequent β-absorption measurement using SM200-monitors (Table 7.1 and 7.2). Subsequently the particle samples were analysed in the laboratory. Additionally PM is measured at the stations in the Copenhagen area using a TEOM (Tapered-element oscillating microbalance) instrument. The TEOM measurements have a time resolution of 30 minutes (Table 7.3). During sampling the collected particles are heated to 50°C. At that temperature some of the volatile compounds evaporate (mainly secondary aerosols). The loss will depend of the actual composition of the aerosols. The European Commission has accepted that TEOM measurements for PM can be used in relation to EU limit values if the measured values are multiplied with a factor 1.3. However, the correction factor depends on the specific measurement site and measurements of PM using TEOM and a correction factor of 1.3 may therefore have considerable uncertainty.

In 2011 the daily limit value for PM_{10} were exceeded in Copenhagen at both traffic stations (HACB/1103 and Jagtvej/1257) while there were no exceedances of the annual limit value for PM_{10} and $PM_{2.5}$ (Table 7.1 and

7.2). However, analysis of the content of sodium chloride in PM_{10} showed that the exceedances of the daily limit value were due to sea salt and winter salting (see paragraph 7.3 for further details).

The EU-directive on air quality (EC, 2008) prescribes that the national average exposure indicator (AEI) has to be determined based on three years average of the average urban background concentration of $PM_{2.5}$. For the years 2009-2011 the AEI is determined to 15 µg/m^3. In Denmark the average exposure indicator is measured in urban background at Copenhagen/1259, Århus/6159 and Aalborg/8158).

Table 7.1. Annual statistics for PM_{10} in 2011. All parameters are calculated as diurnal averages at ambient temperature and pressure.

Unit µg/m^3	Number of results	Average	Median	Days above 50 µg/m^3	90 percentile	Max. day
Traffic						
Copenhagen/1103	348	35	31	46*)	52	103
Copenhagen/1257	354	32	28	43*)	53	105
Århus/6153	364	29	25	27	47	84
Odense/9155	356	27	23	28	46	83
Urban background						
Copenhagen/1259	346	23	20	13	37	77
Rural						
Risø**	295	20	16	7	35	86
Keldsnor/9055	360	20	16	13	36	73
Limit values (2005)	>329	40		35		

* Exceedance of daily limit value

** Based on low volume sampling and gravimetric determination of particle mass

Table 7.2. Annual statistics for $PM_{2.5}$ in 2011. All parameters are calculated as diurnal averages at ambient temperature and pressure. The limit values shall be met in 2015.

Unit µg/m^3	Number of results	Average	Median	90 percentile	Max. day
Traffic					
Copenhagen/1103	352	19	16	33	74
Copenhagen/1257	355	21	18	34	83
Århus/6153	355	18	14	35	74
Aalborg/8151	326	16	13	30	77
Urban background					
Copenhagen/1259	355	17	13	30	68
Århus/6159	340	15	12	29	66
Aalborg/8159	356	17	14	32	90
Rural					
Lille Valby/Risø	262	15	11	28	95
Limit value (2015) (parenthesis gives proposed value for 2020)	>329	25(20)			

Table 7.3. Annual statistics for PM_{10} measured in 2011 using TEOM. The values are calculated based on hourly averages.

Unit µg/m^3	Number of results	Average	Average x 1.3
Traffic			
Copenhagen/1103	7621	26	33
Rural			
Risø	5256	14	18
Limit values			40

Table 7.4. Annual statistics for $PM_{2.5}$ measured in 2011 using TEOM. The values are calculated based on hourly averages.

Unit µg/m^3	Number of results	Average	Average × 1.3
Traffic			
Copenhagen/1103	8147	14	19
Rural			
Risø	4818	9	12
Limit value (2015) (parenthesis gives proposed value for 2020)			25(20)

Table 7.5. Annual statistics for particle number. Average is based on ½-hourly averages. Total annual number of ½-hours is 17520.

Unit µg/m^3	Number of results	Average
Traffic		
Copenhagen/1103	7912	14013
Urban Background		
Copenhagen/1259	10869	10869
Rural		
Risø	9251	3673

7.2 Trends

Up to the year 2000 the particulate matter was measured as Total Suspended Particulate matter (TSP) corresponding to particles with a diameter up to around 25 µm (Figure 7.1). The exact cut-off depend strongly on the wind velocity. From 2001 most of the measurements of particulate matter was changed from TSP to PM_{10} according to the EU directive adopted in 1999 (EC, 1999). PM_{10} measurements are started at all stations except Copenhagen/1103 where the TSP measurements were continued to the end of 2005. The TSP is on the average 30-80% higher than PM_{10} at the street stations, while the difference is less at urban background and rural sites.

A major reduction (7 µg/m^3) in PM_{10} concentration was observed at the measurement station HCAB (Copenhagen/1103) from 2008 to 2009. Detailed examination of all the measurements at HCAB showed that the main reason for this decrease was new asphalt surface on the road laid out during August and September 2008 (Ellermann et al., 2010) that significantly reduced dust generation from road abrasion. PM_{10} were higher in 2011 than in 2009 and 2010 at HCAB. However, the same increase from 2010 to 2011 was observed at Jagtvej. It is therefore believed that the impact of the new asphalt at HCAB continued in 2011.

The measurements of $PM_{2.5}$ started in 2007 at Copgenhagen/1103 and at the other stations in 2008. Figure 7.3 presents all the results from measurements of $PM_{2.5}$ that are done so far. The AEI for 2009-2011 (15 µg/m^3) was slightly higher than the AEI for 2008-2010 (14 µg/m^3).

The measurements show a significant reduction of particle number in ambient air. On HCAB the number of particles has decreased by a factor of about 2 during the period 2002-2011. At the urban background station (HCOE) and rural background station (LVBY) a reduction in particle numbers was also observed though the decrease is smaller than at HCAB. The decreases are only about 30% and 15% at HCOE and LVBY, respectively. More details about particle number can be found in Massling et al. (2011).

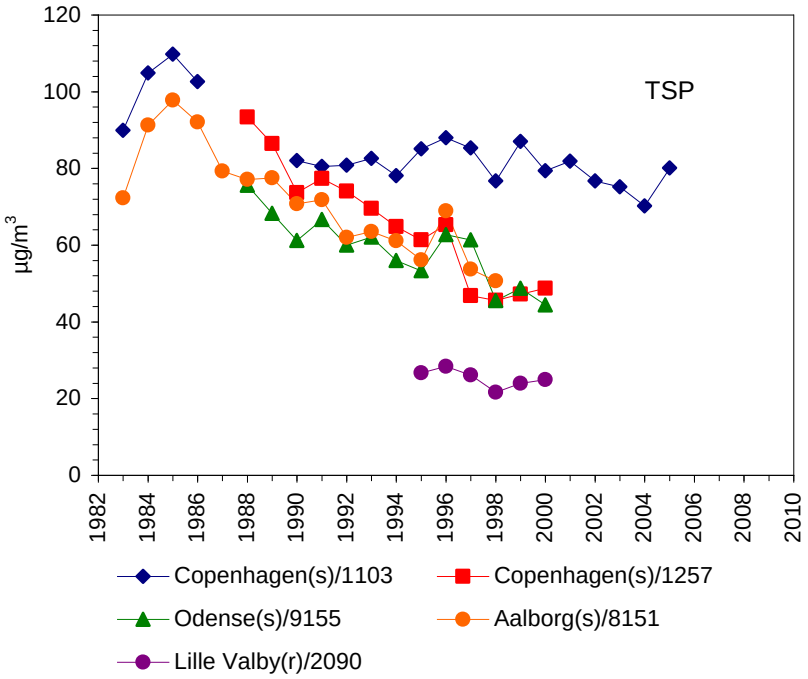


Figure 7.1. Annual averages for TSP measured at street stations (s) and at rural background station (r).

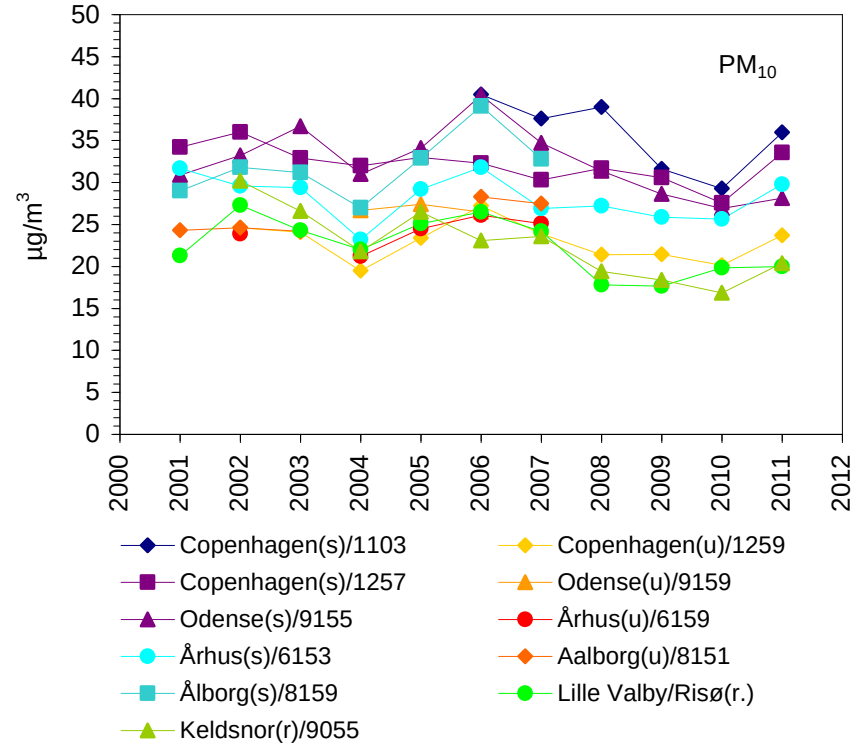


Figure 7.2. Annual averages for PM_{10} measured at street stations (s), urban background stations (u) and at rural background stations (r). The change from gravimetric determination to the use of β-measurements from 2006 gives rise to a 5-10% increase due to the shift of method. The value for PM_{10} at Copenhagen/1103 in 2008 and 2009 is based on the measurements with SM200 and the estimate described above. Data are given at standard temperature and pressure (0ºC and 1 atm.). The difference between ambient temperature and pressure and standard temperature and pressure is – 3% on the annual average.

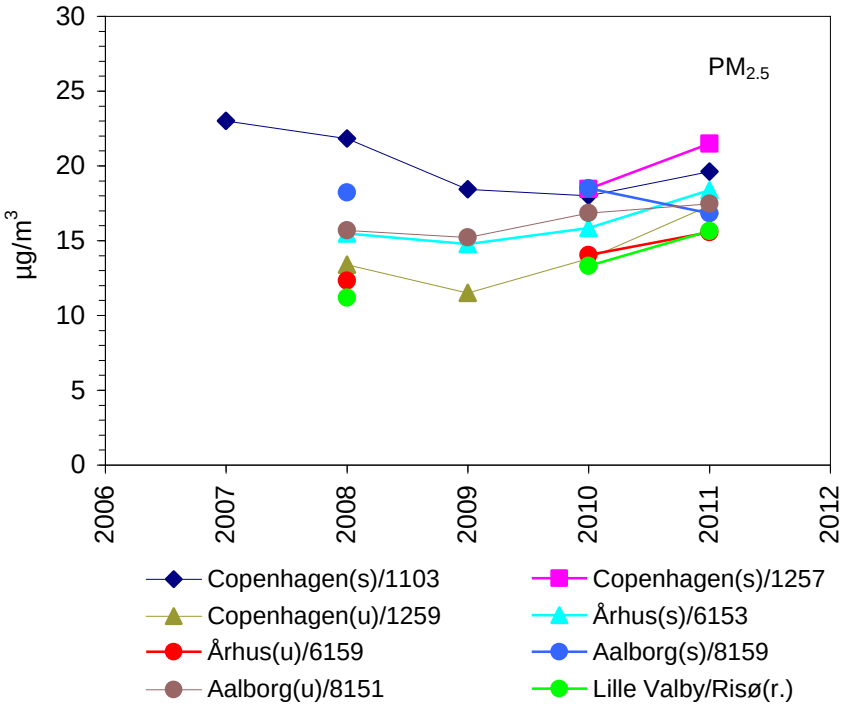


Figure 7.3. Annual averages for $PM_{2.5}$ measured at street stations (s), urban background stations (u) and at rural background station (r). Only annual averages covering more than 2/3 of the years are shown. Data are given at standard temperature and pressure (0ºC and 1 atm.). The difference between ambient temperature and pressure and standard temperature and pressure is – 3% on the annual average.

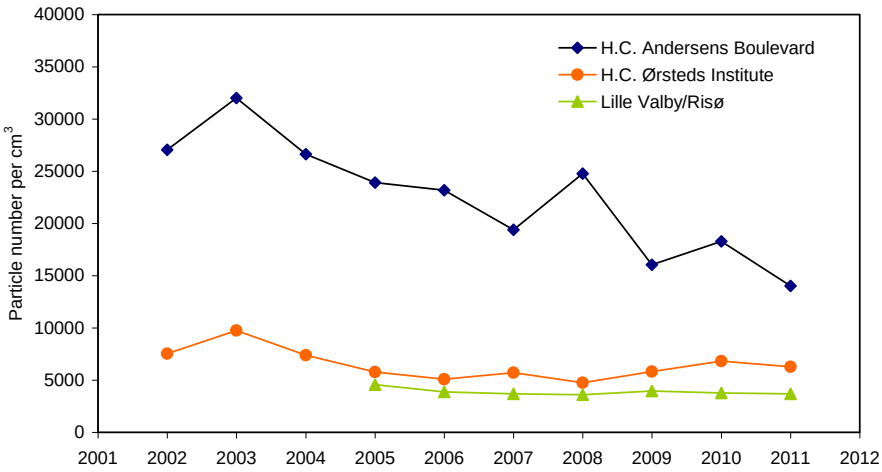


Figure 7.4. Annual averages for particle number. Data for H.C. Andersens Boulevard represents an estimate where annual averages have been corrected for missing data based on comparison with measurements of NOx. This estimate is further described in Massling et al., (2011).

7.3 Impact of salt from winter salting and sea

The EU air quality directive (EC, 2008) gives the member states the possibility to compensate for the impact of salt from sea salt and winter salting on PM_{10} (Article 20 and 21). Salt from sea salt can be subtracted from PM_{10} prior to evaluation of the limit values. If the limit values are exceeded due to winter salting then the member states do not have to prepare an air quality plan in order to reduce the levels of PM_{10}. These rules account for both the annual limit value and the daily limit value that

states that the daily PM_{10} concentration must not exceed 50 µg/m^3 more than 35 days a calendar year.

On this background the monitoring program was expanded in 2010 with daily sampling and analysis of sodium at the street stations H.C. Andersens Boulevard, Copenhagen (1103), Odense (9155) and Aarhus (6153) and at the urban background station in Copenhagen (H.C. Ørsteds Institute/1259). Table 7.5 gives the annual average concentrations for sodium and estimate for total salt (NaCl) in 2011 (calculated from the measured sodium concentration).

Table 7.5 Annual statistics for sodium and estimate of total salt (NaCl) in 2011

	Na µg/m^3	NaCl µg/m^3
Traffic		
Copenhagen/1103	1,5	4,0
Odense/9155	1,3	3,3
Aarhus/6153	1,5	3,9
Urban background		
Copenhagen/1259	0,9	2,4

Figure 7.4 shows the results from measurements of sodium at the street station H.C. Andersens Boulevard, Copenhagen (1103) and at urban background in Copenhagen (H.C. Ørsteds Institute/1259). The high concentrations at the street station during the first 2½ months are due to winter salting of the roads. The high correlation between the sodium concentrations for the remaining part of the year is due to long range transport of sea salt that have equal impact on the two stations.

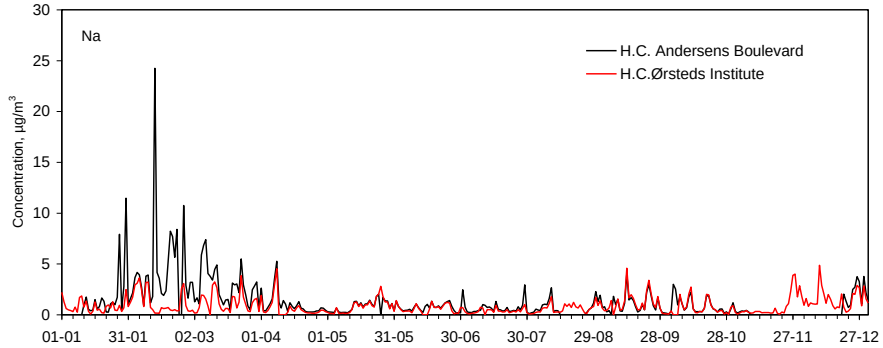


Figure 7.4. Daily concentrations of sodium at H.C. Andersens Boulevard, Copenhagen (1103) and at urban background in Copenhagen (H.C. Ørsteds Institute/1259).

In 2011 there were 46 days with daily average concentrations of PM_{10} above 50 µg/m^3 at H.C. Andersens Boulevard and hence the daily limit value for PM_{10} was exceeded (Table 7.6). The exceedance is partly due to a combination of salt from sea and winter salting. If sodium chloride from sea salt and winter salting is subtracted separately from PM_{10} then

the number of days above 50 µg/m^3 is reduced to 38 days in both cases (Table 7.6). However, if sodium chloride from both sources is subtracted at the same time then there is only 33 days with concentrations above 50 µg/m^3 at H.C. Andersens Boulevard in 2011.

In 2011 there were 43 days with daily average concentrations of PM_{10} above 50 µg/m^3 at Jagtvej and hence the daily limit value for PM_{10} was exceeded at this street also (Table 7.7). At Jagtvej there were only measurements of sodium for the last two thirds of the year, because these measurements were not originally part of the monitoring program. For the first third of the year estimates of the sodium chloride content has been estimated from:

- The average measured sodium content in PM_{10} on H.C. Andersens Boulevard for the winter salting period (1-1-11 – 23-3-11).

- The daily measured sodium content in PM_{10} on the background station H.C. Ørsteds Institute for the remaining period with influence from only long range transported sea salt (24-3-11 – 7-6-11).

Also for Jagtvej the exceedance of the daily limit value for PM_{10} is partly due to a combination of salt from sea and winter salting. Based on the assumptions made above there are only 40 and 32 days with concentrations above 50 µg/m^3 after subtraction of sea salt and winter salting, respectively (Table 7.7). However, if sodium chloride from both sources is subtracted at the same time then there is only 31 days with concentrations above 50 µg/m^3 at Jagtvej in 2011. The main uncertainty here is that it is assumed that winter salting have the same impact on Jagtvej as on H.C. Andersens Boulevard. However, even if the impact of winter salting on Jagtvej is reduced to 50% of the level at H.C. Andersens Boulevard then the number of days will not exceed the limit of 35 days.

Table 7.6 Influence of sea salt and winter salting of roads on the number of days with concentrations of PM_{10} above 50 µg/m^3 at H. C. Andersens Boulevard in 2011. Sea salt is estimated from measurements at urban background during the periode with winter salting.

Date	PM_{10} µg/m^3	PM_{10} without sea salt µg/m^3	PM_{10} without winter salting µg/m^3	PM_{10} without sea salt and winter salting µg/m^3
20-01-2011	59	58	56	56
27-01-2011	59	56	40	40
30-01-2011	73	66	46	46
12-02-2011	99	98	39	39
18-02-2011	52	50	40	40
21-02-2011	53	51	41	41
22-02-2011	64	63	48	48
25-02-2011	103	95	79	79
26-02-2011	70	68	65	65
27-02-2011	56	55	53	53
28-02-2011	70	69	63	63
01-03-2011	76	75	72	72
07-03-2011	52	48	35	35
13-03-2011	62	59	60	60
14-03-2011	80	79	79	79
21-03-2011	69	68	65	65
23-03-2011	51	40	36	36
30-03-2011	52	48	52	48
08-04-2011	51	39	51	39
11-04-2011	51	49	51	49
25-04-2011	53	53	53	53
26-04-2011	52	52	52	52
11-05-2011	58	58	58	58
26-08-2011	56	55	56	55
26-09-2011	62	61	62	61
29-09-2011	61	61	61	61
30-09-2011	76	75	76	75
01-10-2011	79	79	79	79
03-10-2011	77	76	77	76
25-10-2011	55	54	55	54
27-10-2011	51	51	51	51
28-10-2011	62	61	62	61
30-10-2011	52	51	52	51
03-11-2011	81	81	81	81
04-11-2011	90	89	90	89
05-11-2011	80	80	80	80
06-11-2011	83	82	83	82
07-11-2011	66	65	66	65
08-11-2011	53	52	53	52
09-11-2011	51	50	51	50
13-11-2011	71	71	71	71
17-11-2011	56	56	56	56
18-11-2011	68	68	68	68
22-11-2011	56	55	56	55
23-11-2011	64	63	64	63
24-11-2011	51	49	51	49
Number of days above 50 µg/m^3	46	38	38	33

Table 7.7 Influence of sea salt and winter salting of roads on the number of days with concentrations of PM_{10} above 50 µg/m^3 at Jagtvej in 2011. Sea salt is estimated from measurements at urban background during the periode with winter salting.

Date	PM_{10} µg/m^3	PM_{10} without sea salt µg/m^3	PM_{10} without winter salting µg/m^3	PM_{10} without sea salt and winter salting µg/m^3
12-02-2011	84	83	71	71
14-02-2011	53	53	41	40
15-02-2011	65	64	54	53
16-02-2011	59	57	47	46
17-02-2011	53	51	42	40
20-02-2011	60	59	48	47
21-02-2011	61	60	50	49
22-02-2011	57	56	45	44
24-02-2011	105	98	99	92
25-02-2011	105	97	100	92
26-02-2011	82	80	72	70
27-02-2011	62	61	50	49
28-02-2011	69	68	57	56
01-03-2011	75	74	63	62
02-03-2011	65	65	53	53
08-03-2011	55	53	45	43
09-03-2011	52	49	41	39
12-03-2011	53	46	47	40
13-03-2011	72	69	62	59
14-03-2011	74	73	63	62
21-03-2011	54	52	43	41
30-03-2011	57	53	57	53
20-04-2011	53	52	53	52
21-04-2011	64	64	64	64
27-04-2011	51	50	51	50
10-05-2011	55	55	55	55
11-05-2011	61	60	61	60
07-06-2011	53	52	53	52
25-08-2011	51	51	51	51
26-09-2011	55	54	55	54
30-09-2011	55	55	55	55
01-10-2011	84	84	84	84
03-10-2011	63	62	63	62
28-10-2011	60	60	60	60
02-11-2011	60	59	60	59
03-11-2011	77	76	77	76
04-11-2011	91	91	91	91
05-11-2011	76	75	76	75
06-11-2011	77	76	77	76
07-11-2011	56	55	56	55
13-11-2011	65	64	65	64
18-11-2011	61	60	61	60
23-11-2011	65	64	65	64
Number of days above 50 µg/m^3	43	40	32	31

8 Heavy Metals

Collection of PM_{10} is performed on filters which can be used for chemical analysis. Selected filters are analysed by ICP-MS (Inductively Coupled Plasma Mass Spectrometry) for their content of elements. Results for 10 heavy metals are presented in Table 8.1. Comparison between results from the new analysis method and the previously used PIXE-method (Proton Induced X-ray Emission) showed only minor changes in the annual averages, when the low concentration levels are taken in to account.

The table presents also results for analysis of heavy metals in total suspended particulate (TSP) at the measurement station Risø. The content of these heavy metals in PM_{10} and TSP are approximately equal since these metals are mainly found in the fine particle fraction.

The ICP-MS analysis provides the measurements obligatory according to EU Directive 2004/107/EC (EC, 2005) for As, Cr and Ni and EU Directive 2008/50/EC (EC, 2008) for Pb. According to the directive also Hg has to be measured, however, these measurements can be carried out in cooperation with neighbouring countries. As part of a bilateral agreement "Development of the mutual partnership on air pollution" between Denmark and Sweden, it has been agreed that the Swedish measurements at Röå (Table 8.2) can fulfil the Danish obligations on measurements of Hg. This agreement is based on the fact that the spatial variation of background Hg concentrations is small.

8.1 Annual statistics

The annual statistics for the selected heavy metals are shown in Table 8.1 and 8.2. The concentrations are low for all of the heavy metals and there were no exceedances of the target/limit values for the four metals (As, Cd, Ni, Pb) that are regulated by use of target/limit values (EC, 2005, 2008).

Table 8.1. Annual statistics for Vanadium (V), Chromium (Cr), Manganese (Mn), Nickel (Ni), Cupper (Cu), Zink (Zn), Arsenic (As),Selenium (Se), Cadmium (Cd) and Lead (Pb) measured in PM_{10} during 2011. For comparison the table includes also results for these heavy metals measured in total suspended particulate (TSP) at the rural background station Risø.

Unit: ng/m^3	V	Cr	Mn	Ni	Cu	Zn	As	Se	Cd	Pb
PM10, Traffic										
Copenhagen/1103	3,3	7,0	25	2,9	97	45	0,9	0,8	0,2	5,9
Odense/9155	2,2	3,7	14	2,8	42	34	1,0	0,9	0,2	3,2
Århus/6153	2,6	3,7	11	5,7	37	23	0,7	0,6	0,1	3,9
PM10, Urban background										
Copenhagen/1259	2,5	1,2	5,1	3,4	13	15	0,8	0,7	0,1	4,5
TSP, Rural background										
Risø	1,7	0,5	3,0	2,0	2,2	10,5	0,7	0,5	0,1	4,1
EU Target (limit) Values*				20			6		5	500
Guideline value (WHO) **	1000		150						5	
Life time risk level at 1:10^5				25			6.6			

*) Target values for Ni, As and Cd are implemented through EU Council Directive 2004/107/EC (EC, 2005). The limit value for Pb is found in EU Directive 2008/50/EC (EC, 2008).

**) The guidelines and life time risk for the carcinogenic metals are established by WHO (WHO, 2000). The lifetime risk level is defined as the concentration that through a lifelong exposure is estimated to give an excess risk of 1:105 for developing cancer.

Table 8.2. Annual statistics for Mercury 2011. Measured at Råö in southern Sweden by the Swedish Environmental Research Institute.

Unit: ng/m^3	Total Gas Hg (ng/m^3)	Total Particles Hg (ng/m^3)
Råö (SE00014)	1.6	0.009

8.2 Trends

The long term trends for six of the heavy metals are shown in Figure 8.1. For Pb, As, Ni and Mn there are clear reductions in the concentrations due to national and international regulations of the emissions. Most pronounced for Pb where removal of Pb from gasoline has resulted in large reductions of the concentrations. For Mn the long term trend at HCAB deviates from the other stations. This is believed to be due to high Mn concentrations in the asphalt used at HCAB during the period from 1991 to 2008. The concentration of Cu increases mainly due to increased use of Cu in brakes.

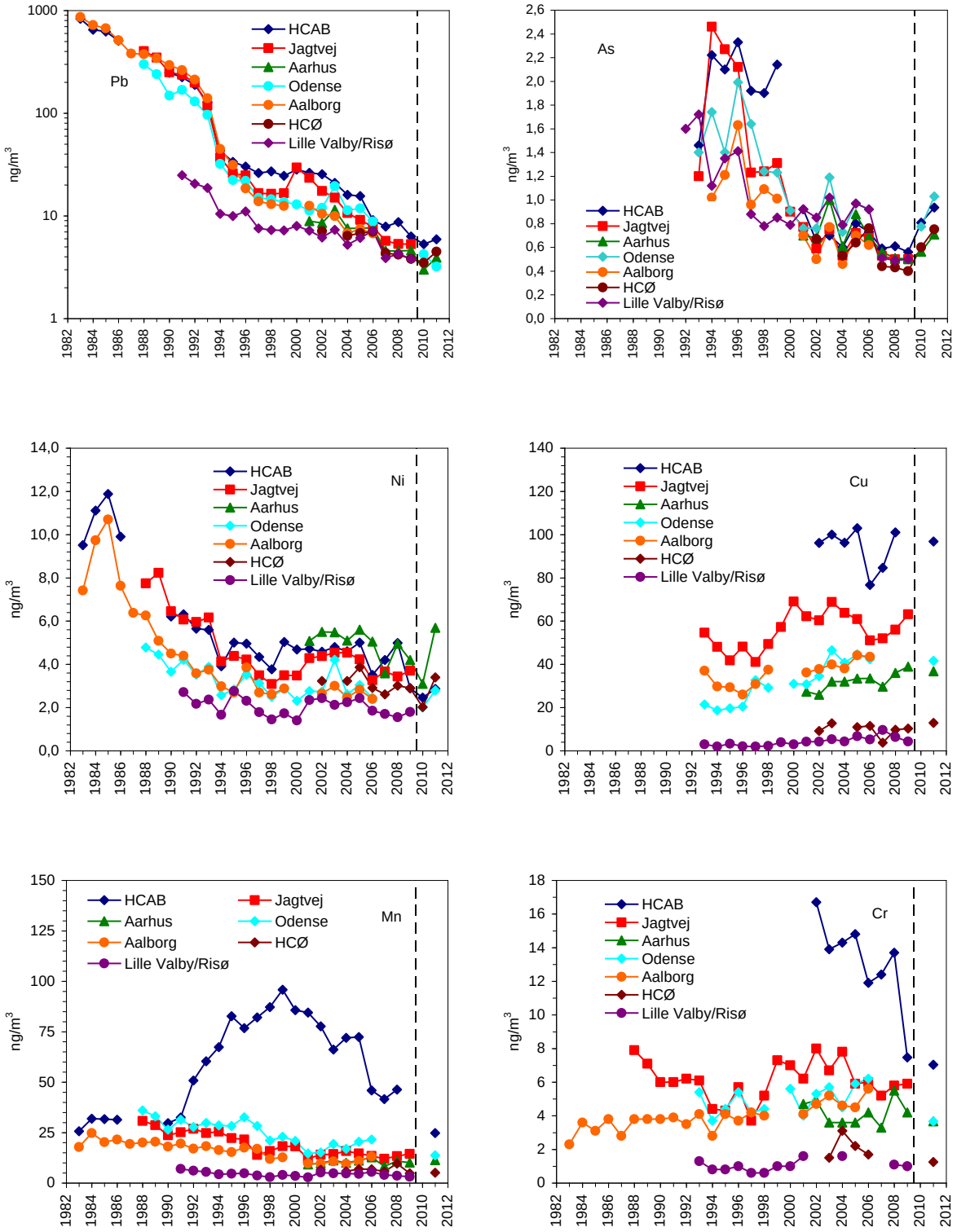


Figure 8.1. Annual averages from selected stations for some heavy metals in particulate matter. Until 2000 in TSP and later in PM_{10} – except for Copenhagen/1103 where PM_{10} replaced TSP from the beginning of 2006. The heavy metals are usually found in fine particles, which make the TSP and the PM_{10} values comparable. Note that the scale for Pb is logarithmic. The dashed line indicate that the analysis method has been changed from 2009 to 2010.

9 Sulphur dioxide

The sulphur dioxide has reached very low levels in Denmark and it is therefore only necessary with a limited monitoring of the concentrations of sulphur dioxide; both with respect to the number of stations and the quality of the measurements. Hence it is only measured at two traffic stations (Copenhagen and Aalborg) with focus on episodes with high concentrations of sulphur dioxide. It is measured using gas monitors based on ultraviolet fluorescence. The concentrations of sulphur dioxide are often below the detection limit of the instruments and hence the uncertainty of the measurements are large. The concentrations are measured continuously throughout the year with a time resolution on minute scale that is aggregated to hourly averages for this reporting.

9.1 Annual statistics

The annual statistics for 2011 for sulphur dioxide are shown in Table 9.1. None of the limit values (EU, 2008) were exceeded in 2011. In 2011 there was no information to the public due to exceedance of the alert threshold for SO_2 (one hour average 500 µg/m^3).

Table 9.1. Annual statistics for SO_2 in 2011. All parameters are calculated based on hourly averages. The detection limit for the monitors is a few µg/m^3, which makes the average and median values encumbered with high relative uncertainties.

Unit: µg/m^3	Number of results	Average year	Average winter	Median	98-percentile	Max. Hour	4th highest diurnal mean
Traffic							
Copenhagen/1103	7854	2,9	2,6	2,5	9,5	24,3	8,8
Aalborg/8151	7956	1,6	2,2	1,3	7,2	20,0	5,6
Limit values	>7467	20	20			350	125

9.2 Trends

The long term trends for sulphur dioxide are shown in Figure 9.1. Since the beginning of the 1980'ties the annual concentrations have decreased with more than a factor of five due to effective national and international regulations of the emissions. The emission reductions are due to use of effective cleaning technologies in combination with decrease of the sulphur content in fuel.

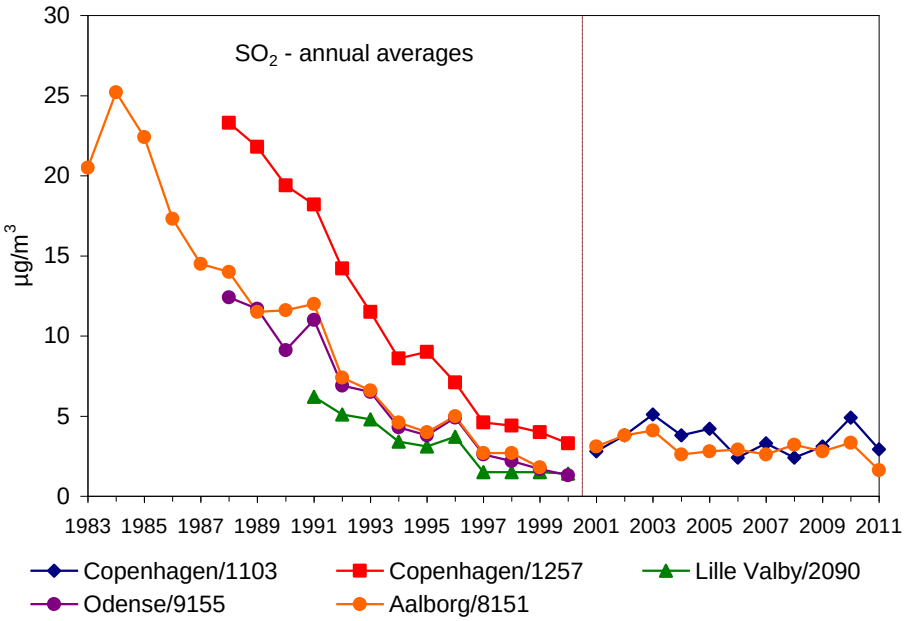


Figure 9.1. Annual averages for SO_2. Until 2001 the results were obtained using KOH impregnated filters for collection of SO_2. These measurements ceased in 2000. After 2000 the SO_2 measurements have been carried out using SO_2-monitors in order to monitor episodic results. The detection limit for the monitors is a few µg/m^3, which makes the average and median values encumbered with high relative uncertainties. The shift in level from 2000 to 2001 is due to shift of the methods.

10 Polyaromatic Hydrocarbons (PAHs)

Following the EU Directive 2004/107/EC (EC, 2005), measurement of atmospheric concentrations of benzo[a]pyrene and other particle bound PAHs have been introduced in the air quality monitoring programme starting from June 2007. The target value for benzo[a]pyrene in ambient air is set to 1 ng/m^3 averaged over a calendar year (EC, 2005). Benzo[a]pyrene is used as a marker for the carcinogenicity of PAHs.

Particulate matter (PM_{10} fraction) is collected at the urban station of H.C. Andersen Boulevard (Copenhagen/1103) in Copenhagen by high volume sampling (HVS) at a flow rate of 0.5 m^3 min^{-1} over a period of 24 hours, for an average total volume of 700 m^3.The filters are kept frozen until analysis. A quarter of a filter is extracted with dichloromethane and cleaned up on silica. Before extraction, the filters are spiked with deuterium-labelled PAH. Analysis of the extracts is carried out by gas chromatography-mass spectrometry (GC-MS). Concentrations of individual PAH in samples are corrected for recovery of a deuterium-labelled PAH standard with the closest molecular weight. A total of 18 PAH's are analyzed in the method.

10.1 Annual Statistics

The average concentration of benzo[a]pyrene measured in Copenhagen was 0.21 ng/m^3 in 2011. The minimum, maximum and average monthly concentrations of benzo[a]pyrene are summarized in Table 10.1.

The average annual concentrations of the other five PAH listed as relevant in the EU Directive were the following: benzo[a]anthracene, 0.20 ng/m^3; benzo[b]fluoranthene, 0.35 ng/m^3; benzo[j+k]fluoranthenes, 0.29 ng/m^3; indeno[1,2,3-cd]pyrene, 0.23 ng/m^3; dibenzo[a,h]anthracene 0.10 ng/m^3.

The seasonal trends in PAH concentrations are summarized in Figure 10.1. As expected, the atmospheric concentrations are low during summer months, while concentrations increase in winter months due to higher emissions and less photochemical degradation of the compounds. It can be concluded that the target value for benzo[a]pyrene on 1 ng/m^3 was not exceeded in 2011.

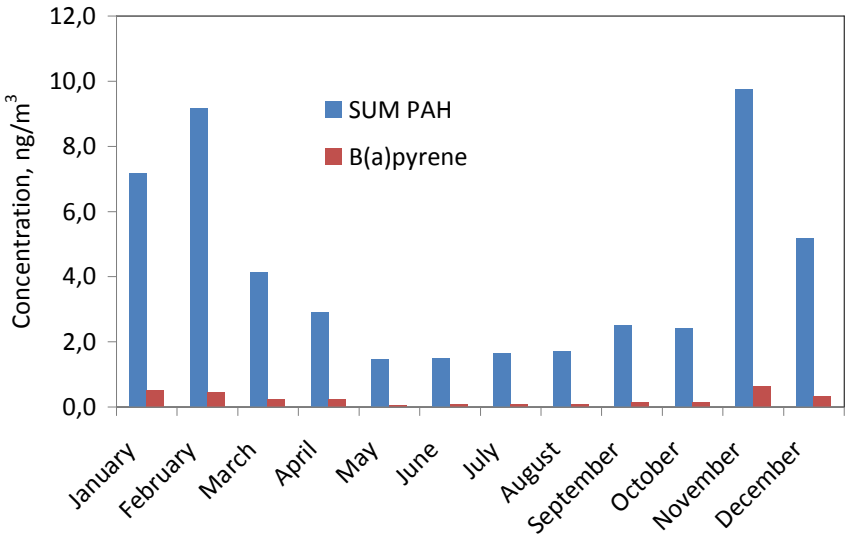


Figure 10.1. Monthly average concentrations in 2011 of benzo[a]pyrene and the sum of the analysed PAH.

Table 10.1. Daily minimum, maximum and average monthly concentrations (ng/m^3) of benzo[a]pyrene during 2011.

Month	Minimum conc.	Maximum conc.	Average conc.
January	0,08	1,39	0,49
February	0,06	1,74	0,44
March	0,08	0,41	0,23
April	0,06	1,68	0,24
May	0,03	0,16	0,06
June	0,03	0,25	0,07
July	0,02	0,17	0,07
August	0,02	0,18	0,06
September	0,06	0,29	0,14
October	0,07	0,33	0,13
November	0,16	1,47	0,63
December	0,06	1,04	0,33
Annual	0,02	1,74	0,21

10.2 Trends

The annual averages of benzo[a]pyrene since 2008 are shown in figure 10.2. A decrease in the annual averages of benzo[a]pyrene is observed, however, longer time series are needed in order to show whether or not this tendency is persistent.

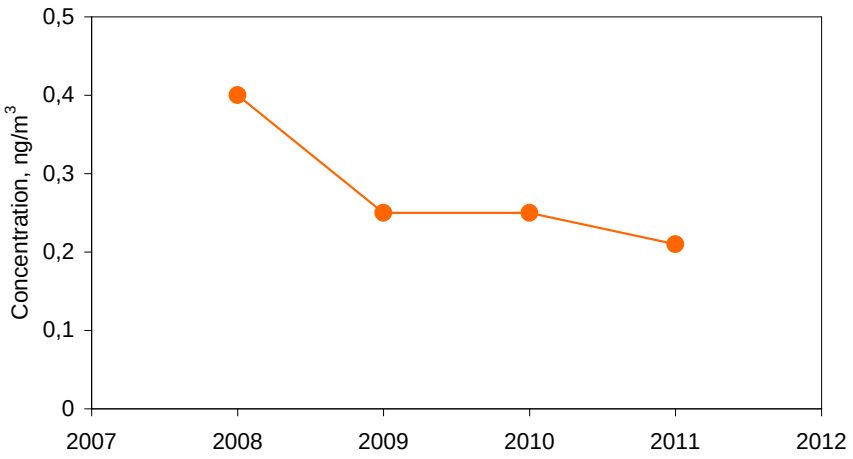


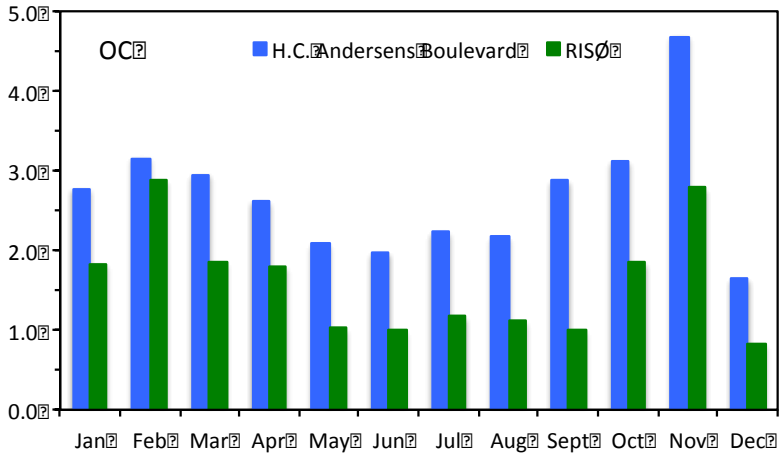
Figure 10.2. Annaul average concentrations of benzo[a]pyrene at H.C. Andersens Boulevard (Copenhagen/1103).

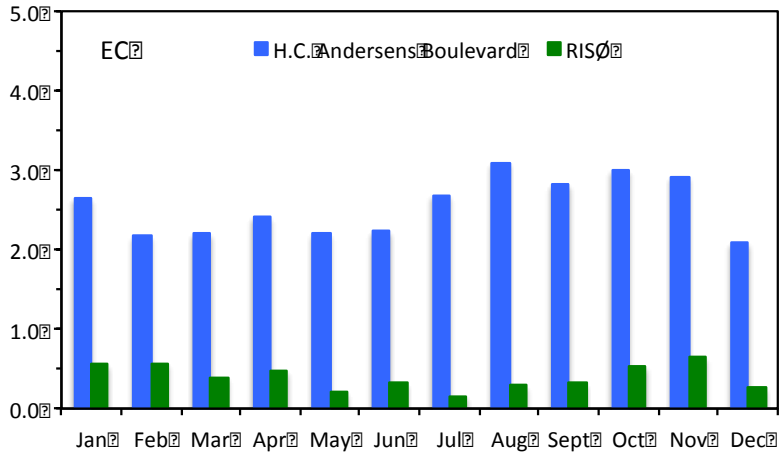
11 Organic carbon and elemental carbon

Ambient concentrations of Organic Carbon (OC) and Elemental Carbon (EC) are measured on the kerb-side station H.C. Andersens Boulevard/1103 and the semi-rural background station Risø. Particulate matter $PM_{2.5}$ is sampled on tandem filters, i.e. quartz-behind-quartz to correct for positive artifacts. The filters are analyzed for OC and EC by a thermal/optical method according to the EUSAAR2 protocol.

11.1 Annual statistics

The measurements of Organic carbon (OC) and elemental carbon (EC) were initiated in 2009.





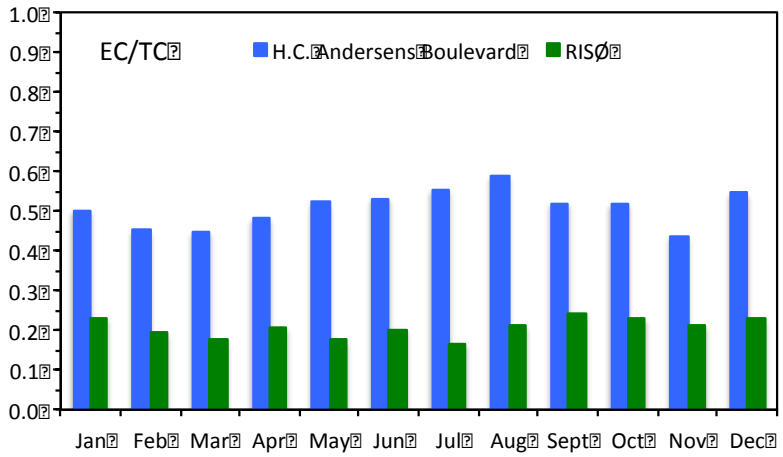


Figure 11.1. Elemental carbon (EC), organic carbon (OC) and the ratio between elemental carbon and total carbon (EC/TC) at H.C. Andersens Boulevard (Copenhagen/1103) and in semi rural background at Lille Valby/Risø in 2011.

The ratio of EC to total carbon (TC), and the absolute concentrations in rural background and the kerb-side station in Copenhagen/1103 differed markedly: Annually EC makes up about 50% of the total particulate carbon at kerb-side compared to about 20% in the urban background (Figure 11.1).

Table 11.1. Annual statistics for OC in 2011. The values are based on daily averages at H. C. Andersens Boulevard (Copenhagen/1103) and in semi-rural background (Risø)

Concentration µg/m^3	Number of results	OC, average	90% percentile
Copenhagen/ 1103	342	2.56	4.60
Lille Valby/ 2090	353	1.53	2.95

Table 11.2. Annual statistics for EC in 2011. The values are based on daily averages at H. C. Andersens Boulevard (Copenhagen/1103) and in semi-rural background (Risø)

Concentration µg/m^3	Number of results	EC, average	90% percentile
Copenhagen 1103	342	2.43	3.63
Lille Valby/ 2090	353	0.38	0.88

A clear seasonal pattern was observed for EC and OC at the rural background with minimum summer concentrations and higher winter concentrations, and consequently only little seasonal variation in the EC/TC ratio. At the kerb-side station, EC/TC showed a maximum ratio in late summer, corresponding to a lower OC and higher EC concentrations in that period.

12 Chemical composition of $PM_{2.5}$

In addition to the measurements of elemental and organic compound, there has also been carried out measurements of the main inorganic compounds in $PM_{2.5}$ (NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-}) at H.C. Andersens Boulevard (HCAB, Copenhagen/1103) and Risø. These measurements are carried out on the basis of the air quality directive from 2008 (EC, 2008). These measurements are carried out by chemical analysis of the daily $PM_{2.5}$ particle filters sampled using the SM200 monitors.

Examples on the daily variations of the concentrations are shown in Figure 12.1 together with the variation of $PM_{2.5}$. For Na^+ the concentrations are similar at HCAB and Risø due to long range transport of sea salt. For the winter months Na^+ are higher at HCAB than Risø due to winter salting of the roads in Copenhagen. The variations of Cl^- follow the variations of Na^+ because the main source is sea salt and winter salting. Mg^{2+} originates only from sea salt and there are therefore similar concentrations at the two stations throughout the year. SO_4^{2-} and NH_4^+ originate mainly from long range transport and there are therefore only minor differences between the two stations (Figure 12.1). This is also the case for NO_3^- and K^+. Ca^{2+} is in general higher at HCAB than at Risø. This is due to road dust at HCAB since asphalt contains large quantities of calcium.

The annual contributions to $PM_{2.5}$ of the different compounds are shown in Figure 12.2. As for the daily variations the annual average concentrations of NH_4^+, Na^+, K^+, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-} are very similar at the two stations. The main variations between the two stations are for EC, OM and Ca^{2+} where the concentrations are higher at the street station compared to the rural background station. This is mainly due to emissions of these compounds from the traffic in Copenhagen. The unknown mass is roughly of the same size at the two stations. The unknown mass is water attached to the particles, dust (to an example SiO_2), heavy metals and other trace constituents.

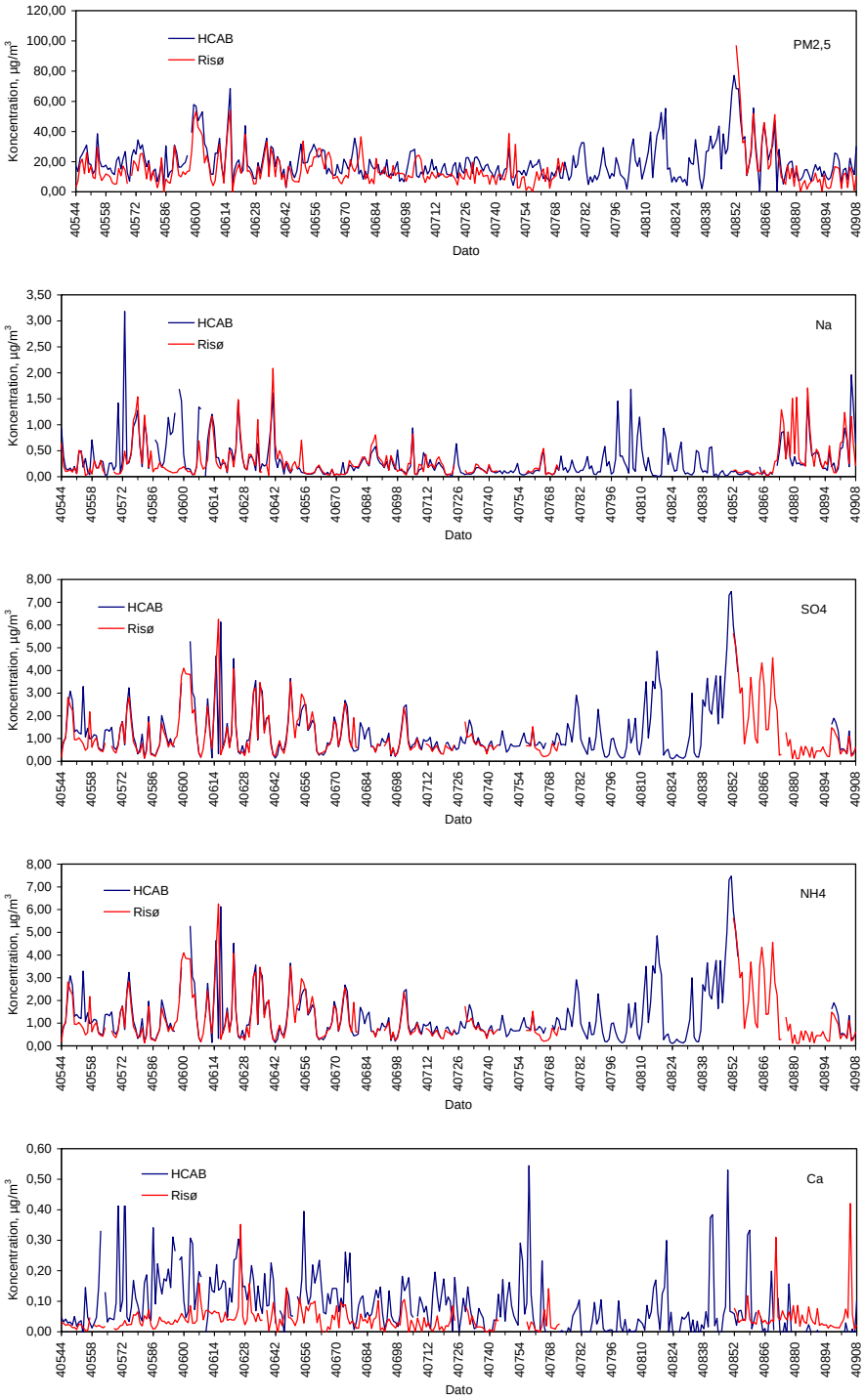


Figure 12.1 Daily variations of the concentrations of $PM_{2.5}$, Na^{+}, SO_4^{2-}, NH_4^{+} og Ca^{2+} at H.C. Andersens Boulevard (HCAB, Copenhagen/1103) and Risø.

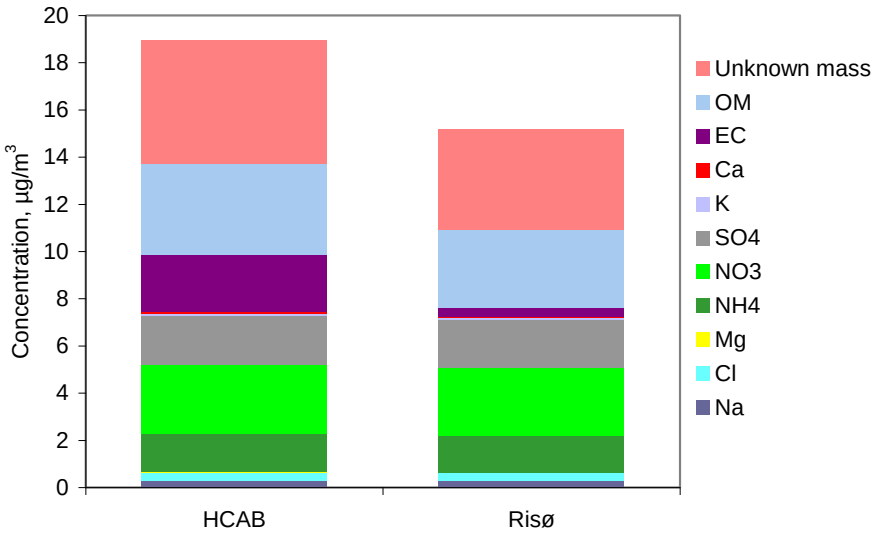


Figure 12.2 Annual average contributions to the chemical composition of $PM_{2.5}$ at H.C. Andersens Boulevard (HCAB, Copenhagen/1103) and Risø in 2011. Organic matter (OM) has been estimated from the measured concentrations of OC by multiplication of OC with a factor of 1.5 and 2.1 at HCAB and Risø, respectively (Turpin and Lim, 2001). This is in order to account for the contribution of hydrogen, oxygen, nitrogen etc. to the mass of the organic compounds.

13 Ozone precursors

Measurements of volatile organic compounds in urban background, which may act as ozone precursors, were initiated in 2009. Ambient air is sampled as 24-hour averages on adsorbent tubes packed with Carbopack X and analysed using Thermal Desorption Gas Chromatography Mass Spectrometry. The major ozone precursors are the aromatic compounds: benzene, toluene, ethylbenzene, xylenes and trimethylbenzenes (TMB), which are also measured at the kerb-side stations in Copenhagen (1103 and 1257), and the C_5-C_7 alkanes: pentane, 2-methylpentane hexane and heptane. The more reactive unsaturated compounds are less abundant.

13.1 Annual statistics

The urban background concentration of the major ozone precursors benzene and toluene are 51% and 44% of the corresponding concentrations at the kerb-side station 1257, respectively. The urban background toluene/benzene ratio is somewhat smaller than at the traffic dominated kerb-side stations, i.e. 2.5 versus 2.9 (1257) and 2.8 (1103). This reflects different sources to benzene and toluene, and a faster atmospheric decomposition of toluene.

Table 12.1. Annual statistics for selected ozone precursors in urban background in Copenhagen (1259) based on daily average concentrations at 1 atm. and 293 K.

Concentration µg/m^3	Number of results	Average concentration	90% Percentile
1-Pentene	296	0.05	0.07
n-Pentane	307	0.62	1.18
Trans-2-pentene	258	0.02	0.04
Isoprene	301	0.05	0.10
2-Methylpentane	306	0.39	0.65
n-Hexane	307	0.19	0.33
Benzene	307	0.64	1.25
n-Heptane	307	0.24	0.42
2,2,2-Trimethylpentane	307	0.09	0.15
Toluene	307	1.61	2.99
n-Octane	303	0.06	0.10
Ethylbenzene	307	0.27	0.46
m,p-Xylene	307	0.37	0.68
o-Xylene	307	0.29	0.51
1,3,5-Trimethylbenzene	300	0.06	0.11
1,2,4-Trimethylbenzene	300	0.23	0.43
1,2,3-Trimethylbenzene	307	0.06	0.11
Σ		5.25	8.74

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Appendix 1

Pollutants measured in the LMP Network

NO and partly NO_2 are formed by combustion at high temperatures. The main sources are power plants and traffic. At the street stations the traffic is the main source. The application of catalytic converter in the exhaust reduces the emission considerably. NO is relatively harmless, but NO_2 can cause respiratory problems.

Most of the NO_2 in the urban atmosphere is produced by oxidation of nitrogen monoxide (NO) by ozone (O_3). The reaction will take place immediately, if sufficient O_3 is present. O_3 is often the limiting component for a complete oxidation in the street canyons, but practically all NO is oxidised at the urban background and rural stations. Within a few hours the NO_2 is further oxidised to nitrate and/or nitric acid, which may cause acid precipitation and eutrofication. NO_2 is a toxic gas, which may cause respiratory problems. There are limit values for the allowed concentration of NO_2 in the atmosphere.

O_3 is formed by photochemical reactions (i.e. by the influence of sunlight) between nitrogen oxides and volatile organic compounds (VOC's). The VOC's can be of natural and anthropogenic origin. The major part of the O_3 measured in Denmark originates from sources outside the country. Usually the highest concentrations are found at rural and urban background sites. O_3 is removed by NO at street level. O_3 is a toxic gas, which may cause respiratory problems and damage on crops and forests. There are so-called target values for the concentration of O_3 in the atmosphere.

The main source of CO in urban air is petrol-fuelled cars. The CO is formed due to incomplete combustion. The application of catalytic converter in the exhaust reduces the emission considerably. CO is only slowly removed from the atmosphere. CO is a toxic gas that may prevent the uptake of oxygen in the blood. There are limit values for the allowed concentration of CO in the atmosphere.

Benzene is present in petrol. It may also be formed in engines due to incomplete combustion. Since 1994 the benzene content in petrol has been reduced by up to a factor of 5. The concentration in the atmosphere has been reduced correspondingly. Benzene is a carcinogenic gas. There is a limit value for the average content in the atmosphere.

Many different VOC's are present in the air. Several of these are emitted by incomplete combustion in e.g. engines and wood burning stoves. Several of the VOC's are carcinogenic. A "target value" is implemented through an EU Council Directive in 2004 for Benzo(a)-pyrene as indicator for PAH (Polycyclic Aromatic Hydrocarbones). Of the VOC's only benzene, toluene and xylenes are measured routinely in LMP IV at present.

The main sources for PM_{10} and $PM_{2.5}$ are combustion and resuspended dust. PM are also produced by chemical reactions in the atmosphere e.g. oxidation of nitrogen dioxide, sulphur dioxide and VOC. The submicron particles, which are formed by combustion and chemical reactions in the atmosphere, are suspected to be the most harmful for the health. There are still a lack of knowledge about the connection between health effects and particle size. Limit values for the PM_{10} concentration in the atmosphere are implemented at present. The limit values are under revision and will include $PM_{2.5}$. The limit values will be currently reviewed when better knowledge about the adverse health effects of fine particles influence on health is obtained.

PM_{10} and $PM_{2.5}$ is measured using two different methods in the LMP program:

- The particles are collected on filters in 24^{h} intervals. The mass on the filters is determined by measurements of β-absorption in the dust. This method is considered to be equivalent to the reference method (EN 12341:1999 and EN14907:2005).
- The particles are collected on a "tapered oscillating microbalance" (TEOM) and heated to 50°C. During heating volatile compounds may evaporate. The loss will be most pronounced for "secondary aerosols" containing ammonium nitrate.

There are a number of different HM's in the atmosphere. They are emitted from e.g. coal and oil fired power plants, waste incinerators and industries. HM's may also be emitted from traffic due to wear on engines, tires and brake pads. Several HM's are toxic even in low concentrations and a few also carcinogenic. A limit value is implemented for lead. Target values are values are implemented for arsenic, cadmium, nickel and mercury. WHO has proposed guideline values for the toxic non-carcinogenic and estimated life time risks for the carcinogenic HM's.

Sulphur dioxide (SO_2) is formed by burning of fossil fuel and biomass. The SO_2 is oxidised in the atmosphere to particulate sulphuric acid and sulphate. The conversion time depends strongly on the temperature and humidity in the air. It is typically of the order of one day. Sulphuric acid contributes to "acid rain" and the deposition of sulphate causes damage to sensitive ecosystems. During the last 20 years the reduction of sulphur in fossil fuel and improved flue gas cleaning has reduced the concentration of SO_2 with one order of magnitude. SO_2 may cause respiratory problems. There are limit values for the allowed concentration of SO_2 in the atmosphere.

THE DANISH AIR QUALITY MONITORING PROGRAMME

Annual Summary for 2011

The air quality in Danish cities has been monitored continuously since 1982 within the Danish Air Quality Monitoring network. The aim is to follow the concentration levels of toxic pollutants in the urban atmosphere and to provide the necessary knowledge to assess the trends, to perform source apportionment, and to understand the governing processes that determine the level of air pollution in Denmark. In 2011 the air quality was measured in four Danish cities and at two background sites. In addition model calculations were carried out to supplement the measurements. At one street station (H.C. Andersens Boulevard) in Copenhagen NO_2 was found in concentrations above EU limit values while NO_2 levels in Odense, Aarhus and Aalborg were below the limit value. Model calculations indicate exceedances of NO_2 limit values at several streets in Copenhagen. Annual averages of PM_{10} and $PM_{2.5}$ were below limit values at all stations. However, concentrations levels in Copenhagen exceeded the daily limit value for PM_{10}. Winter salting of roads was one of the main reasons for this exceedance. The concentrations for most pollutants have been strongly decreasing during the last decades, however, only a slight decrease has been observed for NO_2 and O_3.

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