THE DANISH AIR QUALITY MONITORING PROGRAMME

Annual Summary for 2013

Scientific Report from DCE – Danish Centre for Environment and Energy No. 134 2015

AARHUS
UNIVERSITY
DCE – DANISH CENTRE FOR ENVIRONMENT AND ENERGY

[Blank page]

THE DANISH AIR QUALITY MONITORING PROGRAMME

Annual Summary for 2013

Scientific Report from DCE – Danish Centre for Environment and Energy No. 134 2015

Thomas Ellermann
Jacob Klenø Nøjgaard
Claus Nordstrøm
Jørgen Brandt
Jesper Christensen
Matthias Ketzel
Stefan Jansen
Andreas Massling
Steen Solvang Jensen

Aarhus University, Department of Environmental Science

AARHUS
UNIVERSITY
DCE – DANISH CENTRE FOR ENVIRONMENT AND ENERGY

Data sheet

Series title and no.:	Scientific Report from DCE – Danish Centre for Environment and Energy No. 134
Title:	The Danish Air Quality Monitoring Programme
Subtitle:	Annual Summary for 2013
Authors:	Thomas Ellermann, Jacob Klenø Nøjgaard, Claus Nordstrøm, Jørgen Brandt, Jesper Christensen, Matthias Ketzel, Stefan Jansen, Andreas Massling & Steen Solvang Jensen
Institution:	Aarhus University, Department of Environmental Science
Publisher:	Aarhus University, DCE – Danish Centre for Environment and Energy ©
URL:	http://dce.au.dk/en
Year of publication:	February 2015
Editing completed:	January 2015
Referee:	Ole Hertil, Institute of Environmental Science
Quality assurance, DCE:	Vibeke Vestergaard Nielsen
Financial support:	No external financial support
Please cite as:	Ellermann, T., Nøjgaard, J.K., Nordstrøm, C., Brandt, J., Christensen, J., Ketzel, M. Jansen, S., Massling, A. & Jensen, S.S. 2015. The Danish Air Quality Monitoring Programme. Annual Summary for 2013. Aarhus University, DCE – Danish Centre for Environment and Energy, 72 pp. Scientific Report from DCE – Danish Centre for Environment and Energy No. 134. http://dce2.au.dk/pub/SR134.pdf

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 2013 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.

Keywords:	Atmospheric pollution, urban pollution, nitrogen compounds, ozone, sulphur compounds, heavy metals, volatile organic pollutants, dispersion models and measurements.
Layout:	Ann-Katrine Holme Christoffersen
Front page photo:	Thomas Ellermann
ISBN:	978-87-7156-119-7
ISSN (electronic):	2245-0203
Number of pages:	72
Internet version:	The report is available in electronic format (pdf) at http://dce2.au.dk/pub/SR134.pdf

Contents

Summary and Conclusion

This report presents the result from the Danish Air Quality Monitoring Programme in 2013. 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 eleven monitoring stations; nine stations situated in the four largest cities and two stations located in background areas. These measurements are supplemented with model calculations using DCEs 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 (PAHs). In 2009 the programme was expanded with measurements of a number of volatile organic compounds (VOCs) 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 2013 the permitted number of exceedances 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 values for PM_{10} (40 µg/m^3) and $PM_{2.5}$ (25 µg/m^3 from 2015).

The number of particles in ambient air was about 17000 particles per cm^3 at the street station H.C. Andersens Boulevard. This is a factor of roughly about 3.7 and 6 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 1.8 µg/m^3 corresponding to an estimated annual salt content (NaCl) of about 4.6 µg/m^3. High diurnal values of salt were observed during periods with winter salting of roads.

The annual limit value for NO_2 (40 µg/m^3) 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 were in 2013 on the same level as in 2012. At H.C Andersens Boulevard (Copenhagen/1103) there were still elevated concentrations of NO_2. The main reason for these elevated concentrations is a permanent change in the traffic lanes at the street segment in front of the measurement station.

Model calculations at selected streets in Copenhagen and Aalborg indicate that the limit value was exceeded at 12 out of 98 calculated streets in Copenhagen but not at any streets in Aalborg in 2013.

The ozone levels were in 2013 almost the same as in 2012 at all rural and urban background stations and no clear trend was thus observed. The information threshold at 180 µg/m^3 was not exceeded in 2013. The target value for the max. 8 hours ozone concentration on 120 µg/m^3 was not exceeded, but the long-term objective for this target was exceeded at all non-traffic stations.

Measurements of volatile organic compounds (VOCs) at the urban background in Copenhagen showed concentration levels between 0.04 µg/m^3 and 1.15 µg/m^3 for the selected 17 different compounds. VOCs can act as ozone precursors and the aim of these measurements is to improve the general understanding of the ozone formation on an European level. 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 and at the suburban measurement station at Hvidovre. The average concentration of benzo[a]pyrene was 0.25 ng/m^3 and 0.34 ng/m^3 at H.C. Andersens Boulevard and Hvidovre, respectively. The higher concentrations at Hvidovre are due local use of wood burning for house hold warming. The target value for benzo[a] pyrene (1 ng/m^3) was not exceeded in 2012.

Mearurements of the chemical content in $PM_{2.5}$ showed that 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://dce.au.dk/en/authorities/air/), in Danish (http://dce.au.dk/myndigheder/luft/).

Danish summary - Dansk resumé

Rapporten præsenterer resultater for 2013 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'er) samt udvalgte flygtige kulbrinter (VOC'er), 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'er (EC 2005) samt det nye luftkvalitetsdirektiv (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 2013 er følgende:

- I 2013 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 i 2013 var stort set på niveau med koncentrationerne målt i 2012. På gademålestationen ved H.C. Andersens Boulevard er der fortsat en forhøjet koncentration af NO_2 set i forhold til tidligere. Den væsentligste årsag til den forøgede koncentration på H.C. Andersens Boulevard er en permanent ændring af vejbanerne på den del af H.C. Andersens Boulevard.
- Modelberegninger indikerer, at grænseværdien i 2013 var overskredet på en 12 ud af 98 beregnede gadestrækninger i København, men ikke på udvalgte gadestrækninger i Aalborg.
- I 2013 var der ingen målestationer i måleprogrammet, hvor antallet af overskridelser af den daglige middelværdi for PM_{10} (50 µg/m^3 må ikke overskrides mere end 35 gange årligt) blev overskredet.

- Indholdet af partikler mindre end 2,5 µm ($PM_{2.5}$) overskred ikke den kommende grænseværdi på 25 µg/m^3, som skal overholdes fra 2015.
- Antallet af partikler mellem 6 og 700 nm var omkring 17.000 partikler per cm^3 på gademålestationen H.C. Andersens Boulevard, mens det var betydeligt mindre i by- og landbaggrund. Antallet af partikler steg fra 2012 til 2013, men det overordnede billede er fortsat at antallet af partikler er faldet med omkring en faktor 2 siden 2002 på H.C. Andersens Boulevard.
- Indholdet af natrium i PM_{10} på gademålestationerne var omkring 1,8 µg/m^3 svarende til et estimeret saltindhold (NaCl) på omkring 4,6 µg/m^3.
- Der er ikke fastsat egentlige grænseværdier for ozon (O_3), men kun "målværdier" og "langsigtede mål" (hensigtsværdier). Der var i 2013 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 heller ikke overskredet i 2013.
- 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 0,24 ng/m^3, og 0,34 ng/m^3 på henholdsvis H.C. Andersens Boulevard og ved målestationen i Hvidovre. De højere koncentrationer i Hvidovre skyldes lokal anvendelse af brændeovne til boligopvarmning. Målværdien på 1 ng/m^3 var således ikke overskredet i 2013.
- Målinger af 17 udvalgte flygtige organiske kulbrinter (VOC'er) i bybaggrund i København viser koncentrationsniveauer, som spænder fra 0,04 µg/m^3 til 1,15 µg/m^3 i 2013. Disse VOC'er bidrager til den kemiske dannelse af ozon på europæisk plan og målingerne skal først og fremmest understøtte den generelle forståelse af ozondannelsen i Europa. I Danmark skyldes størstedelen af ozon langtransport af luftforurening fra centrale og sydlige dele af Europa.
- Målinger af det kemiske indhold i $PM_{2.5}$ ved gademålestationen ved H. C. Andersens Boulevard og ved landbaggrundsmålestation på Risø viser ligesom i 2011 og 2012, at de årlige gennemsnitskoncentrationer for NH_4^+, Na^+, K^+, Mg^{2+}, Cl^-, NO_3^- og SO_4^{2-} er stort set ens på de to stationer. Dette 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://dce.au.dk/en/authorities/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 program was revised last time in 2010 and the main changes due to this revision have been described in the previous report (Ellermann et al., 2013). In 2012-2013 there has only been minor changes were the most important are:

- During the course of 2012-13 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 seven stations in the network (HCAB PM_{10} and $PM_{2.5}$; HCØ PM_{10} and $PM_{2.5}$; Jagtvej PM_{10} and $PM_{2.5}$; Risø $PM_{2.5}$) starting during August and September 2012 to replace some of the older SM200 instruments that needed to be renewed.

- A non-permanent measurement station at a suburban area in Hvidovre has been started with measurements of PAHs in relation to use of wood burning as house hold warming.

In the following chapters the results from measurements and model calculations for 2013 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://dce.au.dk/en/authorities/air/, in Danish (http://dce.au.dk/myndigheder/luft/).

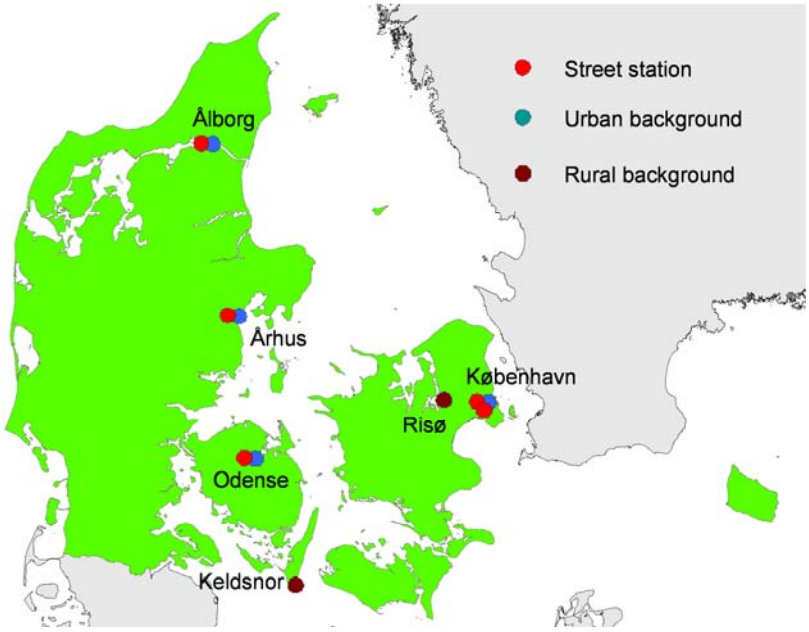


Figure 2.1 Main stations used for monitoring of air quality in relation to health.

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
Hvidovre	Fjelstedvej	Suburban
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 as 24 h averages at all stations except Odense/9159. At five stations (HCAB PM_{10} and $PM_{2.5}$; HCØ $PM_{2.5}$; Jagtvej PM_{10}; Risø $PM_{2.5}$) PM was measured throughout the year by using low volume samplers (LVS) for gravimetric determination of particle mass based on the reference method. At two stations HCØ PM_{10} and Jagtvej $PM_{2.5}$ LVS measurements were used from the 26th June and 16th November respectively: Up to these dates the PM measurements were conducted by the β-absorption technique using the SM200 β-gauges. At the remaining stations PM was determined solely by SM200 β-gauges throughout the year.
- Elements (heavy metals) in PM were measured at Copenhagen/1103, Copenhagen/1257, Copenhagen/1259, Århus/6153, Århus/6159 and 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 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 Risø.
- Benzene and Toluene were measured at Copenhagen/1103 and Copenhagen/1257 using passive sampling on a weekly basis.
- PAHs 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 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, NO_x, 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 the monitoring programme the measurements at the permanent measurement stations are supplemented with model calculations using the THOR modelling system. 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. The system is driven by global meteorological analysed data from National Centres for Environmental Prediction, United States, which is used as input to the meteorological model MM5v7 (Grell et al., 1995).

The meteorological data for 2013 from MM5v7 is subsequently used to drive the air pollution models, including the Danish Eulerian Hemispheric Model, DEHM (Christensen, 1997; Brandt et al., 2012), the Urban Background Model, UBM (Berkowicz, 2000b; Brandt et al., 2001) 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. (2000; 2001 and 2003 or under http://www.au.dk/thor).

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 the model runs under NOVANA, 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 5.6 km x 5.6 km resolution domain and 16,7 km x 16,7 km for the remaining part of Europe. The emissions are based on Danish national emission inventories for the year 2010/2011 made by DCE (http://envs.au.dk/en/knowledge/air/emissions/) and international emission inventories for the year 2012 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 or rural background concentrations on high resolution (1 km x 1 km). The model includes a Gaussian plume approximation for calculation of the dispersion and transport of the air pollutants to every receptor point and a simple chemical model accounting for the photochemical reactions of NO_x and ozone. The basic principles of the model are described in Berkowicz (2000b). In the recent year UBM has undergone many improvements in the formulation of physical processes and now treats both area and point sources in a more

physically correct manner compared to earlier versions of the model. This has improved the overall performance of the model in comparison with measurements, and provides a more realistic spatial distribution of concentrations around large point sources. The emissions used in the UBM model are based on the newly developed SPREAD model that spatially distributes national emissions from 2010 from all sectors on a 1 km x 1 km grid for Denmark (Plejdrup & Gyldenkærne 2011).

Finally, the street canyon model OSPM® (www.au.dk/ospm) is used to calculate the air pollution at 2 m height at the sidewalks of selected streets. Meteorological data from the meteorological model MM5v7 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, turbulence induced by traffic and influence of the street geometry).

The input data for the OSPM model on traffic data and street configurations for the selected urban streets are generated using the AirGIS system based on a GIS road network, GIS foot prints of buildings and GIS calculation points (Jensen et al., 2001;
http://envs.au.dk/videnudveksling/luft/model/airgis/).

The model calculations for 2013 for Copenhagen and Aalborg have been carried out using the full model calculation system based on the THOR system, including MM5v7, DEHM, UBM, and OSPM. The calculations were carried out in order to determine the NO_2 concentration in 98 streets in Copenhagen and 31 streets in Aalborg.

2.2.1 Improved input data and re-calibration of OSPM

The model calculations with OSPM have been improved compared to the version applied for the previous assessment for 2012. This includes changes related to the general building height, revision of NO_x emission factors for Euro 5 and 6 for passenger cars, and use of new travel speeds for the traffic based on GPS data (SpeedMap, speedmap.dk/portal/). Appendix 2 presents documentation for the impact of the improved input data for the model calculations.

The new and improved input data to the model has led to unrealistic high concentrations compared to the measured concentrations from the measurement stations. Especially the new travel speeds have led to substantially higher modelled emissions and thereby higher modelled concentrations. OSPM has therefore been re-calibrated in order to compensate for this. OSPM has been recalibrated against measurements at all street stations based on adjustment of one of the dispersion parameters in the model. More details on these changes are provided below.

A major change in information about travel speed has taken place compared to last year. Previously, information about travel speeds was based on information from the municipalities and qualified estimates, and the applied speeds were generally not based on measurements. The Danish Road Directorate has recently developed a national database of travel speed data for all roads based on GPS measurements from fleets of light-duty and heavy-duty vehicles. The data base is named SpeedMap. Data from SpeedMap has been obtained to provide realistic travel speeds at all calculation points. For Co-

penhagen, travel speeds from SpeedMap are about 20% lower than previous assumptions and the average travel speed used for model calculations has decreased from 41 km/h in 2012 to 32 km/h in 2013. Similar results were seen for Aalborg although only two thirds of the streets where included in the SpeedMap road network (41 km/h in 2012 and 31 km/h in 2013). As NO_x emissions increase substantially with lower speeds in this speed range according to the COPERT 4 emission model, hence OSPM model calculations would overestimate concentrations compared to measurements, if used the same way as previously. Lower speeds will also reduce traffic induced turbulence and hence further increase concentrations. Therefore, the OSPM model has been re-calibrated against measurements from all street measurement stations using the new input data. The higher emissions have been compensated by a calibration of an internal dispersion parameter in OSPM in a way that modelled concentrations in average fit measurements.

The general building height describes the average or typical height for the buildings along the streets. OSPM uses the general building height directly for estimation of several internal parameters in the model, e.g. reaction or residence time of pollution inside the street canyon, the conversion of wind speed at roof level to street level. It is therefore important that the general building heights are described correctly. AirGIS estimates the general building height based on building foot prints, the road segment and the calculation point. AirGIS will take the most abundant height and make it the general building height and the rest exceptions. However, in case of one-side streets with openings in the building side the general building height can become zero. This leads to incorrect and arbitrary model results for such cases. In order to avoid this, OSPM now estimates the general building height based on the inputs from AirGIS on street configuration. The influence of the improved parameterization was successfully tested for several Danish validation datasets (Ketzel et al. 2012). Analysis shows that these changes have relatively little impact on NO_2 concentrations for selected streets in Copenhagen and Aalborg where most streets are street canyons but these changes can also affect the ranking of streets according to NO_2 concentrations.

The methodology of the European COPERT 4 emission model (http://www.emisia.com/copert/) is integrated into OSPM. Emission factors are based on one of the latest versions of the COPERT 4 model (version 10, 2013) and represent 2013 emissions also taking account of the effect of the low emission zones (Jensen at al., 2011). Emission factors for diesel-driven passenger cars for Euro class 5 and 6 have been updated for NO_x emissions. The new assumptions are a 23% increase for Euro 5 and 57% reduction for Euro 6 in comparison to Euro 4. Compared to emission assumptions in our assessment for 2012 this increases total NO_x emissions slightly as previous assumptions were a reduction of Euro 5 in comparison to Euro 4 and a further reduction for Euro 6. These changes can also affect the NO_2 concentration ranking of streets since there are differences in vehicle distribution between streets.

The traffic data used as input for the calculations with OSPM is updated annually for average daily traffic and vehicle distribution for the selected streets based on information obtained from the municipalities of Copenhagen and Aalborg. Traffic data are estimated at the location of the calculation points. For Copenhagen traffic data is based on manual counts

performed annually or in 5-year intervals. Based on information from Copenhagen and Aalborg municipalities the Average Daily Traffic (ADT) and vehicle distribution on all streets have been updated with the most recent available traffic data. The vehicle distribution includes passenger cars, vans, trucks<32t, trucks>32t, and buses. In Copenhagen about half of the 98 calculation points had updated traffic data for 2013. For Aalborg 9 out of 31 streets had updated traffic data.

Manual counts are now carried out annually for the street segments in front of the measurement stations of H.C. Andersens Boulevard and Jagtvej starting from April 2013. This data was also used in the previous assessment for 2012 and there is no difference between 2012 and 2013 for these two road segments. Aalborg does not have a systematic traffic counting program and traffic data is based on available traffic data from manual and automatic counts together with data from a traffic model.

Calculations with the full model chain of DEHM-UBM-OSPM have been compared to measured NO_2 concentrations in 2013 for the fixed street monitoring stations in Copenhagen, Aarhus, Odense and Aalborg. The model system slightly overestimates annual NO_2 concentrations with 3% for Jagtvej (Copenhagen), overestimates by 13% for H.C. Andersens Boulevard (Copenhagen), and slightly underestimates 5% for Aarhus, slightly overestimate for Odense and slightly underestimate for Vesterbro (Aalborg). Calculations with the coupled DEHM-UBM models have also been compared to the fixed urban background monitoring stations in Copenhagen, Aarhus, Odense and Aalborg. Here the model system slightly overestimates annual NO_2 concentrations with 1-5% except for Aarhus where it underestimates by 23% probably due to emissions from nearby trains not fully accounted for.

The comparison of the modelled NO_2 concentrations presented in this report for 2013 with measurements at the 5 street locations shows a good overall agreement within -7 to 13% (Table 2.2).

Detailed traffic data is not obtained for Aarhus and Odense as these cities are not part of the annual assessment based on air quality models. Traffic data originates from the Low Emission Zone Project (Jensen et al., 2011). However, SpeedMap travel speeds have been applied for Aarhus and Odense in the street calculations.

Overall, the changes in the input data to OSPM and the recalibration of the model will lead to changes in the results (concentration levels and ranking of the NO_2 concentrations) between 2012 and 2013 that are larger than normal variations (average daily traffic and vehicle distribution) between two consecutive years.

Table 2.2 Comparison of modelled and measured annual means of NO_2 concentrations in 2013

Unit: µg/m^3	Measure-ments	Model results	Difference %	Models used
Traffic:				
Copenhagen/Jagtvej/1257	38	37	-3	DEHM/UBM/OSPM
Copenhagen/HCAB/1103	55/47*	53	13	DEHM/UBM/OSPM
Aarhus/6153	35	33	-5	DEHM/UBM/OSPM
Odense/9155	28	28	1	DEHM/UBM/OSPM
Aalborg/8151	32	30	-7	DEHM/UBM/OSPM
Urban Background:				
Copenhagen/1259	16	17	5	DEHM/UBM
Aarhus/6159	19	15	-23	DEHM/UBM
Odense/9159	14	14	3	DEHM/UBM
Aalborg/8159	14	14	1	DEHM/UBM
Rural:				
Risø/2090	9.2	13	38%	DEHM/UBM
Keldsnor/9055	7.5	8.0	7%	DEHM/UBM

* 55 µg/m^3 is measured at the monitoring station at HCAB but because of a change in street layout traffic has moved closer to the measuring station, and it is estimated to have led to a jump of about 8-9 µg/m^3 based on parallel measurements. Without the change in street layout, about 47 µg/m^3 is expected. OSPM calculations are more representative of the measurements without the jump as OSPM calculations reflect concentration levels in front of the building facade.

2.2.2 Further development of the model

The detailed investigation on the impact of the changes in road lanes layout on HCAB (Ellermann et al., 2014) showed that the existing OSPM has some shortcomings in reproducing measurements at the location/re-location of the monitor station. The setting at HCAB is complex with multiple road lanes, inhomogeneous distribution of emissions and a measurement point right next to the nearest road lane, and at the same time a relatively long distance to the façade of the buildings. There is a need for further development of OSPM in order to describe the complex setting. A PhD study expects to have a new version of the model in a few years' time that has improved capabilities to describe the complex distribution of emissions in streets, definition of location of calculation point etc. These improvements are expected to improve model calculations for complex street layouts i.e. for HCAB.

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 2013. All parameters are based on hourly averages.

Unit: µg/m^3	**Number**	**Average**	**Median**	**98. percentile**	**19. highest**
Traffic:					
Copenhagen/1257	7989	38	33	94	122
Copenhagen/1103	8046	55*	51	124	152
Aarhus/6153	7983	35	32	85	110
Odense/9155	8256	27	21	82	113
Aalborg/8151	8158	32	27	90	114
Urban Background:					
Copenhagen/1259	8278	16	12	52	68
Aarhus/6159	7882	19	14	67	137
Odense/9159	8078	14	11	47	68
Aalborg/8159	7876	14	9	54	81
Rural:					
Risø	8259	9	6	40	59
Keldsnor/9055	7948	7	5	31	47
Limit value 2010	>7455	40			200

*) Limit value exceeded.

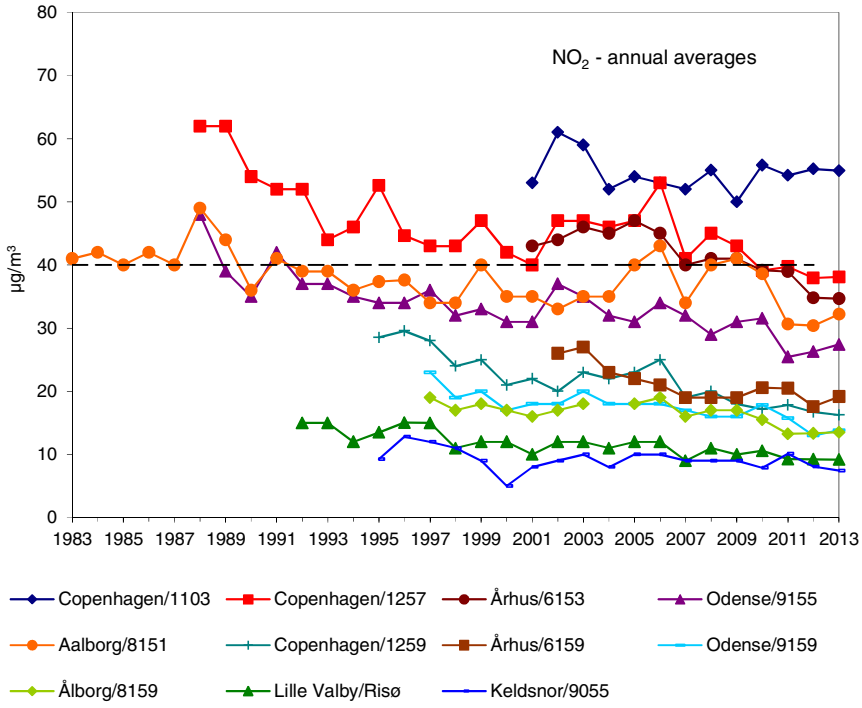
Table 3.2 Nitrogen oxides (NO_x=NO+NO_2) in 2013. All parameters are based on hourly averages.

Unit: µg/m^3 (as NO_2)	Number	Average	Median	98. percentile	19. highest
Traffic:					
Copenhagen/1257	7989	85	63	291	507
Copenhagen/1103	8046	140	110	429	667
Aarhus/6153	7983	79	60	294	617
Odense/9155	8256	66	37	297	592
Aalborg/8151	8158	91	62	359	536
Urban Background:					
Copenhagen/1259	8278	20	14	80	151
Aarhus/6159	7882	28	17	158	343
Odense/9159	8078	19	13	76	234
Aalborg/8159	7876	20	12	102	260
Rural:					
Risø	8259	11	7	53	143
Keldsnor/9055	7948	9	6	38	77

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 downward 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 (called direct 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.



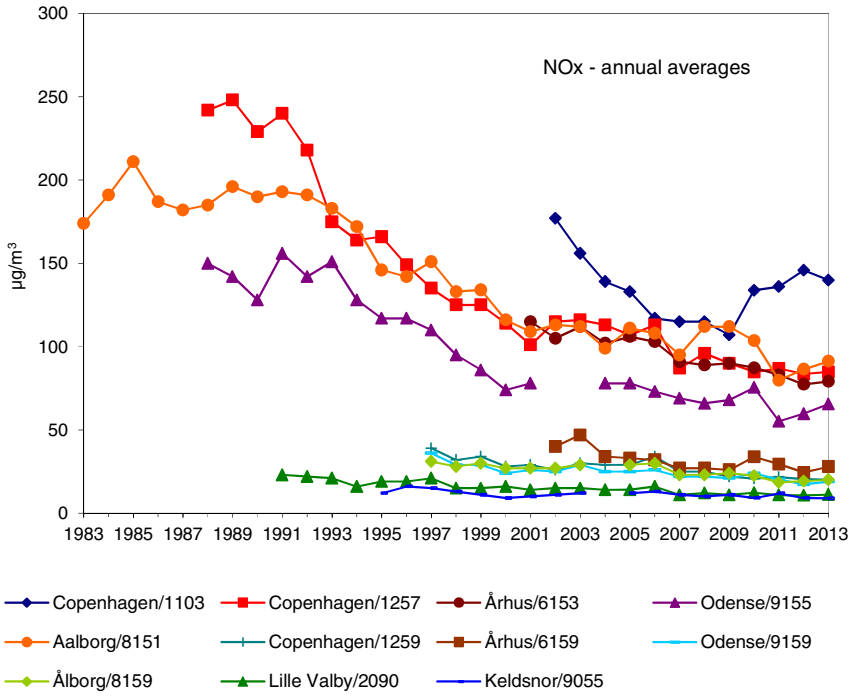


Figure 3.1 The graphs show the time series for the annual average values of NO_2 and NO_x. The dashed line on the upper graph shows the limit value that entered into force in 2010. Previous results from Copenhagen/1103 can be found at the homepage of Copenhagen's Technical and Environmental Administration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

Both NO_2 and NO_x were higher in 2010-2013 compared to 2009 at the street station H.C. Andersens Boulevard (Copenhagen/1103). At all other street stations the levels in 2010-2013 were equal to or lower than observed in 2009. A detailed study at H.C. Andersens Boulevard has shown that the higher concentrations at the measurement station is mainly due to a permanent change in the traffic lanes, and that this is the main reason for the 8-9 µg/m^3 increase in NO_2 that has been observed since the middle of 2010 (Ellermann et al., 2014).

3.3 Results from model calculations

Changes in the input data to OSPM and the recalibration of the model leads to changes in concentration levels and the ranking of NO_2 concentrations between 2012 and 2013 that is larger than normal variations due to changes in average daily traffic and vehicle distribution between two consecutive years. For more details see section 2.2.1. This should be kept in mind when comparing 2012 and 2013.

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

The selected streets represent busy streets and are mainly street canyons. Concentrations are elevated in this type of streets due to the high emissions and restricted dispersion conditions. 98 streets were selected in Copenhagen and 31 in Aalborg.

ADT was between 5,400 and 67,600 vehicles/day in Copenhagen and between 2,700 and 28,300 vehicles/day in Aalborg. On average traffic volumes and heavy-duty share increased about 3-4% in Aalborg from 2012 to 2013 whereas traffic volume on average decreased 1% and heavy-duty share 3% in Copenhagen compared to 2012. 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 µg/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.

3.3.1 Model calculations for Copenhagen

The annual mean concentrations of NO_2 for Copenhagen in 2013 are shown in Figure 3.2 (bar chart) and Figure 3.3 (map).

One street (Vester Voldgade) is not included in the assessment for this year since the street segment has been closed for vehicle traffic where the calculation point is located due to construction of a new Metro line.

The average of NO_2 concentration at all 98 streets has decreased 7% from 2012 to 2013. The general decrease is a result of the many changes made in input data and subsequent re-calibration of OSPM and may not necessarily be assessed as a real decrease from 2012 to 2013. The modelled decrease is a combination of a number of factors that contribute to both decreases and increases in modelled concentrations. Most streets get lower travel speeds but some get higher compared to last year. OSPM was calibrated against measurements to compensate for the higher modelled emissions and lower traffic induced turbulence due to lower travel speeds. Modelled urban

background concentrations decreased by about 1 µg/m^3 that corresponds to a decrease of about 2% for street concentrations. Emissions show a decrease due to the general replacement of the car fleet and lead to decrease in modelled concentrations. There is a slight decrease in ADT of 1% and heavy-duty share of 3% that leads to slightly lower concentrations. Changes in general building height can lead to lower or higher concentrations depending on the street configuration.

In 2013 the limit value for the annual mean concentration was exceeded in 12 out of the 98 selected streets in Copenhagen (Figure 3.2). This is less that in 2012 where the number of streets exceeding the limit value was 19 out of 99. The number of streets exceeding the limit value is very sensitive to small changes in concentrations and uncertainties in the assumptions as can be seen from Figure 3.2 as a number of streets are close to the limit value.

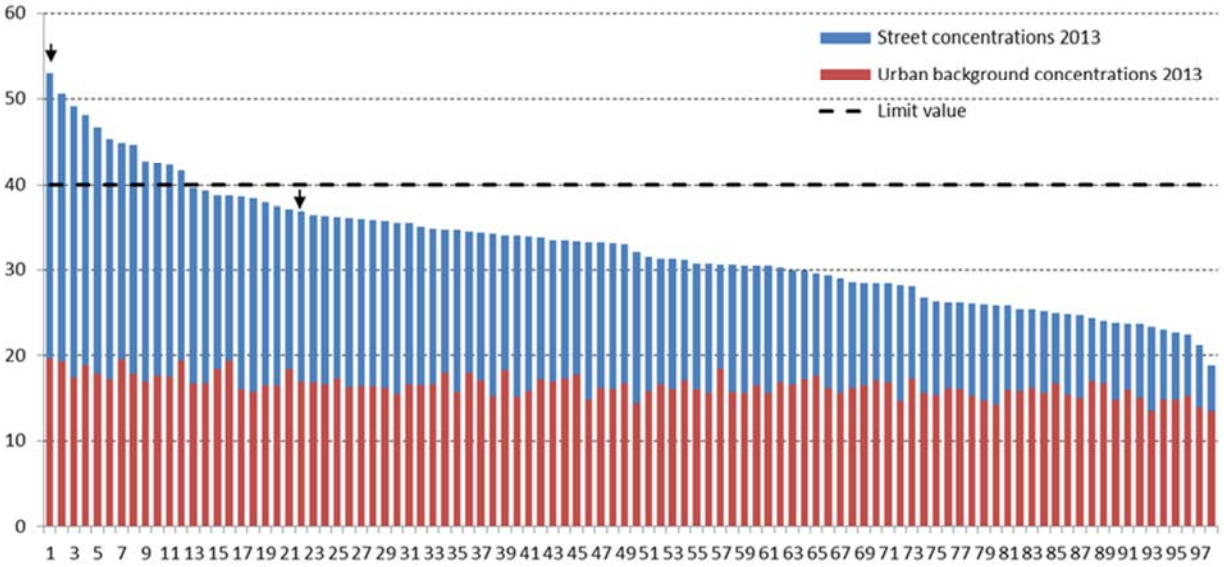


Figure 3.2 Annual mean concentrations of NO_2 in 2013 for 98 streets in Copenhagen. The contribution from traffic in the street canyons is based on the street canyon model OSPM®. The urban background (dark red colour) is obtained from calculations with the urban background model UBM with input from the regional scale model DEHM. The value for a street segment is for the side of the street with the highest annual mean concentration of the two sides. However, for streets with a measurement station it is the side of the location of the station. The names of the streets can be seen in Table 3.3. Arrows indicate street segments with a measurement station.

The streets where the limit value were exceeded all have average daily traffic in the range of 12,200 to 67,600 vehicles per day. However, it is not only the traffic intensity alone which determines the concentration of NO_2. Also the travel speed, vehicle distribution, and street geometry like the width of the streets, the height of the surrounding buildings, openings in the building façade, orientation of the street and background concentrations have impacts on the concentration of NO_2 in a street.

The names of the 98 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.

There have been changes in the ranking of streets according to NO_2 concentrations from 2012 to 2013 mainly due to changes in travel speeds now based on SpeedMap but also changes in Euro 5 and 6 NO_x emission

factors for passenger cars, and changes in the parameterisation of OSPM concerning general building height and re-calibration of OSPM. However, out of 12 exceedances in 2013 8 of these were also exceedances in 2012 leaving 4 new street segments with exceedances in 2013. These street segments are (highest concentrations first): H.C. Andersens Boulevard (3), Vesterbrogade (1), Åboulevard (1) og Bernstorffgade (1). Jagtvej (1) is the location of the monitor station and modelled NO_2 is 37 µg/m^3. Jagtvej has moved up 4 steps in the ranking compared to last year (from 26 to 22). Observed concentrations are 38 µg/m^3.

The highest modelled NO_2 concentration in 2013 is at H.C. Andersens Boulevard (1) (53 µg/m^3) which is the location of the monitoring station. Observed concentrations are 55/47 µg/m^3. This location was ranked number two in 2012.

Table 3.3 Number and names for the street segments that are shown in Figure 3.2 and 3.3. The streets are numbered (1-98) according to NO_2 levels in 2013 (1 = highest, 98 = 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. Note that Vester Voldgade is not included as the road segment, where the calculation point is, has been closed due to construction of new Metro line.

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

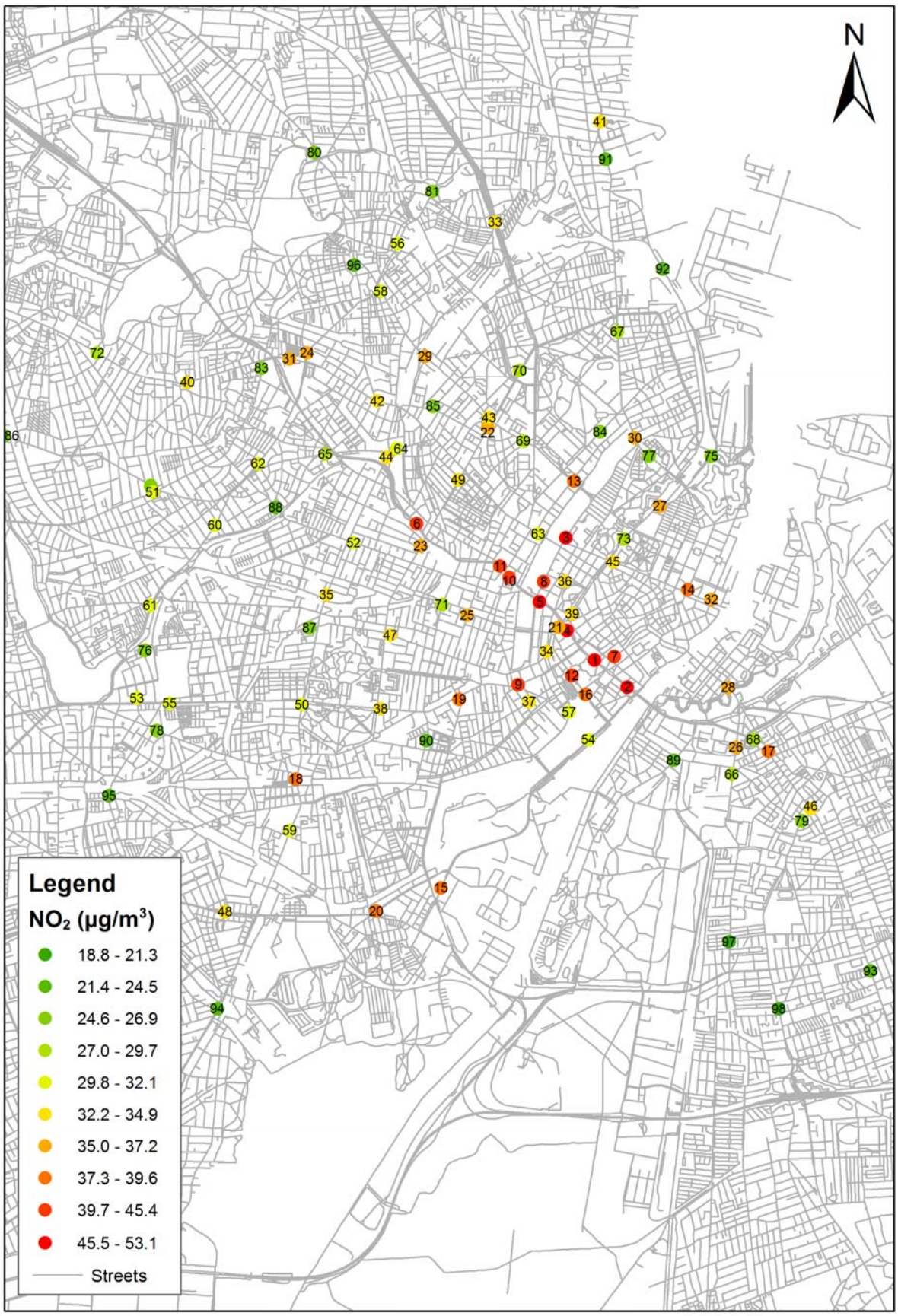


Figure 3.3 Map showing the locations of the selected streets in Copenhagen and the annual mean concentrations of NO_2 for 2013. The contribution from traffic in the street canyons is based on the street canyon model OSPM®. The urban background is obtained from calculations with the urban background model UBM with input from the regional scale model DEHM. The value for a street segment is for the side of the street with the highest annual mean concentration of the two sides. However, for streets with a measurement station it is the side of the location of the station. The names and numbers for the streets are shown in Table 3.3.

3.3.2 Model calculations for Aalborg

For Aalborg the modelled street concentrations show an average decrease of 12% for NO_2 compared to 2012 when only considering the 22 out of 31 street segments that had SpeedMap travel speeds. 9 out of 31 streets did not get updated SpeedMap travel speeds as they were not located on the LTM road network (Landstrafikmodellen). Therefore, for these 9 streets a too high travel speed is assumed that leads to lower modelled concentrations than would otherwise have been the case with lower travel speeds from SpeedMap. Only considering these streets a decrease of 21% is modelled. The general decrease is a result of the many changes made in input data and subsequent re-calibration of OSPM and may not necessarily be assessed as a real decrease from 2012 to 2013. Other factors also influence the results. Modelled urban background concentrations decrease by about 0.3 µg/m³, corresponding to about 1% decrease in street concentrations. Emissions show a decrease due to the general replacement of the car fleet that partly explains the decrease. Changes in general building height can be a part of the explanation as some streets will have lower or higher concentrations due to changes in calculated general building heights. In general, the decrease is not due to changes in ADT and vehicle distribution as the average was slightly higher in 2013 compared to 2012. ADT was 3% higher and heavy-duty share was 4% higher. The average NO_2 street concentration considering all 31 street segments has a modelled decrease of 14%.

According to the model calculations the limit value for the annual mean concentration in 2013 was not exceeded at any of the 31 selected streets which was also the case in 2012 (Figure 3.4 and Figure 3.5). The order of the streets has changed slightly due to the above changes.

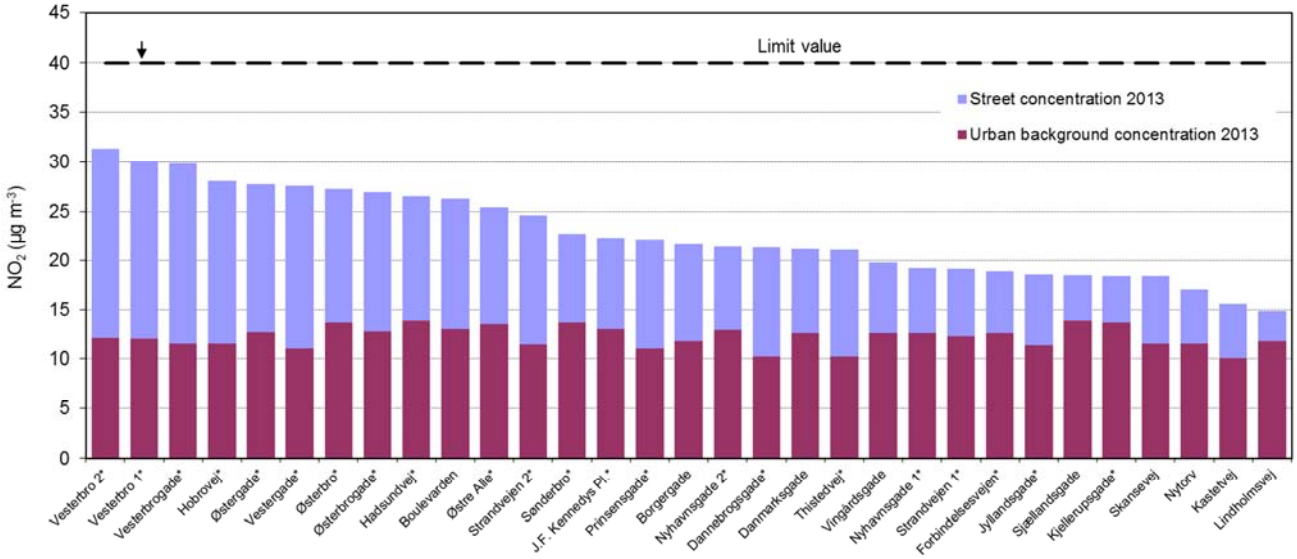


Figure 3.4 Modelled annual mean concentrations of NO_2 in 2013 for 31 streets in Aalborg. The contribution from traffic in the street canyons is based on the street canyon model OSPM®. The urban background (dark red colour) is obtained from calculations with the urban background model UBM with input from the regional scale model DEHM. The value for a street segment is for the side of the street with the highest annual mean concentration of the two sides. However, for streets with a measurement station it is the side of the location of the station. The arrow indicates the street segment (Vesterbro 1) with the measurement station. '*' at the end of the street name indicates that calculations were based on SpeedMap data.

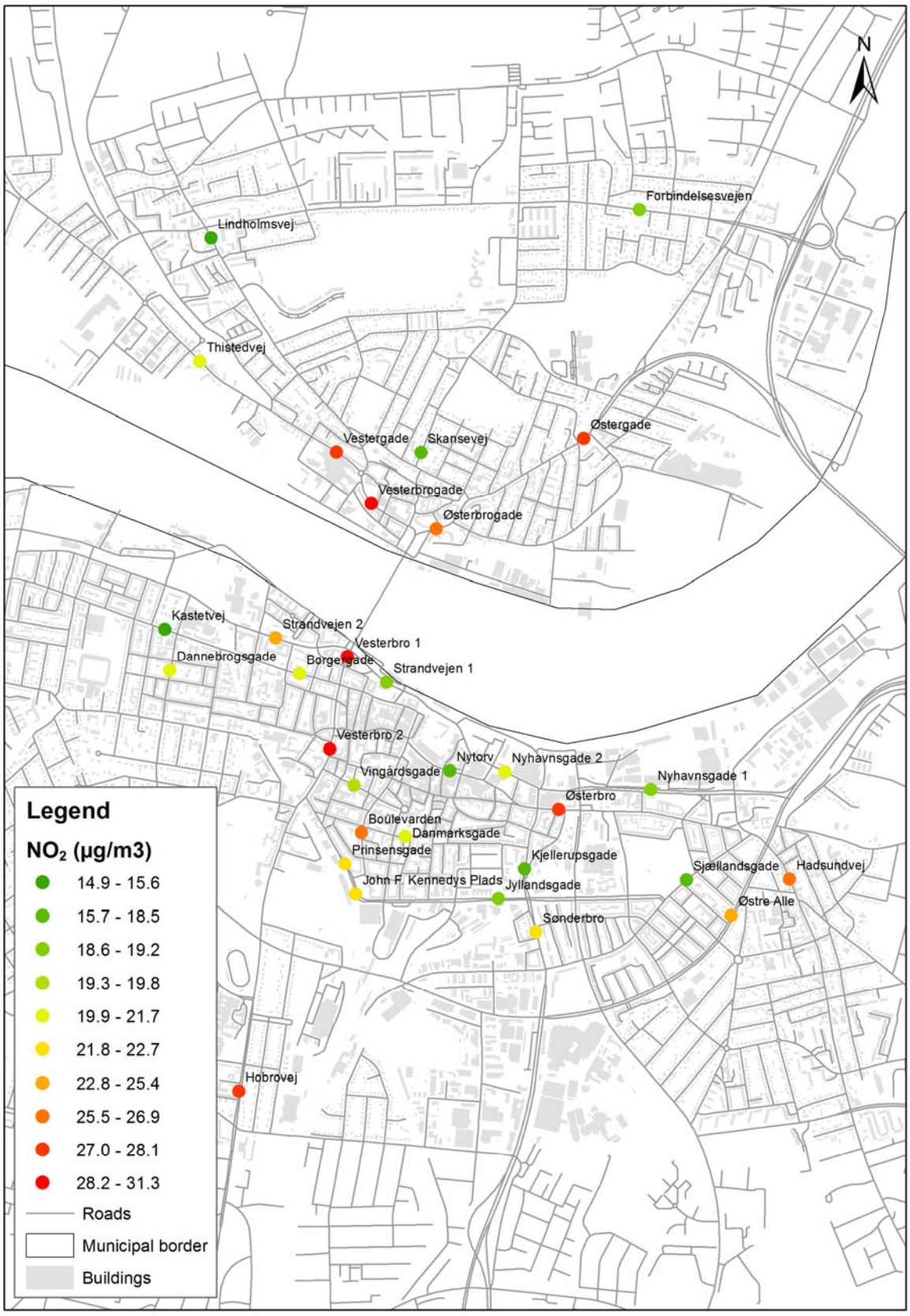


Figure 3.5 Map showing the location of the selected streets in Aalborg and the annual mean concentrations of NO_2 for 2013. The contribution from traffic in the street canyons is based on the street canyon model OSPM®. The urban background is obtained from calculations with the urban background model UBM with input from the regional scale model DEHM. The value for a street segment is for the side of the street with the highest annual mean concentration of the two sides. However, for streets with a measurement station it is the side of the location of the station. 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 2013 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 2011-2013 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 2013 there was no 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.

Table 4.1 Ozone (O_3) in 2013. 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.	Days above target value	Max.
				8 hours	8 hours	1 hour
Urban Background:						
Copenhagen/1259	7988	57	58	121	4	129
Århus/6159	7608	53	56	117	4	128
Odense/9159	7700	58	60	142	5	168
Aalborg/8158	7796	58	60	116	2	127
Rural						
Risø/2090	7972	64	65	139	9	142
Keldsnor/9055	7756	60	61	132	3	142
Traffic						
Copenhagen/1103	7944	34	33	91	0	101
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 (NO_x, 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.

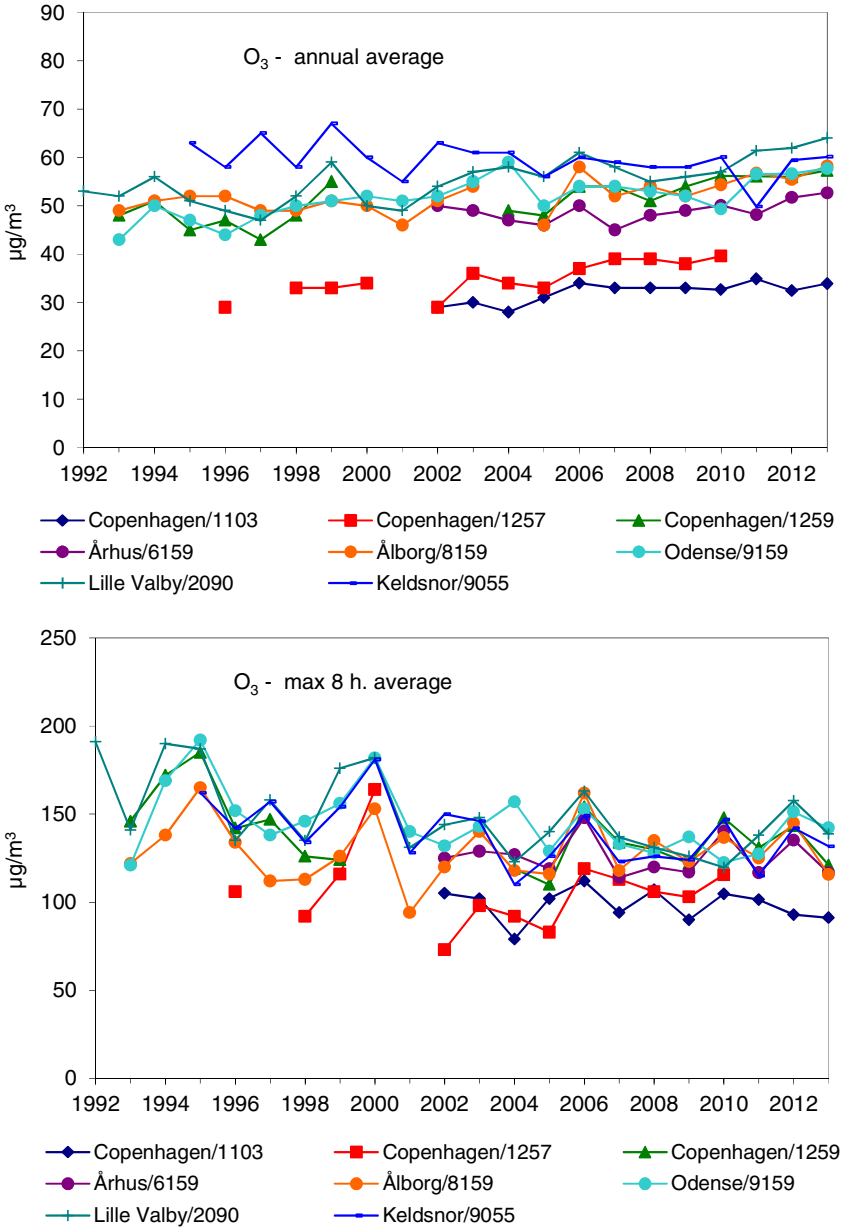


Figure 4.1 Annual average values and the max. 8 hour average value. The latter is calculated as 8 hourly running averages according to the provisions in the EU Directive (EC, 2008). Previous results from Copenhagen/1103 can be found at the Website of the Copenhagen Environmental Protection Agency (www. 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 µg/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 µg/m^3. The target value and long term objective are given in the EU Directive (EC, 2008). Results from the model calculations for 2013 show that the maximum daily 8 hour mean value of 120 µg/m^3 was only exceeded up to 5 days during 2013 (Figure 4.3). Similar results were obtained for 2010 - 2012 and hence the target value was not exceeded. However, the long term objective was exceeded at in large parts of Denmark (Figure 4.4). The highest 8 hour mean concentrations were observed at Bornholm, because it is a small island sourround by sea and the long range transported ozone is only deposited slowly over sea.

According to the directive (EC, 2008) the public has to be informed if the one hour average concentration exceeds the information threshold at 180 µg/m^3. Both measurements and model calculations shows that this threshold was not exceeded in 2013 (Figure 4.5). The model calculations underestimate the maximum one hour mean concentration with about 10-20%. One of the 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.

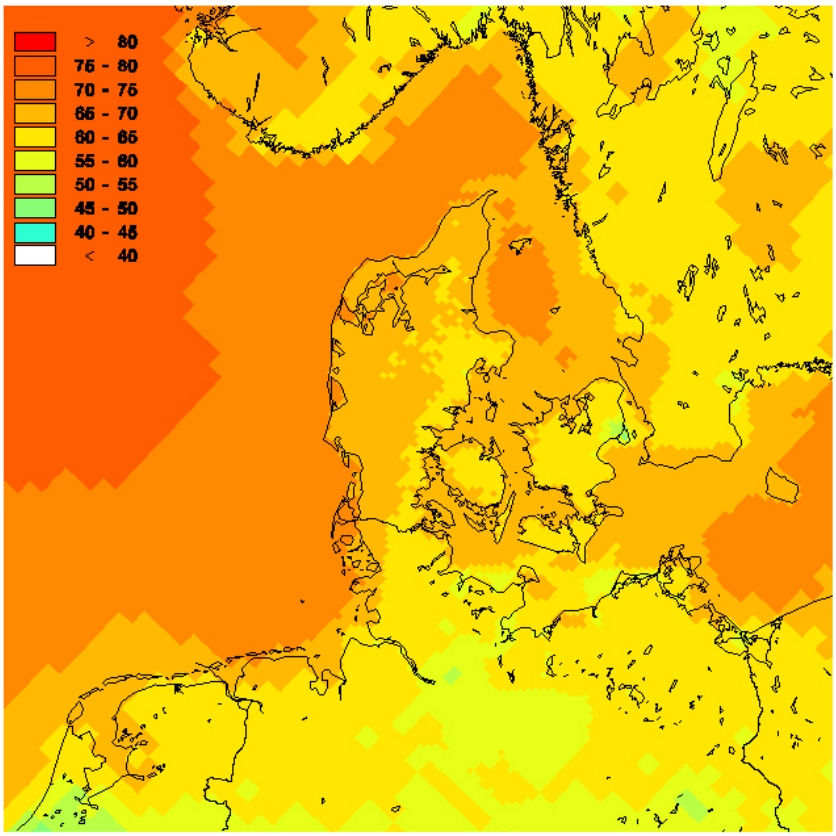


Figure 4.2 Annual mean concentrations of O_3 (µg/m^3) for 2013 calculated using DEHM. The figure shows the average concentrations for the 6 km x 6 km grit cells used in the model.

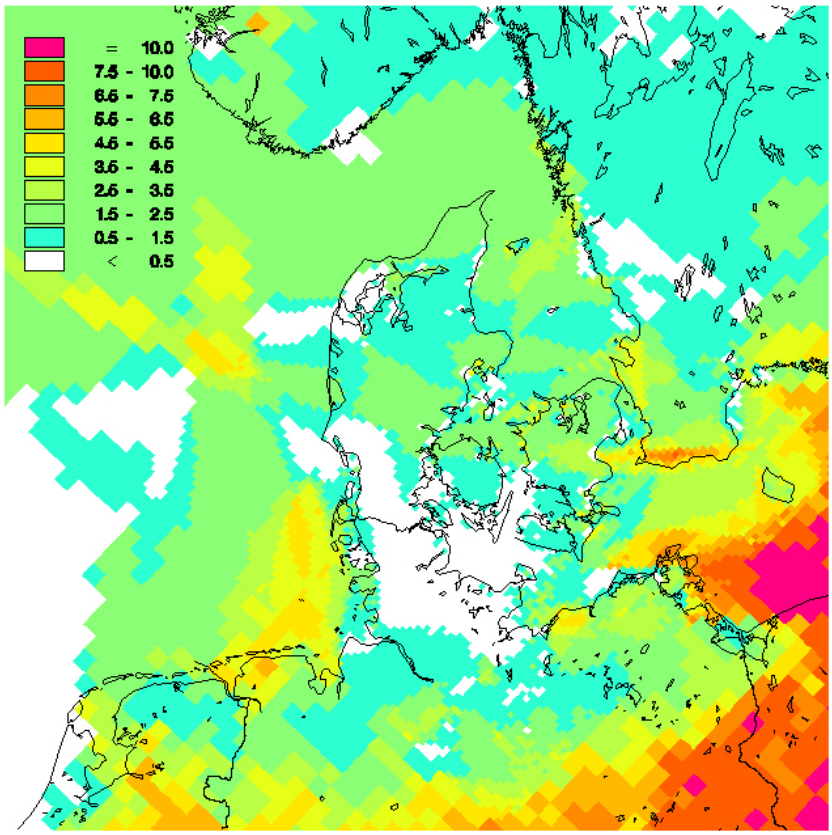


Figure 4.3 Number of exceedances of 120 µg/m^3 for 8-hour running mean concentrations of ozone in 2013. The calculations were carried out using DEHM.

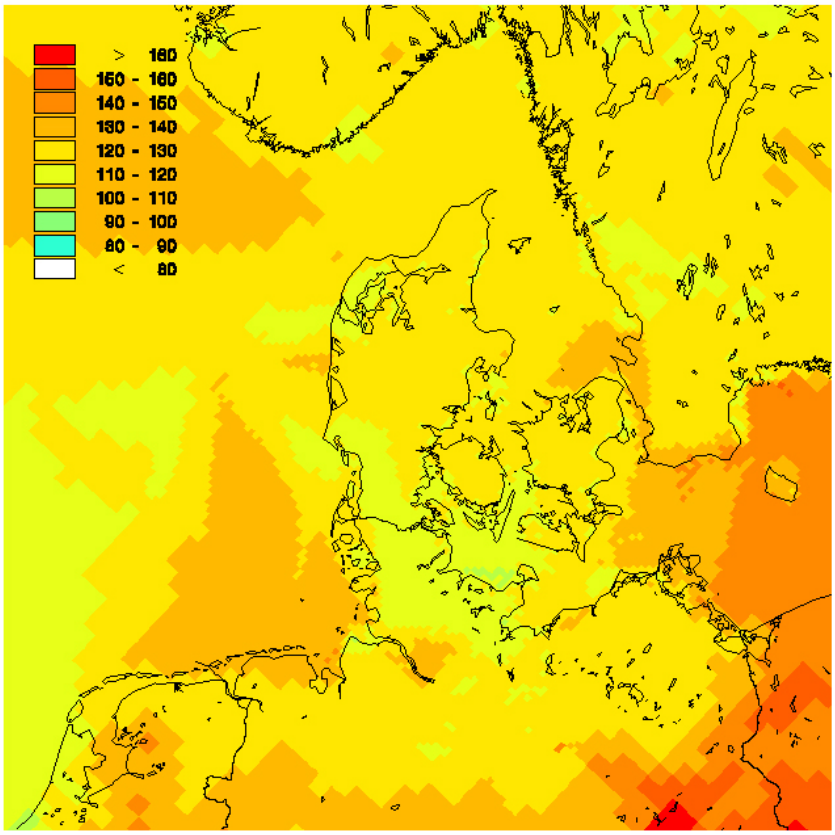


Figure 4.4 Maximum 8 hour running mean concentration (µg/m^3) of ozone in 2013 calculated using DEHM.

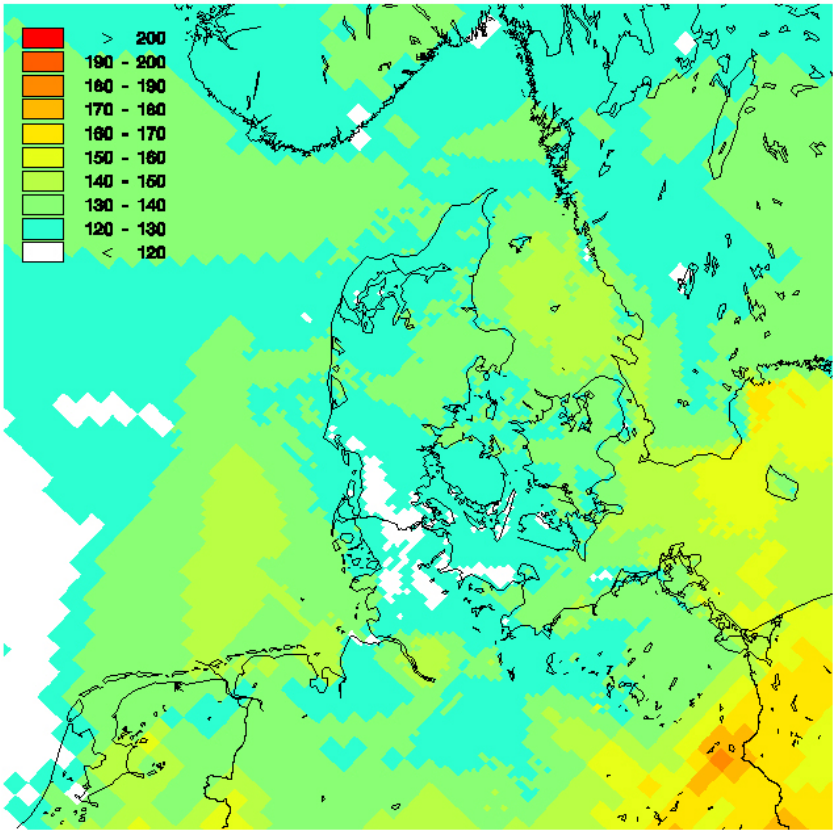


Figure 4.5 Maximum one hour mean concentration of ozone (µg/m^3) in 2013 calculated using DEHM.

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 2013 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 2013. 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	8263	361	325	789	1211	1074	1727
Århus/6153	8033	286	255	665	1411	1434	1764
Odense/9155	8174	363	289	1022	1868	1904	2513
Aalborg/8151	8024	396	350	801	1272	1056	1403
Urban Background:							
Copenhagen/1259	8148	240	226	480	755	828	1085
Rural							
Risø	8271	199	170	456	809	845	955
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.

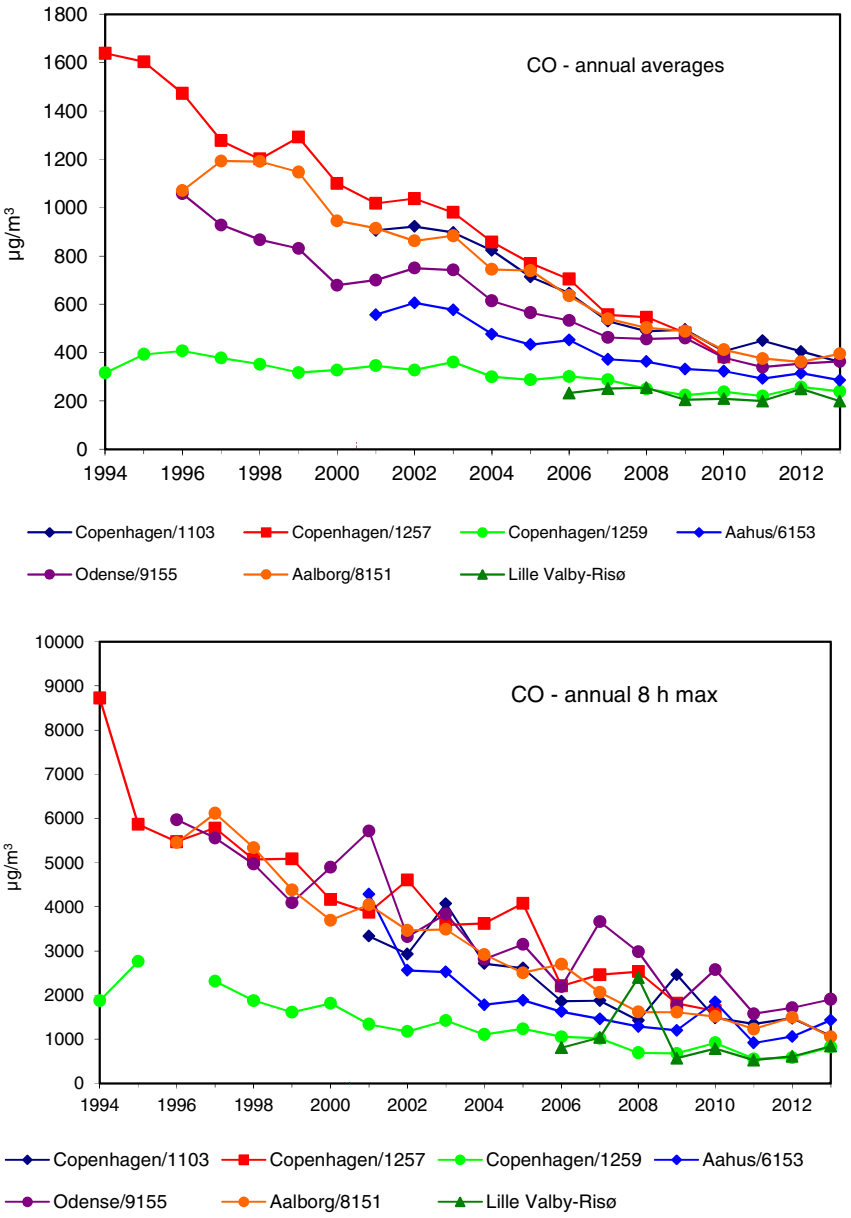


Figure 5.1 Annual average values and highest 8-hour values calculated based on an hourly moving average.

6 Benzene and Toluene

Benzene and toluene are measured at two kerb-side stations in Copenhagen, Jagtvej/1257 and H.C. Andersen's Boulevard/1103, using a passive sampling method of weekly time resolution. Benzene, toluene and 15 other ozone precursors are also measured in urban background (H.C. Ørsted Institute/-1259) using active sampling of daily time resolution (Chapter 12).

6.1 Annual statistics

The annual averages of benzene and toluene in 2013 are listed in Table 6.1 and Table 6.2. The annual average of benzene was about 20% of the EU-limit value (EC, 2008) and the annual average for toluene was only about 15% of the WHO guide line value (WHO, 2000).

The annual averages of benzene and toluene in urban background/1259 were 0.46 µg/m^3 and 1.1 µg/m^3, respectively as described in Chapter 12. The different ratios are influenced by the distance to sources and atmospheric degradation. The high toluene/benzene ratio of ~ 3 at the street stations is typical for traffic sources, whereas wood combustion is characterised by a factor < 1 (Hedberg et al., 2002). For this reason, the toluene/benzene ratio is not constant throughout the year, but lowest in the heating season, where benzene from wood combustion adds to the ambient benzene concentration.

Table 6.1 Annual statistics for benzene in 2013 based on weekly average concentrations at 1 atm. and 293 K. The limit value is based on the 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	1.1	2.2
Limit value		5	

Table 6.2 Annual statistics for toluene in 2013 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	2.9	4.2
Copenhagen/1257	52	2.9	5.1
Guideline value	-	-	260

The concentrations of benzene are not measured directly in Aarhus, Odense, and Aalborg, however, since the concentrations are below the lower assessment threshold limit an objective estimate of the concentrations can be used to determine the concentration levels.

The objective estimate for benzene is based on the correlations between the average concentrations of benzene and CO. Ellermann et al. (2012) documented that the benzene concentrations can be estimated based on the simple empirical model:

Benzene = 0.0044·CO - 0.37

where benzene and CO are in units of µg/m³.

Based on this and the concentrations of CO (Table 5.1) the annual average concentrations of benzene is estimated to about 1 µg/m³ for all the three street stations in Aarhus, Odense and Aalborg in 2013.

6.2 Trends

Benzene has decreased from approximately 6 µg/m³ on Jagtvej (Copenhagen/1257) in 1998, to a value below the lower assessment threshold (EC, 2008) of 2 µg/m³ since 2007. In 2013 the annual averages were 1.1µg/m³ at both street stations in Copenhagen. Toluene shows a similar trend, which indicates that benzene and toluene are mainly emitted from traffic. Annually averages for toluene were 2.9 µg/m³ at both kerbside stations. The main reasons for the significant decreases of benzene and toluene up to 2008 are reductions of the emissions from gasoline-fuelled traffic due to increased use of catalysts and higher ratio of diesel cars.

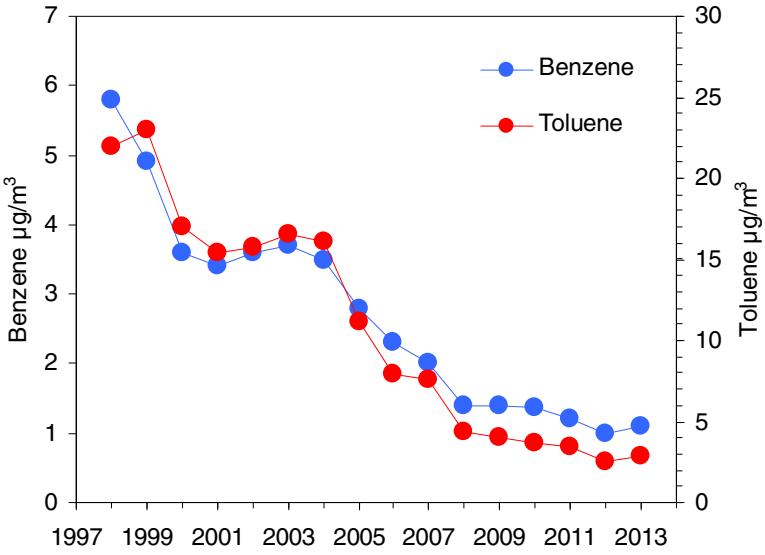


Figure 6.1 Annual average concentrations of benzene and toluene on the kerbside station Jagtvej, Copenhagen/1257.

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 sampled on the filters. 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 (LVS) i.e. a flow of 2,3 m^3/hr with following gravimetric determination of the sampled mass in the laboratory. During the course of 2012-13 LVS were introduced into the regular measuring programme to replace some of the older SM200 instruments that needed to be renewed and installed at seven stations in the network (HCAB PM_{10} and $PM_{2.5}$; HCØ PM_{10} and $PM_{2.5}$; Jagtvej PM_{10} and $PM_{2.5}$; Risø $PM_{2.5}$) with the first measurements running from August 2012. At Jagtvej $PM_{2.5}$ a LVS 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 $PM_{2.5}$ data. In 2013 at five stations (HCAB PM_{10} and $PM_{2.5}$; HCØ $PM_{2.5}$; Jagtvej PM_{10}; Risø $PM_{2.5}$) PM was measured throughout the year by using LVS. At two stations HCØ PM_{10} and Jagtvej $PM_{2.5}$ LVS instruments replaced SM200 measurements from the 26th June and 16th November 2013 respectively why the data series in 2013 from these two stations consists of a combination of SM200- and LVS measurements. Preliminary results from comparing LVS 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 LVS instruments.

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

In 2013 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 [from 2015]) 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 2011-2013 the AEI is determined to 13 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 2013. All parameters are based on 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[1]	339	29	28	14	43	100
Copenhagen/1257[1]	342	24	22	6	39	89
Århus/6153[2]	362	21	19	4	33	80
Odense/9155[2]	343	23	19	16	43	103
Urban background						
Copenhagen/1259*	329	17	15	1	27	60
Rural						
Risø[2]	344	14	13	0	24	46
Keldsnor/9055[2]	339	16	14	3	30	64
Limit value (2005)	>328**	40		35***		

[1] Measurements based on LVS with gravimetric determination of particle mass

[2] Measurements based on SM200 beta gauge determination of particle mass

* Combination of LVS gravimetric and SM200 beta gauge determination of particle mass

** 90% data capture of number of diurnal measurements in relation to number of days in 2013

*** 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 2013.
All parameters are based on diurnal averages at ambient temperature and pressure.

Unit µg/m^3	Number of results	Average	Median	90 percentile	Max. day
Traffic					
Copenhagen/1103[1]	328	17	15	28	52
Copenhagen/1257*	347	14	12	24	52
Århus/6153[2]	356	11	10	21	49
Aalborg/8151[2]	362	13	12	21	48
Urban background					
Copenhagen/1259[1]	351	11	9	19	47
Århus/6159[2]	362	10	9	17	48
Aalborg/8158[2]	355	9	8	16	45
Rural					
Risø[1]	349	10	8	19	44
Limit value (2015) (parenthesis gives proposed value for 2020)	>328**	25(20)			

[1] Measurements based on LVS with gravimetric determination of particle mass.

[2] Measurements based on SM200 beta gauge determination of particle mass.

* Measurements based on a combination of LVS gravimetric and SM200 beta gauge determination of particle mass.
** 90% data capture of number of diurnal measurements in relation to number of days in 2013.

Table 7.3 Annual statistics for PM_{10} measured in 2013 using TEOM. The values are based on ½-hourly averages. Total annual number of ½-hours is 17520.

Unit: µg/m^3	Number of results	Average	Average x 1.3
Traffic:			
Copenhagen/1103	---	---	---
Rural:			
Risø	14072	13	16
Limit value			40

Table 7.4 Annual statistics for $PM_{2.5}$ measured in 2013 using TEOM. The values are based on ½-hourly averages. Total annual number of ½-hours is 17520.

Unit: µg/m^3	Number of results	Average	Average
Traffic:			
Copenhagen/1103	16283	12	16
Rural:			
Risø	15300	8	10
Limit value (2015) (parenthesis gives proposed value for 2020)			25(20)

Table 7.5 Annual statistics for particle number measured in 2013 using DMPS. All values are based on ½-hourly averages. Total annual number of ½-hours is 17520.

Unit: µg/m^3	Number of results	Average
Traffic:		
Copenhagen/1103	11289	16864
Urban Background:		
Copenhagen/1259	12863	4506
Rural:		
Lille Valby	11198	2819

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) and PM_{10} measurements were 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 all 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 µg/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 from 2008 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 µg/m^3, 2009-2011: 15 µg/m^3, 2010-2012: 14 µg/m^3, 2011-2013: 13 µg/m^3).

The measurements show a significant reduction of particle number in ambient air (Figure 7.4) over the total measuring period. On HCAB the number of particles has decreased by a factor of about 2 during the period 2002-2012. At the urban background station (HCØ) 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 HCØ and LVBY/Risø, respectively.

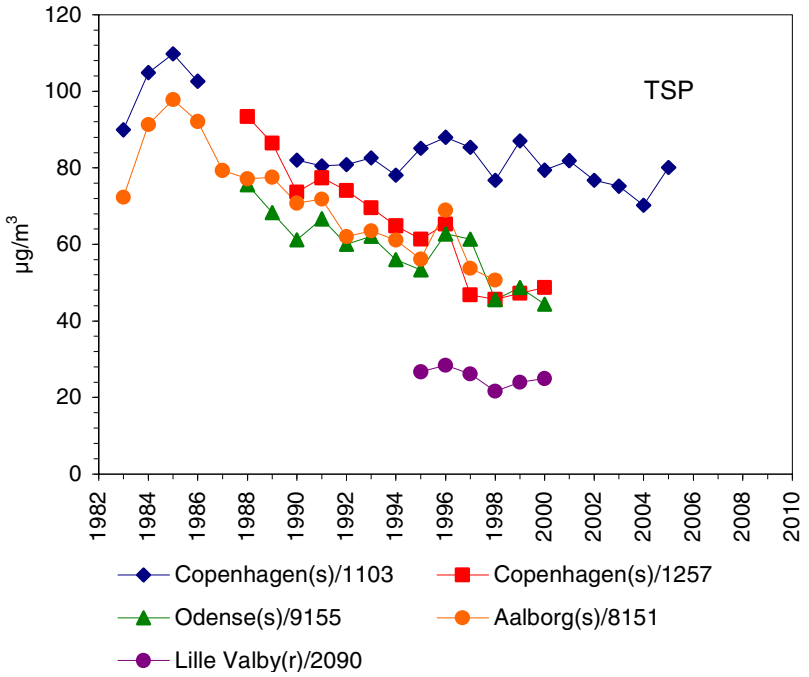


Figure 7.1 Annual averages for TSP measured at street stations (s) and at rural background station (r).

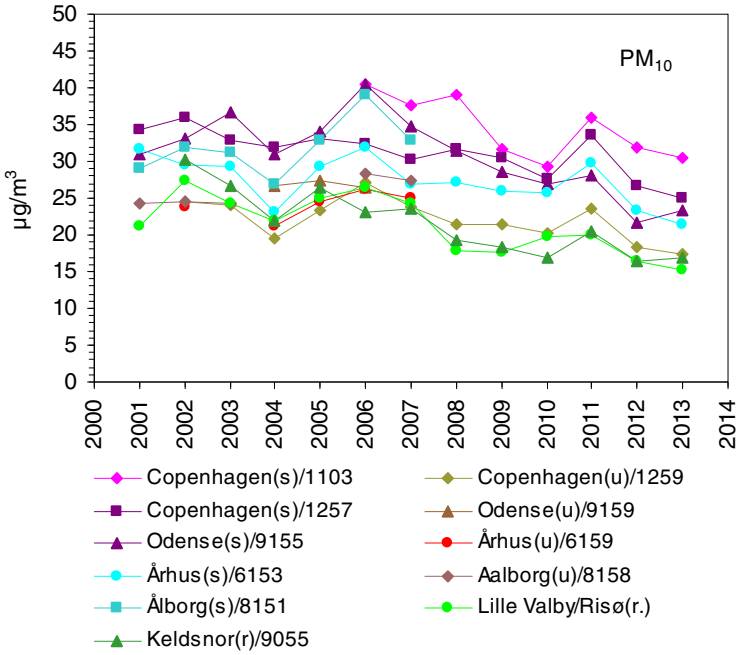


Figure 7.2 Annual averages for PM_{10} measured at street stations (s), urban background stations (u) and at rural background stations (r). The change from gravimetric determination using the SM200 as a filter sampler to the use of the same instrument as a β-gauge from 2006 gives rise to a 5-10% increase 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 (HCAB/1103 and Jagtvej-/1257 from Aug/Sep. and HCØ/1259 from 26 Jun. 2013) PM_{10} is measured by the LVS gravimetric reference method. Data are given at standard temperature- and pressure conditions (0ºC and 1 atm.). PM given at ambient temperature and pressure conditions is on an annual average approximately 3% lower than PM-results given at standard conditions.

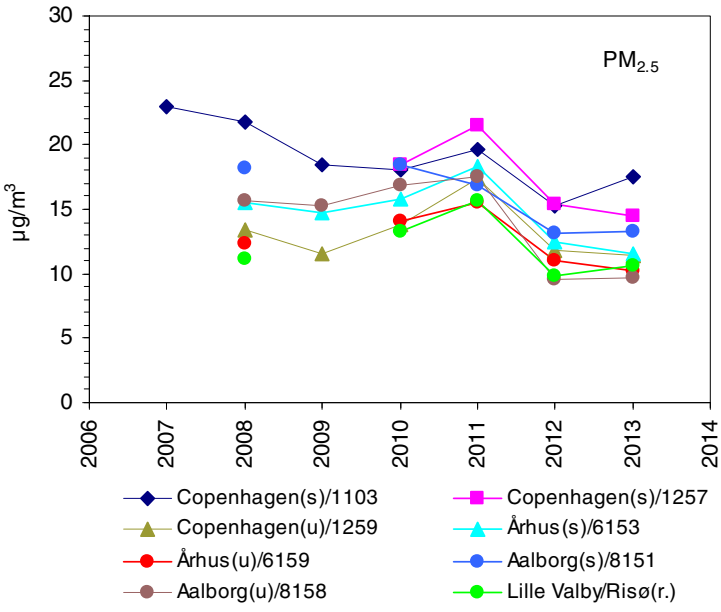


Figure 7.3 Annual averages for $PM_{2.5}$ measured at street stations (s), urban background stations (u) and at rural background station (r). Only annual averages covering more than 2/3 of the years are shown. At the stations HCAB/1103 and HCØ/1259 and at Risø $PM_{2.5}$ from Aug./Sep. 2012 and Jagtvej/1257 from 16 Nov. 2013 is measured by LVS gravimetric reference method. Data are given at standard temperature- and pressure conditions (0ºC and 1 atm.). PM given at ambient temperature and pressure conditions is on an annual average approximately 3% lower than PM-results given at standard conditions.

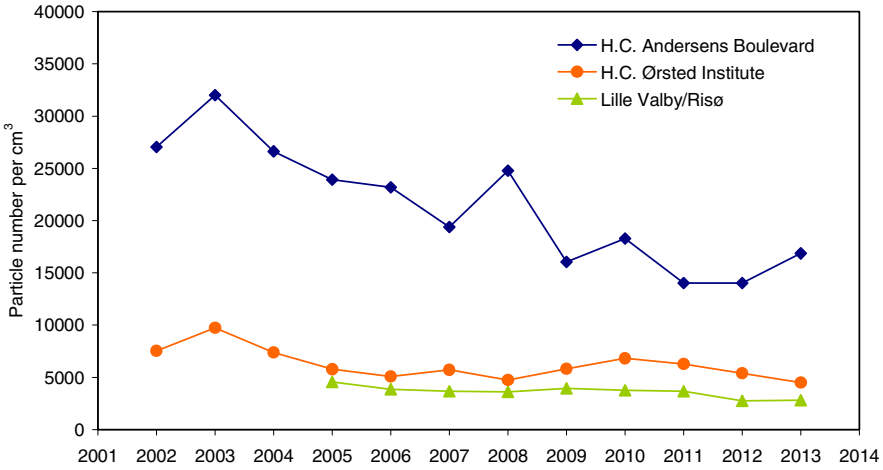


Figure 7.4 Annual averages for particle number. Data for H.C. Andersens Boulevard represents an estimate where annual averages have been corrected for missing data based on comparison with measurements of NO_x. This estimate is further described in Massling et al. (2011).

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 prepare an air quality plan in order to reduce the levels of PM_{10}. These rules account for both the annual limit value and the daily limit value that states that the daily PM_{10} concentration must not exceed 50 µg/m^3 more than 35 days a calendar year.

On this background the monitoring program was expanded in 2010 with daily sampling and analysis of sodium at the street stations H.C. Andersens Boulevard, Copenhagen (1103), Odense (9155) and Aarhus (6153) and at the urban background station in Copenhagen (H.C. Ørsted Institute/1259). Table 7.6 gives the annual average concentrations for sodium and estimate for total salt (NaCl) in 2013 (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	1.5	3.7
Odense/9155	2.3	5.8
Aarhus/6153	1.7	4.3
Urban Background:		
Copenhagen/1259	1.0	2.6

Figure 7.5 shows the results from measurements of sodium at the street station H.C. Andersen's Boulevard, Copenhagen (1103) and at urban background in Copenhagen (H.C. Ørsted 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 main part of the remaining year is due to long range transport of sea salt that have equal impact on the two stations.

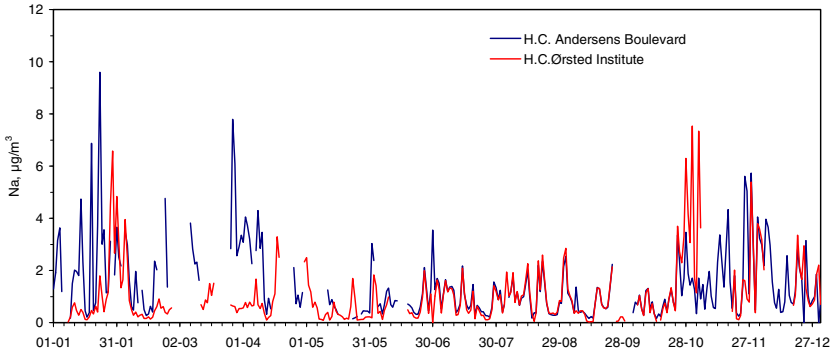


Figure 7.5 Diurnal concentrations of sodium at H.C. Andersen's Boulevard, Copenhagen (1103) and at urban background in Copenhagen (H.C. Ørsted Institute/1259).

In 2013 the permitted number of exceedances in a year of the diurnal limit value of 50 µg/m^3 for PM_{10} was not passed at any stations in the measuring network and therefore it has not been necessary to correct PM_{10} 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 Rööå (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 2013. 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	2.6	7.8	22	3.4	82	41	0.8	0.7	0.1	3.7
Odense/9155***	2.0	4.0	15	2.4	37	37	0.7	0.7	0.1	4.4
Aarhus/6153***	2.0	3.7	7.7	4.0	34	23	0.6	0.6	0.1	1.7
PM_{10},Urban background:										
Copenhagen/1259	1.2	2.7	5.0	2.2	9.5	13	0.5	0.5	0.1	2.8
TSP, Rural Background										
Risø	1.3	0.8	2.6	1.8	2.7	11	0.6	0.4	0.1	2.3
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.

***) Vanadium has low data representativity for Odense and Aarhus due to technical problem with the analysis instrument.

Table 8.2 Annual statistics for Mercury 2013. 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	0.005

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.

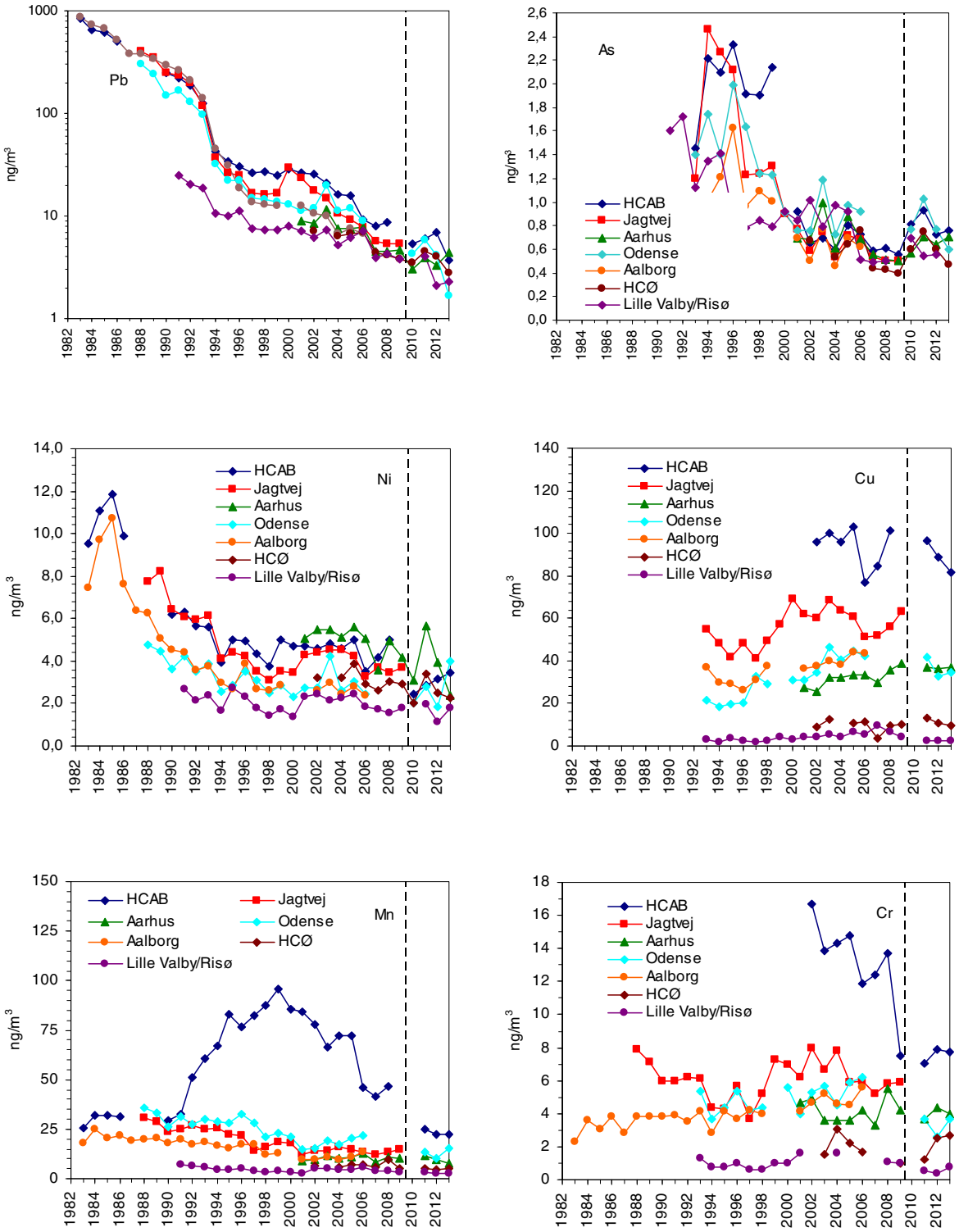


Figure 8.1 Annual averages from selected stations for some heavy metals in particulate matter. Until 2000 in TSP and later in PM_{10} – except for Copenhagen/1103 where PM_{10} replaced TSP from the beginning of 2006. The heavy metals are usually found in fine particles, which make the TSP and the PM_{10} 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 2013 for sulphur dioxide are shown in Table 9.1. None of the limit values (EU, 2008) were exceeded in 2013. In 2013 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 2013. 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. Hour	4th highest diurnal mean
Traffic							
Copenhagen/1103	8239	2.3	2.3	1.8	8.3	23.4	9.5
Aalborg/8151	8079	1.8	2.0	1.2	7.7	18.0	8.7
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's 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.

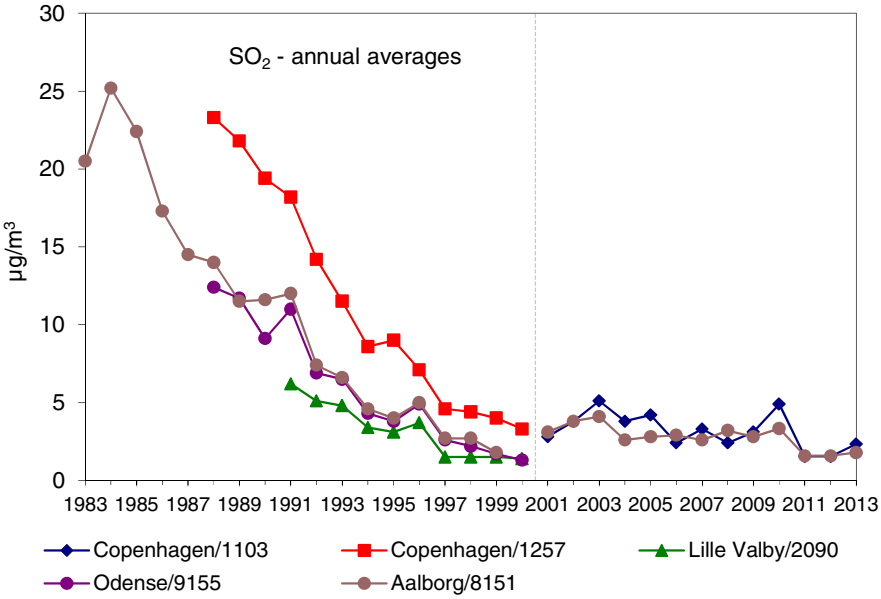


Figure 9.1 Annual averages for SO_2. Until 2001 the results were obtained using KOH impregnated filters for collection of SO_2. These measurements ceased in 2000. After 2000 the SO_2 measurements have been carried out using SO_2 monitors in order to monitor episodic results. The detection limit for the 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. Andersens Boulevard (Copenhagen/1103) in Copenhagen and at a temporary station in a suburban area in Hvidovre. PM is collected 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-labeled PAH. Analysis of the extracts is carried out by gas chromatography-mass spectrometry (GC-MS). Concentrations of individual PAHs in samples are corrected for recovery of a deuterium-labelled PAH standard with the closest molecular weight. A total of 18 PAHs are analysed with the method.

10.1 Annual Statistics

The average concentration of benzo[a]pyrene in 2013 measured was 0.24 ng/m^3 and 0.34 ng/m^3 at the street station on HCAB and suburban station in Hvidovre, respectively. The higher concentrations in Hvidovre are due to local wood burning for house hold heating. The minimum, maximum and average monthly concentrations of benzo[a]pyrene are summarized in Table 10.2 and 10.3.

The average annual concentrations of the other five PAHs listed as relevant in the EU Directive were the following: benzo[a]anthracene, 0.22 ng/m^3; benzo[b]fluoranthene, 0.34 ng/m^3; benzo[j+k]fluoranthenes, 0.34 ng/m^3; indeno[1,2,3-cd]pyrene, 0.33 ng/m^3; dibenzo[a,h]anthracene 0.06 ng/m^3.

Table 10.1 Annual average concentrations for the six PAHs listed in the EU Directive.

	HCAB ng/m^3	Hvidovre ng/m^3
Benzo[a]pyrene	0.24	0.34
Benzo[a]antracene	0.22	0.29
Benzo[b]fluoranthene	0.34	0.45
Benzo[j+k]flouranthenes	0.34	0.57
Indeno[1,2,3-cd]pyrene	0.33	0.38
Dibenzo[a,h]anthracene	0.06	0.08

The seasonal trends in PAH concentrations are summarized in Figure 10.1 and 10.2. 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 2013.

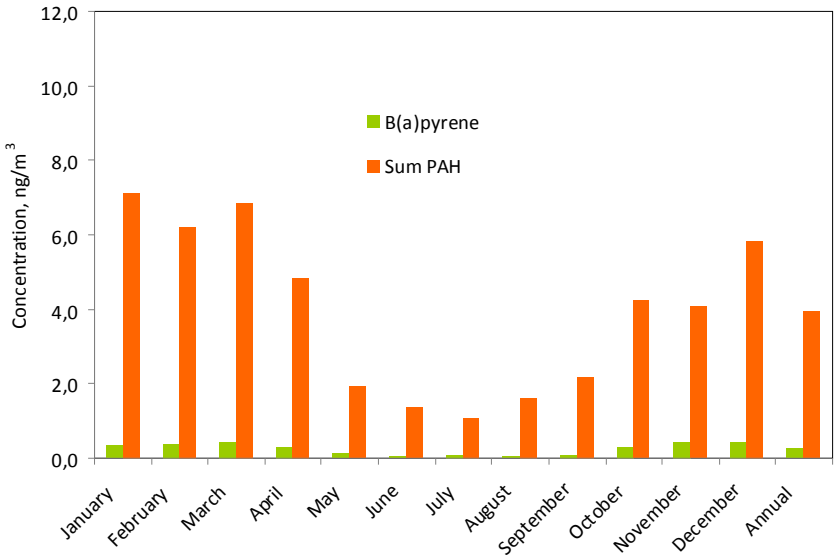


Figure 10.1 Monthly average concentrations in 2013 of benzo[a]pyrene and the sum of the analysed PAHs in Copenhagen.

Table 10.2 Daily minimum, maximum and average monthly concentrations (ng/m^3) of benzo[a]pyrene during 2013 in Copenhagen.

Month	Minimum conc.	Maximum conc.	Average conc.
January	0.16	0.63	0.36
February	0.26	0.72	0.39
March	0.38	0.50	0.42
April	0.15	0.37	0.28
May	0.06	0.20	0.11
June	0.03	0.07	0.06
July	0.04	0.11	0.08
August	0.05	0.08	0.06
September	0.07	0.16	0.10
October	0.22	0.39	0.29
November	0.17	0.37	0.41
December	0.33	0.61	0.43
Annual	0.03	1.06	0.24

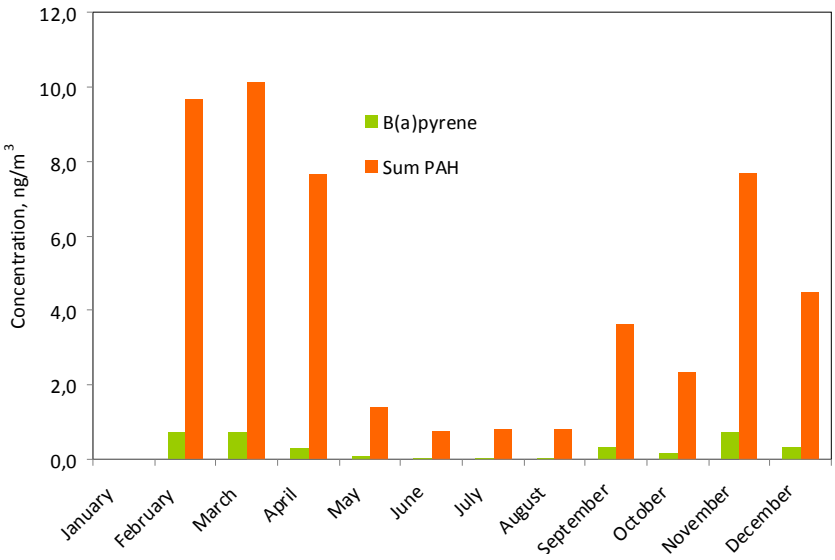


Figure 10.2 Monthly average concentrations in 2013 of benzo[a]pyrene and the sum of the analysed PAHs in Hvidovre.

Table 10.3 Daily minimum, maximum and average monthly concentrations (ng/m^3) of benzo[a]pyrene during 2013 in Hvidovre.

Month	Minimum conc.	Maximum conc.	Average conc.
February	0.25	1.01	0.73
March	0.42	0.87	0.71
April	0.22	0.56	0.32
May	0.06	0.11	0.08
June	0.04	0.05	0.05
July	0.04	0.06	0.05
August	0.04	0.07	0.05
September	0.08	0.63	0.33
October	0.08	0.28	0.18
November	0.34	1.21	0.74
December	0.27	0.40	0.33
Annual	0.04	1.21	0.34

10.2 Trends

The annual averages of benzo[a]pyrene since 2008 at the street station on HCAB are shown in figure 10.3. 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.

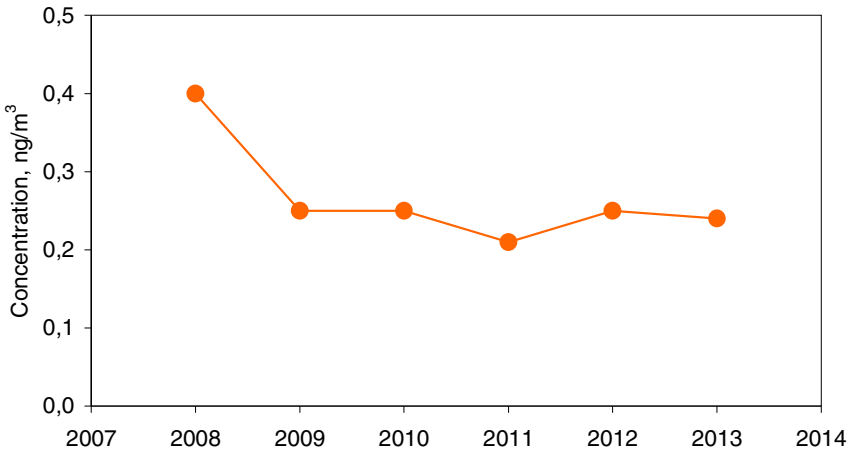


Figure 10.3 Annual average concentrations of benzo[a]pyrene at H.C. Andersens Boulevard (Copenhagen/1103).

11 Organic carbon and elemental carbon

Ambient concentrations of Organic Carbon (OC) and Elemental Carbon (EC) are measured on the street station H.C. Andersens Boulevard/1103 in Copenhagen and the semi-rural background station Risø North of Roskilde. $PM_{2.5}$ particulate matter is sampled on two filters in tandem, i.e. quartz-behind-quartz, to correct for positive artifacts from adsorption of volatile and semivolatile organic compounds. The filters are analyzed for OC and EC by a thermal/optical method according to the European EUSAAR2 temperature 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 street station in Copenhagen/1103 differed markedly: EC makes up about 50% of the total particulate carbon at kerb-side compared to about 20% in 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. On the kerbside station HCAB, EC and OC showed only minor variation.

Table 11.1 Annual statistics for OC in 2013. 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	99%	2.6	4.1
Risø	95%	1.3	2.4

Table 11.2 Annual statistics for EC in 2013. 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	99%	1.8	2.7
Risø	95%	0.3	0.6

EC at the street station in Copenhagen/1103 has decreased more than 22% relative to the period 2010-2012, which could to be due to reduced traffic emissions. At the same time, however, OC has increased slightly. Decreasing concentrations of both EC and OC have generally been observed over the last 4 years at the rural site Risø. As a result hereof, the ratio of EC to total carbon (TC) has been relatively constant in that period. While rural EC is likely to have decreased as a result of reduced anthropogenic emissions, the reason for lower OC concentrations is less clear. Moreover, EC and OC have only been measured in full calendar years since 2010. Thus, the reduction of OC may be due to natural variation. Generally, the largest contributor to ambient OC is atmospheric oxidation of biogenic compounds.

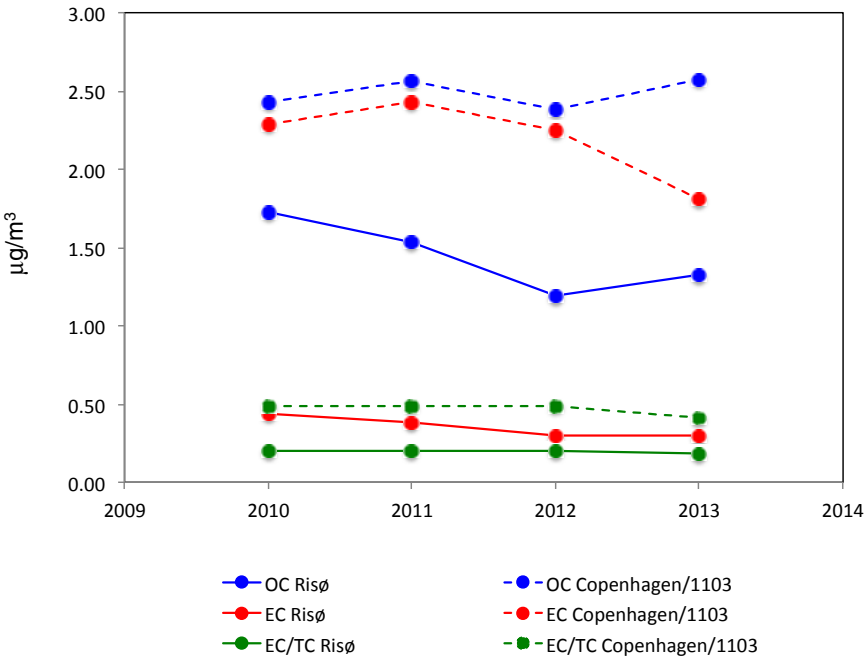


Figure 11.1 Elemental carbon (EC), organic carbon (OC) and the ratio between elemental carbon and total carbon (EC/TC) at H.C. Andersens Boulevard (Copenhagen/1103) and in semi-rural background at Risø in 2013.

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. Andersen's 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. As in 2012, the unknown mass is higher at HCAB than at Risø. 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.

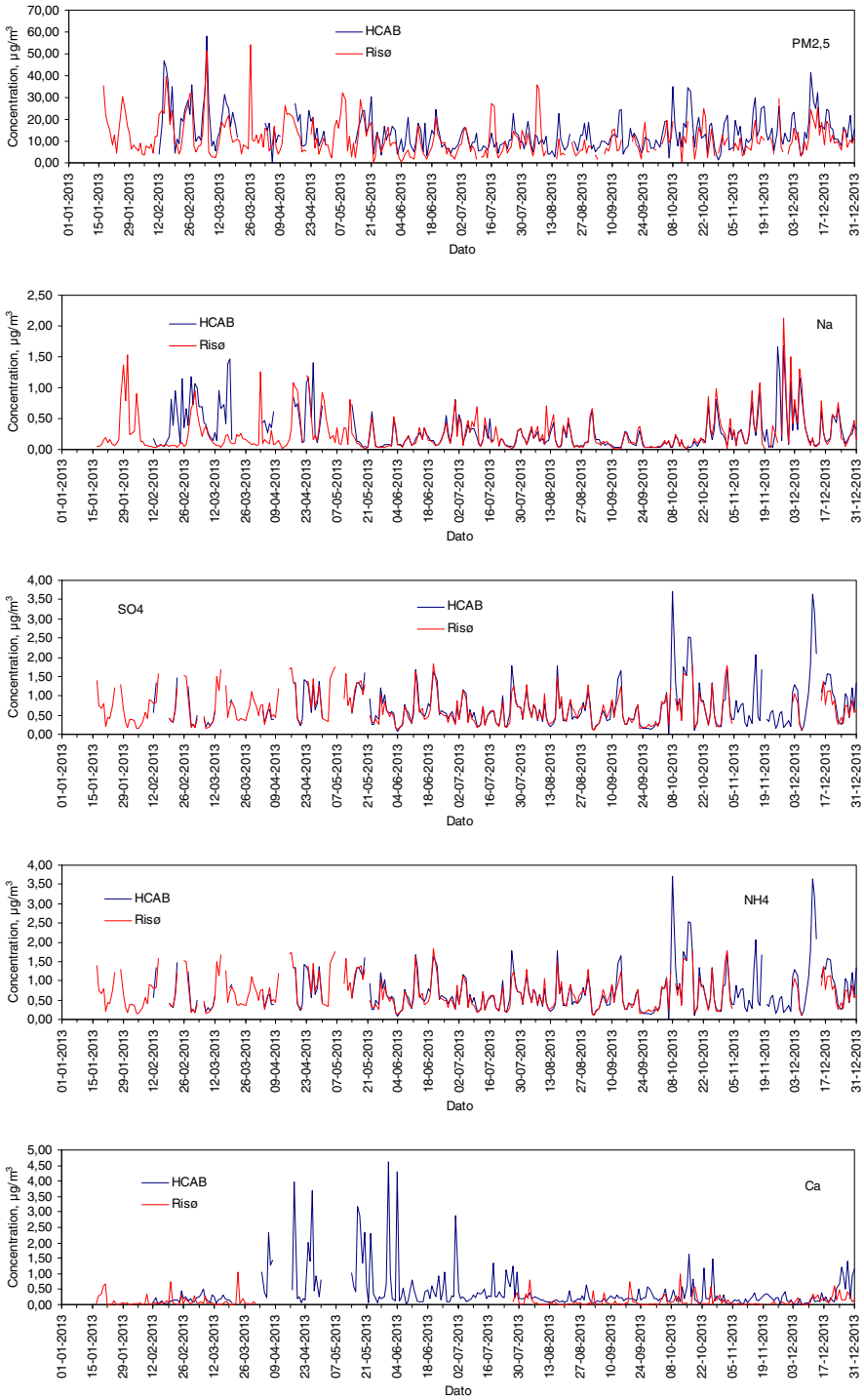


Figure 12.1 Daily variations of the concentrations of $PM_{2.5}$, Na^+, SO_4^{2-}, NH_4^+ and Ca^{2+} at H.C. Andersens Boulevard (HCAB, Copenhagen/1103) and Risø in 2013. The large gap in data for calcium on Risø is due to problems with filter material.

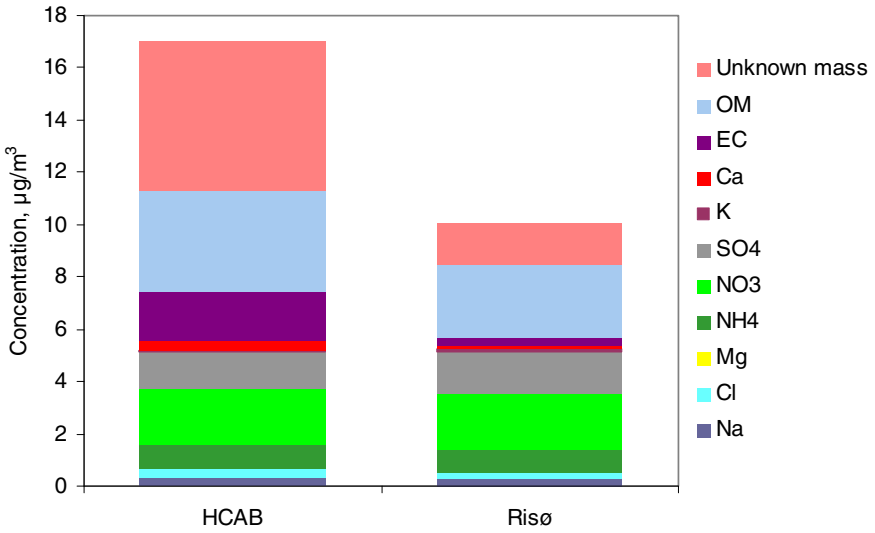


Figure 12.2 Annual average contributions to the chemical composition of $PM_{2.5}$ at H.C. Andersens Boulevard (HCAB, Copenhagen/1103) and Risø in 2013. Organic matter (OM) has been estimated from the measured concentrations of OC by multiplication of OC with a factor of 1.5 for the fresh OM at HCAB 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

14 References

Berkowicz, R., 2000a: OSPM - A parameterized street pollution model, Environmental Monitoring and Assessment 2000, 65, 323-331. doi: 10.1023/A:1006448321977.

Berkowicz, R., 2000b: A simple model for urban background pollution, Environmental Monitoring and Assessment 2000, 65, 259-267. doi: 10.1023/A:1006466025186.

Brandt, J., Christensen, J.H., Frohn, L.M., Berkowicz, R. & Palmgren, F. 2000: The DMU-ATMI THOR Air Pollution Forecast System: System Description, National Environmental Research Institute, Roskilde Denmark 60 pp. -NERI Technical Report No. 321.

Brandt, J., Christensen, J.H., Frohn, L.M. & Berkowicz, R., 2003: Air pollution forecasting from regional to urban street scale – implementation and validation for two cities in Denmark. Physics and Chemistry of the Earth, Vol. 28, pp. 335-344.

Brandt, J., Christensen, J.H. Frohn, L.M. Palmgren, F. Berkowicz R. & Zlatev, Z., 2001: Operational air pollution forecasts from European to local scale. Atmospheric Environment, Vol. 35, Sup. No. 1, pp. S91-S98.

Brandt, J., Silver, J.D., Frohn, L.M., Geels, C., Gross, A., Hansen, A.B., Hansen, K.M., Hedegaard, G.B., Skjøth, C.A., Villadsen, H., Zare, A. & Christensen, J.H., 2012: An integrated model study for Europe and North America using the Danish Eulerian Hemispheric Model with focus on intercontinental transport, Atmospheric Environment, Volume 53, June 2012, pp. 156-176, doi:10.1016/j.atmosenv.2012.01.011.

Christensen, J.H., 1997: The Danish Eulerian Hemispheric Model – a three-dimensional air pollution model used for the Arctic, Atm. Env., 31, 4169–4191.

EC, 1999: Directive 1999/30/EC of 22 April 1999 relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air. J. Europ. Commun. L163/41.

EC, 2000: Directive of the European Parliament and of the council 2000/69/EC of 16 November 2000 on limit values for benzene and carbon monoxide in ambient air. J. Europ. Commun. L313/12.

EC, 2002: Directive 2002/3/EC of the European Parliament and of the Council of 12 February 2002 relating to ozone in ambient air. Official Journal of the European Union L 067 /14.

EC, 2005: Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air. Official Journal of the European Union L23/3.

EC, 2008: Directive 2008/50/EC of the European Parliament and of the Council of 15 December 2004 on ambient air quality and cleaner air for Europe: Official Journal of the European Union L152/1.

Ellermann, T., Ketzel, M., Winther, M., & Nordstrøm, C., 2012: Foreløbige resultater for NO2 i 2011 og vurdering af årsag til de høje koncentrationer på H.C. Andersens Boulevard. Thomas Ellermann, Notat til Miljøstyrelsen 31. januar 2012, 7 s. Available at:
http://dce.au.dk/fileadmin/dmu.au.dk/Notat_NO2_2011.pdf

Ellermann, T., Wåhlin, P., Nordstrøm, C., & Ketzel, M. 2010: Vejbelægningens indflydelse på partikelforureningen (PM_{10}) på stærkt trafikerede gadestrækninger i Danmark. Paper presented at Trafikdage 2010, University of Aalborg; Aalborg, Denmark. August 2010. Paper. Available at:
http://www.trafikdage.dk/papers_2010/380_ThomasEllermann.pdf

Grell, G.A., Dudhia, J. & Stauffer, D.R., 1995: A description of the fifth-generation Penn State/NCAR Mesoscale Model (MM5). Mesoscale and Microscale Meteorology Division, National Centre for Atmospheric Research, Boulder, Colorado, USA. NCAR Technical Note, NCAR/TN-398+STR, pp. 114.

Harrison, D. 2006: UK Equivalence Programme for Monitoring of Particulate Matter. Report BV/AQ/AD202209/DH/2396 Bureau Veritas London, England (for: Defra
http://www.airquality.co.uk/archive/reports/cat05/0606130952_UKPMEquivalence.pdf)

Jensen, S.S., Berkowicz, R., Hansen, H. Sten. & Hertel, O. 2001: A Danish decision-support GIS tool for management of urban air quality and human exposures. Transportation Research Part D: Transport and Environment, Volume 6, Issue 4, 2001, pp. 229-241.

Jensen, S.S., Ketzel, M., Nøjgaard, J.K. & Becker, T. 2011: Hvad er effekten af miljøzoner for luftkvaliteten? - Vurdering for København, Frederiksberg, Aarhus, Odense, og Aalborg. Slutrapport. Danmarks Miljøundersøgelser, Aarhus Universitet 110 s. – Faglig rapport nr. 830. Available at:
http://www.dmu.dk/Pub/FR830.pdf

Ketzel, M., Jensen, S.S, Brandt, J., Ellermann, T., Olesen, H.R., Berkowicz, R. & Hertel, O. 2013: Evaluation of the Street Pollution Model OSPM for Measurements at 12 Streets Stations Using a Newly Developed and Freely Available Evaluation Tool. J Civil Environ Eng, S1:004. doi:10.4172/2165-784X.S1-004

Massling, A., Nøjgaard, J.K., Ellermann, T., Ketzel, M. & Nordstrøm, C., 2011: Particle project 2008 – 2010. National Environmental Research Institute, Roskilde Denmark. -NERI Technical Report No. 837.

Miljøministeriet, 2010: Bekendtgørelse om vurdering og styring af luftkvaliteten. Bekendtgørelse nr. 851 af 30.06.2010 (In Danish). Ministry of Environment; Copenhagen, Denmark.

Plejdrup, M.S. & Gyldenkærne, S., 2011: Spatial distribution of emissions to air – the SPREAD model. National Environmental Research Institute, Aarhus University, Denmark. 72 pp. – NERI Technical Report no. FR823. Available at: http://www.dmu.dk/Pub/FR823.pdf

Turpin, B.J. & Lim, H.-J., 2001: Species Contributions to PM2.5 Mass Concentrations: Revisiting Common Assumptions for Estimating Organic Mass, Aerosol Science and Technology, 35: 1, 602 — 610, First published on: 30 November 2010 (iFirst). DOI: 0.1080/02786820119445URL. Available at: http://dx.doi.org/10.1080/02786820119445

WHO, 2000: Air Quality Guidelines for Europe, Second Edition, WHO Regional Publications, European Series, No. 91, Copenhagen 2000. Availabel at: http://www.euro.who.int/air

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.

Appendix 2. Validation of OSPM with updated input data

Purpose of this chapter is to document the performance of the OSPM with the new model configuration and input data used first time in the NOVANA 2013 report. Also the effect of the changes between the previous (2012) results and the present results will be documented by showing the influence of one change at the time.

The main changes between the previous and present OSPM model configurations are explained in detail in Chapter 2, therefore here only a brief list is given:

- New travel speeds based on GPS data (SpeedMap).
- Revised / updated emission factors for EURO 5/6 diesel passenger cars.
- Update in the way the general building height is calculated.
- Recalibration of OSPM using some internal dispersion parameter.

A2.1 Overall influence of changes in model configuration and input data

The influence of the above mentioned changes is illustrated by using the 99 street sections as reference and presenting results in a similar way as in Chapter 3. Please note that in this appendix calculation results are presented and compared for 99 street sections as also used in the previous NOVANA report. However, in Chapter 3 of the present report one street was removed from the results (it is temporarily closed due to Metro construction) and only 98 streets are presented.

The overall comparison between the calculations for 2012 and 2013 is shown in Figure A2.1 where the results for both years are plotted in the same diagram. In both cases the results are ordered after highest NO_2 value, i.e. the ranking of individual streets is different and cannot be compared. For the majority of the streets the results in 2013 are lower than previously due to the generally decreasing trend in the vehicle emission factors. Also the number of exceedances of the 40 $\mu g/m^3$ NO_2 annual limit value has decreased from 19 in 2012 to 12 in 2013.

However, the contrast between the highest and lowest NO_2 concentrations have increased, moreover the 5 street sections with the highest concentrations are higher in 2013 than previously. This is due to the fact that the travel speed at the highest polluted street (also highest traffic volume) is in average reduced more than for the less polluted/busy streets. This is also illustrated in Figure A2.2. Here the same results for 2013 and 2012 are plotted just using the same order of streets in both cases. The new SpeedMap based travel speeds for the individual streets are plotted in Figure A2.2 as well. A clear anti-correlation between travel speed and NO_2 concentrations is visible since low travel speeds are connected with higher NO_x emissions. Also visible is the general trend with average higher travel speeds for streets with lower traffic. In the 2012 calculations the assumed travel speeds were very similar for all streets (around 40 to 50 km/h).

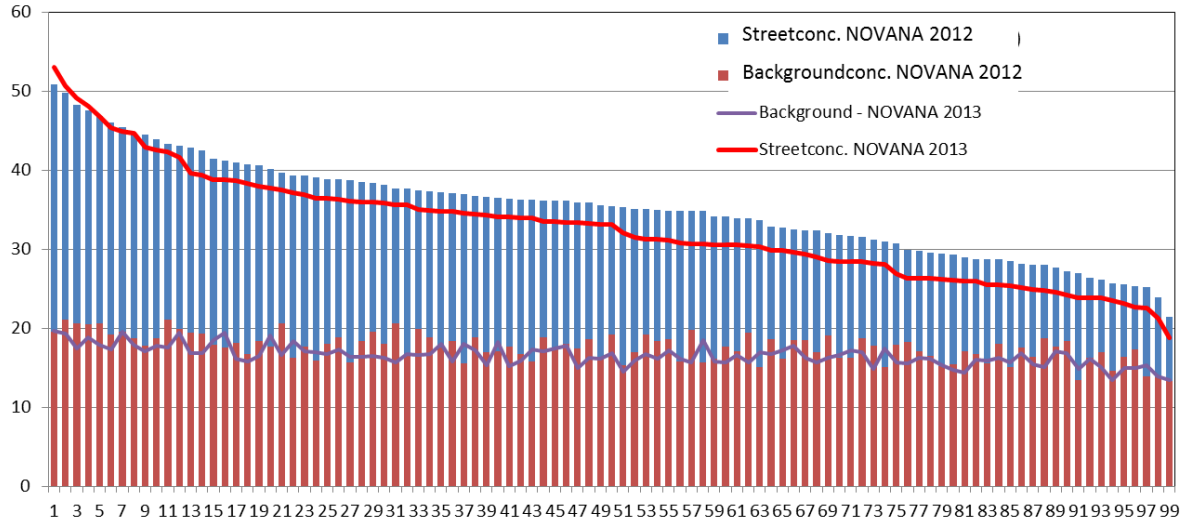


Figure A2.1. Annual mean concentrations of NO_2 in 2013 for 99 streets in Copenhagen (lines) compared with the results presented for 2012 in the previous NOVANA report (Bar chart). In both years the streets are independently sorted according to NO_2 concentrations. See also Figure 3.2 for more explanations.

.

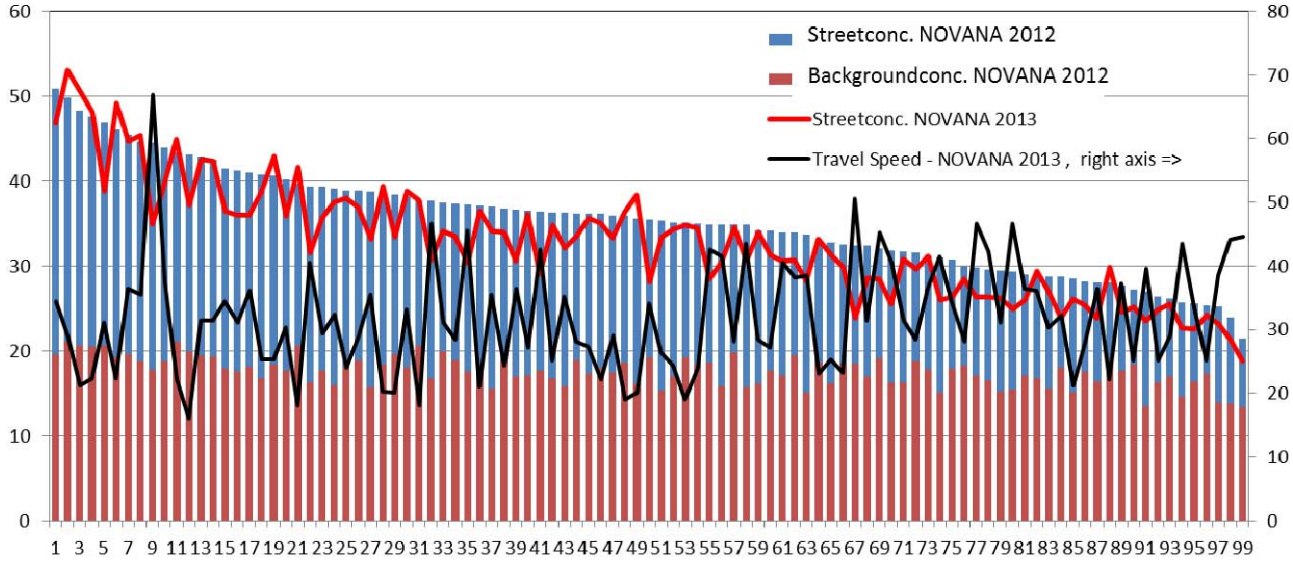


Figure A2.2. Annual mean concentrations of NO_2 in 2013 for 99 streets in Copenhagen (red line) compared with the results presented for 2012 in the previous NOVANA report (Bar chart). Same order of streets for both years according to NO_2 ranking in 2012. Travel speeds in 2013 are shown as black line using the right axis.

.

A2.2 Influence of updated travel speeds

Figures A2.1 and A2.2 include a combination of all the changes listed above. In order to illustrate the isolated influence of changing the travel speeds a scatter plot in Figure A2.3 shows the difference in NO_2 concentration as a function of the change in travel speeds. In the first model calculation the new speeds were used and in a second model run all travel speeds were set to 40 km/h (approximately the situation in the previous NOVANA reports). Due to the reduction in travel speed the NO_2 concentrations in average increase with about 3 µg/m³ and in several cases even up to 10 µg/m³. To compensate for this the OSPM had to be recalibrated using all available measurements from the 5 NOVANA street stations.

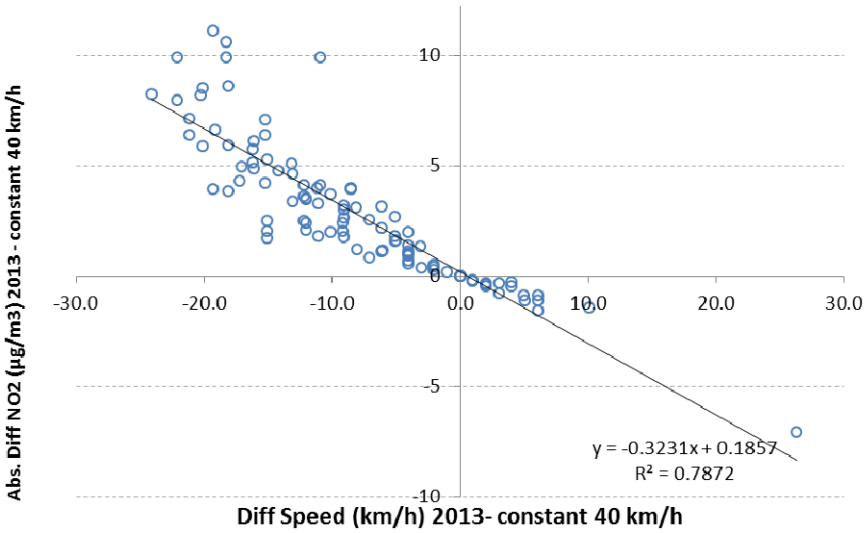


Figure A2.3. Scatter plot showing the influence of changing the travel speed between two model runs. Each point shows the result for one of the 99 streets in Copenhagen as difference between the new assumption of travel speed (SpeedMap) and the approximate situation before with constant travel speed of 40 km/h. X-axis gives the difference in speed (New-Old) and Y-axis the difference in NO_2 concentration..

A2.3 Influence of updated emission factors for EURO 5/6 diesel passenger cars

The changes in the assumed emission factors for EURO 5/6 diesel passenger cars are illustrated in Figure A2.4. The results of two model runs are shown with one change in parameter at the time while all other parameters are kept constant. Changes/updates have some small notable influence and contribute to the overall changes in concentration levels and in the street ranking between the 2012 and 2013 results. However, the updated emission factors have much less dramatic effects than the change in travel speeds as demonstrated above.

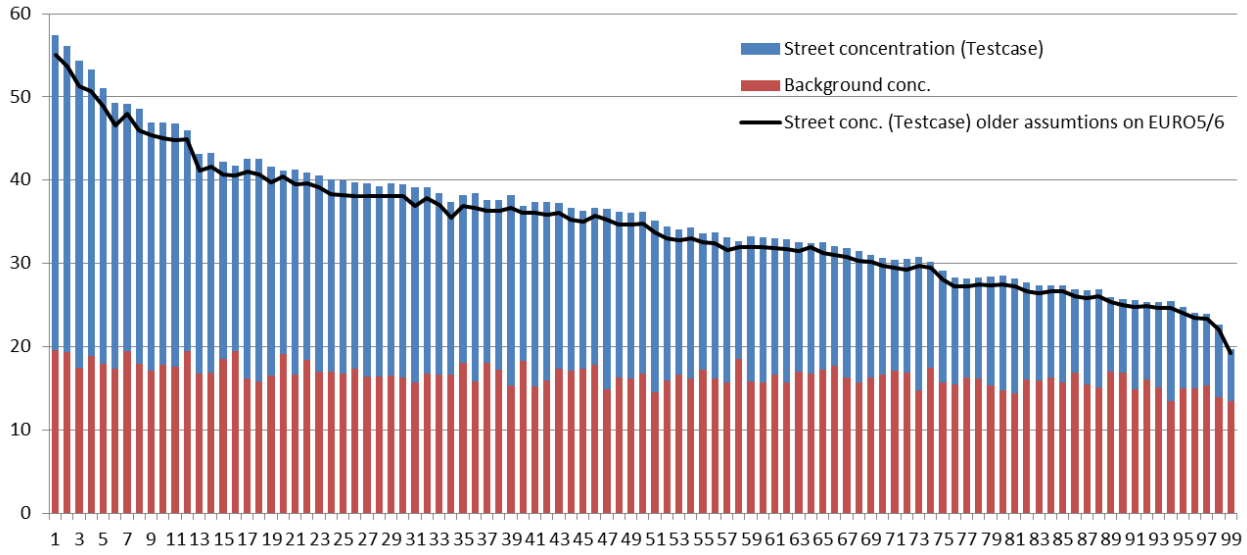


Figure A2.4. Annual mean concentrations of NO_2 for two model runs with new / old assumptions about EURO 5 and 6 emissions for diesel passenger cars. All other parameters are kept constant..

A2.4 Influence of updated general building height

The changes in the treatment of the general building height are illustrated in Figure A2.5. Results of two model runs are shown with one change in parameter at the time while all other parameters are kept constant. Changes/updates have influence for few streets and have minor contribution to the overall changes in concentration levels and in the street ranking between the 2012 and 2013 results.

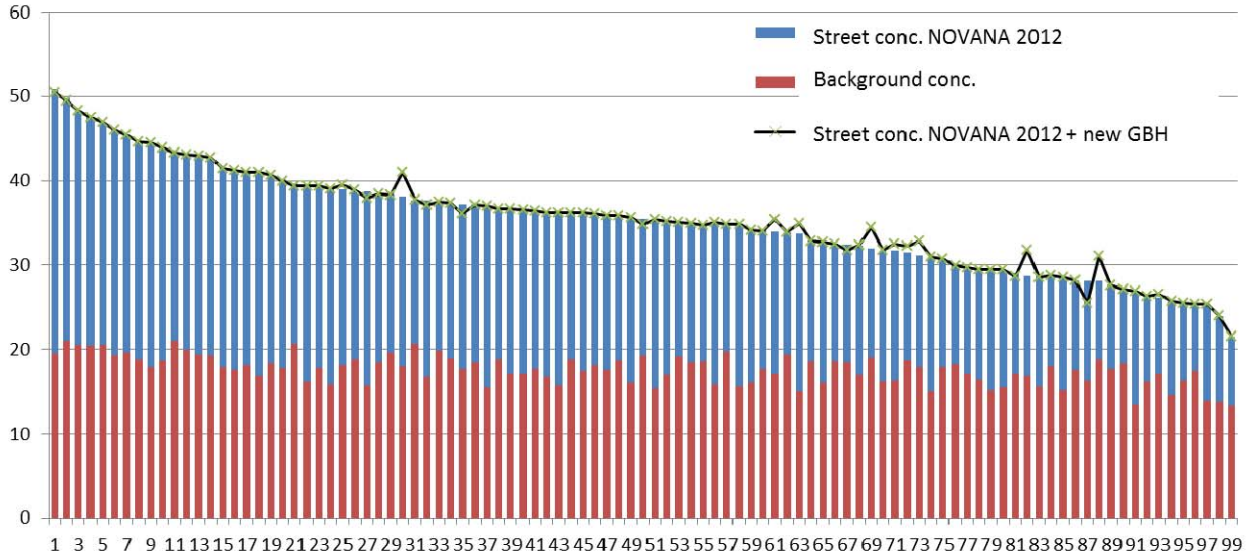


Figure A2.5. Annual mean concentrations of NO_2 for two model runs with new / old way of treating the general building height in OSPM. All other parameters are kept constant.

.

A2.5 Validation of OSPM with various measurements

As discussed in Chapter 2 the OSPM model has been recalibrated after implementing the new travel speeds, the new EURO 5 and 6 emissions and the new description of the general building heights, using the 5 NOVANA street stations and focussing on 2013 NO_2 measurements.

Validation of OSPM at 5 fixed monitor stations for 2013

Table A2.1 shows the comparison been the calculations with the full model chain of DEHM-UBM-OSPM (after recalibration) and measured NO_2 concentrations in 2013 for the fixed street monitoring stations in Copenhagen, Aarhus, Odense and Aalborg. For HCAB the recalibration assumed a situation before the concentration jump in 2010, i.e. the model was calibrated against a value of 47 µg/m^3 NO_2 (see footnote in Table A2.1). The overall agreement is satisfying and lies within -7% and 13%. A more detailed discussion including a separate validation of the DEHM/UBM part of the model chain is given in chapter 2.

Table A2.1. Comparison of modelled and measured annual means of NO_2 concentrations in 2013 at 5 traffic stations. (Same as Table 2.2 in Chapter 2)

Unit: µg/m^3	Measurements	Model results	Difference	Models used
Traffic:				
Copenhagen/Jagtvej/1257	38	37	-3%	DEHM/UBM/OSPM
Copenhagen/HCAB/1103	55/47*	53	13%	DEHM/UBM/OSPM
Aarhus/6153	35	33	-5%	DEHM/UBM/OSPM
Odense/9155	28	28	1%	DEHM/UBM/OSPM
Aalborg/8151	32	30	-7%	DEHM/UBM/OSPM

* 55 µg/m^3 is measured at the monitoring station at HCAB but because of a change in street layout traffic has moved closer to the measuring station, and it is estimated to have led to a jump of about 8-9 µg/m^3 based on parallel measurements. Without the change in street layout about 47 µg/m^3 is expected. OSPM calculations are more representative of the measurements without the jump as OSPM calculations reflect concentration levels in front of the building facade.

Validation of OSPM for Jagtvej and H.C. Andersens Boulevard 1994-2010

In the following we illustrate the performance of the recalibrated model for longer time series at the two NOVANA streets stations in Copenhagen, Jagtvej (JGTV) and H.C. Andersens Boulevard (HCAB) for NO_x and NO_2. There are, however, a few limitations when running the model for many years since not all input data are available at the same details as for the most recent year. These assumptions are listed below:

- For the multi-year model runs we have assumed measured urban background and meteorology from the Copenhagen background monitoring station at H.C. Ørsted Institute (HCØ) being representative for both streets, since no full model chain THOR/DEHM/UBM calculations are available yet in the same detail/quality as for NOVANA 2013. The difference between HCØ measured background and detailed background model is relatively small for Jagtvej (about +- 1 µg /m^3 for NO_2) while for HCAB the background is likely to be underestimated by 2-3 µg/m^3 for NO_2 using measured data from HCØ as background. That should be kept in mind when evaluating the model performance for HCAB.

- The same traffic speeds from SpeedMap and dispersion parameter as in the NOVANA 2013 calculations are used back in time. No detailed information about travel speed many years back is available.

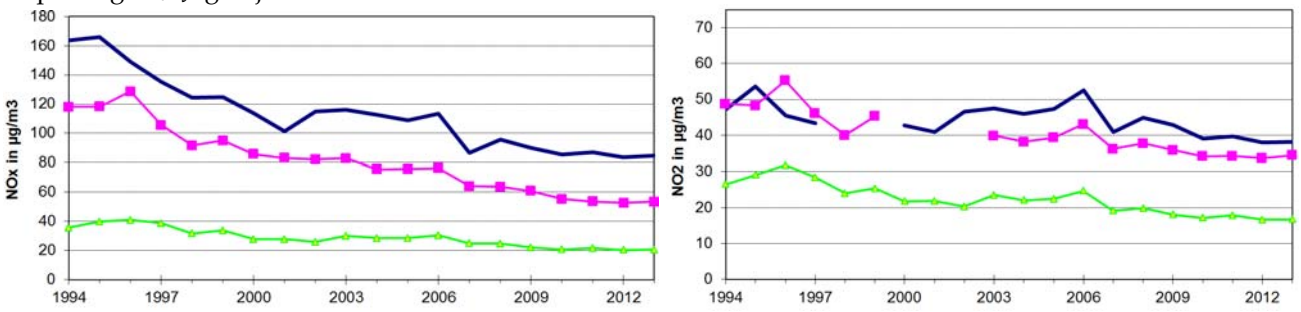
- We use the same ADT / HD-share back in time for all years – no possible changes in traffic back in time have been considered since limited traffic data is available that represents traffic directly at the monitoring stations.

Figure A2.6 shows the comparison between model results using the same assumptions as in NOVANA 2013 with the above mentioned limitations and measurements for JGTV and HCAB and the pollutants NO_x and NO_2. For comparison we show in Figure A2.7 the same type of validation with the earlier OSPM model configuration published in *Ketzel et al.* (2012).

We observe clear underestimation of both NO_x and NO_2 at JGTV in the most recent model runs (Figure A2.6) compared to the older results. It looks like the model performs at JGTV not as good as previously. Since the recalibration was performed with the intention to reduce the overall bias for all 5 streets in the NOVANA monitoring programme, JGTV is one of the sites where the model underpredicts. A reason for the lower values in the model is that the measurement station at JGTV is located close to the traffic, while the model is representing the situation at the building façade. However, this is subject to further investigation.

The model performance at HCAB is good, both with the new and the previous model configuration. It is clearly visible that the model is not able to reproduce the concentration jump in 2010 and represents the situation from before 2010.

Copenhagen / Jagtvej



Copenhagen / H.C. Andersens Boulevard

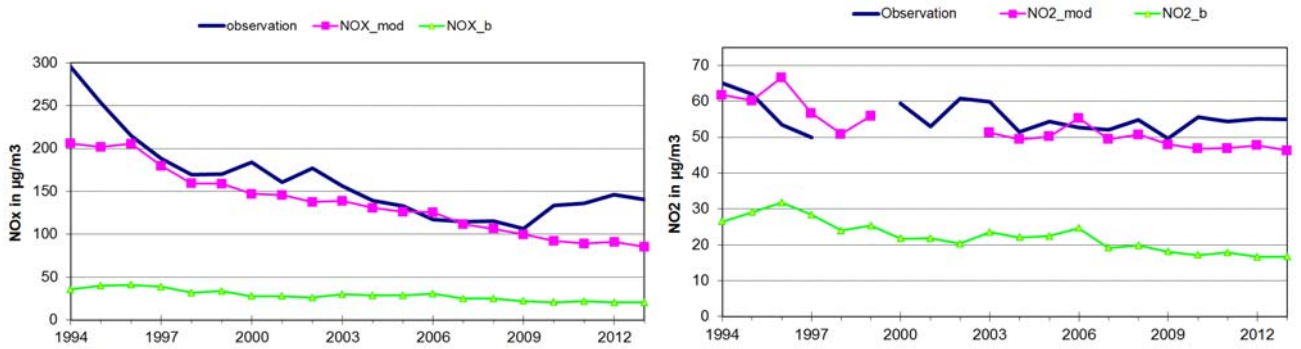
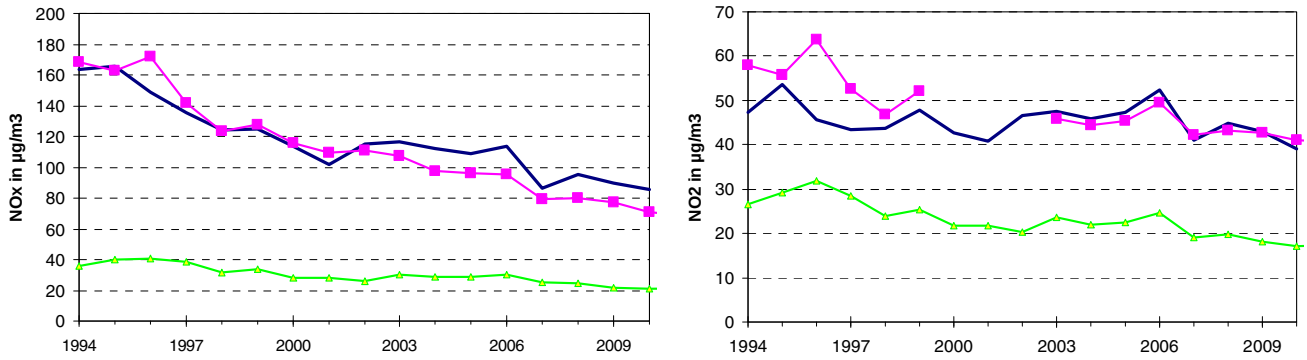


Figure A2.6 Trends in annual averages of NO_x (left panel) and NO_2 (right panel). Plotted are observed and modelled street concentrations for JGTV and HCAB as well as observed urban background concentrations (HCØ) between 1994 and 2013. Calculations using a model configuration as close as possible as in NOVANA 2013, however, with few limitations mentioned in the text, that result in small differences between the results for 2013 in this plot compared to Table A2.1. See as well foot note in Table A2.1 regarding the jump of measured NO_x/NO_2 concentrations in 2010.

Copenhagen / Jagtvej



Copenhagen / H.C. Andersens Boulevard

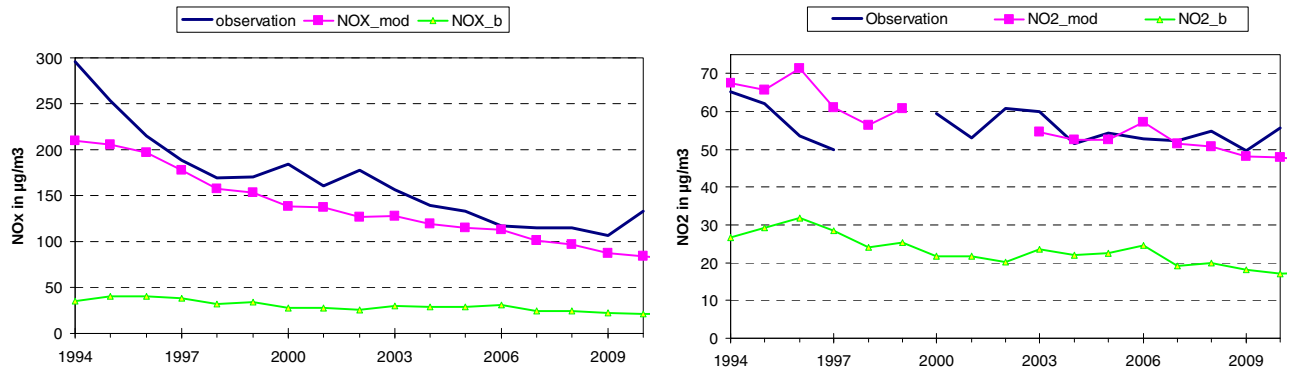


Figure A2.7 As in Figure A2.6 using an earlier model set-up and time series up to 2010 only.
Published as: Ketzel M, Jensen SS, Brandt J, Ellermann T, Olesen HR, Berkowicz R and Hertel O (2012): Evaluation of the Street Pollution Model OSPM for Measurements at 12 Streets Stations Using a Newly Developed and Freely Available Evaluation Tool. J Civil Environ Eng, S1:004.

Validation of OSPM for 10 streets in Copenhagen

Finally, the performance of the recalibrated model was additionally tested against measurements from a 5 week passive sampling campaign performed by Force Technology A/S financed by the Danish EPA in 2011/2012, that also previously has been used for model testing (Ellermann et al., 2012, Ketzel et al., 2012). The measurement and model period was 24. Oct. – 28. Nov. 2011.

Results are shown in Figure A2.8 for 10 streets. Measurements are shown only for 9 streets since one of the instruments was stolen. Model results are shown as bar-chart both for the original model configuration as well as for the new re-calibrated model. Changing from the old to the new model configuration involves as well a change to the new lower travel speeds (SpeedMap) at the 10 locations. The old and new travel speeds have been included as line chart in Figure A2.8.

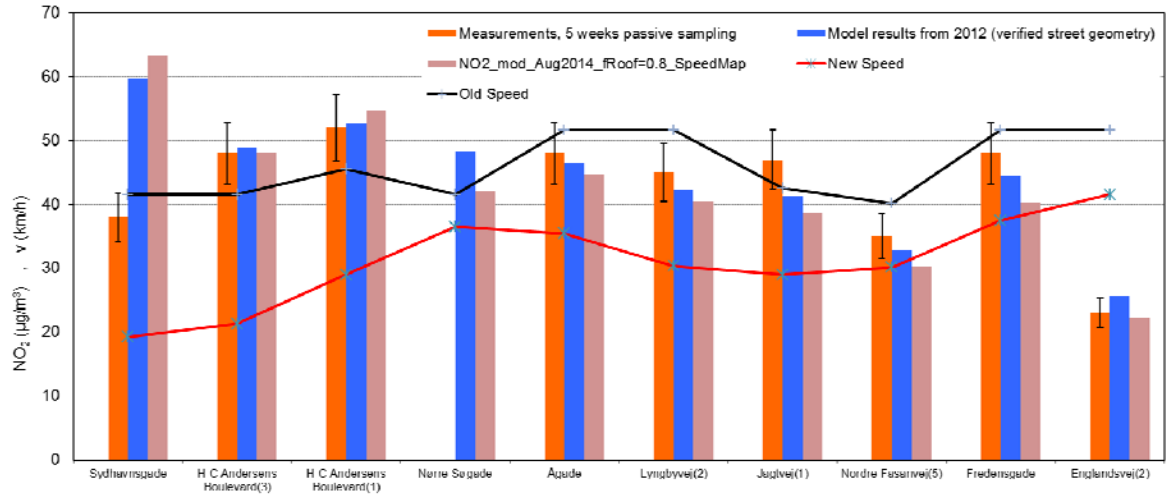


Figure A2.8. Measurements and model results for NO_2 in the period 24. Oct. – 28. Nov. 2011 at 10 selected streets as reported in (Ellermann et al. 2012). Model results are given for the situation with "verified street geometry" with original model configuration from 2012 (blue bars) and the recalibrated model as used in report for NOVANA 2013 (light red). Also shown are the travel speeds estimated for the 10 streets and used in the original (black lines) and the new model configuration (red lines), the latter based on SpeedMap data.

Similar to the situation shown in Figure A2.1, the new model gives larger gradients between the high and low polluted streets. This is again related to the fact, that the busiest streets with highest concentration have lower travel speeds in the new model configuration leading to higher emissions, compared to the less polluted streets. For the streets with the highest model results (Sydhavnsgade and 2x HCAB) the new model configuration gives higher or similar results while for the rest of the streets the new model gives slightly lower results. The large discrepancy between measurements and model for Sydhavnsgade is caused by an overestimation in the assumed traffic volume in the calculations; this has been corrected later on. The comparison with the measurements for the rest of the streets is satisfying, however, the model shows a tendency for underestimation.

Conclusions on validation of OSPM

In conclusion the results in this chapter show that the new model configuration has been successfully validated against all available measurements. Some challenges remain in having the model to reproduce the concentration jump at HCAB. Related to this, some new model development is ongoing as also discussed in Chapter 2.2.2.

References in Appendix 2:

Ellermann, T., Ketzel, M. & Solvang Jensen, S. 2012. Sammenligning af NO_2-målinger og OSPM-beregninger for 10 gadestrækninger i København. Aarhus Universitet, DCE – Nationalt Center for Miljø og Energi, 26 s. - Teknisk rapport fra DCE – Nationalt Center for Miljø og Energi nr. 9.
http://www.dmu.dk/Pub/TR9.pdf

Ketzel M, Jensen SS, Brandt J, Ellermann T, Olesen HR, Berkowicz R and Hertel O (2012): Evaluation of the Street Pollution Model OSPM for Measurements at 12 Streets Stations Using a Newly Developed and Freely Available Evaluation Tool. J Civil Environ Eng, S1:004.
http://dx.doi.org/10.4172/2165-784X.S1-004

[Blank page]

THE DANISH AIR QUALITY MONITORING PROGRAMME

Annual Summary for 2013

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 2013 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.

ISBN: 978-87-7156-119-7
ISSN: 2245-0203