THE DANISH AIR QUALITY MONITORING PROGRAMME

Annual Summary for 2012

Scientific Report from DCE – Danish Centre for Environment and Energy No. 67 2013

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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 2012 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. The concentrations for most pollutants have been decreasing during the last decades.

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Summary and Conclusion

This report presents the result from the Danish Air Quality Monitoring Programme in 2012. 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 2012 the daily limit value for PM_{10} were not exceeded at any station in the measuring network including stations where exceedances previously have occurred (e.g. the two traffic stations in Copenhagen). There were likewise no exceedances of the annual limit values for PM_{10} (40 $\mu g/m^3$) and $PM_{2.5}$ (25 $\mu g/m^3$ 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 a factor of about 2.5 and 5 higher than in urban and rural background, respectively. A significant reduction in particle number has been observed since 2002.

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

The annual limit value for NO_2 (40 $\mu g/m^3$) 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 2011 to 2012 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. The background for these elevated concentrations are currently investigated in an on-going project for the Danish Environmental Protection Agency.

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 2012. 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 level around the average for the 31 selected streets in Aalborg.

The ozone levels were in 2012 almost the same as in 2011 at all rural and urban background stations and no clear trend was thus observed. The information threshold at 180 $\mu g/m^3$ was exceeded once in 2012. The target value for the max 8 hours ozone concentration on 120 $\mu g/m^3$ 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 0.25 ng/m^3. The target value for benzo[a] pyrene (1 ng/m^3) was not exceeded in 2012.

For the second 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), in Danish (http://dce.au.dk/myndigheder/luft/).

Danish summary - Dansk resumé

Rapporten præsenterer resultater for 2012 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.

De væsentligste konklusioner fra overvågningsprogrammet i 2012 er følgende:

- I 2012 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 2011 til 2012, mens der på de øvrige målestationer var stort set uændrede koncentrationer. På gademålestationen ved H.C. Andersens Boulevard er der fortsat en forhøjet koncentration af NO_2. Årsagerne til den forøgede koncentration på H.C. Andersens Boulevard er ved at blive undersøgt i et igangværende projekt for Miljøstyrelsen.
- Modelberegninger indikerer, at grænseværdien i 2012 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 Køben-

havn 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 2012 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}. Ej heller blev antallet af overskridelser af den daglige middelværdi for PM_{10} (50 µg/m^3 må ikke overskrides mere end 35 gange årligt) overskredet ved nogen målestation i måleprogrammet.
- 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 µg/m^3 svarende til et estimeret saltindhold (NaCl) på omkring 4,0 µg/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 2012 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 overskredet én gang i 2012.
- 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 0,25 ng/m^3. Målværdien på 1 ng/m^3 var således ikke overskredet i 2012.
- For fjerde 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 anden gang præsenteres resultater for bestemmelse af det kemiske indhold i $PM_{2.5}$ ved gademålestationen ved H. C. Andersens Boulevard og ved landbaggrundsmålestation 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 skyldes, 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 Energy (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 , in Danish (http://dce.au.dk/myndigheder/luft/). 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 sec-

ond 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.

- Five low volume samplers (LVS) for gravimetric determination of particle mass based on the reference method were introduced into the regular measuring programme and installed at four stations in the network (HCAB PM_{10} and $PM_{2.5}$; HCØ $PM_{2.5}$; Jagtvej PM_{10} ; Risø $PM_{2.5}$) during August and September 2012 to replace some of the older SM200 instruments that needed to be renewed. At Jagtvej $PM_{2.5}$ a low volume sampler was running for three months (June, July and August) for control of a SM200 and these measurements were also used for the reporting the 2012 PM data.

In the following chapters the results from measurements and model calculations for 2012 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, in Danish (http://dce.au.dk/myndigheder/luft/).

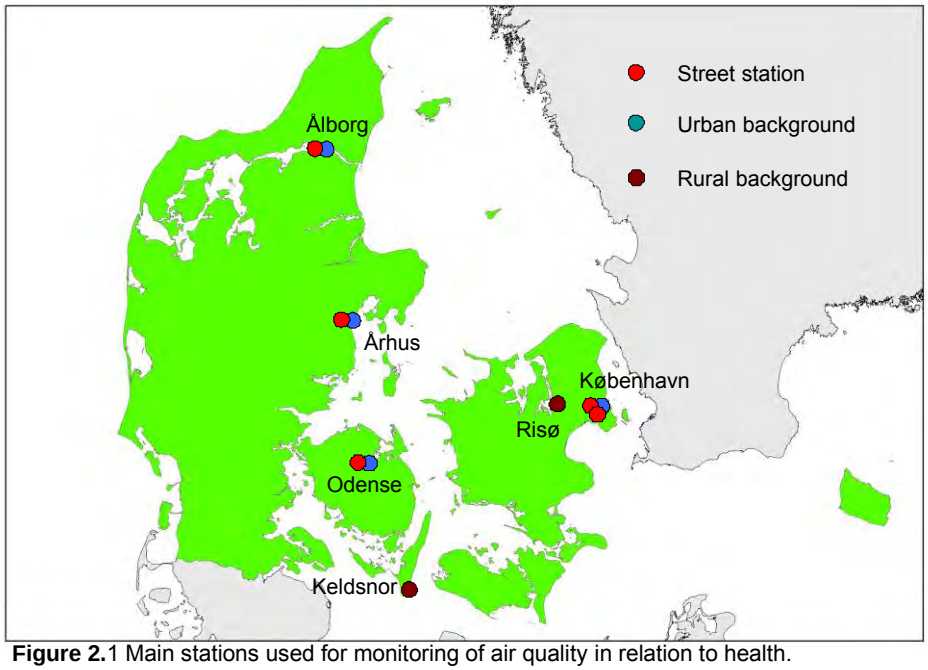


Figure 2.1 Main stations used for monitoring of air quality in relation to health.

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 2012:

- Nitrogen oxides (NO, NO_2 and NO_x (= NO + NO_2)) were measured at all stations.
- Particle mass (PM_{10} and $PM_{2.5}$) were measured at all stations except Odense/9159. PM was at these stations measured by means of β-absorption as 24 h averages.
- In addition to the β-measurements, five low volume samplers (LVS) for gravimetric determination of particle mass based on the reference method were introduced into the network and installed at four stations (HCAB PM_{10} and $PM_{2.5}$; HCØ $PM_{2.5}$; Jagtvej PM_{10} and $PM_{2.5}$; Risø $PM_{2.5}$) during the summer 2012.
- 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} and $PM_{2.5}$ was measured at both Copenhagen/1103 and Risø by means of TEOM that measures on a half hourly basis making it possible to resolve the diurnal variation. 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 low volume sampling (gravimetric method) 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 analysed 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; Ketzel et al., 2012). 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 de-

scribed 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 assessments 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://envs.au.dk/videnudveksling/-luft/model/airgis/

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 2012 for nitrogen dioxide and nitrogen oxides are shown in Table 3.1 and 3.2. There was only exceedance of the annual limit value for NO_2 (EC, 2008) at H.C. Andersens Boulevard (Copenhagen/1103). There were no exceedances of the hourly limit value for NO_2 on 200 µg/m^3. This value must not be exceeded more than 18 times in a calendar year (see 19th highest hourly concentration in Table 3.1). In 2012 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 2012. All parameters are based on hourly averages.

Unit: µg/m^3	Number	Average	Median	98. percentile	19. highest
Traffic:					
Copenhagen/1257	7981	38	33	96	121
Copenhagen/1103	7845	55*)	51	126	150
Aarhus/6153	7577	35	31	86	113
Odense/9155	7233	26	20	84	117
Aalborg/8151	8003	30	25	90	121
Urban Background:					
Copenhagen/1259	7864	17	13	50	69
Aarhus/6159	6951	17	14	57	84
Odense/9159	7922	13	10	43	62
Aalborg/8159	8270	13	10	48	77
Rural:					
Risø	7922	9	6	37	59
Keldsnor/9055	7364	8	8	32	49
Limit value 2010	>7455	40			200

*) Limit value exceeded

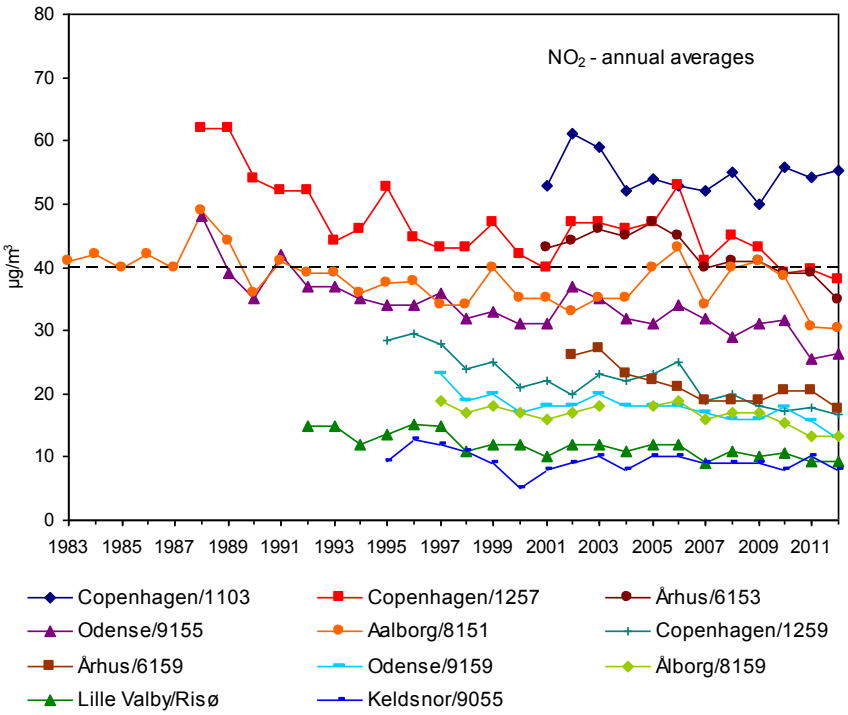
Table 3.2. Nitrogen oxides (NO_x = NO + NO_2) in 2012. All parameters are based on hourly averages.

Unit: µg/m^3	Number	Average	Median	98. percentile	19. highest
Traffic:					
Copenhagen/1257	7981	83	62	284	465
Copenhagen/1103	7845	145	116	465	633
Aarhus/6153	7577	77	60	265	515
Odense/9155	7233	60	33	303	526
Aalborg/8151	8003	87	58	350	532
Urban Background:					
Copenhagen/1259	7864	20	15	75	147
Aarhus/6159	6951	24	16	106	262
Odense/9159	7922	17	12	67	195
Aalborg/8159	8270	19	12	92	254
Rural:					
Risø	7922	11	7	46	90
Keldsnor/9055	7364	9	6	39	68

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 emit 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.



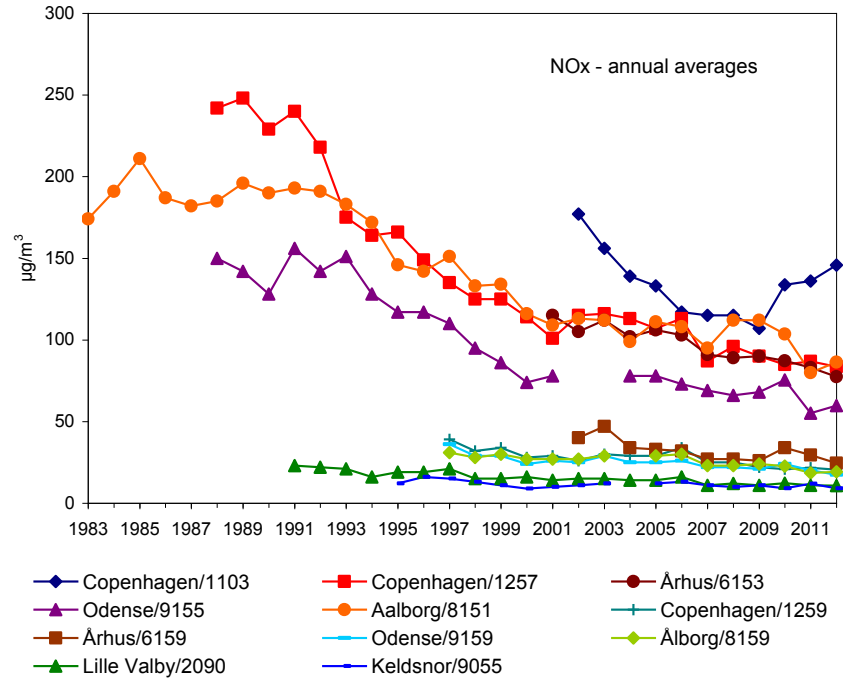


Figure 3.1 The graphs show the time series for the annual average values of NO_2 and NO_x. The dashed line on the upper graph shows the limit value that entered into force in 2010. Previous results from Copenhagen/1103 can be found at the homepage of Copenhagen Environmental Protection Agency (www.Miljoe.kk.dk)

Both NO_2 and NO_x were higher in 2010-2012 compared to 2009 at the street station H.C. Andersens Boulevard (Copenhagen/1103). At all other street stations the levels in 2010-2012 were equal to or lower than observed in 2009. In an on-going project for the Danish Environmental Protection Agency DCE are currently investigating the reasons behind this difference between H.C. Andersens Boulevard and the other street stations. Results from this project will be published by DCE during autumn 2013.

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 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 5,400 and 67,600 vehicles/day in Copenhagen and between 2,700 and 28,600 vehicles/day in Aalborg. On average traffic volumes are 1% lower in Aalborg and about 7% lower in Copenhagen compared to 2011. Based on information from Copenhagen and Aalborg municipalities the ADT and vehicle distribution on all streets have been updated with the most recent available traffic data. Last year the vehicle distribution for Copenhagen was based on the percentage of heavy-duty vehicles. Therefore, assumptions about the average percentage of vans, and the average distribution of heavy-duty on trucks (<32, >32t) and buses had to be made. This year the vehicle distribution (passenger cars, vans, type of trucks, type of buses) have been obtained based on manual counts.

Furthermore, manual traffic counts were for the first time available at the street segments in front of the measurement stations of H.C. Andersens Boulevard and Jagtvej. Compared to previous assumptions for H.C. Andersens Boulevard average daily traffic is about 8% higher compared to 2011, and the percentage of vans is higher and the percentage of heavy-duty vehicles is lower. Compared to previous assumptions for Jagtvej average daily traffic is about 26% lower compared to 2011, and the percentage of vans is higher and the percentage of heavy-duty vehicles is slightly higher.

Travel speeds have not been changed for any of the streets. However, analysis of travel speed data based on GPS measurements from a new national database of the Danish Road Directorate (SpeedMap) show that travel speeds are lower compared to previous assumptions for H.C. Andersens Boulevard and Jagtvej. Therefore, it is likely that lower travel speeds can be expected for all other roads. The next assessment for 2013 will include travel speed data for all 99 streets based on SpeedMap.

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 $\mu g/m^3$. The number of exceedances is also given. An exceedance is registered if the calculated

concentration is higher than 40.5 µg/m^3 since 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.

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, Ketzel et al. 2012).

Calculations with the full model chain of DEHM-UBM-OSPM have been compared to measured NO_2 concentrations in 2012 for the fixed street monitoring stations in Copenhagen and Aalborg. The model system predicts annual NO_2 concentrations within 2% for Jagtvej (Copenhagen), -10% for H.C. Andersens Boulevard (Copenhagen), -11% for Vesterbro (Aalborg). Calculations with the coupled DEHM-UBM models have also been compared to the fixed background monitoring stations in Copenhagen and Aalborg. Here the model system predicts annual NO_2 concentrations within 13% for H.C. Ørsted Institute (Copenhagen) and -7% Østerbro (Aalborg).

The comparison of the modelled NO_2 concentrations presented in this report for 2012 with measurements at the 3 street locations and 2 background locations in Copenhagen and Aalborg shows a good agreement within ± 15%.

3.3.1 Model calculations for Copenhagen

The annual mean concentrations of NO_2 for Copenhagen in 2012 are shown in Figure 3.2 (bar chart) and Figure 3.3 (map).

In 2012 the limit value for the annual mean concentration was exceeded in 19 out of the 99 selected streets in Copenhagen (Figure 3.2). In 2011 the number of streets exceeding the limit value was 17 out of 99.

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. The total average of NO_2 concentrations at all 99 streets has decreased very little while the average of the concentrations at the 20 streets with the highest concentration has increased slightly leading to a small increase in the number of exceedances, both changes below 1 µg/m^3 in difference.

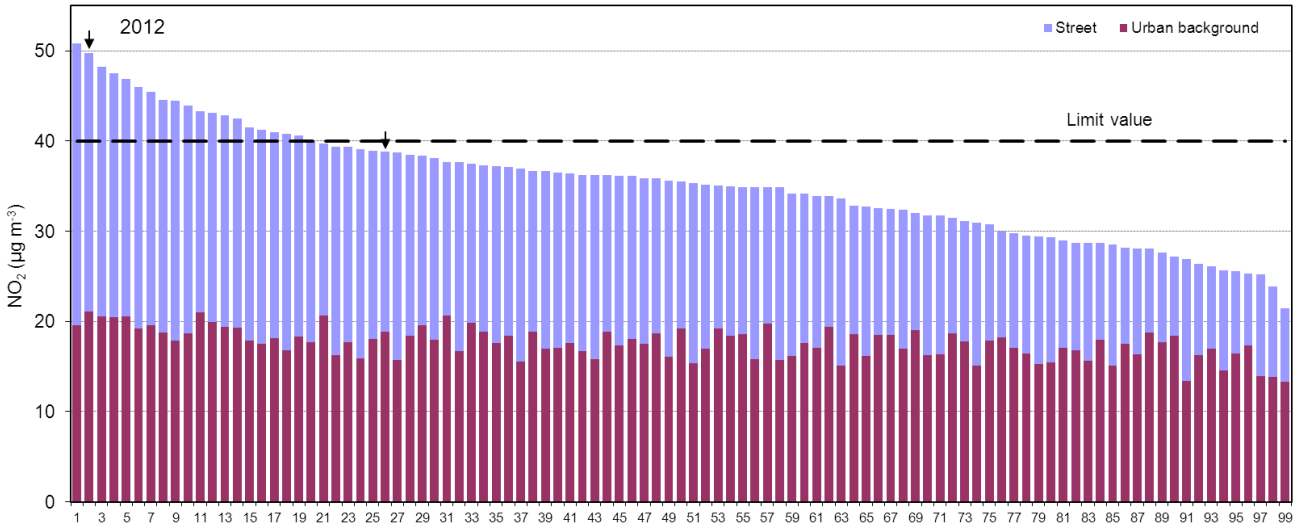


Figure 3.2 Annual mean concentrations of NO_2 in 2012 for 99 streets in Copenhagen. The contribution from traffic in the street canyons is based on the street canyon model OSPM®. The urban background (dark red colour) is obtained from calculations with the urban background model UBM with input from the 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 11,000 to 67,600 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 (1-99) according to NO_2 levels in 2012 (1 = highest, 99 = 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	Gyldenløvesgade	34	Tagensvej (3)	67	Strandvænget (2)
2*	H.C. Andersens Boulevard (1)	35	Hulgårdsvej (2)	68	Amager Boulevard
3	H.C. Andersens Boulevard (2)	36	Falkoner Alle (2)	69	Jagtvej (2)
4	H.C. Andersens Boulevard (3)	37	Frederikssundsvej (8)	70	Slotsherrensvej (2)
5	Bernstorffsgade (2)	38	Frederikssundsvej (1)	71	Roskildevej (1)
6	Øster Søgade	39	Tagensvej (1)	72	Hillerødgade (3)
7	Nørre Søgade	40	Amagerfælledvej	73	Kalvebod Brygge
8	Ågade	41	Østerbrogade (1)	74	Frederiksborgvej (1)
9	Lyngbyvej (2)	42	Nordre Fasanvej (1)	75	Dag Hammerskjölds Allé
10	Fredensgade	43	Søndre Fasanvej (2)	76	Bülowsvej (2)
11	Stormgade	44	Nordre Fasanvej (3)	77	Folke Bernadottes Allé
12	Hammerichsgade	45	Østerbrogade (4)	78	Peter Bangs Vej (1)
13	Åboulevard (1)	46	Toldbodgade	79	Ålholmvej (2)
14	Åboulevard (3)	47	Gammel Kongevej (1)	80	Slotherrensvej (1)
15	Tomsgårdsvej (2)	48	H.C. Ørsteds Vej (2)	81	Tuborgvej (1)
16	Torvegade	49	Toftegårds Allé (1)	82	Røde Mellemvej (1)
17	Øster Voldgade (1)	50	Øster Voldgade (2)	83	Frederikssundsvej (2)
18	Amagerbrogade (2)	51	Amagerbrogade (1)	84	Vesterfælledvej
19	Vesterbrogade (1)	52	Vesterbrogade (3)	85	Englandsvej (1)
20	Tagensvej (2)	53	Vester Farimagsgade	86	Blegdamsvej
21	Bernstorffsgade (1)	54	Istedgade	87	Strandvejen (2)
22	Jyllingevej (1)	55	Tagensvej (4)	88	Hillerødgade (1)
23	Frederikssundsvej (3)	56	Grøndals Parkvej	89	Godthåbsvej (2)
24	P. Knudsens Gade (2)	57	Nørre Farimagsgade	90	Halmetgade
25	Enghavevej	58	Gammel Køge Landevej (1)	91	Amagerbrogade (3)
26*	Jagtvej (1)	59	Strandvejen (1)	92	Peter Bangs Vej (2)
27	Folehaven (1)	60	Godthåbsvej (3)	93	Bellahøjvej
28	Bredgade	61	Rebildvej	94	Vigerslevvej (2)
29	Gothersgade (1)	62	Ingerslevsgade	95	Frederiksborgvej (2)
30	Scandiagade	63	Frederikssundsvej (5)	96	Artillerivej
31	Vester Voldgade	64	Jagtvej (3)	97	Gammel Køge Landevej (2)
32	Tuborgvej (2)	65	Ålholmvej (1)	98	Røde Mellemvej (2)
33	Nørre Voldgade (2)	66	Nørrebrogade	99	Englandsvej (2)

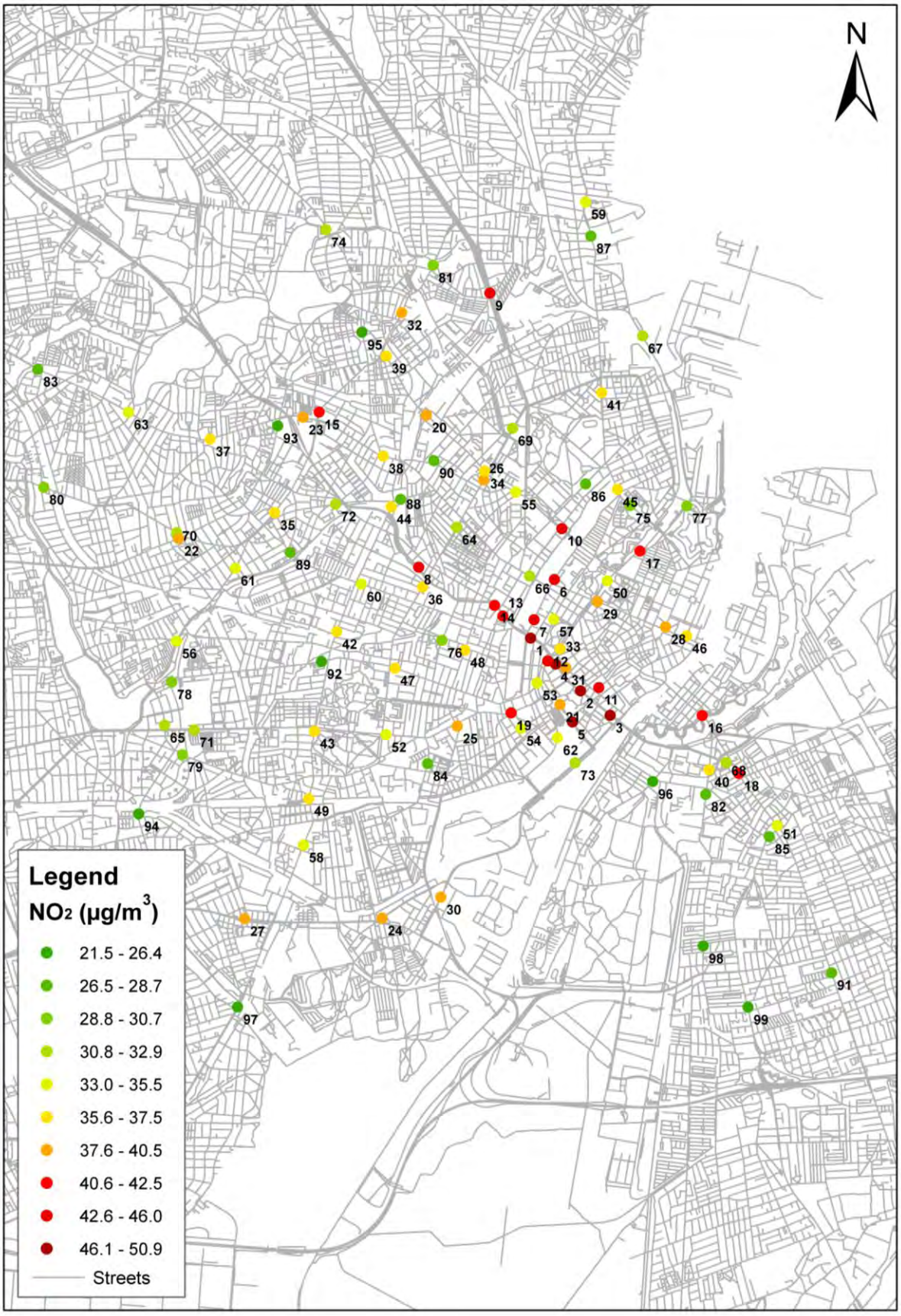


Figure 3.3. Map showing the locations of the selected streets in Copenhagen and the annual mean concentrations of NO_2 for 2012. The contribution from traffic in the street canyons is based on the street canyon model OSPM®. The urban background is obtained from calculations with the urban background 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 the same level in the NO_2 concentrations compared with 2011 for the same reasons given for Copenhagen in the previous section. The average NO_2 concentration at street level has changed by less than 1 µg/m^3 compared to 2011 due to small changes in vehicle fleet and traffic data. A small reduction in the street contribution (Street level minus background concentrations) has been compensated by a slight increase in the modelled urban background levels due to changes in emissions and meteorology.

According to the model calculations the limit value for the annual mean concentration in 2012 was not exceeded at any of the 31 selected streets which was also the case in 2011 (Figure 3.4 and Figure 3.5). The order of the streets has changed slightly due to updated traffic data.

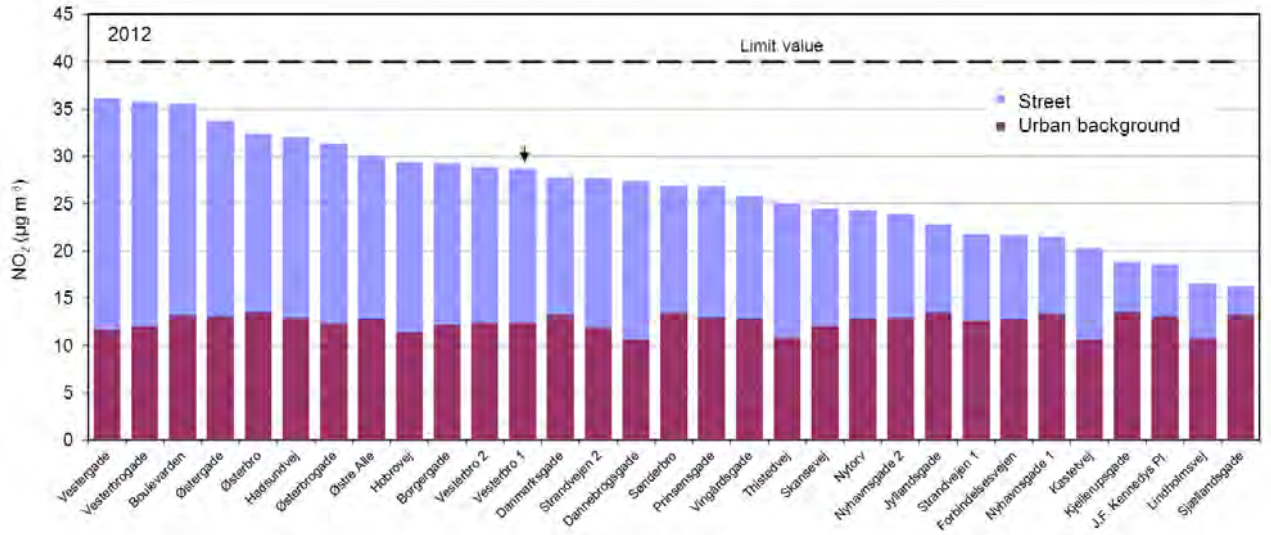


Figure 3.4. Annual mean concentrations of NO_2 in 2012 for 31 streets in Aalborg. The contribution from traffic in the street canyons is based on the street canyon model OSPM®. The urban background (dark red colour) is obtained from calculations with the urban background model UBM with input from the regional scale model DEHM. The value for a street is for the kerb side with the highest annual mean concentration. The arrow indicates the street segment (Vesterbro 1) with the measurement station.

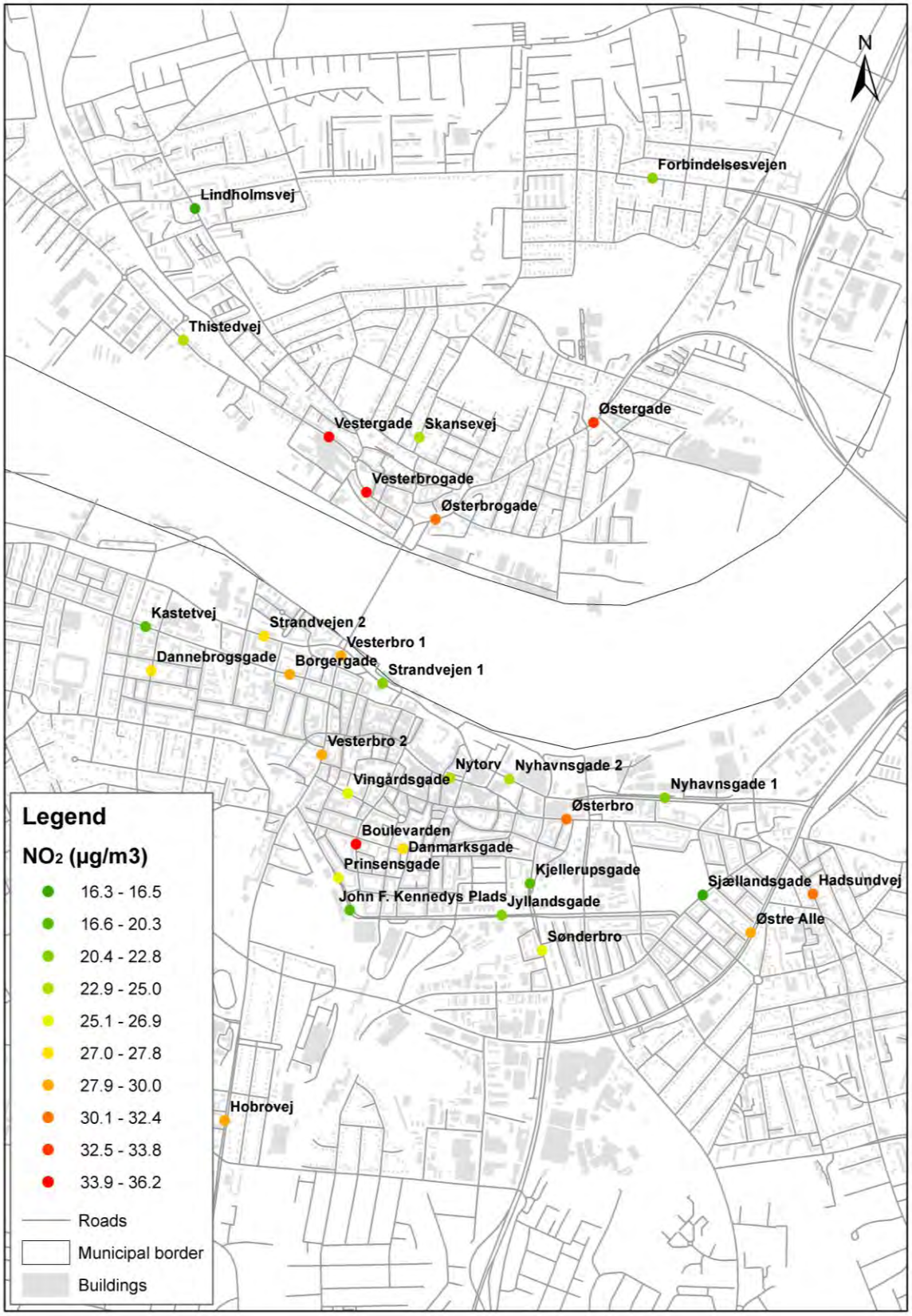


Figure 3.5. Map showing the location of the selected streets in Aalborg and the annual mean concentrations of NO_2 for 2012. The contribution from traffic in the street canyons is based on the street canyon model OSPM®. The urban background is obtained from calculations with the urban background model 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 2012 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 2010-2012 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) was exceeded at five of the stations. However, the long term objective has not entered into force.

In 2012 there was one exceedance of the information threshold (hourly average 180 µg/m^3) and no exceedance of the alert threshold (hourly average 240 µg/m^3) for ozone. The exceedance of the information threshold took place at the rural background station at Risø on the 20th August 2012 with a duration of only one hour. By a mistake no information to the public was given about the exceedance.

Table 4.1. Ozone (O_3) in 2012. 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 that the maximum running eight hour average exceeds 120 µg/m^3.

Unit: µg/m^3	Number of results	Average	Median	Max 8 hours	Days above target value 8 hours	Max 1 hour
Traffic:						
Copenhagen/1259	7603	56	58	143	4	173
Aarhus/6159	7233	52	54	135	1	144
Odense/9159	7735	57	58	151	6	160
Aalborg/8158	7124	55	58	145	2	156
Rural:						
Risø	7941	62	64	93	7	185
Keldsnor/9055	7698	59	61	142	5	157
Traffic						
Copenhagen/1103	7728	32	31	93	0	104
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.

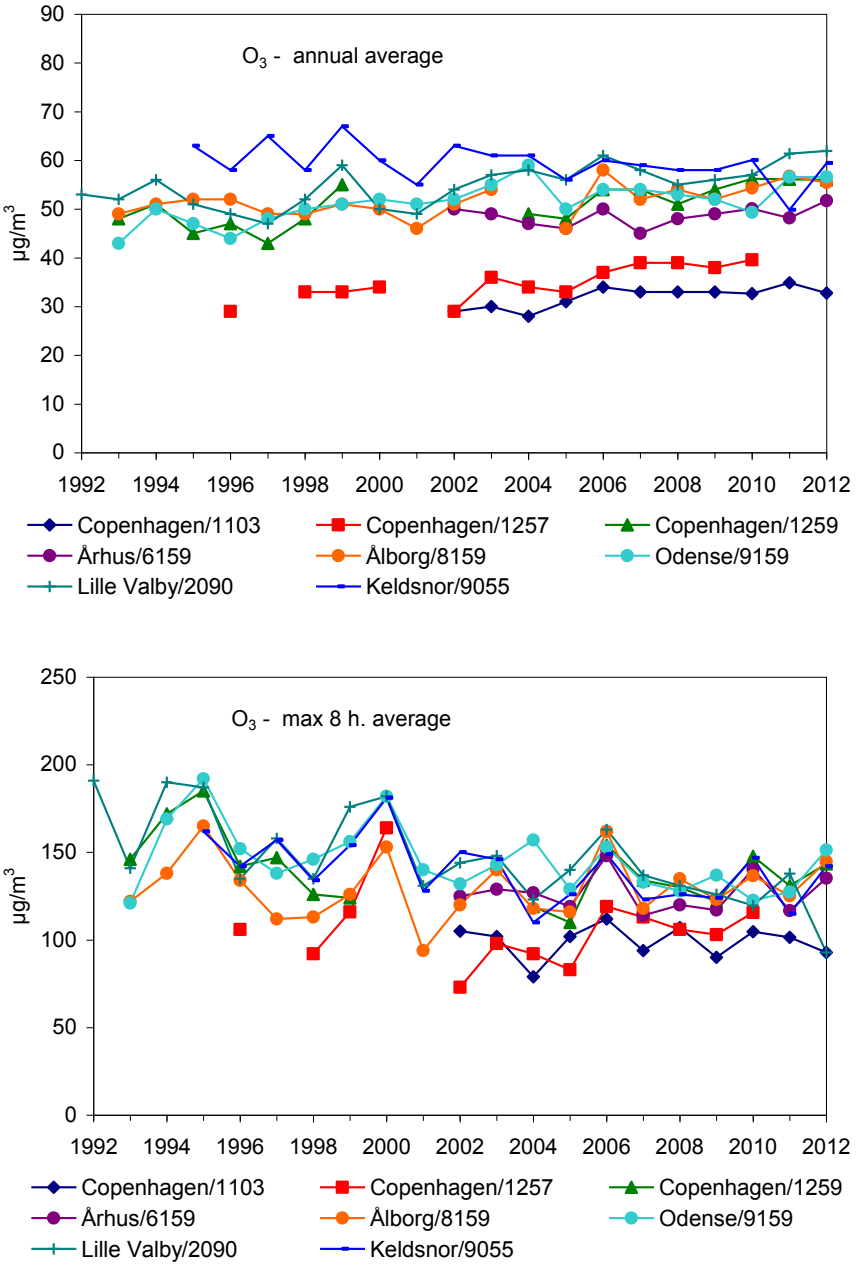


Figure 4.1 Annual average values and the max. 8 hour average value. The latter is calculated as 8 hourly running averages according to the provisions in the EU Directive (EC, 2008). Previous results from Copenhagen/1103 can be found at the Website of the Copenhagen Environmental Protection Agency (www. 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 2012 show that the maximum daily 8 hour mean value of 120 $\mu g/m^3$ was only exceeded up to 6 days during 2012 (Figure 4.3). Similar results were obtained for 2010 and 2011 and hence the target value was not exceeded. However, the long term objective was exceeded at in large parts of Denmark, while no exceedances were observed in northern Jutland and north east Zealand (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 one time in 2012, while the model calculations show that the one hour mean concentration was not exceed 180 $\mu g/m^3$ in 2012 (Figure 4.5). This difference is due to an underestimation of the model calculated ozone concentrations with about 10-20%. One of the main reasons for this discrepancy is most likely that the model does not include emissions of ozone precursors from wild fires that are known to increase episodic ozone concentrations.

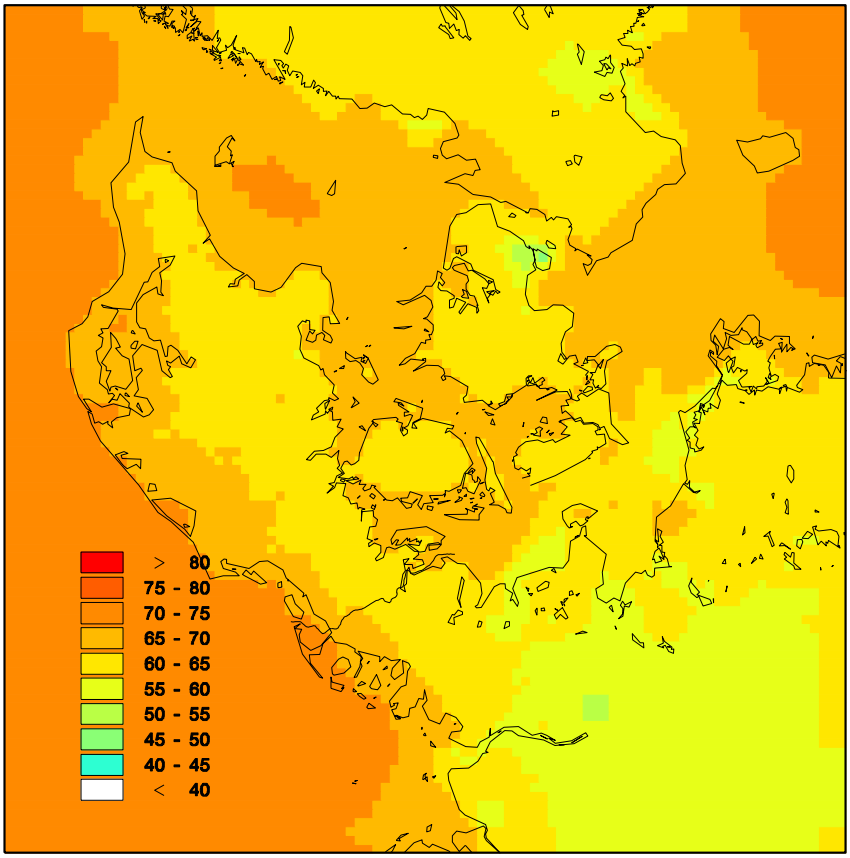


Figure 4.2. Annual mean concentrations of O_3 (µg/m^3) for 2012 calculated using DEHM. The figure shows the average concentrations for the 6 km x 6 km grit cells used in the model.

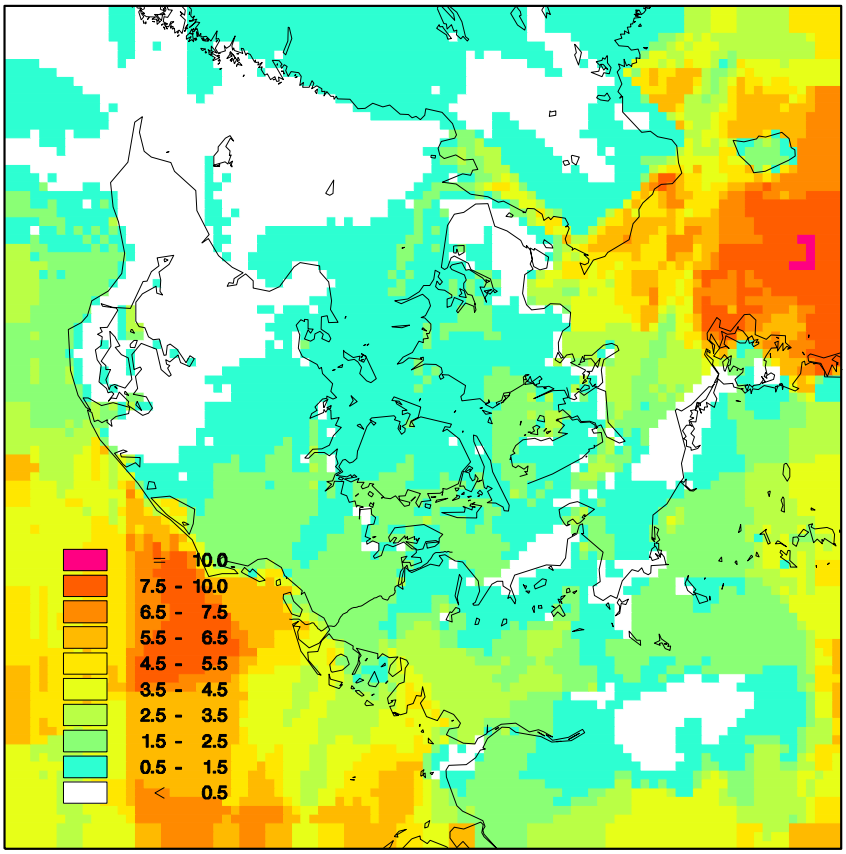


Figure 4.3. Number of exceedances of 120 µg/m^3 for 8-hour running mean concentrations of ozone in 2012. The calculations were carried out using DEHM.

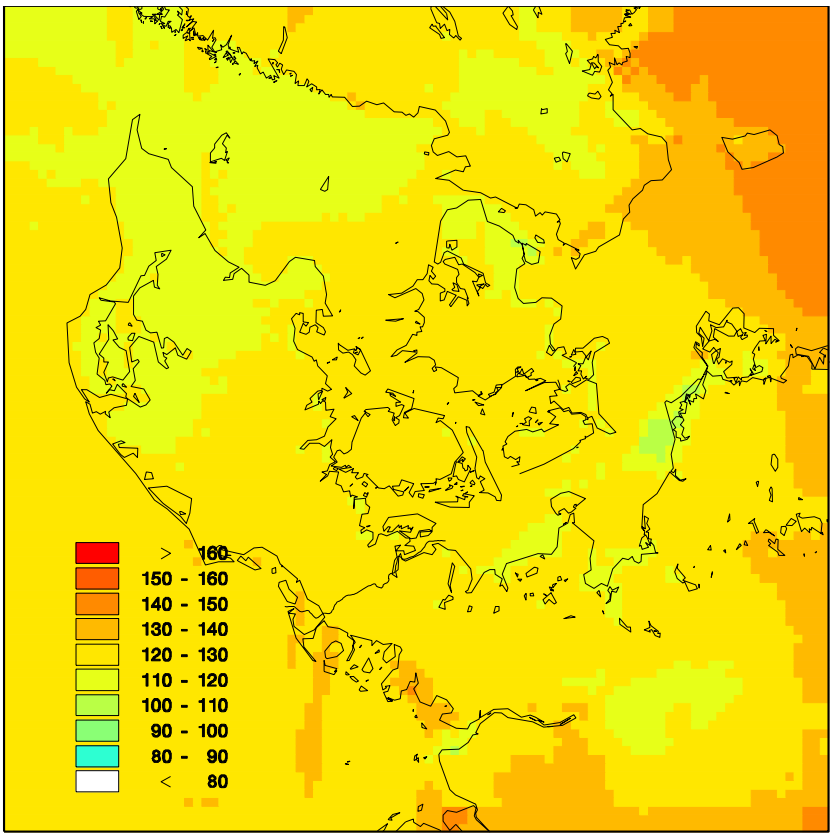


Figure 4.4. Maximum 8 hour running mean concentration (µg/m^3) of ozone in 2012 calculated using DEHM.

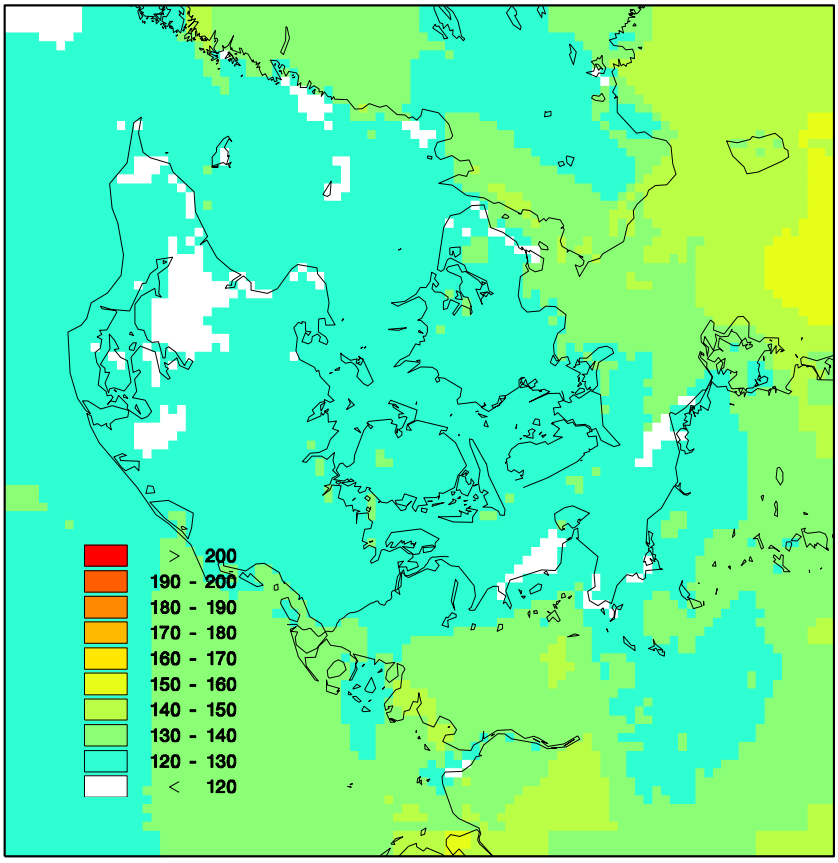


Figure 4.5. Maximum one hour mean concentration of ozone (µg/m^3) in 2012 calculated using DEHM.

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 2012 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 2012. 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	8060	405	374	831	1235	1101	2443
Aarhus/6153	6948	314	278	700	1310	1426	1973
Odense/9155	7666	355	276	1087	2276	2202	4283
Aalborg/8151	8024	362	307	893	1327	1269	2042
Urban Background:							
Copenhagen/1259	7663	258	238	492	744	698	1049
Rural:							
Risø	7479	250	230	439	751	773	841
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.

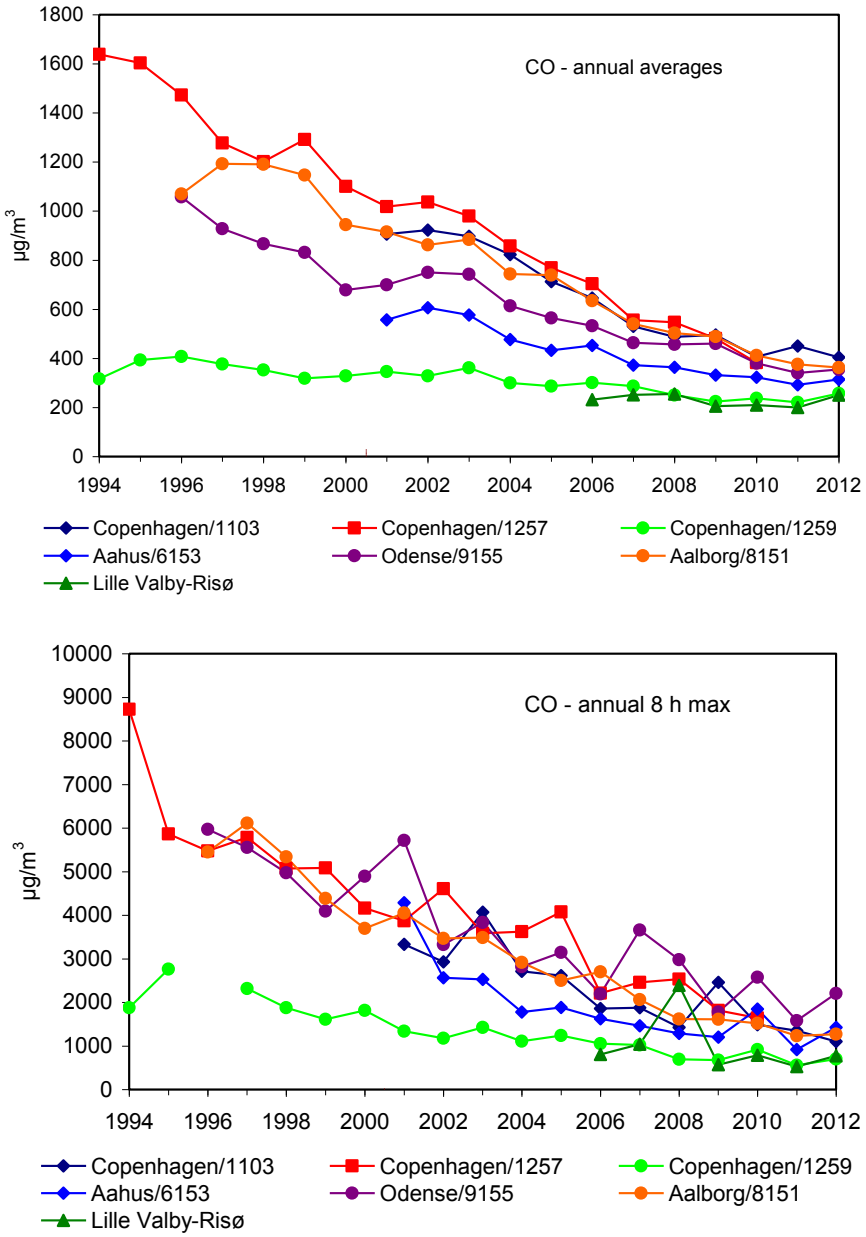


Figure 5.1. Annual average values and highest 8-hour value calculated based on an hourly moving average. Previous results from Copenhagen/1103 can be found at the website of the Copenhagen Environmental Protection Agency (www.Miljoe.kk.dk).

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. 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

The annual average of benzene and toluene in 2012 are listed in Table 6.1 and Table 6.2. The annual average for benzen were only about 20% of the EU-limit value (EC, 2008) and the annual average for toluene were only about 15% of the guide line value fro WHO (WHO, 2000)

The annual averages of benzene and toluene in urban background/1259 were 0.55 µg/m^3 and 1.15 µg/m^3, respectively as described in Chapter 12.

Table 6.1. Annual statistics for benzene in 2012 based on weekly average concentrations at 1 atm. and 293 K. The limit value is based on EU Directive 2008/50/EC (EC, 2008).

Concentration µg/m^3	Number of results	Average	Max weekly average
Copenhagen/1103	52	1.1	2.4
Copenhagen/1257	52	1.0	1.9
Limit value		5	

Table 6.2. Annual statistics for toluene in 2012 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). The guideline value is established by WHO (WHO, 2000).

Concentration µg/m^3	Number of results	Average	Max weekly average
Copenhagen/1103	52	2.8	3.9
Copenhagen/1257	52	2.5	3.7
Guideline value	-	-	260

6.2 Trends

Benzene has decreased from approximately 6 µg/m^3 on Jagtvej (Copenhagen/1257) in 1998 to a value below the lower assessment threshold (EC, 2008) of 2 µg/m^3. In 2012 the annual averages were 1.0 and 1.1 µg/m^3 at the kerbside stations 1257 and 1103 in Copenhagen. Toluene shows a similar trend, which indicates that benzene and toluene are mainly emitted from traffic. Annually averages for toluene were 2.5 and 2.8 µg/m^3, 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.

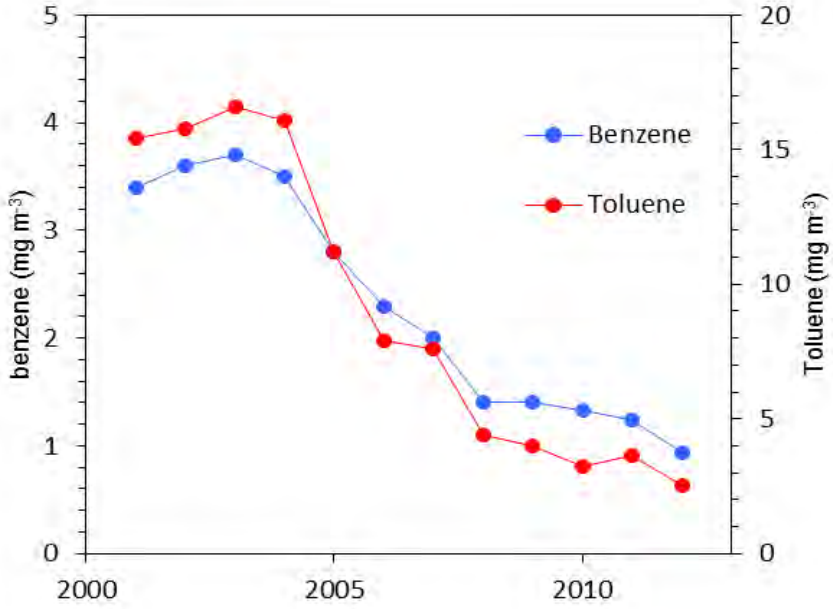


Figure 6.1. Annual average concentrations of benzene and toluene on the kerbside station Jagtvej, Copenhagen/1257.

7 Particles (TSP, PM_{10}, $PM_{2.5}$ and 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 from 2007 been extended to also 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 using the SM200 as a filter sampler for PM_{10} (Harrison, 2006). For this reason we have decided from 2006 and onwards to report results from the β-method. Previously, only results from weighing of the filters collected by the SM200 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.

As part of an overall maintenance plan for the measuring programme it has been decided to substitute the old SM200 samplers with measurements of PM that follows the reference method for the determination of PM_{10} and $PM_{2.5}$ (EN 12341: 1998 and EN 14907:2005). The basic measuring principle of the reference method uses low volume sampling i.e. a flow of 2,3 m^3/hr with following gravimetric determination of the sampled mass . Five low volume samplers (LVS) were installed at four stations in the network (HCAB PM_{10} and $PM_{2.5}$; HCØ $PM_{2.5}$; Jagtvej PM_{10} ; Risø $PM_{2.5}$) during August and September 2012 to replace some of the older SM200 instruments that needed to be renewed. At Jagtvej $PM_{2.5}$ a low volume sampler was running for three months (June, July and August) for control of a SM200 and these measurements were also used for the reporting of the 2012 PM data. Preliminary results from comparing low volume sampler gravimetric determination and the SM200 β-method for PM measurements has not documented any systematic deviation between the two measuring methods except for an improved reproducibility using the new samplers. 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. Parallel with the SM200 monitoring, PM measurements using the LVS gravimetric reference method were initiated in the summer 2012 in Copenhagen at HCAB (street), Jagtvej (street), HCØ (urban background) and at Risø (rural background) near Roskilde. 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 2012 the permitted number of exceedences in a year of the diurnal limit value of 50 µg/m^3 for PM_{10} were not exceeded at any stations in the measuring network, even at stations where exceedances previously has occurred (the two traffic stations in Copenhagen (HACB/1103 and Jagtvej/1257)). There were likewise no exceedances of the annual limit value for PM_{10} (of 40 µg/m^3) and $PM_{2.5}$ (of 25 µg/m^3) at any measuring station.

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 2010-2012 the AEI is determined to 14 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 2012. 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*	354	31	29	24	44	90
Copenhagen/1257*	345	26	23	15	41	80
Aarhus/6153	341	23	21	5	36	95
Odense/9155	312	21	18	5	34	74
Urban Background:						
Copenhagen/1259	334	17	16	2	29	68
Rural:						
Risø	338	16	14	4	27	71
Keldsnor/9055	270	16	14	3	28	66
Limit value (2005)	>329**	40		35***		

* Based part of the year on low volume sampling with gravimetric determination of particle mass

** 90% data capture of number of diurnal measurements in a year.

*** Permitted number of exceedences in a year of the diurnal limit value of 50 µg/m^3

Table 7.2. Annual statistics for $PM_{2.5}$ in 2012. All parameters are calculated as diurnal averages at ambient temperature and pressure.

Unit: µg/m^3	Number of results	Average	Median	90 percentile	Max day
Traffic:					
Copenhagen/1103*	351	15	13	26	61
Copenhagen/1257*	357	15	14	26	65
Aarhus/6153	326	12	10	23	59
Aalborg/8151	201	13	12	23	44
Urban Background:					
Copenhagen/1259*	361	11	10	21	60
Aarhus/6159	264	11	9	21	40
Aalborg/8158	360	9	8	17	54
Rural:					
Risø*	340	10	8	18	56
Limit value (2015) (parenthesis gives proposed value for 2020)	>329**	25(20)			

* Based part of the year on low volume sampling with gravimetric determination of particle mass

** 90% data capture of number of diurnal measurements in a year.

Table 7.3. Annual statistics for PM_{10} measured in 2012 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	7425	30	40
Rural:			
Risø	5495	13	16
Limit value			40

Table 7.4. Annual statistics for $PM_{2.5}$ measured in 2012 using TEOM. The values are calculated based on hourly averages.

Unit: µg/m^3	Number of results	Average	Average
Traffic:			
Copenhagen/1103	7567	12	16
Rural:			
Risø	7485	8	10
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	14542	14042
Urban Background:		
Copenhagen/1259	12264	5407
Rural:		
Lille Valby	7709	2744

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 depends 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.

The measurements show a tendency to a decrease in PM_{10} at the majority of the measurement stations since 2001, where the measurements began (Figure 7.2). Although the measurements at HCAB (Copenhagen/1103) began later, there is also a decrease in PM_{10} at this station. However, this is mainly due to a major reduction (7 $\mu g/m^3$) in PM_{10} from 2008 to 2009. Detailed examination of all the measurements at HCAB showed that the main reason for this decrease from2008 to 2009 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.

The measurements of $PM_{2.5}$ started in 2007 at Copenhagen/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. There seems to be a tendency to a small reduction in $PM_{2.5}$, although this tendency is uncertain due to the relatively short period with measurements. There has so far not been any trend in the average exposure index (AEI) (2008-2010: 14 $\mu g/m^3$, 2009-2011: 15 $\mu g/m^3$, 2010-2012: 14 $\mu g/m^3$).

The measurements show a significant reduction of particle number in ambient air (Figure 7.4). On HCAB the number of particles has decreased by a factor of about 2 during the period 2002-2012. At the urban background station (HCØE) and rural background station (LVBY/Risø) a reduction in particle numbers was also observed though the decrease is smaller than at HCAB. The decreases are only about 30% at HCØE and LVBY/Risø, respectively.

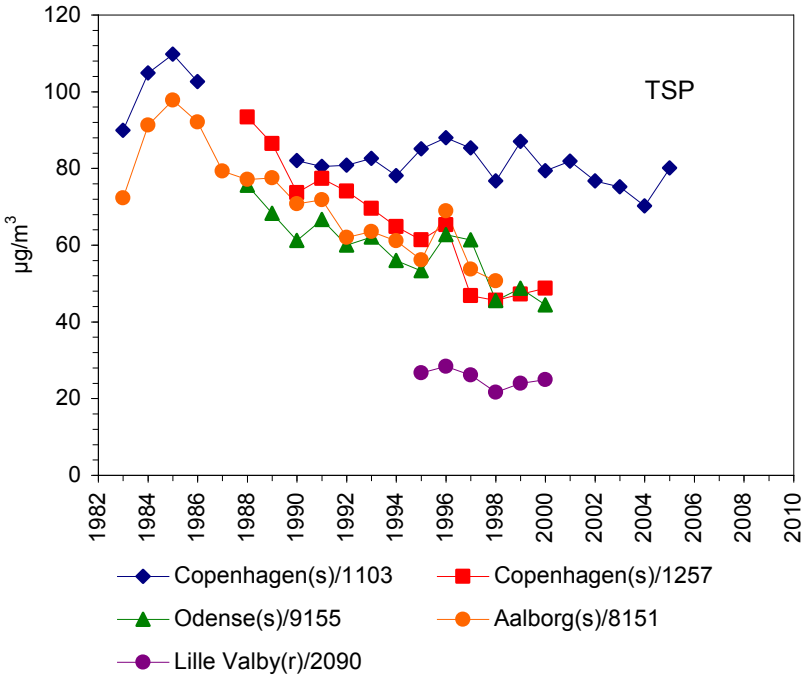


Figure 7.1. Annual averages for TSP measured at street stations (s) and at rural background station (r).

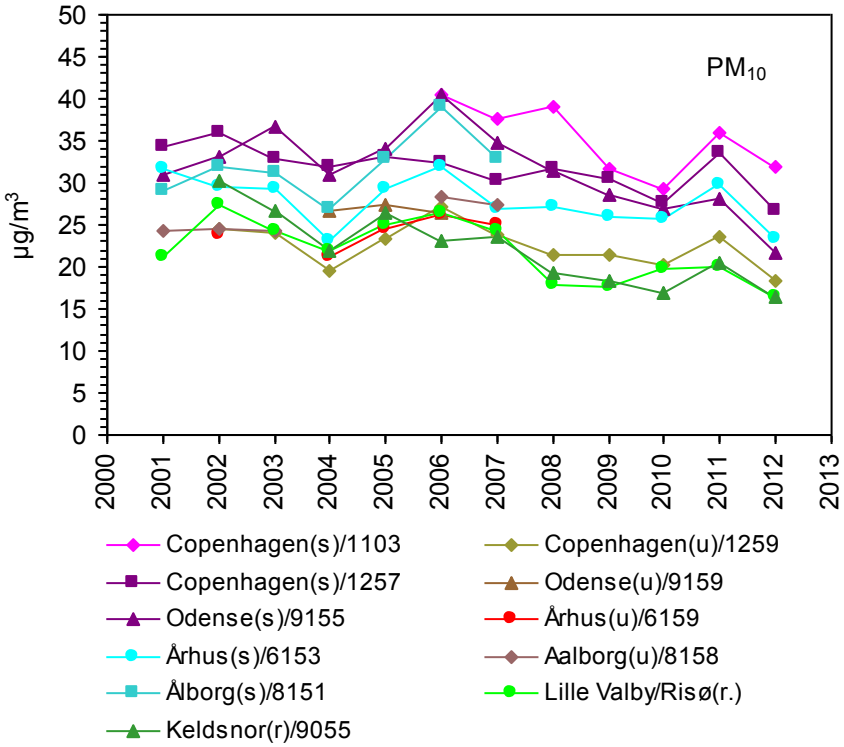


Figure 7.2. Annual averages for PM_{10} measured at street stations (s), urban background stations (u) and at rural background stations (r). The change from gravimetric determination using the SM200 to the use of the same instrument as a β-gauge from 2006 gives rise to a 5-10% increase due to the shift of method. The value for PM_{10} at Copenhagen/1103 in 2008 and 2009 is based on the measurements with SM200 in combination with an estimated value. At the Copenhagen stations (1103 and 1257) PM_{10} from Aug/Sep. - 31 Dec. 2012 is measured by LVS gravimetric reference method. 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.

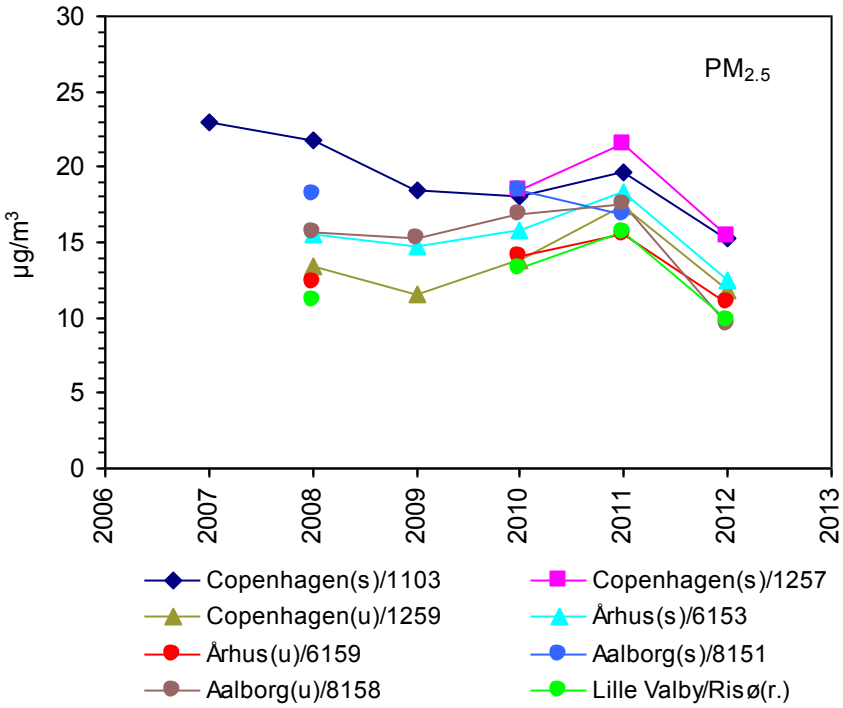


Figure 7.3. Annual averages for $PM_{2.5}$ measured at street stations (s), urban background stations (u) and at rural background station (r). Only annual averages covering more than 2/3 of the years are shown. At the Copenhagen stations (1103 and 1259) and at Risø $PM_{2.5}$ from August/September 2012 is measured by LVS gravimetric reference method Data are given at standard - and pressure (0°C and 1 atm.). The difference between ambient temperature and pressure and standard temperature and pressure is – 3% on the annual average.

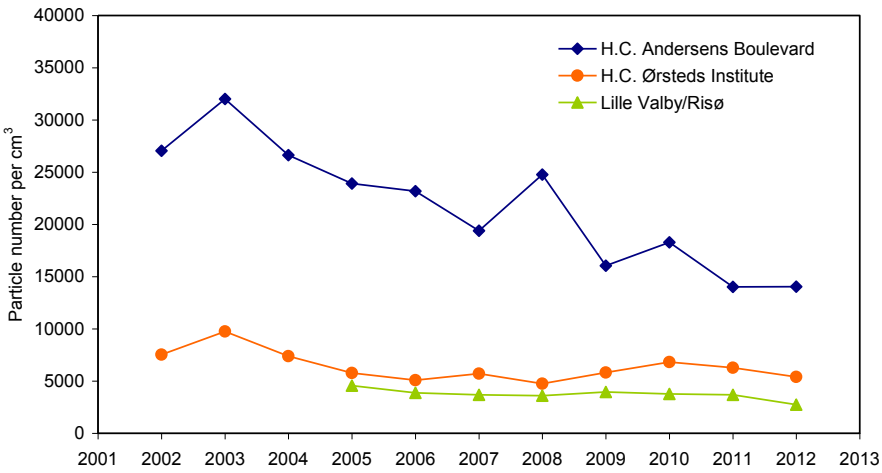


Figure 7.4. Annual averages for particle number. Data for H.C. Andersens Boulevard represents an estimate where annual averages have been corrected for missing data based on comparison with measurements of NO_x. This estimate is further described in Massling et al., (2011).

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 pre-

pare 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 7.6 gives the annual average concentrations for sodium and estimate for total salt (NaCl) in 2012 (calculated from the measured sodium concentration).

Table 7.6. Annual statistics for sodium and estimate of total salt (NaCl) in 2012.

	Na µg/m^3	**NaCl µg/m^3**
Traffic:		
Copenhagen/1103	1.6	4.1
Odense/9155	1.3	3.4
Aarhus/6153	1.5	4.1
Urban Background:		
Copenhagen/1259	1.0	2.7

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 winter 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.

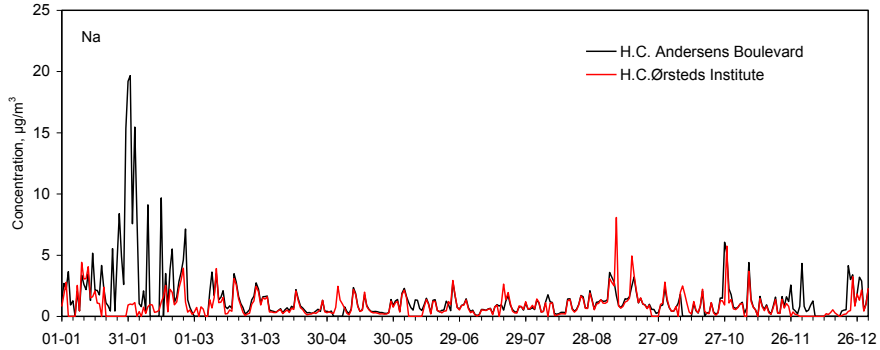


Figure 7.4. Daily concentrations of sodium at H.C. Andersens Boulevard, Copenhagen (1103) and at urban background in Copenhagen (H.C. Ørsteds Institute/1259).

In 2012 there were no exceedances of the daily limit value for PM10 and therefore it has not been necessary to correct PM10 for the content of NaCl due to sea salt and winter salting of the roads

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, and 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 2012. 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
PM_{10}, Traffic:										
Copenhagen/1103	1.9	7.9	22	3.1	89	45	0.7	0.6	0.1	6.9
Odense/9155	1.6	2.6	10	1.9	33	35	0.8	0.6	0.1	4.1
Aarhus/6153	1.8	4.4	9.4	4.0	36	26	0.6	0.6	0.1	3.3
PM_{10},Urban background:										
Copenhagen/1259	2.1	2.5	4.7	2.5	11	17	0.6	0.6	0.1	4.0
TSP, Rural Background										
Risø	1.3	0.4	2.5	1.2	2.3	8.3	0.5	0.4	0.1	2.1
EU Target (Limit) Values *				20			6		5	500
Guideline value (WHO)**	1000		1.5						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)	1.5	0.007

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.

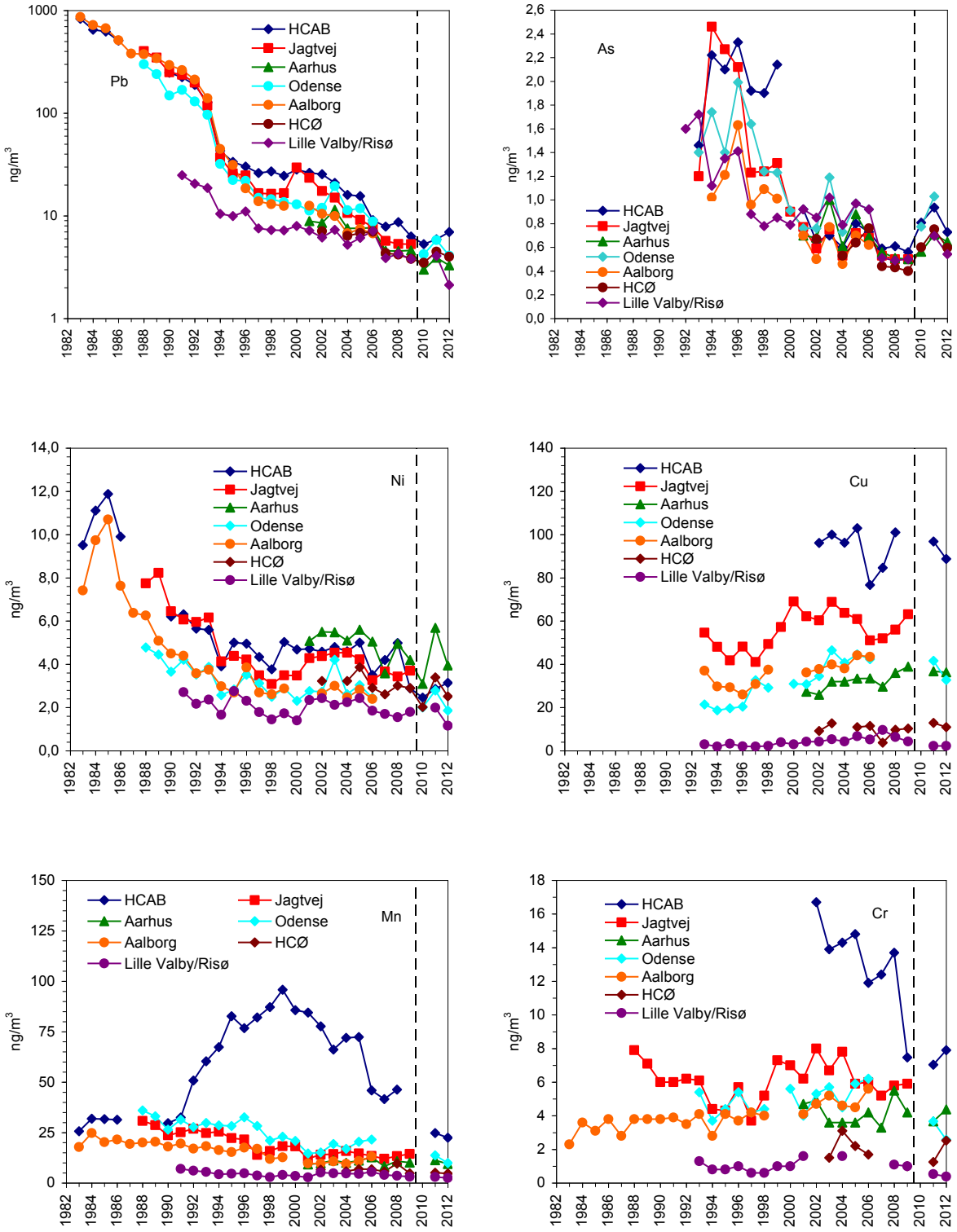


Figure 8.1. Annual averages from selected stations for some heavy metals in particulate matter. Until 2000 in TSP and later in PM_{10} – except for Copenhagen/1103 where PM_{10} replaced TSP from the beginning of 2006. The heavy metals are usually found in fine particles, which make the TSP and the PM_{10} 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 uncertainties 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 2012 for sulphur dioxide are shown in Table 9.1. None of the limit values (EU, 2008) were exceeded in 2012. In 2012 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 2012. All parameters are calculated based on hourly average. 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 hours	4th highest diurnal mean
Traffic:							
Copenhagen/1103	7859	1.5	1.8	1.2	7.1	16.5	6.9
Aalborg/8151	8014	1.6	1.7	1.0	7.2	23.8	5.4
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'ies 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.

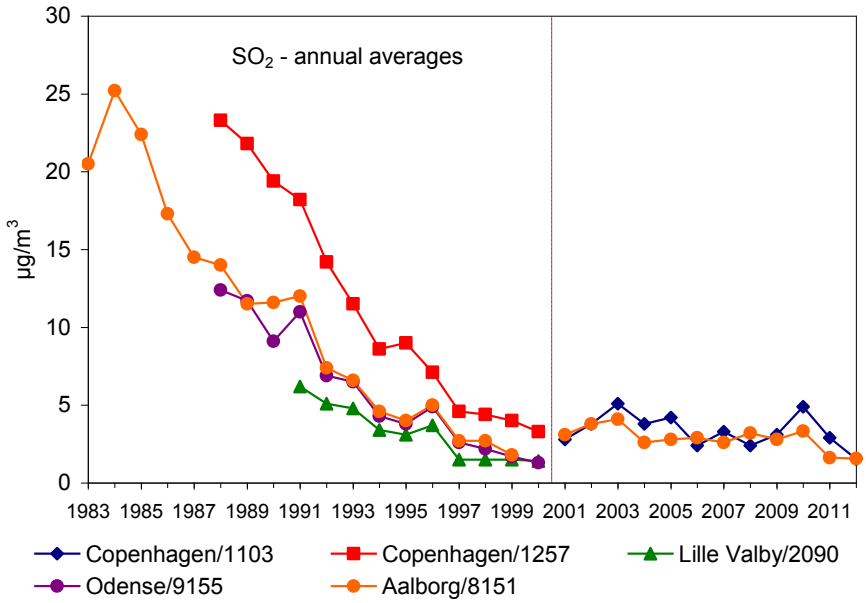


Figure 9.1. Annual averages for SO_2. Until 2001 the results were obtained using KOH impregnated filters for collection of SO_2. These measurements ceased in 2000. After 2000 the SO_2 measurements have been carried out using SO_2-monitors in order to monitor episodic results. The detection limit for 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. Weekly based PAH concentrations are obtained by analysis of pooled fractions of daily collected samples. For each day 4 x 1,5 cm^2 are taken from the filter and the fractions from the whole week are pooled and extracted. The pooled filters are 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 analysed in the method.

10.1 Annual Statistics

The average concentration of benzo[a]pyrene measured in Copenhagen was 0.25 ng/m^3 in 2012. 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, 0.23 ng/m^3; benzo[b]fluoranthene, 0.35 ng/m^3; benzo[j+k]fluoranthenes, 0.38 ng/m^3; indeno[1,2,3-cd]pyrene, 0.44 ng/m^3; dibenzo[a,h]anthracene 0.12 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 2012.

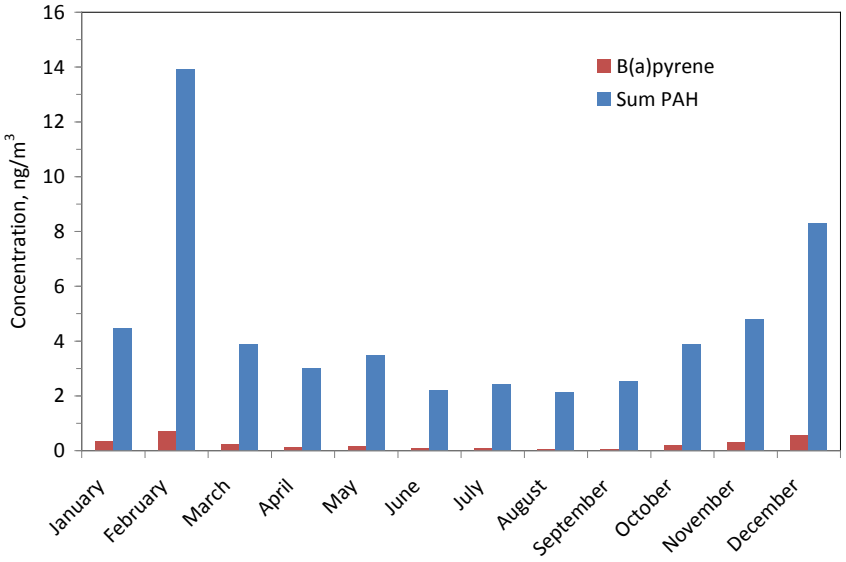


Figure 10.1. Monthly average concentrations in 2012 of benzo[a]pyrene and the sum of the analysed PAH.

Table 10.1. Daily minimum, maximum and average monthly concentrations (ng/m^3) of benzo[a]pyrene during 2012.

Month	Minimum conc.	Maximum conc.	Average conc.
January	0,22	0,45	0,33
February	0,46	0,95	0,71
March	0,17	0,29	0,24
April	0,09	0,21	0,14
May	0,06	0,29	0,17
June	0,08	0,12	0,10
July	0,06	0,12	0,10
August	0,06	0,08	0,06
September	0,06	0,09	0,07
October	0,11	0,35	0,20
November	0,24	0,45	0,31
December	0,40	0,74	0,58
Annual	0,06	0,95	0,25

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.

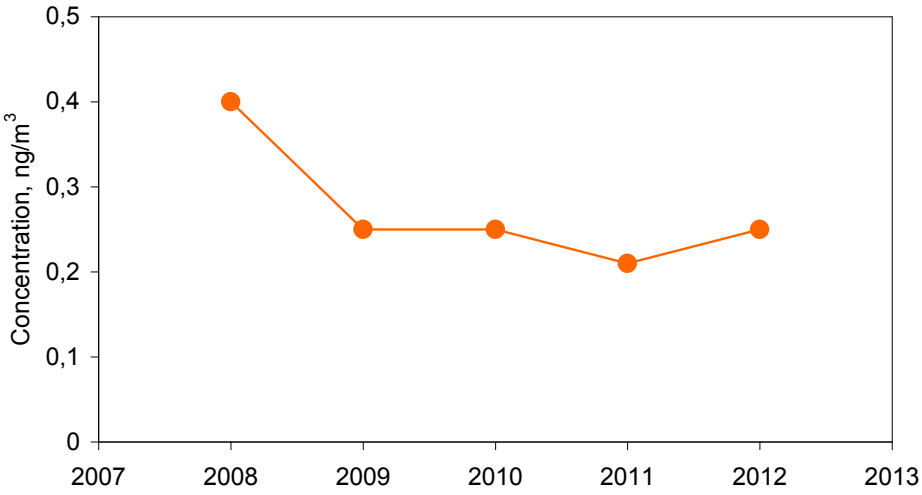


Figure 10.2. Annual average concentrations of benzo[a]pyrene at H.C. Andersens Boulevard (Copenhagen/1103).

11 Organic carbon and elemental carbon

Ambient concentrations of Organic Carbon (OC) and Elemental Carbon (EC) are measured on the kerbside 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. 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 rural background (Figure 11.1, Table 11.1 and 11.2).

A clear seasonal pattern was observed for EC and OC at the rural background with minimum summer concentrations and higher winter concentrations. The EC/TC ratio showed little seasonal variation. 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.

Table 11.1. Annual statistics for OC in 2012. The values are based on daily averages at H. C. Andersens Boulevard and in semi-rural background

Concentration µg/m^3	Data capture	OC, average.	90% percentile
Copenhagen/1103	98%	2.38	4.02
Risø	93%	1.19	2.26

Table 11.2. Annual statistics for EC in 2012. The values are based on daily averages at H. C. Andersens Boulevard and in semi-rural background

Concentration µg/m^3	Data capture	EC, average.	90% percentile
Copenhagen/1103	98%	2.25	3.48
Risø	93%	0.30	0.58

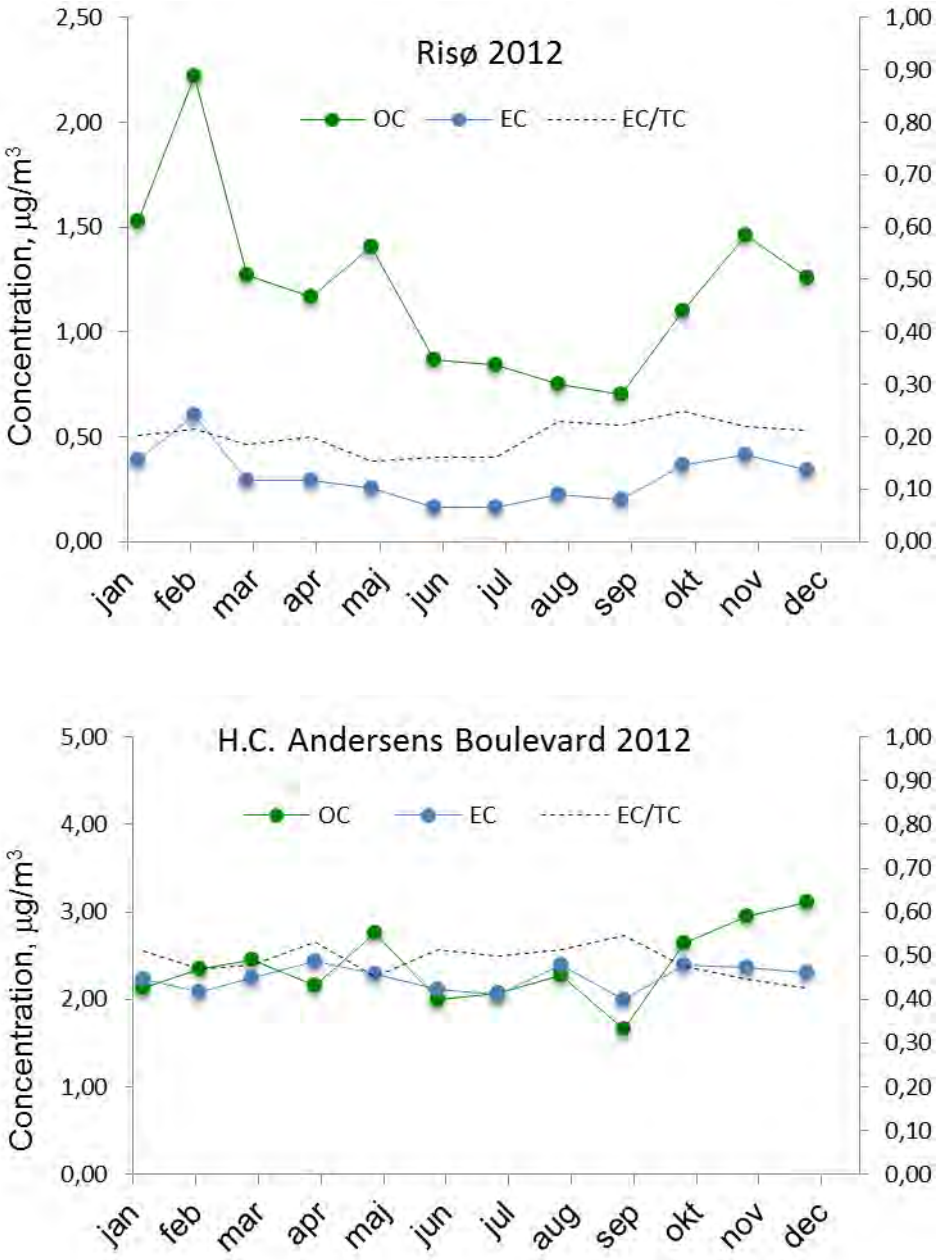


Figure 11.1. Elemental carbon (EC), organic carbon (OC) and the ratio between elemental carbon and total carbon (EC/TC) at H.C. Andersens Boulevard (Copenhagen/1103) and in semi-rural background at Risø in 2012.

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. In 2012 the unknown mass is higher at HCAB than at Risø while the unknown mass was on the same level at the two stations in 2011. However, the mass of the unknown is very uncertain because it is calculated from the difference between $PM_{2.5}$ and the sum of all the analysed constituents. More measurements are therefore needed in order to determine whether or not there is a difference in the unknown mass 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.

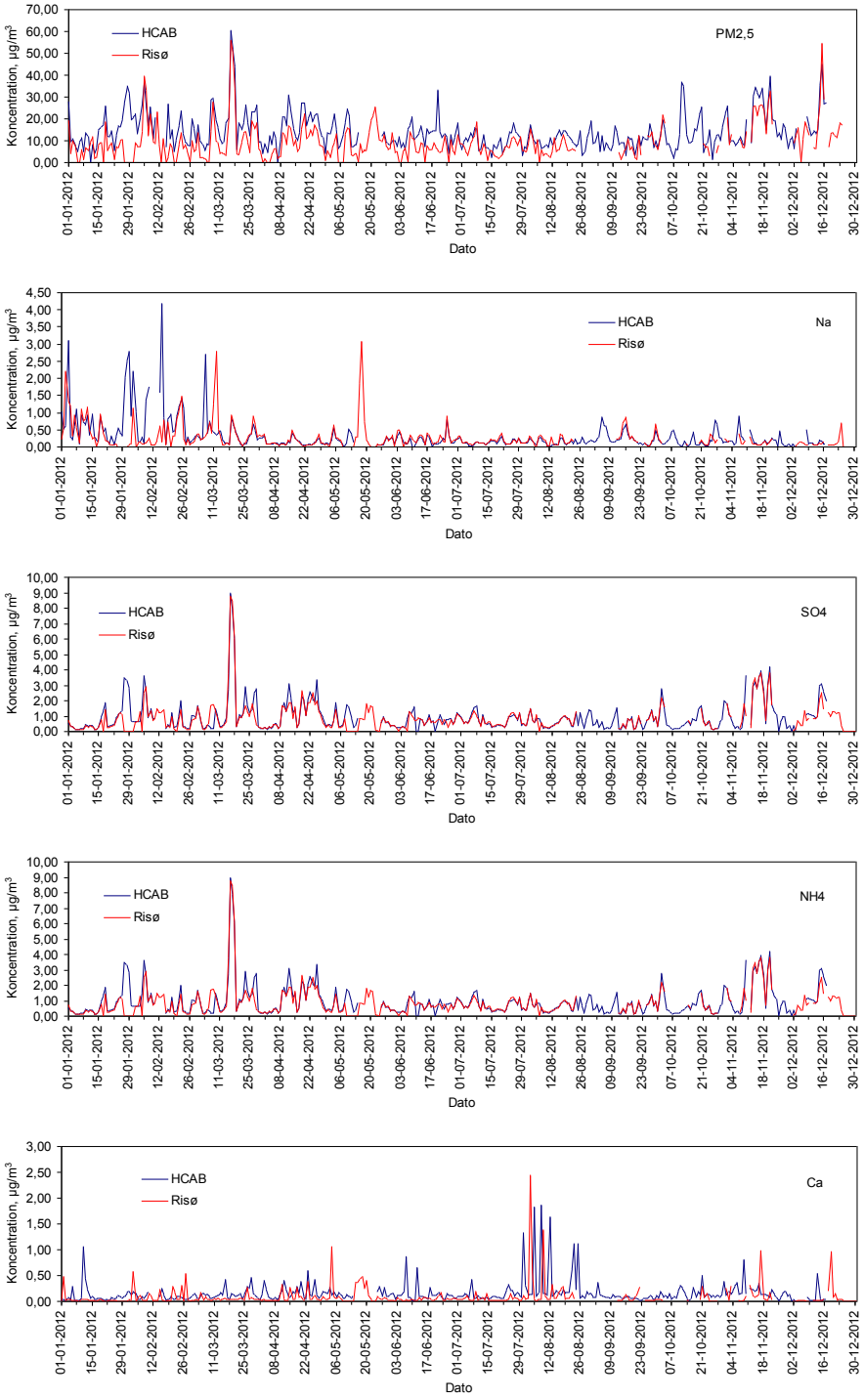


Figure 12.1 Daily variations of the concentrations of $PM_{2.5}$, Na^+, SO_4^{2-}, NH_4^+ and Ca^{2+} at H.C. Andersens Boulevard (HCAB, Copenhagen/1103) and Risø in 2012.

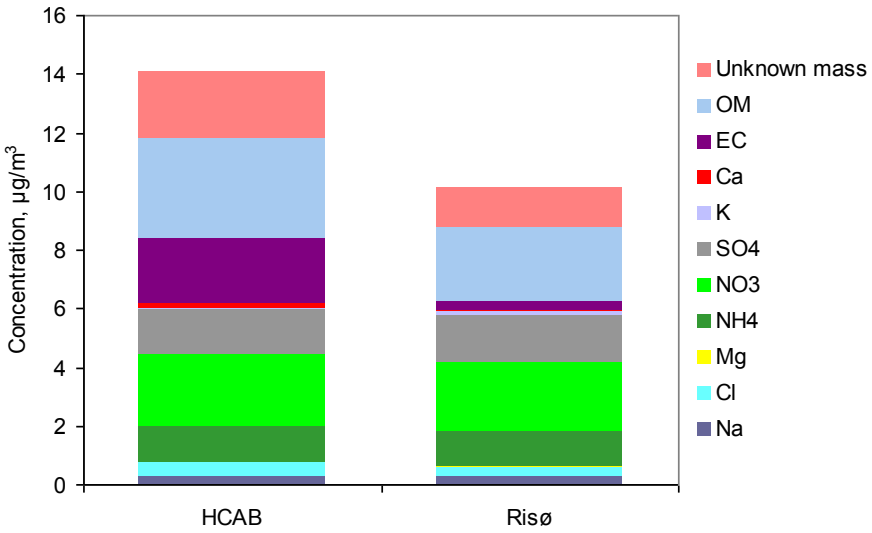


Figure 12.2 Annual average contributions to the chemical composition of $PM_{2.5}$ at H.C. Andersens Boulevard (HCAB, Copenhagen/1103) and Risø in 2012. Organic matter (OM) has been estimated from the measured concentrations of OC by multiplication of OC with a factor of 1,5 for the fresh OM at HCAB and 2,1 for the aged OM 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 mainly anthropogenic 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 correspond to 54% and 46% of the corresponding concentrations at the kerb-side station 1257, respectively. The urban background ratio between toluene and benzene is somewhat smaller than at the traffic dominated kerb-side stations, i.e. 2.1 versus 2.5 (1257) and 2.6 (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	321	0.04	0.06
n-Pentane	344	0.58	0.95
Trans-2-pentene	312	0.02	0.03
Isoprene	330	0.05	0.11
2-Methylpentane	256	0.35	0.55
n-Hexane	246	0.16	0.27
Benzene	345	0.55	1.02
n-Heptane	345	0.16	0.27
2,2,2-Trimethylpentane	316	0.05	0.09
Toluene	345	1.15	1.97
n-Octane	337	0.05	0.09
Ethylbenzene	345	0.22	0.36
m,p-Xylene	345	0.32	0.54
o-Xylene	344	0.23	0.39
1,3,5-Trimethylbenzene	102	0.05	0.08
1,2,4-Trimethylbenzene	295	0.19	0.31
1,2,3-Trimethylbenzene	333	0.05	0.09
Σ		4.21	7.19

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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 eutrophication. 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.

TITLE SCIENTIFIC

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 2012 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. The concentrations for most pollutants have been decreasing during the last decades.

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