National Environmental Research Institute
Ministry of the Environment · Denmark

Aerosols in Danish Air (AIDA)

Mid-term report 2000-2002

NERI Technical Report, No. 460

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Data sheet

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Abstract:

In year 2000 the Danish Parliament decided to fund a four-year particle research programme, which should include characterization of physical and chemical properties of the particles in Denmark and their sources and also assess the adverse health effects and the socio-economic impact in the Danish society. The overall objective of the particle programme is to provide new and broader knowledge in Denmark on the health effect of atmospheric particles with the aim to develop strategies to reduce the adverse health effect of man-made and natural sources. The activities should be closely related to other activities in Denmark and internationally. Specifically National Environmental Research Institute (NERI) shall investigate emissions, size distributions, chemical composition, transformation and dispersion of particles.

The present report is the mid-term report on the activities at NERI, and is a summary of the experimental results, analysis of particle in relation to sources - especially road traffic - and the papers published in connection with the programme.

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1 Summary

A four-year project

In year 2000 the Danish Parliament decided to fund a four-year particle research programme, which should include characterisation of physical and chemical properties of the particles in Denmark and their sources and also assess the adverse health effects and the socio-economic impact in the Danish society. A steering group chaired by the Danish Environmental Protection Agency (DEPA) co-ordinates the programme, and the National Environmental Research Institute (NERI) carries out the characterisation of particles and their sources and the socio-economic aspects. The health effect studies are carried out at different institutions and universities, e.g. Danish Cancer Society and University of Copenhagen (Environmental and Occupational Medicine, Institute of Public Health).

Objectives

The overall objective of the particle programme is to provide new and broader knowledge in Denmark on the health effect of atmospheric particles with the aim to develop strategies to reduce the adverse health effect of man-made and natural sources. The activities should be closely related to other activities in Denmark and internationally.

Specifically National Environmental Research Institute (NERI) shall investigate emissions, size distributions, chemical composition, transformation and dispersion of particles.

The present report is the mid-term report on the activities at NERI.

Approach

The experimental research is mainly taking outset in the Danish air quality monitoring programme operated by NERI (Kemp & Palmgren, 2003), which include continuous, long time series of the main pollutants related to the most important sources in Denmark. The monitoring programme is supplemented by special particle related measurement campaigns. This combination of long time series of traditional pollutants and the special particle campaigns permits establishment of relationships between sources and the properties of the particles (sizes and physical/chemical properties).

The studies

The investigations included emission inventories of Danish stationary and mobile sources, experimental studies of PM_{10}, $PM_{2.5}$ and ultrafine particles in Denmark in busy street canyons, urban background and rural locations. The studies included chemical composition, e.g. the content of elemental carbon, and size distributions. Emission factors of particles from traffic were estimated under actual driving on the basis of the air quality measurements. Finally, also the penetration and deposition op particles (PM_{10}, $PM_{2.5}$ and ultrafine particles) in an apartment facing a busy street was estimated. The results of the experimental studies were applied for development and validation of NERI's air quality and exposure models for particles.

Main conclusions

The road traffic and wood stoves are the particle sources, which cause the highest outdoor human exposure due to high emissions, at low release heights and in urban areas, where the population lives, works and goes about.

Diesel vehicles are the dominating source of nano-particles and ultrafine particles. Modern petrol cars do only contribute a little the PM pollution. In addition to the tailpipe, the non-exhaust emissions from wear of road surfaces, tires, brakes etc contributes significantly to the PM_{10} pollution from diesel as well as from petrol vehicles. The non-exhaust emission depends on many factors, e.g. wind speed, salting and sanding of roads in winter, precipitation and properties of the road surface.

The highest emissions of particles take place from traditional diesel vehicles without filters or catalysts. The particle filters are generally very efficient (>95%) for all particles including nano particles and ultrafine particles. The oxidising catalysts on diesel vehicles remove a significant part of the semi-volatile particles (condensates, which are fuel, lubricants or reaction products).

Long-range transported particles, i.e. primary particles and secondary particles formed by oxidation of SO_2 and NO_x emitted at the European continent, are dominating in urban background and comparable with the traffic contribution in busy streets (mass concentration, $PM_{10}/PM_{2.5}$).

Many more results are reviewed in this report and published in reports and international journals, see the references under the authors of this report.

2 Introduction

Significant health effects of PM

Studies of long-term exposure to air pollution, especially to particulate matter (PM), suggest an increased mortality, increased risk of chronic respiratory illness, and of developing various types of cancer. World Health Organisation (WHO, 1999) has estimated that in Europe air pollution has caused 168,000 (range of estimate 100,000 – 400,000) excess deaths annually; in the United States the corresponding figure has been estimated to be approximately 100,000. The best estimate on the reduction in life expectancy in Central Europe is about 1 year (Katsouyanni et al., 1997 and Künzli et al., 2000).

Especially fine PM is considered to be causing a significant burden of disease and excess deaths in Europe and North America (Pope et al., 1995, 1999 and 2002 and Dockery et al., 1993 and 1994). However, it is not known, which chemical and physical characteristics of the PM are responsible for these effects, and which source categories are responsible for the most harmful exposures (Pekkanen et al., 1997 and Peters and Wichmann, 2001). A reliable assessment of urban PM pollution and the subsequent adverse health effects is therefore crucial in terms of the promotion of public health (WHO, 2000).

Chemical and physical properties

The chemical and physical properties of PM are important for assessment of deposition of material in the lungs and the assessment of adverse health effects. The important properties - in addition to size - include state (liquid/solid), volatility, hygroscopicity, chemical composition (content of organics, metals, salts, acids etc.), morphology and density. These properties also need to be taken into account in selecting methods for regulation and control of PM emissions.

The particle size

The particle size is believed to be an important parameter in relation to health effects. The particle size can also reveal the origin/sources and the history of the particles. Traditionally, they are described as appearing in 3-4 modes. The coarse mode particles can be defined as the particles with diameters larger than 2 µm. In urban areas these particles are typically formed mechanically by abrasion of road material, tyres and brake linings, dust raised by wind and traffic turbulence, etc. Natural sources are soil dust and sea spray (sea salt). The fine mode particles (accumulation mode in the range 0.1 -2 µm) are typically formed by chemical reactions (e.g., SO_2 and NO_x to form sulphate and nitrate), or other relatively slow processes in the atmosphere; the fine PM are therefore commonly aged particles and transported over long distances. The ultrafine particles are less than 0.1 µm and they are often divided in the Aitken nuclei between 0.1 µm and 0.02 µm, and the very small particles, nucleation mode. They are both in general primary particles formed during combustion, e.g. in engines or directly in the atmosphere by nucleation from gases. The particles may grow by coagulation of primary particles, and by condensation of gases on particles.

Monitoring of PM

Monitoring data for particles are normally given as mass per volume of air, e.g. $\mu g/m^3$, and the limit values are given in this unit. Previously total suspended particulates were measured, which in practice

cover particles smaller than 20-30 µm in aerodynamic diameter. The international limit values are now given for PM_{10} or $PM_{2.5}$, which cover all particles below 10 and 2.5 µm in aerodynamic diameter. The concentration of coarse mode particles is often defined as PM_{10}-$PM_{2.5}$. The ultrafine particles do not contribute to significantly to PM_{10} and $PM_{2.5}$. The total number of particles is dominated by the ultrafine particles. It is therefore considered to use other measures for the particle concentration, e.g. PM_1, $PM_{0.1}$ or the particle number. However, a combination of particle mass (coarse particles) and particle number (ultrafine and fine particles) may be the best option for defining limit values for particles in the future.

The limit values

The limit values for the EU and Denmark are given in *Table 1*. The limit values for 2010 are proposals and a review will be done in 2003/2004.

Table 1 Limit values in accordance with the EU directive (EC, 1999) and the Danish Regulation no....

Pollutant	Limit value (µg/m^3)	Averaging time	Statistics	For protection	Date of compliance
PM_{10}	50	24 hours	35 times per year	Human	2005
	40	-	Annual average	Human	2005
	50	24 hours	7 times per year	Human	2010 (proposal)
	20	-	Annual average	Human	2010 (proposal)

The Nordic countries

In Nordic countries, atmospheric long-range transport constitutes an important part of the total urban background $PM_{2.5}$ concentration (e.g., Johansson et al. 1999; Pakkanen et al., 2001; Karppinen et al. 2002). In urban areas in Sweden, it even constitutes the most important single contribution to both urban background $PM_{2.5}$ and PM_{10}, which is clearly illustrated by the spatially uniform urban background concentrations of these particulate fractions (Areskoug et al. 2000).

The long-range transported aerosol dominates the accumulation mode of the aerosol size distribution even in urban areas, whereas its contribution to the ultra-fine and coarse mode is small, in comparison to that of the local particle emissions (Johansson and Burman, 2001). For cities in Nordic countries, the coarse particle fraction is important for the elevated PM_{10} concentrations, especially in spring (e.g., Johansson, 1999, Pohjola et al, 2002).

Other countries

In the UK, numerous sources of fine particles have been recognised in urban centres (QUARG 96, APEG 1999); these include contributions from natural sources, road transport, stationary combustion and industrial processes. Road transport nationally can contribute about 25 % of PM_{10}, whereas in urban centres the contribution rises to approximately 80-90 % (QUARG 96, APEG 1999). The coarse fraction (particles with aerodynamic diameters 2.5-10 µm) tend to consist mainly of soil, sea salt, biogenic and airborne dust components, whereas the fine fraction (diameters below 2.5 µm) consists of contributions from mobile (mainly diesel) and stationary combustion processes, and secondary aerosols (such as sulphates, nitrates and ammonium).

In Budapest, Hungary, the highest PM_{10} concentrations occur in the vicinity of major urban roads (Bozó et al. 2001), indicating that local traffic is mainly responsible for the elevated coarse particle concentrations. The amount of major industrial pollution sources has substantially decreased in urban areas in Central Eastern Europe during the last decade. In Budapest, heat energy production is based mainly on natural gas, regarding both thermal power plants and domestic heating.

Ultrafine particles

A major contribution to particulate pollution in urban areas is believed to be attributed especially to emissions from diesel powered vehicles (Palmgren et al. 2002). Ultrafine particles emitted from petrol as well as diesel engines are formed at high temperature in the engines, in the exhaust pipe, or immediately after emission to the atmosphere. Some of these particles may be in the so-called nucleation mode (nano particles < 30 nm). The ultrafine particle mode dominating the number concentration has a peak in the range of 30-50 nm. The ultrafine particles in urban air are mainly emitted from diesel and petrol fuelled vehicles.

Measurement campaigns carried out in two cities in Denmark included monitoring of the ultrafine particles from traffic under normal driving conditions and in ambient air, in order to be able to establish the relationship between the sources and the exposure of the population. Measurements of ultrafine particles were carried out by a DMPS (Differential Mobility Particle Sizer) with a high time resolution that corresponds to the variation in traffic and meteorological variables.

The particles were segregated in 29 size fractions, ranging from 0.01 to 0.7 µm. It was shown that particles originating from diesel engines in 1999 were smaller than in 2000. The average size changed after the sulphur content in diesel was reduced. These very small particles are probably mainly droplets formed in or immediately after the tailpipe. The sulphur content plays a key role as condensation nuclei for fuel, lubrication oil and volatile combustion products. The particle number concentration may therefore depend strongly on the sulphur content of the diesel oil consumed.

EC/OC

In Copenhagen, hourly elemental and organic carbon (EC/OC) measurements of PM_{10} were carried out in a busy street, related to measurements of other traffic-originated pollutants. The statistical correlations between EC and CO and also OC and NO_x /CO were relatively low. However, a clear correlation between EC and NO_x was observed, indicating a significant contribution to EC from diesel traffic (Palmgren et al. 2002).

Soot

Particles from diesel as well as petrol engines comprise also solid, mainly carbonaceous, particles, which may have a crucial role regarding the adverse health effects. The measurements of ultrafine particles in Copenhagen have identified this mode of the particle size distribution (Wåhlin et al. 2001a).

The results from Stockholm (Kristensson et al. 2001) and Nantes (Despiau et al. 2001) suggest that local traffic is the main source of ultrafine particles, and most of the particles close to traffic are in the

range from 3 to 30 nm. The size distributions change rapidly with distance from the traffic sources. At the rooftop location, the size distributions shift towards larger sizes compared with those in the street level.

Biomass/wood

In residential areas of North European cities, biomass burning for domestic heating may be an important source of fine particles during winter. For instance in Sweden, wood is most frequently burned in boilers constructed for multiple energy sources (oil, wood and electricity). Recently, low emission boilers have been introduced into the market, but stoves have come into use as an additional heating device, commonly also in urban areas.

Emissions from wood combustion may be important for particulate matter, but also for many particle-bound hydrocarbons, such as polycyclic aromatic hydrocarbons. The aerosol originated from biomass combustion may substantially differ from that originated from vehicle exhausts, both regarding chemical composition and particle size distribution. For instance, PM from biomass burning may contain a larger fraction of hygroscopic particles (Hedberg et al. 2002).

Trends in Denmark

The PM pollution in Denmark has been assessed to cause adverse health effects. The PM pollution in Denmark is in general lower than in many other European countries, and the concentration level has with a few exceptions been decreasing during the last 20 years, *Figure 1*. However, the PM_{10} levels at some locations in Denmark still exceed the new EU limit values, which have been implemented in Danish law by regulations. The main contributions to the PM pollution are from traffic, heating, long range transported pollution and natural sources.

Health assessments in Denmark

Several studies based on Danish air quality data and international health data suggest increased mortality and morbidity in Denmark due to PM pollution (reviewed in Palmgren et al., 2001a).

This sub-project

In year 2000 the Danish Parliament decided to fund a four-year particle research programme, which should include characterisation of physical and chemical properties of the particles in Denmark and their sources and also assess the adverse health effects and the socio-economic impact in the Danish society. A steering group chaired by the Danish Environmental Protection Agency (DEPA) co-ordinates the programme, and the National Environmental Research Institute (NERI) carries out the characterisation of particles and their sources and the socio-economic aspects. The health effect studies are carried out at different institutions and universities, e.g. Danish Cancer Society and University of Copenhagen (Environmental and Occupational Medicine, Institute of Public Health).

The present report is the mid-term report on the activities at NERI.

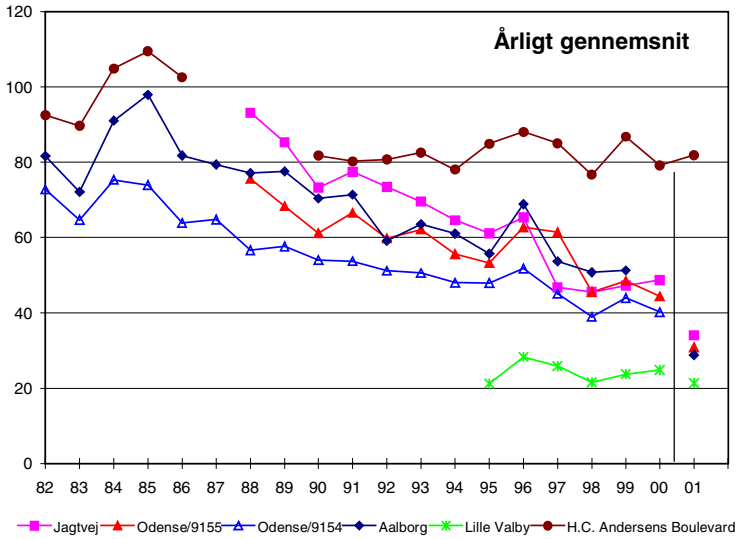

Figure 1 The trends in TSP at Danish monitoring stations. PM_{10} measurements were started at many stations in 2001. The stations are located at streets near the kerb side except Lille Valby, which is a rural station.

3 Objectives

The overall objective of the particle programme is to provide new and broader knowledge in Denmark on the health effect of atmospheric particles with the aim to develop strategies to reduce the adverse health effect of man-made and natural sources. The activities should be closely related to other activities in Denmark and internationally.

Specifically National Environmental Research Institute (NERI) shall investigate emissions, size distributions, chemical composition, transformation and dispersion of particles.

The Danish co-operation on emissions from the Danish car fleet and the health effect studies should be continued and strengthened. The activities will also strengthen the Danish participation in the international co-operation.

The research at NERI shall more specifically include the following issues:

- Characterisation of particles, i.e. size distributions, other physical properties and chemical composition of particles (ATMI).
- Inventories of emissions from different sources and determination of emission factors (SYS and ATMI).
- Particle emissions from road traffic (fuel, engine types etc.) (ATMI, SYS and TI).
- The effect of reduction measures (ATMI)
- Air quality and exposure models (ATMI)
- Socio-economic assessment (SYS and ATMI)
- International activities/co-operation (ATMI)

4 Approach

National and international co-operation

The programme is based on careful reviewing of the international literature, participation in international networks/projects, Danish studies on emissions, Danish studies on air quality, the Danish air quality monitoring programme and development of air quality and exposure models for particles.

NERI and DEPA participate actively in the following international networks related to PM: Development of EU directives, CAFE (Clean Air For Europe), SATURN (...), EMEP, Motor Vehicle Emission Group (MVEG) and others. In addition, NERI is a participant in a FP5[1] project, SAPPHIRE, on source apportionment of PM, and participant in several Expression of Interest (EoI) to FP6[2].

The general approach in the Danish studies is to build the research on existing activities in Denmark and on established and new international co-operation projects.

Emission inventories

The emission studies are based on existing work with national emission inventories in relation to CORINAIR and extended to include more detailed emission studies in relation to Danish emissions. The studies include mobile as well as stationary sources. An important issue is determination of emission factors.

Support from monitoring networks

The experimental research is mainly taking outset in the Danish air quality monitoring programme operated by NERI (Kemp & Palmgren, 2003), which include continuous, long time series of the main pollutants related to the most important sources in Denmark. The monitoring programme is supplemented by special particle related measurement campaigns. This combination of long time series of traditional pollutants and the special particle campaigns permits establishment of relationships between sources and the properties of the particles (sizes and physical/chemical properties). Meteorological data and activity data, e.g. traffic statistics, is available from the monitoring programme for the analysis and interpretation of data.

Air quality models

NERI has a complete hierarchy of air quality models, from European, regional, urban and local scale (streets and near stationary sources). These models are developed and validated for the traditional gaseous air pollutants. The results from the present studies will be applied for development and validation of particle modules to be included in the models. The air quality models are linked to the exposure models, which are used for determination of the human exposure of specific cohorts in the populations. The air quality and exposure models are necessary for assessment of the effect of different abatement scenarios.

[1] The EU's Fifth Framework Programme for Research and Technological Development.

[2] The EU's Sixth Framework Programme for Research and Technological Development.

The models are also necessary as tools in socio-economic assessments.

5 Danish emission inventory

International obligations

At the beginning of 2002 the first Danish emission inventory of particulate matter was carried out. The emission inventory was part of the Danish emission inventories reported under the UN-ECE Convention on Long-Range Transboundary Air Pollution (CLRTAP). The inventory includes total suspended particles (TSP), PM_{10} and $PM_{2.5}$. Emission of particles was reported for the first time in 2002 and the inventory for the year 2000 is considered to be a provisional version based on activity data and emission factors presently available.

Detailed emission inventories

A more detailed emission inventory of particle emission from Danish sources has been prepared in connection with this programme. The basis of input data of the emission inventory was improved and the method of calculation documented. The project will contribute to improve the quality of the Danish emission inventories of particulate matter reported under the UN-ECE CLRTAP.

Method, results and primary sources of the provisional emission inventory of the year 2000 are discussed. Revised emission factors are determined and an improved emission inventory for the year 2000 is presented. More details are given in annex A & B.

5.1 Emission inventory for particulate matter from stationary sources

The improved particulate emission inventory of stationary combustion plants is shown in *Table 2* and *Table 3*. The detailed emission inventory further disaggregated to fuel level is enclosed in Nielsen et al. 2003.

Table 2 Improved emission inventory year 2000, main SNAP[3] categories. Unit: Tons.

snap1	snap1 name	TSP	PM_{10}	$PM_{2.5}$
01	Combustion in energy and transformation industry	1131	948	810
02	Non-industrial combustion plants	3058	2899	2734
03	Combustion in manufacturing industry	741	575	448
Stationary combustion plants		4930	4423	3992

[3] SNAP: Selected Nomenclature for Air Pollution

Table 3 Improved emission inventory year 2000, SNAP-2 level. Unit: tons.

snap1	snap1 name	snap2	snap2 name	TSP	PM_{10}	$PM_{2.5}$
01	Combustion in energy and transformation industry	0101	Public power	826	702	594
		0102	District heating plants	161	115	91
		0103	Petroleum refining plants	142	129	122
		0104	Solid fuel transformation plants	0	0	0
		0105	Coal mining, oil / gas extraction, pipeline compressors	3	3	3
02	Non-industrial combustion plants	0201	Commercial and institutional plants (t)	136	132	123
		0202	Residential plants	2793	2665	2529
		0203	Plants in agriculture, forestry and aqua-culture	129	102	81
03	Combustion in manufacturing industry	0301	Comb. in boilers, gas turbines and stationary engines	447	339	254
		0303	Processes with contact	294	235	194
Stationary combustion plants				4930	4423	3992

TSP emissions from stationary combustion plants add up to 18% of the overall emission. The percentage from stationary combustion plants is higher, if only fine particulate fractions are considered. Thus $PM_{2.5}$ emission from stationary combustion plants ads up to 34 % of the overall emission.

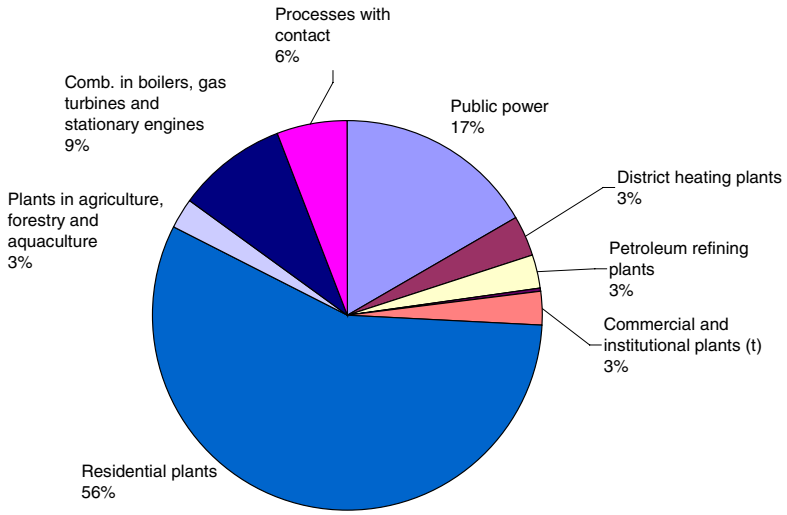

Figure 2. The improved emission inventory for TSP (Nielsen et al. 2003).

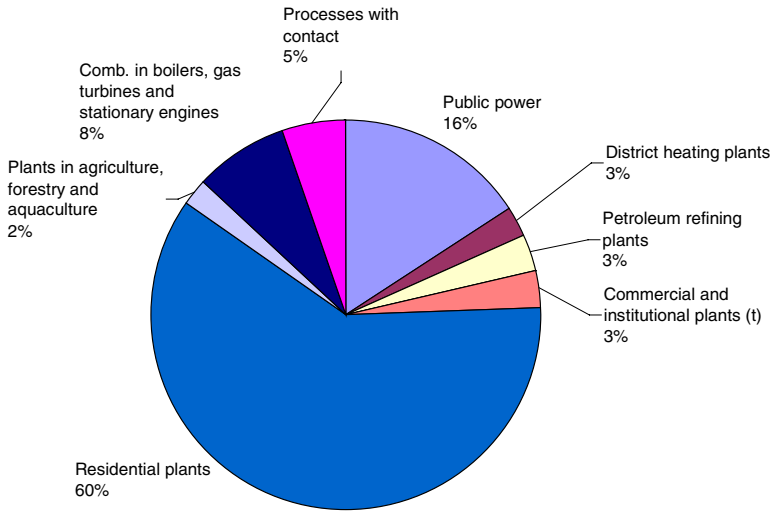

Figure 3 The improved emission inventory for PM_{10} (Nielsen et al. 2003).

An improved particulate matter emission inventory for stationary combustion plants for the year 2000 has been prepared. The revision is based on a survey of primary emission sources. Several emission factors have been changed as a result of improved knowledge of emission measurements performed on Danish plants and from literature surveys.

According to the improved emission inventory the primary sources of particulate (PM_{10}) emission are:

- Residential boilers, stoves and fireplaces combusting wood
- Farmhouse boilers combusting straw
- Power plants primarily combusting coal

– Coal and residual oil combusted in industrial boilers and processes

Further there is considerable emissions from:
– Residential boilers using gas oil
– Refineries

Emissions from wood burning

The PM emission from wood combusted in residential plants is the predominant source. Thus 40% of the $PM_{2.5}$ emission from stationary combustion is emitted from residential wood combustion. This corresponds to 13% of the overall Danish emission. $PM_{2.5}$ emission from burning straw in farmhouse boilers accounts for 19% of the total emission of stationary combustion plants.

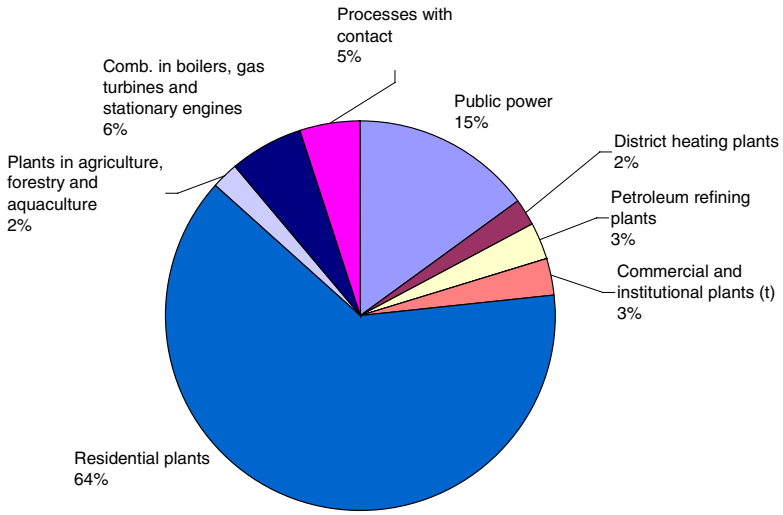

Figure 4 The improved emission inventory for $PM_{2.5}$ (Nielsen et al. 2003).

The literature survey revealed that the uncertainty in the emission factors for residential combustion of wood in stoves and boilers is immense and it can not be rejected that Danish emission factors should be increased more than a factor 10. Still, other references supported the current emission factor, and at present the emission factor has not been changed. Further studies of this emission factor are of great importance for further improvements of the inventory.

5.2 Emission inventory for particulate matter from road transport and other mobile sources

The direct contribution from road transport to ambient air concentration of particles originates from several processes. These are the direct exhausts from vehicles in the street, abrasion of material from tyre and break/clutch wear, road abrasion and the re-suspension of particles already emitted. Until recently the annual Danish particulate emissions estimates only comprised the exhaust emissions from diesel vehicles. However this limitation is not expedient since also exhaust emissions from petrol vehicles and not least the emissions

from the non-exhaust emission sources contribute significantly to the particulate emissions load.

The focus on the "new" sources of particulate emissions has also influenced national obligations in terms of emission information: From 2000 and onwards countries, which are parties to the UNECE convention are obliged to produce national estimates including both exhaust emission totals and non-exhaust figures for tyre and brake wear.

Exhaust emission factors

The Danish particulate exhaust emissions from diesel road transportation vehicles are calculated with the European COPERT model (Ntziachristos and Samaras 2000) including both the contribution from operationally hot engines and during cold start. In the model all present vehicle types are grouped into vehicle layers. This is a subdivision of all vehicle classes into groups of vehicles with the same average fuel use and emission behaviour. For petrol vehicles no PM emission data is available in the COPERT model. Instead relevant petrol emission factors, see TNO (2001), are derived from Dutch measurements (Klein et al., 2002), and to carry out the emission calculations for these vehicles a new database has been developed at NERI using the COPERT model principle.

For further details see, Nielsen et al., 2003.

Table 4 Emission factors (hot and cold aggregated) used in the Danish inventory (Nielsen et al. 2003).

Vehicle class	Fuel type	Engine/weight	Urban (g/km)	Rural (g/km)	Highway (g/km)
PC	Petrol	< 1.4 l.	0.01	0.01	0.01
PC	Petrol	1.4 – 2 l.	0.01	0.01	0.01
PC	Petrol	> 2 l.	0.01	0.01	0.01
PC	Diesel	< 2 l.	0.17	0.06	0.10
PC	Diesel	> 2 l.	0.17	0.06	0.10
LDV	Petrol		0.02	0.02	0.02
LDV	Diesel		0.33	0.19	0.21
Trucks	Diesel	3.5 – 7.5 tonnes	0.27	0.18	0.15
Trucks	Diesel	7.5 – 16 tonnes	0.53	0.36	0.29
Trucks	Diesel	16 – 32 tonnes	0.59	0.40	0.33
Trucks	Diesel	> 32 tonnes	0.63	0.43	0.36
Urban buses	Diesel		0.49	0.33	0.26
Coaches	Diesel		0.48	0.32	0.26
Mopeds	Petrol		0.12	0.12	
Motorcycles	Petrol	2 stroke	0.12	0.12	0.12
Motorcycles	Petrol	< 250 cc 4 stroke	0.04	0.04	0.04
Motorcycles	Petrol	250 – 750 cc 4 stroke	0.04	0.04	0.04
Motorcycles	Petrol	> 750 cc 4 stroke	0.04	0.04	0.04

Non exhaust emission factors

The non-exhaust emission sources treated in this study are tyre, break and road-asphalt wear. Different factors affect tyre wear such as tyre construction, composition, size, accumulated mileage, driving behaviour, vehicle type, vehicle settings and maintenance, road surface characteristics and weather. Brake wear only occurs during forced decelerations, and therefore most of the emissions should be observed near busy junctions, traffic lights, pedestrian crossings, and corners. Most of the emission factors used in the Danish inventory come from TNO (2001) which has conducted a literature study targeted at proposing particulate emission factors of TSP, PM_{10} and $PM_{2.5}$ relevant for national inventories in the context of the UNECE con-

vention. The data originate from Dutch roadside measurements, as the only source of information. The tyre and break wear factors have been established from mass balance experiments for passenger cars, while for other vehicle types the tyre wear factors have been estimated using information from people employed in the tyre business and industry. Break wear factors for the same vehicle types have been estimated using the same ratio between brake and tyre wear as for passenger cars. The road abrasion factors are taken from an emission inventory by RIZA (Institute for Inland Water Management and Waste Water Treatment) in the Netherlands in 1994. Modifications of the TNO (2001) emission data are made for tyre wear (PM2.5) and brake wear (PM10 and PM2.5) using the findings from USEPA (1995) and TNO (1997).

For further details see, Nielsen et al., 2003.

Table 5 Non exhaust emission factors (mg/km) per vehicle category in the Danish inventory (Nielsen et al. 2003).

	Brake wear			Tyre wear			Road abrasion		
Vehicle category	TSP	PM_{10}	$PM_{2.5}$	TSP	PM_{10}	$PM_{2.5}$	TSP	PM_{10}	$PM_{2.5}$
Passenger cars	6	5.9	2.4	69	3.5	2.5	145	7.3	0
Light duty vehicles	7.5	7.4	3.0	90	4.5	3.2	190	9.5	0
Heavy duty vehicles	32.25	31.6	12.9	371.25	18.6	13.0	783	39.2	0
Buses	32.25	31.6	12.9	371.25	18.6	13.0	783	39.2	0
Mopeds	1.5	1.5	0.6	17.25	0.9	0.6	36.5	1.85	0
Motorcycles	3	2.9	1.2	34.5	1.7	1.2	73	3.7	0

The total exhaust PM emissions are calculated separately for operationally hot engines and for engines driving under cold start conditions. The total fuel use is estimated in parallel and finally a fuel balance is made in order to remove the gap between the simulated fuel use with the national fuel sale statistics provided by the Danish Energy Agency (DEA). The non-exhaust emissions are simulated using the hot engine emission calculation method.

Trends

The total PM exhaust emissions have decreased substantially since the mid-1990s due to the stepwise strengthening of emission standards for all vehicle types. This decrease will continue in the future as new low emitting vehicles complying with future emission standards substitute older and more polluting vehicles. In absolute amounts the conventional types of diesel light duty and heavy-duty vehicles have the highest emissions and for these vehicles the future emission reductions will become most effective. Conventional passenger cars still contribute significantly to this vehicle type's PM total. However the conventional emission share will be negligible in the future following the penetration of catalyst vehicles into the Danish traffic.

In the Danish inventory a database has been constructed especially to estimate the emissions from brake and tyre wear and road abrasion. The basic calculation principle is to multiply the total annual mileage per vehicle category with the correspondent average emission factors for each source type.

The total emissions from all mobile sources are summarised in *Table 6*. For further details see, Nielsen et al., 2003.

Table 6 Particulate emission totals for all transport modes in 2000 (Nielsen et al. 2003).

Category	TSP [tons]	PM10 [tons]	PM2.5 [tons]
Road traffic	3969	3969	3969
Brake wear	400	392	160
Tyre wear	4632	234	163
Road abrasion	9751	490	0
Military	19	19	19
Railways	162	162	162
Inland waterways	72	69	66
National sea traffic	352	335	318
National fishing	398	378	359
Domestic LTO	2	2	2
Domestic cruise	2	2	2
Agriculture	2174	2066	1963
Forestry	2	2	2
Industry	1145	1090	1037
Household and gardening	27	27	27
Total	23106	9235	8249
International sea traffic	7618	7237	6875
International LTO	4	4	4
International cruise	34	34	34

5.3 Total emissions

The total emissions of particles in Denmark are summarised in *Figure 5*.

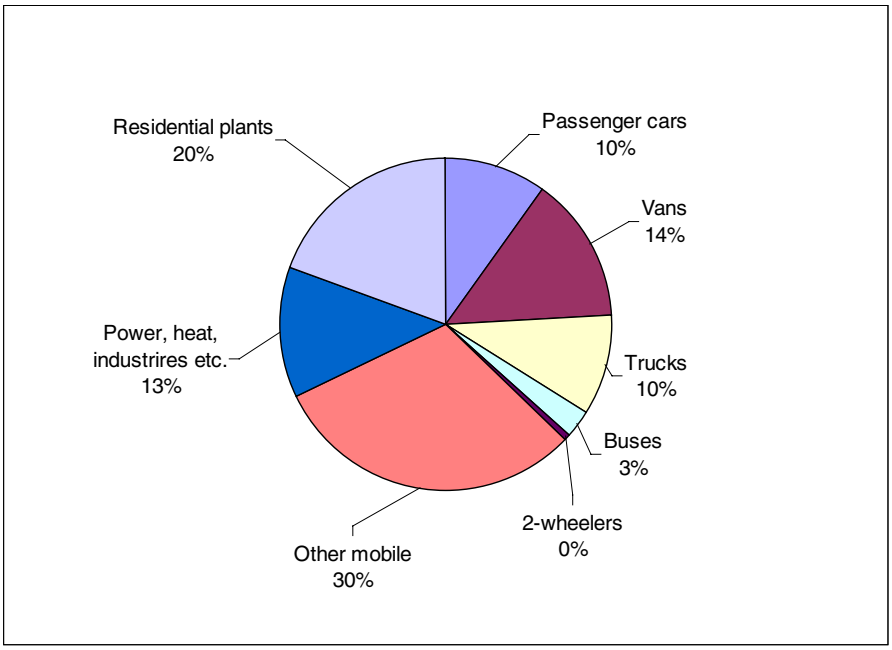

Figure 5 Total emissions of PM_{10} in different categories. "Other mobile" includes tractors, machinery for building and constructions and other off-road machinery. The emissions from this category are very uncertain.

6 Experimental studies

6.1 Traffic particle field studies

Size distributions

The particle size distribution is an important factor that needs to be addressed whenever the particle pollution is concerned. A major contribution to harmful particulate pollution in urban areas is believed to be attributed to traffic, and especially, to emissions from diesel powered vehicles. Ultrafine particles emitted from petrol as well as diesel engines are formed at high temperature in the engines, in the exhaust pipe, or immediately after release to the atmosphere. Some of these particles may be in the so-called nucleation mode (nano-particles < 30 nm). The dominating ultrafine particle mode has a number concentration peak in the range 20-50 nm. These particles are formed by coagulation of primary particles, and by condensation of gases on particles. The fine particles (accumulation mode in the range 0.1 µm - 2 µm) are typically formed by chemical reactions (e.g. SO_2 and NO_x to form sulphate and nitrate), or other relatively slow processes in the atmosphere. The last mode is the coarse particles > 2 µm, which in urban areas typically are formed mechanically by abrasion of road material, tyres and brake linings, soil dust raised by wind and traffic turbulence, etc. These larger particles may also cause health effects.

The chemical and physical properties

The physical and chemical properties are important for assessment of the deposition in the lungs and further for assessment of the adverse health effects. The important properties - in addition to size - are state (liquid/solid), volatility, hygroscopicity, chemical composition (content of organics, metals, salts, acids etc.), morphology, and density. These properties are also important for selection of methods for regulation and control of emissions. The ultrafine particles in urban ambient air are mainly emitted from diesel and petrol fuelled vehicles and the test cycles on the emission from the engines can be based on measurements on dynamometers using dilutions systems, which, however, not always are comparable with the real emission conditions in a street. The control parameter is normally the mass of the particles that will be dominated by larger particles. The mass include often only the solid part of the particles, which is measured after heating of the exhaust gas to e.g. 300 °C; this will remove semi-volatile compounds, e.g. organic condensates, which are likely to be present in the urban air.

Real driving conditions

It is important to measure and determine the particle emission under normal driving conditions and in ambient air, in order to establish the relationship between the sources and the exposure of the population. An important part of the particle research programme is dedicated to experimental field studies of the particles from traffic, including exhaust as well as non-exhaust particles.

6.2 Objectives of the experimental studies

The aim of the studies is to quantify the emissions of ultrafine particles from different types of vehicles with respect to chemical composition, physical properties and number-size as well as mass-size distributions. The results will be applied for development and validation of quality and exposure models for particles and as input (e.g. emission factors) to the models.

6.3 Experimental techniques

Relationship to monitoring networks

The project includes field studies of particle size distributions, chemical composition and physical properties of particles in ambient air. Investigations of particle sources and laboratory studies of particle emissions from vehicles supplemented the studies. The measurements were performed at several locations, which all are related to the Danish Air Quality Monitoring Programme (Kemp and Palmgren, 2003), and make use of logistics and data from routine monitoring.

Jagtvej

The most comprehensive studies were performed in a street canyon close to central Copenhagen (Jagtvej), which is a street canyon with a 10 m wide 2 lane road, which during rush hours in practise is a 4 lane road. At both sides of the roadway are bicycle lanes, pavements and rows of 5-6 storey houses. The traffic density is approx. 26,000 vehicles per 24 hours, including 6-8% heavy vehicles, i.e. buses, lorries and larger vans. A fixed monitoring station of the Danish Air Quality Monitoring Programme has been in operation at this location since 1988. Data from this station include half-hour measurements of NO_x, CO, TSP/PM_{10} and other traditional pollutants. Measurements were also performed at a nearby urban background station (H.C. Ørsted Institute, HCOE), where monitoring data and representative meteorological data are also available.

Odense

Similar measurements were performed at another monitoring station under the Danish Air Quality Monitoring programme at Albanigade in Odense, which also is a 2 lane road with bicycle lanes, pavements, but only 1-2 storey houses along the road. The traffic density is approx. 22,000 vehicles per 24 hours, including 12% heavy vehicles.

H.C. Andersen Boulevard

Other important studies were performed at H.C. Andersen's Boulevard (HCAB), which is a broad street with 3-4-storey house on the eastern side and the amusement park "Tivoli" on the other side. It is a 6-lane street with more than 60,000 vehicles per 24 hours and approx. 10% heavy vehicles. The monitoring station is operated in a cooperation between the Environmental Protection Agency of the Municipality in Copenhagen and NERI, and the monitoring programme include all standard pollutants, and recently also PM_{10} and $PM_{2.5}$ measured by TEOM.

DMPS

The Differential Mobility Particle Sizer (DMPS) used for the particle measurements consist of 28 cm Hauke-type Differential Mobility Analyser (DMA) (Winklmayr et al., 1991), built at the Lund Institute of Technology, employing a re-circulating flow system (Jokinen and

Makela, 1997) connected to a TSI Model 3010 Condensation Particle Counter (CPC). Corrections for reduced counting efficiency at lower sizes, multiple charging (Wiedensohler, 1988) and particle sampling losses were made. The scanning time for each size spectrum is approximately 3 min, using alternating up- and down-scans. Average spectra for each half-hour were calculated and used for the analysis in relation to the trace gas and meteorological measurements. The total particle number, surface and volume was calculated for each half-hour based on the single scans assuming spherical particles.

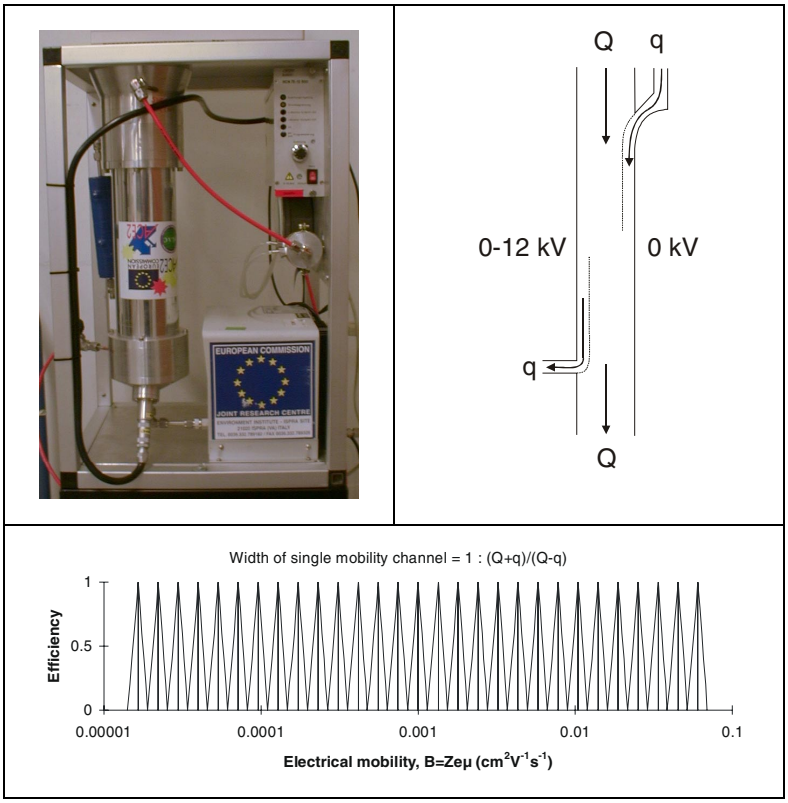

Figure 6 Upper left is a DMPS (Differential Mobility Particle Sizer). To the right is shown the principle of a DMA (Differential Mobility Analyzer), which is the heart of the DMPS. Below is shown how the particles are sorted in relation to the mobility (related to the voltage over the DMA electrodes).

Traffic counts

Starting in July 2001 automated traffic counts are available at Jagtvej, close to the monitoring station, using a Autoscope Solo video sensor system counting traffic volume and traffic speed in the different lanes.

TSP and soot

The measurement techniques are related to different definitions of particle parameters. Particles were earlier normally defined as TSP ("total suspended particulates") or soot. TSP is the mass concentration ($\mu g/m^3$) of the particles, which were collected by specific air samplers and included often all particles with a diameter up to around 30 µm, but the cutoff diameter varies typically between 10 and 50 µm. depending on e.g. the wind speed. The mass is determined by weighing of the filter before and after collection of the particles on the filter. Determination of soot takes place by measurement of the blackness of the filter after collection of particles on the filter. Large mechanically

formed particles, e.g. soil dust, contributes much to the TSP concentration. Soot is comprised of coloured (black) particles, which primarily consist of material from combustion processes, e.g. combustion of oil and coal.

PM_{10} and $PM_{2.5}$

During the last decade greater emphasis is on the smaller particles and measurements of PM_{10} mass concentration in the air (particles with a diameter less than 10 µm) is now more common in monitoring programmes. There are two main reasons for measuring PM_{10} rather than TSP. The PM_{10} measurement method has a more well-defined and wind-speed independent size cut-off at 10 µm. PM_{10} seems to be more relevant in relation to assessment of adverse health effects, and by this more relevant for establishment of air quality limit values.

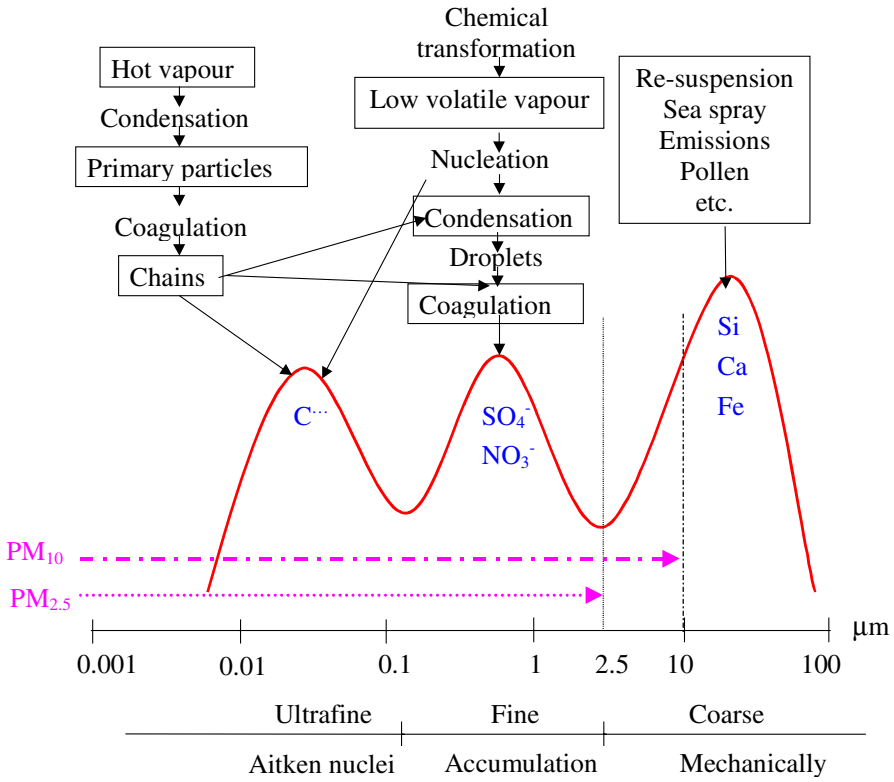

Figure 7 Schematic description of the particle size distribution. The vertical axis is artificial. The ultrafine mode would be very small, if the vertical axis was the mass concentration, and the coarse mode would be very small, if it was the number concentration.

PM_{10}

As shown in *Figure 7* PM_{10} is probably not the most appropriate parameter for description of the fine particles. The cut-off is located somewhere in the coarse mode and is probably sensitive to changes in the position of the mode. $PM_{2,5}$ is perhaps a better parameter, because it separates the fine and the coarse mode and includes the fine and the ultrafine mode. Better assessment of the health effects may be obtained but other particle parameters may be important, e.g. particle number and their chemical properties, because the smallest (ultrafine) particles only contributes negligible to the mass concentration of the particles.

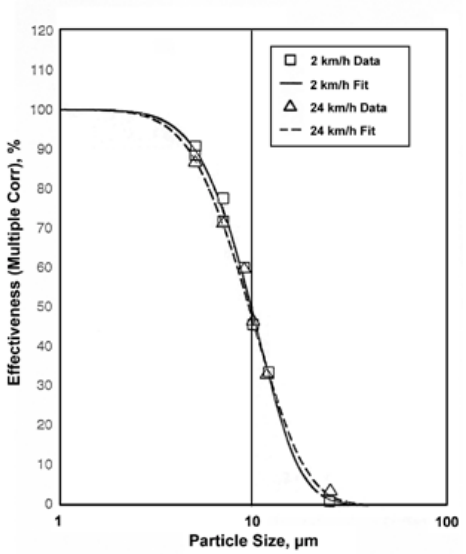

Figure 8 PM_{10} is measured by collection of particles on a filter. The inlet (shown left) cuts off particles > 10 µm. The graph (shown right) shows that the cutoff is not sharp, but defined by the reference method.

Determination of mass

The mass concentrations (TSP, PM_{10} and $PM_{2.5}$) can be determined by several measurement techniques. The EU reference method is based on increased weight of a filter after collection of particles (gravimetric method). This requires weighing in the laboratory of the filters before and after collection of the particles.

Automatic methods are developed, because actual (online) data are required, e.g. for providing information to the public. One of these methods (SM200 from the Swedish company OPSIS) is used in LMP for measurements of 24 hour average concentrations of PM_{10} ($PM_{2.5}$ is also possible). The method is based on increased absorption of beta radiation in the filter after collection of particles. The SM200 monitor method used at NERI is accredited by DANAK, the Danish Accreditation Organisation. Satisfactory agreement with the reference method has been demonstrated in Berlin and Oslo.

TEOM

Another method is TEOM (Tapered Electronic Oscillating Microbalance), which is based on reduced oscillation frequency of a vibration unit with a collection filter. The advantage of the method is the high time resolution (1/2-1 hour), which makes the method very useful for measurements close to sources with fast variations of the emissions, e.g. the road traffic. TEOM monitors are installed at H.C. Andersens Boulevard (central Copenhagen) for measurements of PM_{10} og $PM_{2.5}$ in addition to a gravimetric TSP sampler. A disadvantage is that the filter has to be heated to around 50 °C in order to remove water, and this leads to loss of volatile compounds or decompose other compounds, e.g. semi-volatile organic compounds and ammonium nitrate. A correction in relation to the reference method is needed, but the problem is that the correction depends on the composition of the particles, and therefore also on the location.

Other parameters

The new EU air quality limit values are defined for PM_{10}. They are mainly based on health effect studies in USA in the early and mid 1990's and also more recent studies in Europe. A review of the limit

values is planned for 2003-2004, because it is recognised that the better and more health related measures of the particulate matter could be defined, e.g. $PM_{2.5}$, PM_1, $PM_{0.??}$, particle number concentration, surface area of the particles, surface activity etc.

6.4 Urban background measurements in Copenhagen

How representative is the urban background site?

The permanent urban background station in Copenhagen is located on the rooftop of the H.C. Ørsted Institute. The elevation above ground level is approximately 20 m. Some doubts have been raised concerning this height, because urban background stations often are placed at ground level in parks or similar. During a measuring campaign in July-August 2002 a temporary urban background station was established at ground level on the lawn of the H.C. Ørsted Institute close to the permanent station, but on the backside of the building, so it was shielded from the heavily trafficked road Nørre Allé (*Figure 9*). The PM_{10} and the concentration of the gases CO, NO_x and NO_2 were measured in parallel on a half-hour basis using similar monitors at both sites.

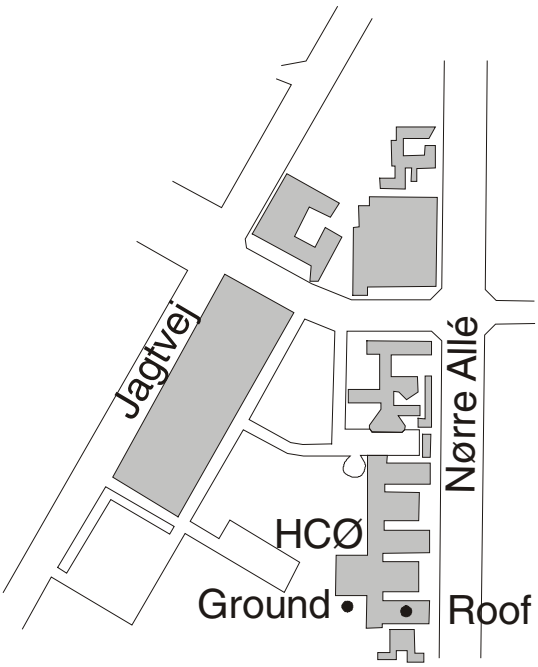

Figure 9 The location of the two measuring sites on the ground and on the roof of the H.C. Ørsted Institute.

The measurements at the two sites were compared using scatter plots as shown in *Figure 10*. It is readily seen that the agreement between the measurements is rather good. The ratios between the standard deviations are in the range 0.89 – 1.03, not indicating serious lower values on the roof than on the ground.

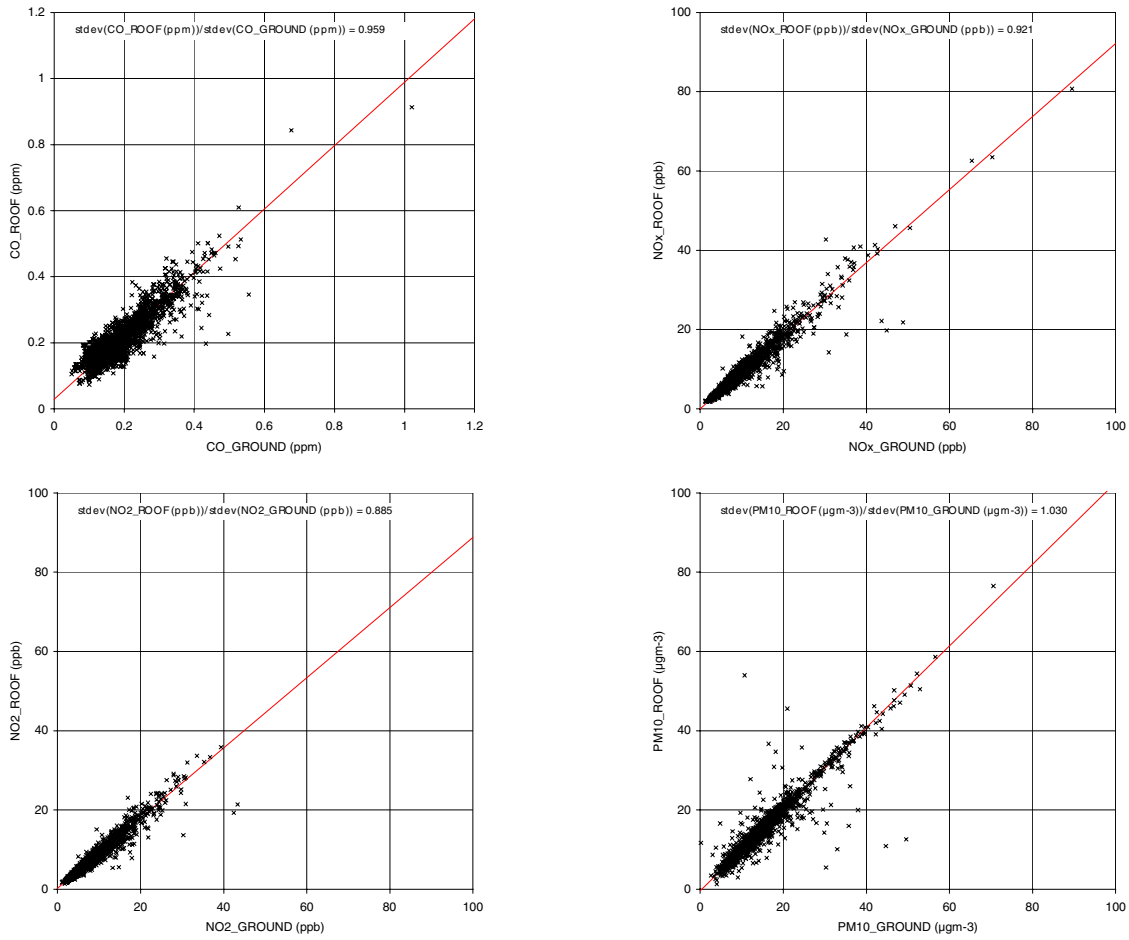

Figure 10 Comparison of simultaneous half-hour measurements of CO, NO_x, NO_2 and PM_{10} in urban background air in two heights at the H.C.Ørsted Institute in Copenhagen.

6.5 Level and trends of TSP and PM_{10} in Denmark

Monitoring of air quality in Denmark

The PM pollution in Denmark has been investigated for more than 20 years, especially under the Danish Air Quality Monitoring (LMP). *Figure 11* shows the trend of TSP since 1982 at trafficked streets in the biggest Danish cities. The trend at a rural monitoring station Lille Valby near the town Roskilde approx. 40 km. west of Copenhagen is also shown. The first systematic PM_{10} measurements were carried out in 2001. They showed that PM_{10} is approx. 65% of TSP, which roughly corresponds to the literature values.

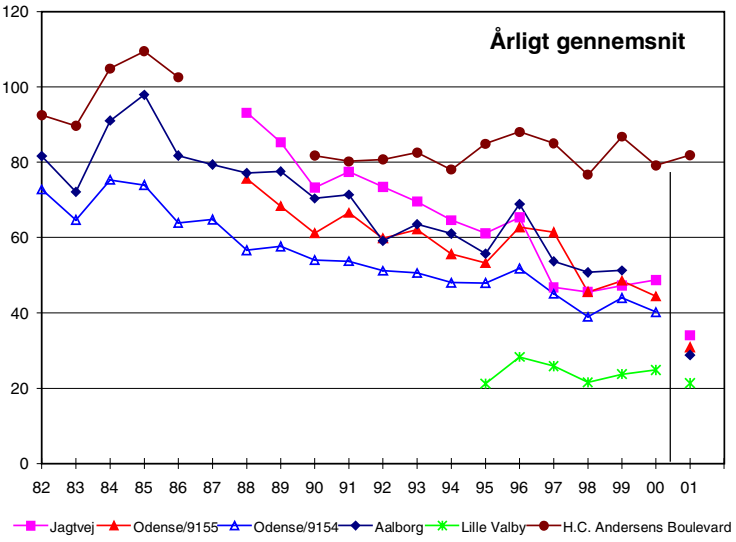

Figure 11 Annual averages of TSP (and in 2001 PM_{10}) measured in the 4 biggest cities in Denmark and at one rural background station.

General decreasing trends

Most of the stations showed clear decreasing trends, which may have different reasons. One important reason is the decreasing contribution from long range transported air pollution, e.g. the reduced sulphur pollution in Europe, *Figure 12*.

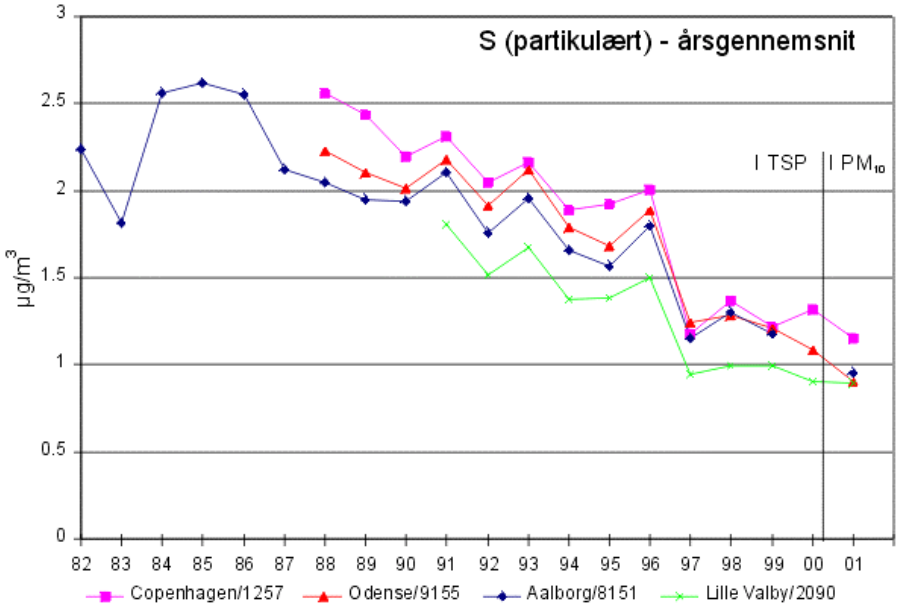

Figure 12 The trend of particulate sulphur measured under LMP IV.

Other factors are better control of industries, power plants and other point sources. "Green fields" and reduced emissions from traffic do also play a role.

HCAB

The nearly constant level at HCAB is probably due to a significant non-exhaust contribution from the very dense traffic at this main street (> 60.000 vehicles per day), and this traffic has been increasing.

Compliance with limit values?

The PM_{10} annual averages are, except for HCAB, below the limit value, 40 µg/m^3, which the Member States in EU have to meet before 2005. (EC, 1999). However, the 24 hour average limit value on 50 µg/m^3 is exceeded more than the permitted 35 time per year. This is illustrated in *Figure 13* and *Table 7* for Jagtvej in Copenhagen. The proposed limit values to be met by 2010 are in general exceeded all over the country like in all other European countries. These very stringent limit values may be revised in connection with the review of the EU limit values.

Table 7 PM_{10} measured at Jagtvej in Copenhagen

Year	Number of measurements	Average (µg/m^3)	Number of measurements above 50 µg/m^3	Percent exceedances
1999	356	35.3	53	15%
2000	310	29.9	38	12%
2001	261	35.1	44	17%

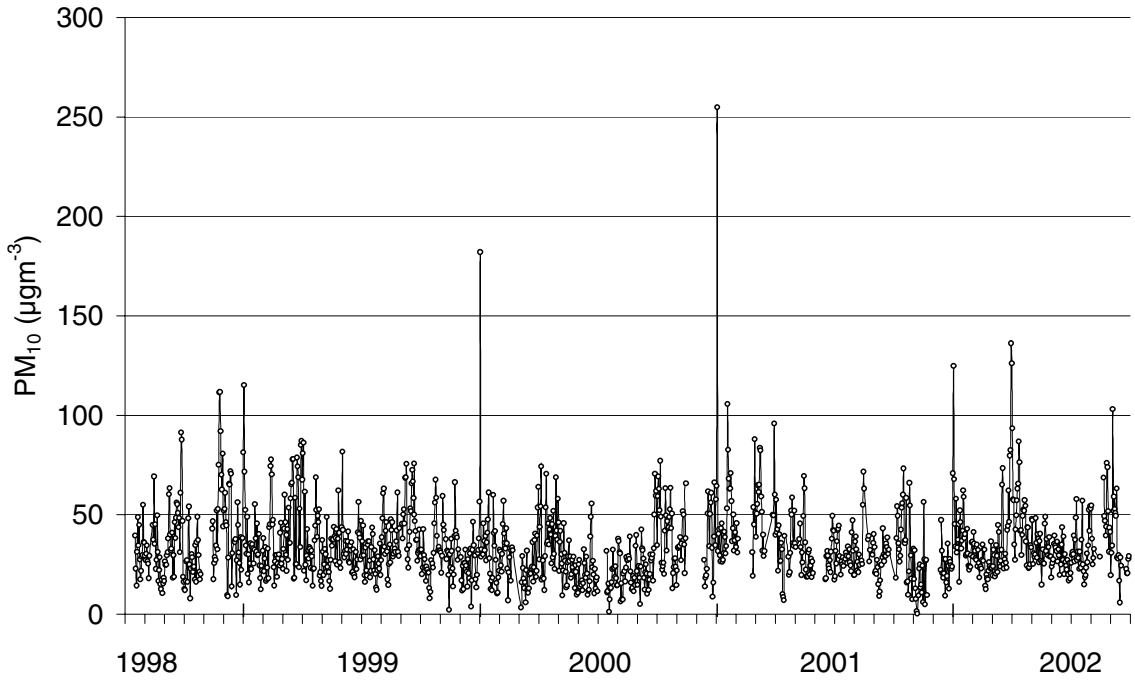

Figure 13 All measurements by the SM200-monitor of PM_{10} at Jagtvej from July 1998 to September 2002.

6.6 Source contributions to PM_{10}

Long range transport important

A more detailed analysis of the PM pollution at streets, urban background and at rural sites confirms that the long range transported contribution is significant, *Table 8*. It is partly primary (directly emit-

ted) and partly secondary particles formed by oxidation of SO_2 and NO_x from traffic, power plants and industries in Europe.

The upper regression line at *Figure 14* shows PM_{10} versus NO_x at Jagtvej measured by SM200 (a beta-absorption method equivalent to the reference method). The PM_{10} level at NO_x=0 corresponds to the non-traffic (background) part, i.e. mainly long range transport and natural sources. The background level is approx. 22 µg/m^3. The level is around 33 µg/m^3 measured by SM200 at a busy street like Jagtvej. The lower regression line represents TEOM measurements These measurements are carried out at 50 °C, which lead to losses of ammonium nitrate (long range transported secondary particles), volatile organic compounds and water. The shift of the regression line corresponds to the losses due to the NO_4NO_3 and the volatiles in PM_{10}.

Table 8 Averages of simultaneous PM_{10} measurements by SM200 at Jagtvej in Copenhagen, at HCOE and at rural background sites Keldsnor at the southern part of Langeland and Lille Valby near Roskilde. Unit, µg/m^3.

	Jagtvej	HCØ	Keldsnor	Lille Valby
17.10.2001 - 29.09.2002	34.4		26.4	24.7
03.05.2002 – 29.09.2002	30.8	25.3	22.7	21.1

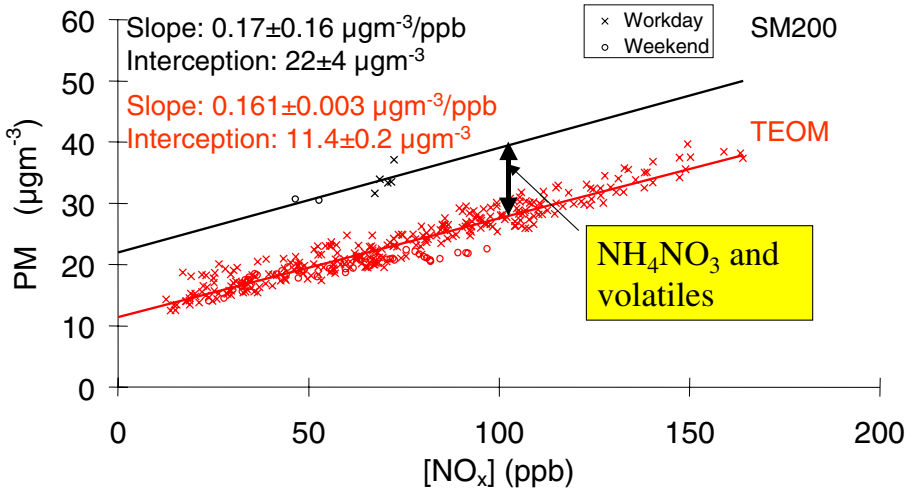

Figure 14 PM_{10} measured by SM200 and TEOM at Jagtvej in Copenhagen. The shift is due to losses of ammonium nitrate or other volatile compounds of the TEOM measurements carried out at 50 °C.

Rural sites

Measurement results of PM_{10} at the two rural background stations, Lille Valby og Keldsnor, are shown at *Figure 15*. PM_{10} at these two locations are strongly correlated and at the same level, which confirm dominating contribution from distant sources (long range transport).

Measurements in Copenhagen

Complete data are available for PM measured by TEOM (PM_{10}) and DMPS (6 –700 nm in 29 size classes) since July 2001. From May are TEOM ($PM_{2.5}$) also available. Elemental carbon (EC) data are available from a 4-5 months campaign in the autumn of 2001. CO, NO and NO_x data are always available from the monitoring programme, LMP IV.

All measurements are carried out as half-hour averages and can be compared directly.

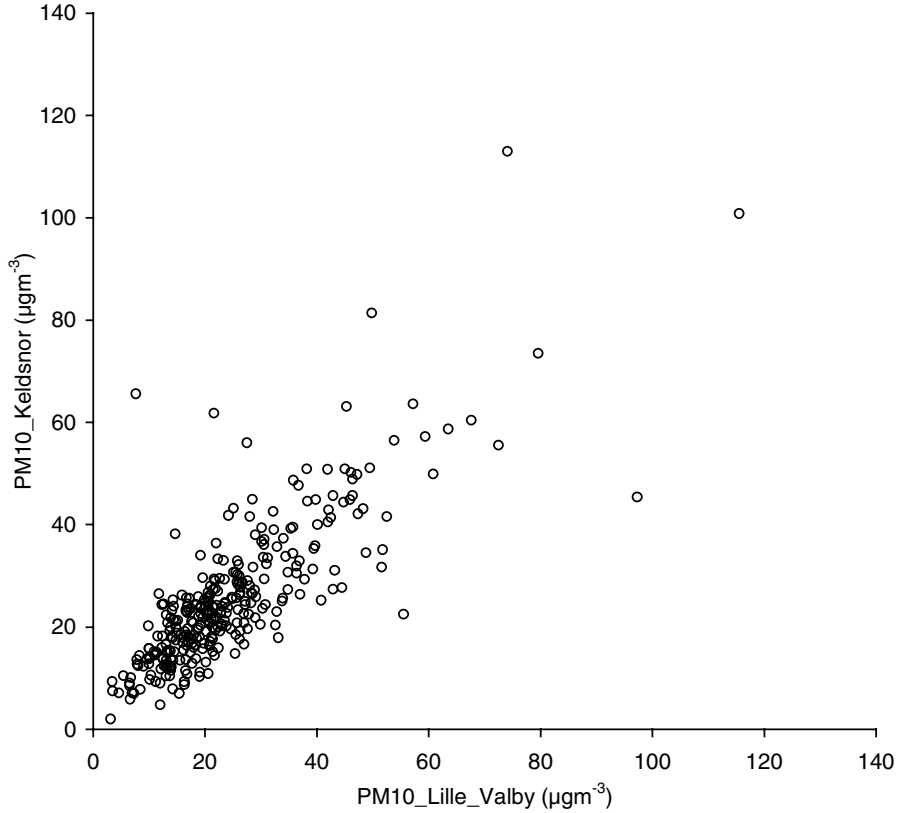

Figure 15 Simultaneous data of PM_{10} at two rural background stations in Denmark (Keldsnor and Lille Valby). The distance between the stations is 142 km. The agreement confirms the strong influence from long-range transported particles.

The measurement results

The averages, medians and percentiles are shown in *Table 9*. The DPMS data are based on 80,000 single measurements of the size distributions during the measurement period.

Table 9 Averages, medians and percentiles in the period July 2001 - July 2002 at H.C Andersen Boulevard in Copenhagen.

	PM_{10}*	$PM_{2.5}$	CO	NO	NO_x	NO_2*	Particle number	Volume	EC
Unit	μgm^{-3}	μgm^{-3}	ppm	ppb	ppb	ppb/μgm^{-3}	cm^{-3}	$\mu m^3 cm^{-3}$	μgm^{-3}
Average	35,8	15,3	0,78	57,3	87,4	30,1/57,7	40389	16,0	2,7
Median	30,5	14,0	0,67	45,1	75,5	29,3/56,2	31710	12,8	2,3
98%-percentile	102,0	33,8	2,18	186,2	234,3	58,2/111,6	130462	46,3	7,1
19. highest						71,3/136,7			

*The measurement results of PM_{10} are not directly comparable with limit values, because they are measured by TEOM at 50 °C. The limit values for NO_2 is 40 μgm^{-3} (annual average), and 18 permitted exceedances of 200 μgm^{-3} per year (date of compliance 2010).

Weekly variation

All measurements of PM show a distinct diurnal and weekly variation correlated with the road traffic. *Figure 16* and *Figure 17* show the hour by hour averages over an average week of the gases, PM_{10}, EC and particles number concentration. The correlation is weakest for PM_{10}, particle volume and NO_2. The reason for this for PM_{10} and parti-

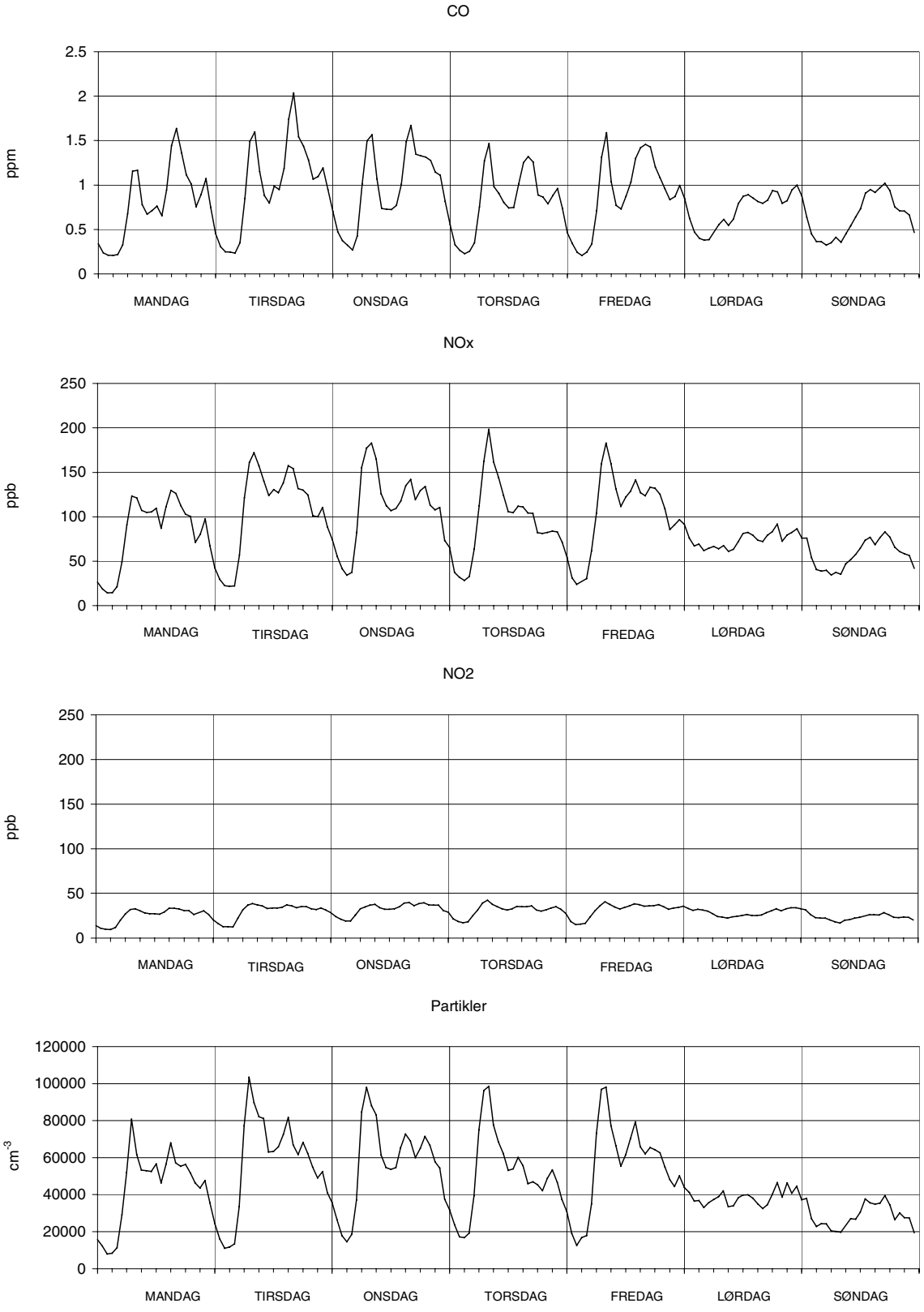

Figure 16 Variation - at HCAB - of gases and particles (unit number per cm^3 over an average week. The traffic and the meteorology (dispersion) mainly influence the variation. The NO_2 is limited by the long range transported ozone

cle volume is that there are significant contributions from sources, which do not correlate with traffic, i.e. long-range transport. However, the correlation with PM_{10} measured by TEOM is much better than with PM_{10} measured by the reference method. This is due to the heating of the TEOM filter 50° C, which removes a large portion of the long-range transported particles (approx. 50% corresponding to 11 μgm^{-3}). The explanation for the poor correlation for NO_2 is that NO_2 mainly is a secondary pollutant formed by oxidation of NO by ozone:

$$NO + O_3 \rightarrow NO_2 + O_2,$$

In streets this process is normally limited by the available amount of regional ozone, which in this case was 25 ppb O_3 (50 $\mu g/m^3$) in average at Lille Valby.

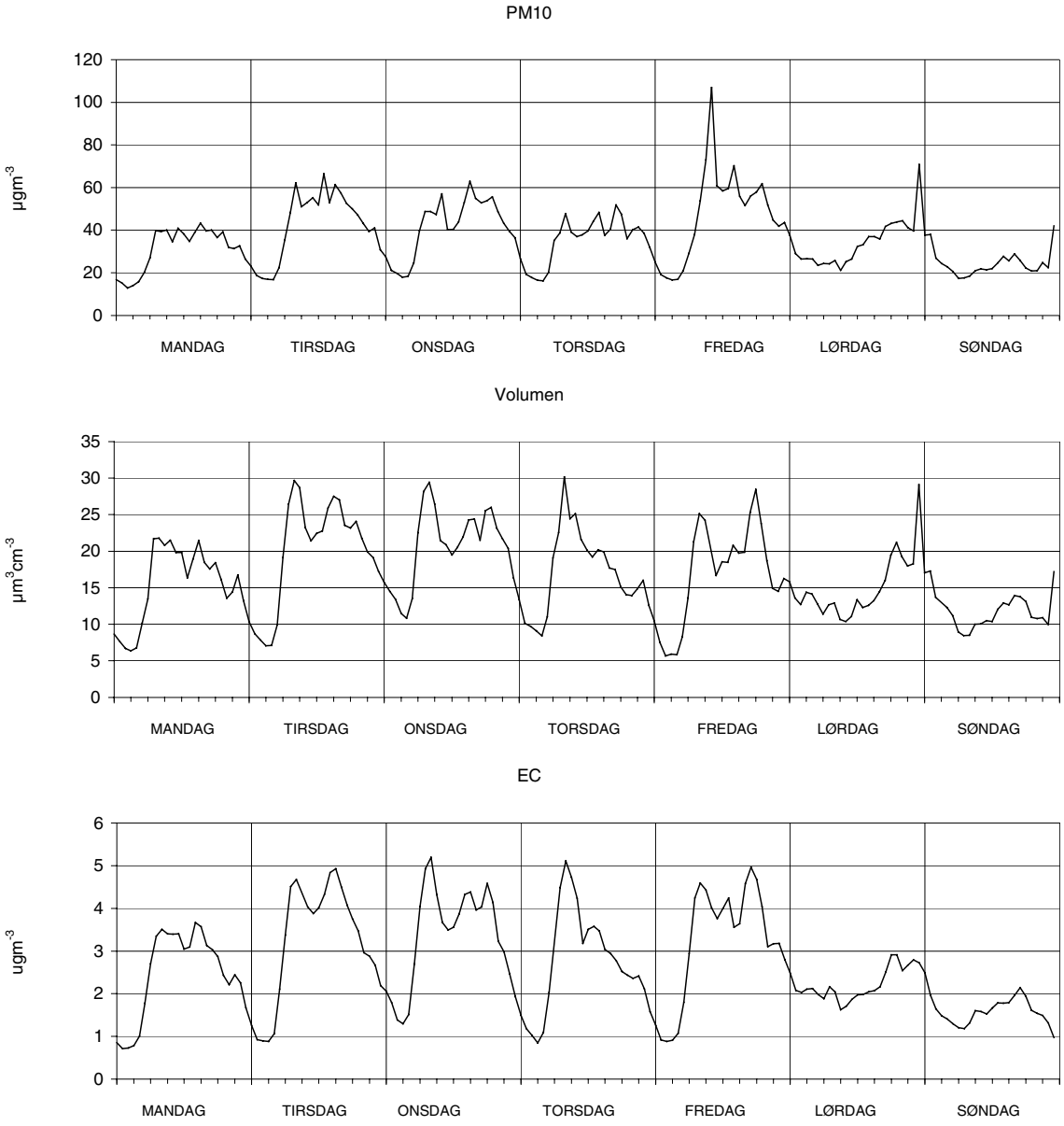

Figure 17 Variation - at HCAB - of PM_{10}, particle volume (unit: μm^3 pr. cm^3) and EC over an average week. The traffic and the meteorology (dispersion) mainly influence the variation. There is an important contribution to PM_{10} and particle volume from other sources, i.e. long range transport and sometimes the fireworks from the Tivoli amusement park.

Two methods for PM_{10}

The limit values for PM_{10} are defined for 24 hours averages, measured by the reference method or an equivalent method, which in general is done in the Danish Air Quality Monitoring programme. Measurement results of PM_{10} by TEOM monitor as well as the SM200 monitor are available at the monitoring station at Jagtvej (street) and at HCØ (urban background). The TEOM monitor underestimates PM_{10} compared to the SM200-monitor. The differences between the two methods are more or less similar at the two stations. The contribution to PM_{10} from traffic density is much higher at Jagtvej than at HCØ (6 times). It has been shown that the TEOM monitor measures the traffic contribution nearly correctly and the differences only are due to long range transport and natural sources. The losses at HCAB are thus assumed to be the same as at Jagtvej, and the TEOM data from HCAB can be corrected for losses using data from Jagtvej. The black graph in *Figure 18* shows the 24-hour values of uncorrected data and the red graph the corrected data.

Exceedances of limit values at H.C. Andersen Boulevard

The annual averages and the number of exceedances per year can be estimated by the limited number of measurements (164 measurements out of 365). The corrected annual average is probably a good estimate, since all seasons are represented in the data set (*Table 10*). The limit value, 40 µg/m^3 is exceeded. The best estimate of the annual number of exceedances of 50 µg/m^3 is 365/164*59 = 131, which is not in compliance with the limit values (35 exceedances per year).

Table 10 Average of PM_{10} measured by TEOM 24-hour averages from the period July 2001 - July 2002. The first column is based on all data, and the second column corresponds to measurements, which could be corrected for losses. Unit µg/m^3.

	TEOM-PM_{10}	TEOM-PM_{10}	Correction	PM_{10} (Corrected)
Average	35,8	36,1	10,7	46,7
Number of measurements	233	164	164	164
Number of exceedances of 50 µg/m^3	59			

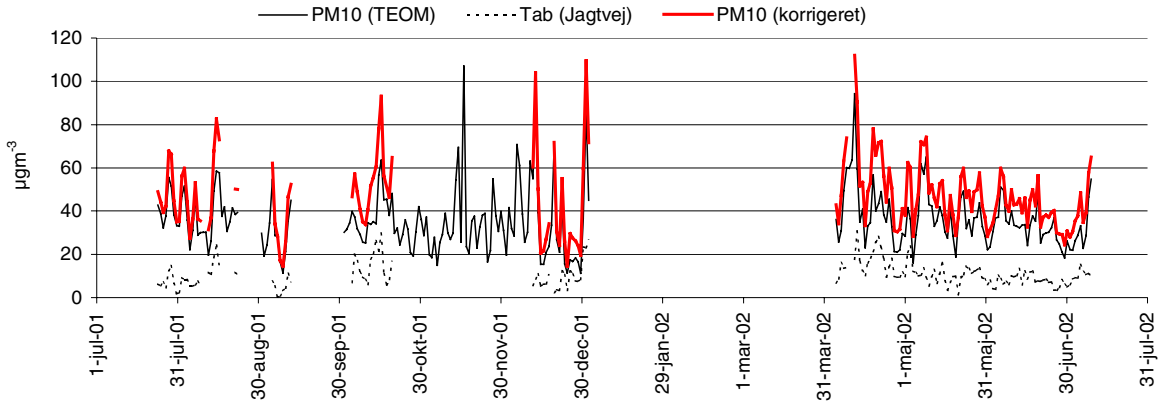

Figure 18 The black graph shows the 24-hour values calculated from ½ hour values of PM_{10} measured by TEOM at HCAB. The broken line shows the available data on PM_{10} losses in the TEOM monitors at Jagtvej and HCØ in the actual period. The red graph shows the corrected concentrations at HCAB, where the correction has been made by the adding the losses determined at Jagtvej and HCØ.

Long range transport and local sources

The calculated averages of PM_{10} at HCAB show that the limit value of annual averages, 40 µg/m^3, will be exceeded also in the coming years. Considerations about possible measures to reduce the PM_{10} pollution have to be based on knowledge about the contribution from different sources. Simultaneous TEOM measurements at Jagtvej and HCØ show a strong correlation, but the concentrations are always larger at Jagtvej than at HCØ. The correlation is due to a large long range transported contribution, which is the same at the two locations. The difference is mainly caused by the proximity of the traffic at Jagtvej, a street canyon, where the dispersion is limited between the building rows, whereas the dispersion in urban background takes place over a larger area, which also include the areas between the streets. The dispersion is the same for gases and fine and ultrafine particles in the urban scale. Traffic is the main source to elevated NO_x concentrations in streets, whereas PM_{10} also originates from other local sources like constructions and wind generated dust.

6.7 Use of Particulate Elemental Carbon for Source Apportionment

EC/OC measurements

Carbon monoxide (CO) is commonly used to trace petrol cars. Diesel vehicles are recognised to be high emitters of particulate matter. This is largely composed of elemental carbon. This proposes an assessment of the elemental carbon (EC) as a tracer for diesel emissions. The measurement of the particulate elemental carbon has been performed using the automatic speciation analyser 5400 Ambient Carbon Particulate Monitor (R & P). This is based on a thermal-CO_2 technique.

The method

Sampling was operated through a PM_{10} inlet, on an hourly basis. Then the temperature of the particulate matter was raised firstly to 340°C, secondly to 750°C. The detection of CO_2 during the second step has been used for determining the EC concentration. The measurements reported here were performed at H.C.Andersen Boulevard in June/July 2001. Data from this monitoring station include half-hour measurements of NO_x, CO and other traditional pollutants.

Receptor modelling

Principal component analysis (PCA) of the measured data was performed for the identification of the important sources. It shows that two factors are responsible for almost all the variation (97%) of the concentrations of CO, NO_x, and particulate elemental carbon. The factor loadings are presented in *Figure 19*. One factor can be linked to traffic in general, the second one to the fact that diesel and petrol traffic densities are not totally correlated in time. Nevertheless this representation should be discussed because the importance of the first factor is largely superior to the second one (90% and 7% respectively). The efficiency of the application of PCA is based on the difference between the petrol and diesel traffic patterns. However, the NO_x at H.C. Andersen Boulevard is dominated by emissions from diesel traffic. As a consequence, the correlation between the NO_x and EC is high compared with the correlation between NO_x and CO, and therefore the NO_x contributions from the two sources cannot be split precisely.

Other streets in Copenhagen are relatively stronger influenced by petrol traffic, and might be better candidates for the source apportionment.

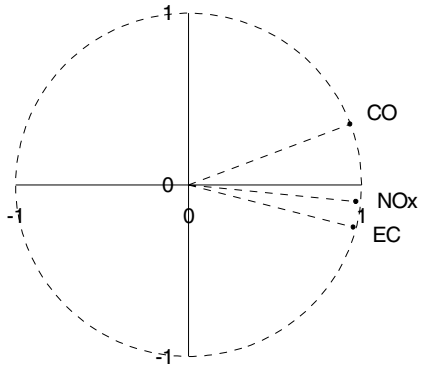

Figure 19 Factor loadings in two dimensions of EC, CO and NO_x. The circle represents unit communality (100% explained variance).

The total concentration of NO_x can be calculated as the sum of the petrol and diesel emissions (Eq. 1). Each contribution corresponds to the multiplication of its tracer by a coefficient (Eq. 2).

$$[NO_x] = [NO_x(diesel)] + [NO_x(petrol)] \qquad \textit{Eq. 1}$$

$$[NO_x] = \alpha[EC] + \beta[CO] \qquad \textit{Eq. 2}$$

A fitting has been carried out to determine the coefficient, using the least squares method. *Table 11* contains the results.

Table 11 Results from the fitting of the data to Eq 2.

Coefficient α	22 ppb/µgm^{-3}
Coefficient β	43 ppb/ppm
Correlation between the measured NO_x and the calculated NO_x	94 %

Figure 20 shows the result as the average weekly variation of NO_x ('Measured') and the fit ('Model') calculated as the sum of contributions of from the two sources ('Petrol' and 'Diesel'). The analysis indicates that diesel traffic is the main source of NO_x.

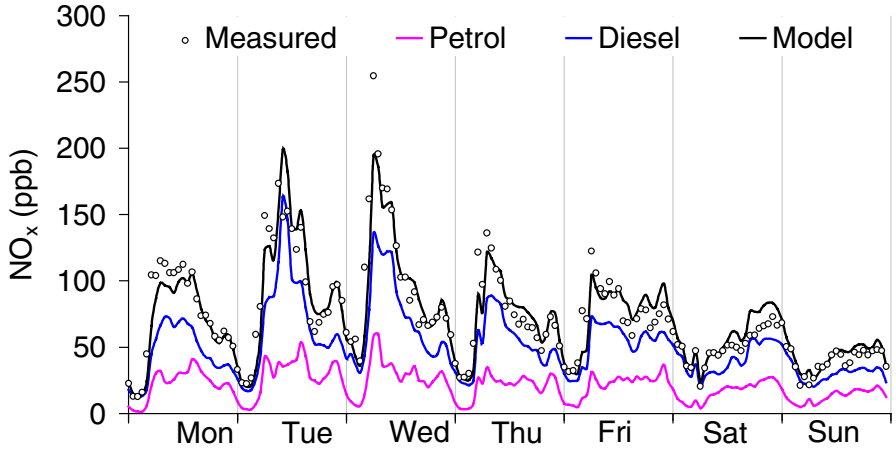

Figure 20 Ambient concentrations of NO_x for an average week. The measured values are fitted with contributions from diesel and petrol traffic using EC and CO as tracers (eq. 2)

EC from diesel vehicles

The analysed data show that the correlation between NO_x and EC at this station is much better than the correlation between NO_x and CO, limiting the application of the source apportionment method for the assessment of the NO_x contributions from petrol traffic. Nevertheless, it has been shown that EC is strongly correlated with the traffic emitted NO_x. Consequently, the use of EC as a tracer for diesel appears to be promising.

6.8 PM_{10} and $PM_{2.5}$ and their sources

The measurement period

A series of NO_x, PM_{10} and $PM_{2.5}$ monitoring data with high time resolution from the time period 20.05.2002-30.09.2002 has been analysed (Wåhlin and Palmgren 2003). The sampling site is the monitoring station at H.C. Andersens Boulevard (HCAB) in Copenhagen where simultaneous TEOM-PM_{10} and TEOM-$PM_{2.5}$ measurements were initiated at the beginning of the period (Palmgren et al., 2003).

The analysis

The average working day cycle of simultaneous $PM_{2.5}$ and NO_x measurements is shown in *Figure 21*. The NO_x is here used as a tracer for the traffic emissions. Over such a long time period we expect that the average long-range contribution will be time of day independent. Therefore we will estimate the long-range contribution by the interception of a regression line with the vertical line representing the average NO_x concentration in background air (< 5 ppb). As can be seen in *Figure 21*, it complicates the analysis that the $PM_{2.5}/NO_x$ ratio from the local sources is not constant during a working day. The displacement of the two drawn tangent lines indicates a significant day/night difference. The explanation for this may be a hysteresis effect due to particle deposition, but it might also be influenced from more dry and turbulent conditions in daytime. This introduces some uncertainty in the analysis. We assess that the interception of the lower tangent line with the $PM_{2.5}$ axis at 9 μgm^{-3} is the best estimate of the

average long-range contribution (ignoring the fact that the NO_x concentration in background air is not exactly zero).

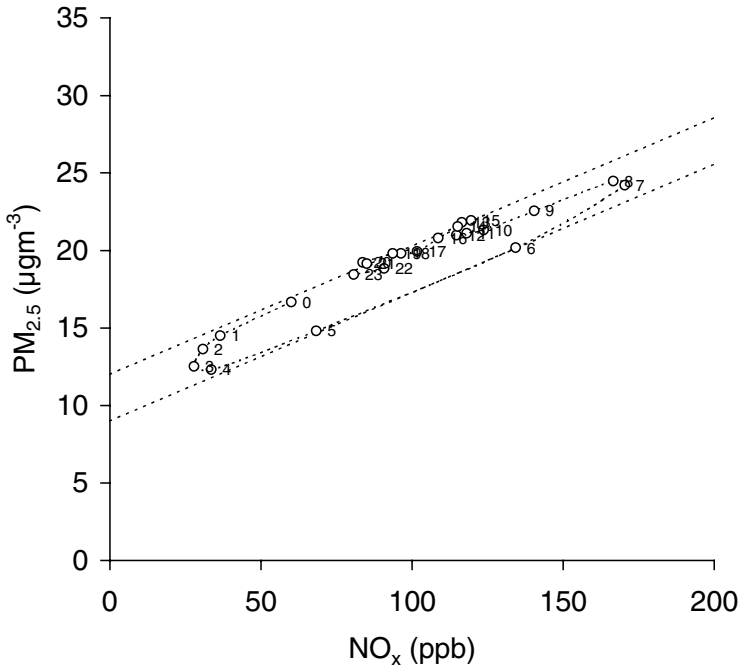

Figure 21 Average workday cycle of simultaneous $PM_{2.5}$ and NO_x one-hour measurements at H.C.Andersens Boulevard in the period 20.05.2002-30.09.2002. The labels on the data points indicate the hour of the day. The two lines have the same slope (0.083 μgm^{-3}/ppb), which can be considered as an estimate of the direct $PM_{2.5}/NO_x$ traffic emission ratio. The displacement of the two lines indicates a significant day/night difference. The interception of the lower line with the $PM_{2.5}$ axis at 9 μgm^{-3} is used as an estimate of the average long-range contribution.

Figure 22 shows the average working day cycle of simultaneous $PM_{2.5}$ and PM_{10} half-hour measurements at HCAB in the period 20.05.2002-30.09.2002. The slope of the regression line is used to estimate the average $PM_{10}/PM_{2.5}$ local (traffic) emission ratio = 2.59. The point on the line at $PM_{2.5}$ = 9μgm^{-3} as estimated in *Figure 22* is used to find the average long-range $PM_{10}/PM_{2.5}$ ratio = 1.27 and the average long-range contribution of PM_{10} = 11.4 μgm^{-3}.

Re-suspension of PM

A closer inspection of the distributions of the measured points in *Figure 22* reveals that the points are not totally randomly scattered around the regression line. This is analysed in more details in *Figure 23* where the $PM_{10}/PM_{2.5}$ ratio is calculated for each point after subtraction of the estimated long-range contributions. It can seen that a noticeable peak in the morning appears just when the morning traffic begins, as indicated by the increase of the NO_x concentration. This peak is probably a result of re-suspension of road dust that has settled during the night.

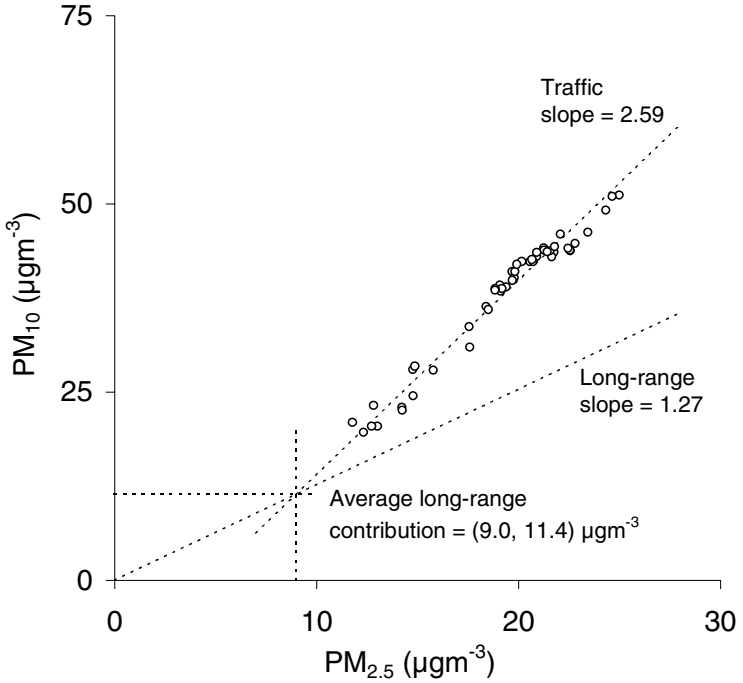

Figure 22 Average workday cycle of simultaneous $PM_{2.5}$ and PM_{10} half-hour measurements at H.C.Andersens Boulevard in the period 20.05.2002-30.09.2002. The slope of the regression line is used to estimate the average $PM_{10}/PM_{2.5}$ local (traffic) emission ratio = 2.59. The point on the line at PM2.5 = 9 µgm-3 is used to find the average long-range PM_{10} /$PM_{2.5}$ ratio = 1.27.

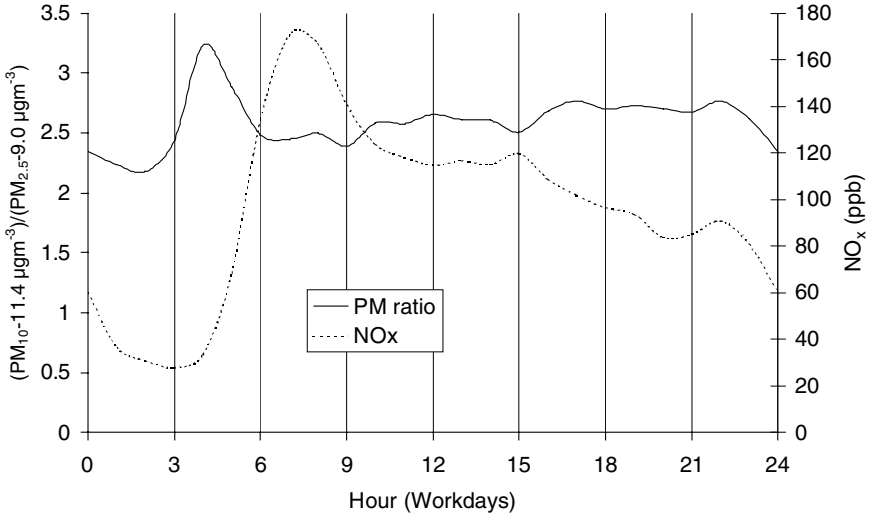

Figure 23 The $PM_{10}/PM_{2.5}$ ratio during an average workday after correction for the long-range contributions (half-hour measurements). The peak appears when the morning traffic begins, as indicated by the increase of the NO_x concentration. The peak is probably due to resuspension of road dust that has settled during the night.

The average variation in *Figure 23* of the $PM_{10}/PM_{2.5}$ traffic emission ratio during a working day is much smaller than the day-to-day variation. This is demonstrated in *Figure 24* by a scatter plot showing all simultaneous $PM_{2.5}$ and PM_{10} half-hour measurements at HCAB in

the period 20.05.2002-30.09.2002. The average long-range PM_{10} /$PM_{2.5}$ ratio = 1.27 as estimated in *Figure 22* is in good agreement with the lower edge of the cloud of points. This indicates that the long-range ratio is rather constant in time. Unlike this, the agreement between the average $PM_{10}/PM_{2.5}$ traffic emission ratio = 2.59 and the upper edge of the cloud is not so good indicating that the traffic emission ratio is not constant in time. The *Figure 23* shows that it is often as high as 3.5, sometimes even higher. The reason for this is probably that the efficiency of the re-suspension process is not only related to the traffic, but also to independent parameters such as wind speed and the dryness of the road surface.

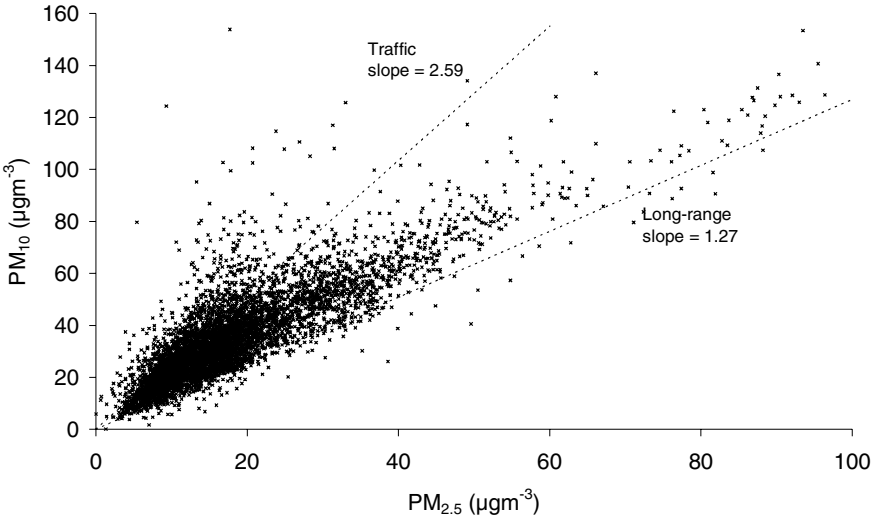

Figure 24 Scatter plot showing all simultaneous PM2.5 and PM10 half-hour measurements at H.C.Andersens Boulevard in the period 20.05.2002-30.09.2002. The average long-range $PM_{10}/PM_{2.5}$ ratio = 1.27 as estimated in *Figure 22* is in good agreement with the lower edge of the cloud of points. This indicates that the ratio is rather constant in time. The agreement between the average $PM_{10}/PM_{2.5}$ traffic emission ratio = 2.59 and the upper edge of the cloud is not so good indicating that the emission ratio is not constant in time. The figure shows that it is often as high as 3.5, sometimes even higher.

Application of TEOM data

The PM_{10} and $PM_{2.5}$ values measured by TEOM monitors are significantly lower than the values measured by the reference method due to evaporation of volatile material. We can find the losses by comparison of simultaneous measurements of PM_{10} at the same site using a TEOM monitor in parallel with a SM200 monitor, which measures in good agreement with the reference method. The losses (PM10_SM200 – PM10_TEOM) at the kerbside station Jagtvej (JGTV) and at the urban background station H.C. Ørsted Institute (HCOE) are compared in *Figure 25*. The line was calculated using orthogonal regression analysis. At JGTV there is a significant contribution of PM_{10} from the traffic source, while at HCOE there is an approximately 5 times smaller contribution. No significant difference between the two monitoring stations can be observed in *Figure 25*, indicating that the losses do not relate to the traffic source. On the other hand, for the long-range transported particles we do expect losses of this magnitude due to evaporation of ammonium nitrate and water. These com-

pounds are entirely related to the secondary particles in the fine fraction.

Source apportionment

Analysis of the TEOM half-hour measurements at JGTV and HCOE permit separation of PM_{10} in a traffic fraction, which is proportional to the NO_x concentration (0.15 μgm^{-3}/ppb*[NO_x]) and a rest (PM_{10} - 0.15 μgm^{-3}/ppb*[NO_x]), which is approximately the same at the two locations. Moreover, subtracting 2.5 μgm^{-3} we compensate for a day-night average displacement of approximately 5 μgm^{-3} in analogy with the method applied in *Figure 21*. The rest can be attributed only to sources far from the two locations. Tall stacks in Copenhagen may contribute, but we think that the distant sources dominate, e.g. point sources in Central Europe and natural sources (sea spray and soil dust). The long-range contributions must be the same at HCOE, JGTV and HCAB. Therefore, we can use the long-range fraction of PM_{10} measured by TEOM at HCOE, the long-range TEOM $PM_{10}/PM_{2.5}$ ratio = 1.27, and the particle losses measured at HCOE and JGTV, in a calculation, which on a diurnal basis separates the PM_{10} and $PM_{2.5}$ at HCAB in a local (traffic) part and a long-range part, and corrects for the evaporation losses. The results are shown in *Figure 26* The average values and totals are listed in *Table 12*, as absolute values as well as percentages. The number of exceedances of 50 μgm^{-3} was 14 out of 81 possible (17%). The totals in Table 1 are quite well determined, whereas the separation into source categories must be considered as the best estimate on the available data. It should be noted that a rather limited part of PM_{10} at HCAB (• 14%) is fine particles from tailpipe exhaust.

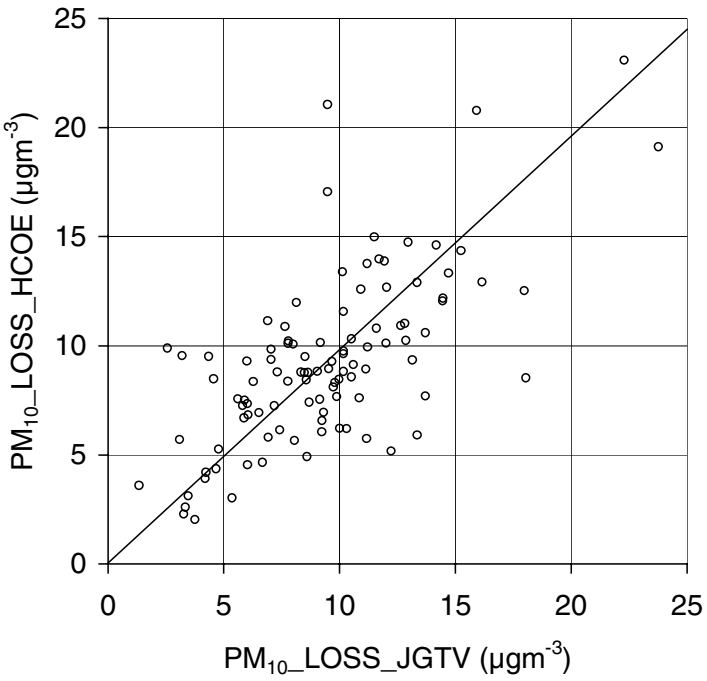

Figure 25 Comparison of PM_{10} loss (PM10_SM200 – PM10_TEOM) at the kerbside station (JGTV) and at the urban background station (HCOE). The line was calculated using orthogonal regression analysis. There is no significant difference between the two monitoring stations, indicating that the losses do not relate to the PM_{10} from the traffic source.

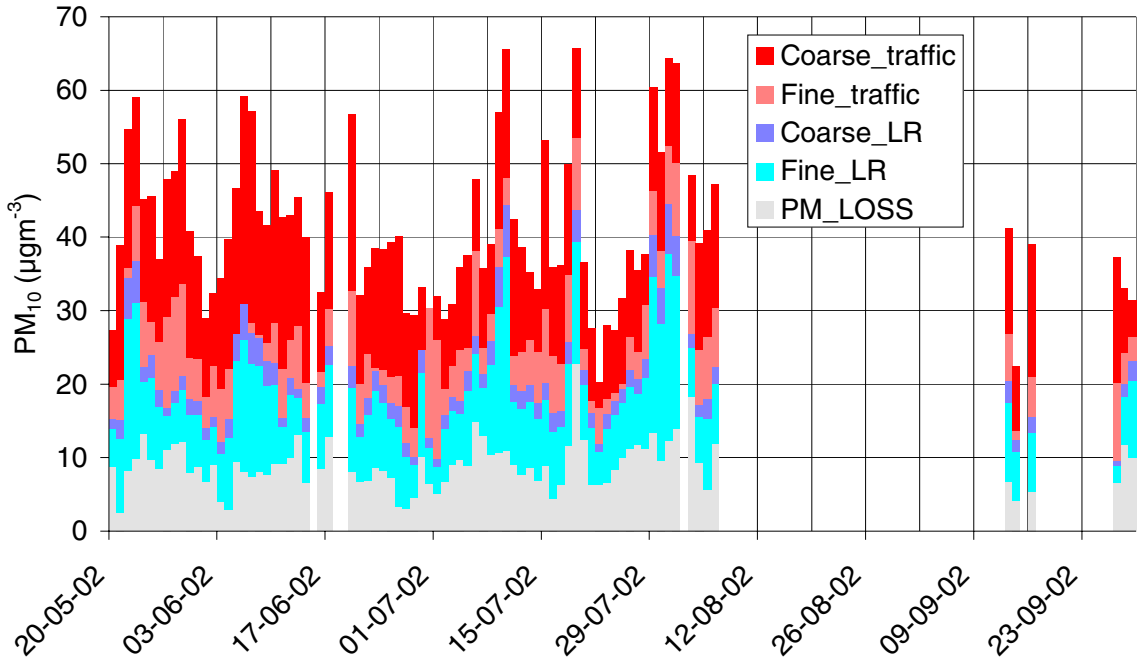

Figure 26 PM_{10} measured by TEOM monitor at H.C.Andersens Boulevard in the period 20.05.2002-30.09.2002. The data are corrected for the PM loss calculated as the average of the PM_{10} losses measured at Jagtvej and at the H.C. Ørsted Institute (*Figure 25*). Measurements of $PM_{2.5}$ at H.C. Andersens Boulevard, and of PM_{10} and NO_x at the H.C. Ørsted Institute (PM10_LR = PM10 – 2.5 µgm-3 –0.15 µgm-3/ppb*[NO_x]), were used for the source apportionment, and for the split of the data into fine and coarse fractions. The periods with missing data are mainly due to malfunction of the TEOM PM_{10} monitor at the H.C. Ørsted Institute.

Table 12 Averages and totals of the data shown in *Figure 26*. Unit: µgm-3.

	Fine ($PM_{2.5}$)	Coarse (PM_{10}-$PM_{2.5}$)	Sum (PM_{10})
Traffic	5.7 (14%)	14.0 (34%)	19.7 (48%)
Long-range	18.7 (46%)*)	2.6 (6%)	21.4 (52%)
Sum	24.5 (60%)	16.6 (40%)	41.1 (100%)

*) Corrected for the average losses of volatile material in the TEOM monitor (= 9.0 µgm-3).

6.9 Ultrafine particles

DMPS measurements

Average weekly cycles of the measurement periods at the street stations of ultrafine particles (measured by DMPS), NO_x and CO concentrations were generally used for the analysis (the cycles of CO, NO_x and total particles at Albanigade can be seen in *Figure 27*). A clear diurnal variation of the three parameters with a sharp rush-hour peak in the morning and another rush-hour peak especially for CO during the afternoon was observed on workdays at both street stations. The pattern is different on Saturdays and Sundays. Although the correlation between particles, NO_x and CO is generally good, some deviations were observed. These differences can be related to differences in the traffic patterns for petrol and diesel vehicles (diesel taxies compared with other traffic peaks at night, petrol cars during rush hours) (Wåhlin et al. 2001a).

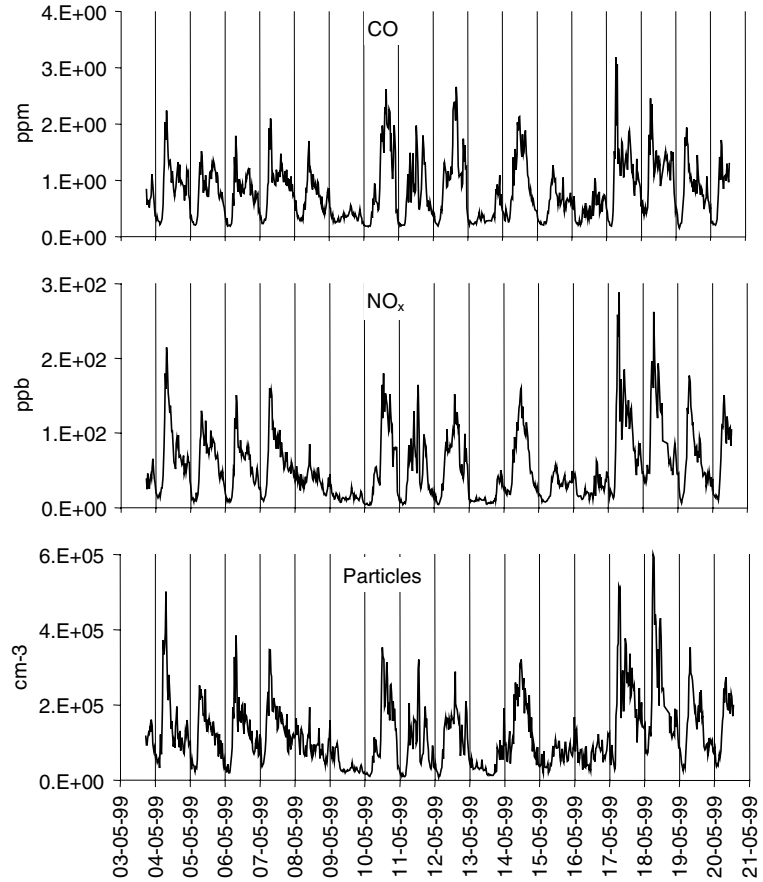

Figure 27 The time series of NOx, CO and particle number concentrations measured at Albanigade, 03.05.99-20.05.99. (Wåhlin et al. 2001a)

The workday cycles

The average particle spectra representing all working days at the two street sites Jagtvej and Albanigade and at an urban background station in Copenhagen, HCØ, are1 shown in *Figure 28*. Although the shapes seem very similar with a peak of the size distribution at approx. 20 nm, small differences exist with shifts to larger size in the spectra collected at the urban background location, indicating some growth of the particles or large contributions from other sources (Wåhlin et al. 2001a).

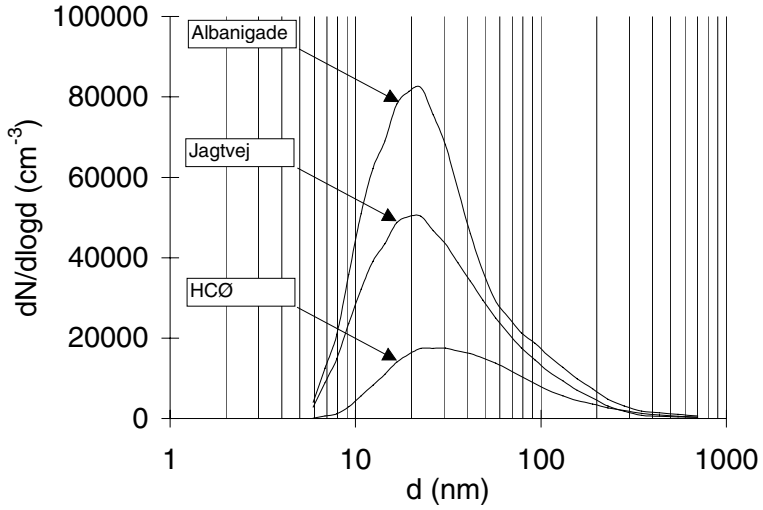

Figure 28 The average particle number distributions during the respective sampling periods for Albanigade, Jagtvej, and H.C. Ørsted Institute (roof station close to Jagtvej) (Wåhlin et al. 2001a).

Data analysis

Receptor modelling of the ultrafine particle contributions from petrol and diesel vehicles and non-traffic has been performed. The data analysis was based on long time series of air pollution concentrations measured routinely at the normal air quality monitoring stations and measurement campaigns of the pollutants under investigation, e.g. particulates (Palmgren et al. 2003). The time series from the campaigns, typically for several months, were analysed using statistical methods. Traffic data for different vehicle categories and with high time resolution are also available. The basic tool was a receptor model for identification and quantification of different types of sources.

Linear receptor models are based on the assumption that the original receptor site concentrations can be adequately explained by a linear combination of contributions from various relevant sources with fixed composition. Factor analysis (or principal component analysis) can be used in the search of important sources.

A factor analysis on half-hour average concentrations at Jagtvej of CO, NO_x and particles, including the average particle size spectra (29 spectrum derivatives dN/dlogd), has been performed (Wåhlin et al. 2001a). The correlation matrix of the 32 variables was diagonalised, and 95.6% of the total variance turned out to be accumulated in a 3-dimensional subspace. The rotation was performed in such a way that three easily recognisable sources could be identified: 'Non-traffic', 'Petrol+diesel', and 'Diesel'.

Non-traffic sources

The 'Non-traffic' factor (small CO and NO_x loadings) gives only a minor contribution to the total particle number, and is concentrated in the coarse part of the spectrum. The size range indicates that the particles are secondary, long-range transported particles.

Traffic sources

The 'Petrol+diesel' factor describes the general emissions from traffic, because the loadings of CO and NO_x are high. All petrol traffic is attributed to the general traffic factor, but due to the fact that petrol

traffic is highly correlated with diesel traffic, it is obvious that diesel traffic contributes substantially to the variation. The major part of the particles is apportioned to this factor.

The 'Diesel' factor is attributed to diesel traffic alone (low loading of CO). A considerable part of the finest particles is apportioned to the 'Diesel'-factor. It is a consequence of the differences in the diurnal and weekly pattern of diesel and petrol traffic that two traffic factors are found. Otherwise 'petrol' and 'diesel' would have merged into one single factor.

Size distributions in streets and urban background

The following analysis is based on 3740 half-hour average values of size distributions at Jagtvej and HCØ during summer 15 May 2001 – 4 September 2001 and winter 8 January 2002 – 6 February 2002. Simultaneous ½ hour data of NO_x and CO are also available. *Figure 29* shows calculated average size distributions at both locations and the difference between the two locations. The number size distribution is shown to the left and the volume size distribution to the right. The volume is calculated assuming spherical particles by multiplication by $4/3*\pi(d/2)^3$. The vertical axis is the concentration per size decade.

Total concentrations

The total average concentrations are the areas below the curves, where the width of the size decade is 1. The mass can be calculated assuming a specific gravity at 1 g/cm^3 by replacement of the unit $\mu m^3 cm^{-3}$ at the vertical axis with μgm^{-3}. The values at Jagtvej HCOE are given in *Table 13* The NO_x and CO concentrations are also plotted in the figure. The difference between the two locations represents the traffic-generated pollution from the street, because the traffic contribution at the urban background site HCØ is much smaller (4-5 times). The regional contribution (including the long range transported part) is eliminated by the subtraction.

The regional contribution

The regional contribution to particles and CO can be calculated assuming the ratio, particles/NO_x, to be the same at urban background and the street location. This is calculated by a simple down scaling to the regional NO_x concentration (3.5 ppb). The average traffic contribution can be calculated by multiplication of the NO_x difference between urban background and regional background by this ratio; the regional background is approx. 3.5 ppb. The results are shown in *Table 13* and *Figure 30*. The chemical transformation of NO_x and coagulation and evaporation of the particles during transport from street to urban background is not included in this simple model, but the results are in accordance with measurements carried out at Lille Valby, which indicates that these processes are unimportant.

Three log-normal distributions of particles

The size distribution of the traffic generated particles can be fitted to the sum of three log-normal distributions for every single ½ hour averages. The medians of these log-normal distributions are 12 nm, 23 nm and 57 nm, respectively. However, the relative contributions for the single half-hour averages can differ from the graphs in *Figure 29*.(see later).

The mass of the ultrafine particles is negligible

The ultrafine particles (d < 100 nm) dominate in number at the streets as well as at urban background, whereas the volume (mass) is negligible, see *Figure 29*. The particles in the regional background domi-

nate over the traffic particles, *Figure 30* and *Table 7*, especially the volume (mass).

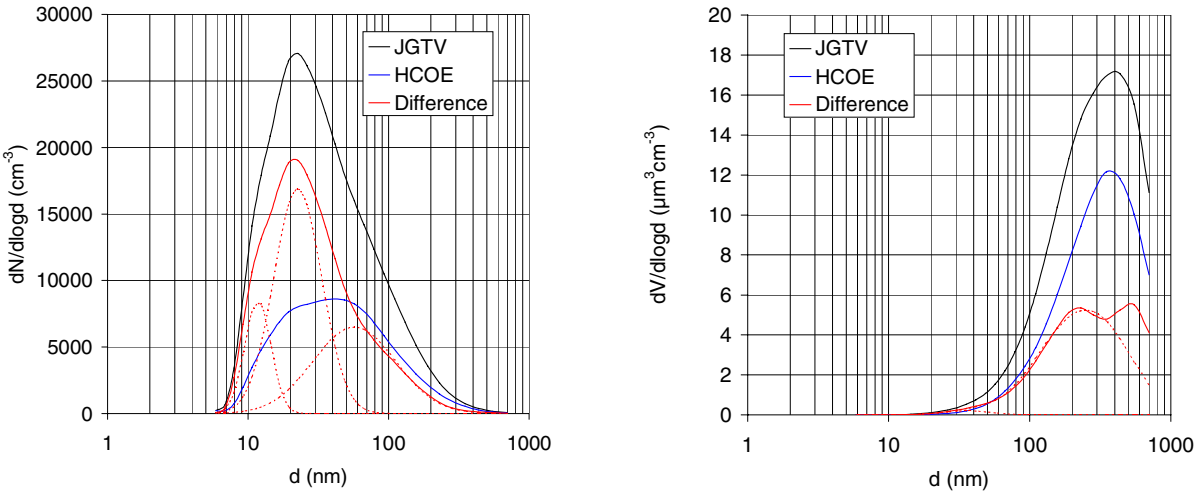

Figure 29 The average particle distributions at Jagtvej and HCØ and the difference the two locations. The left graph is the number size distributions and the right is the volume distributions calculated by multiplication with $\pi d^3/6$, assuming spherical particles.

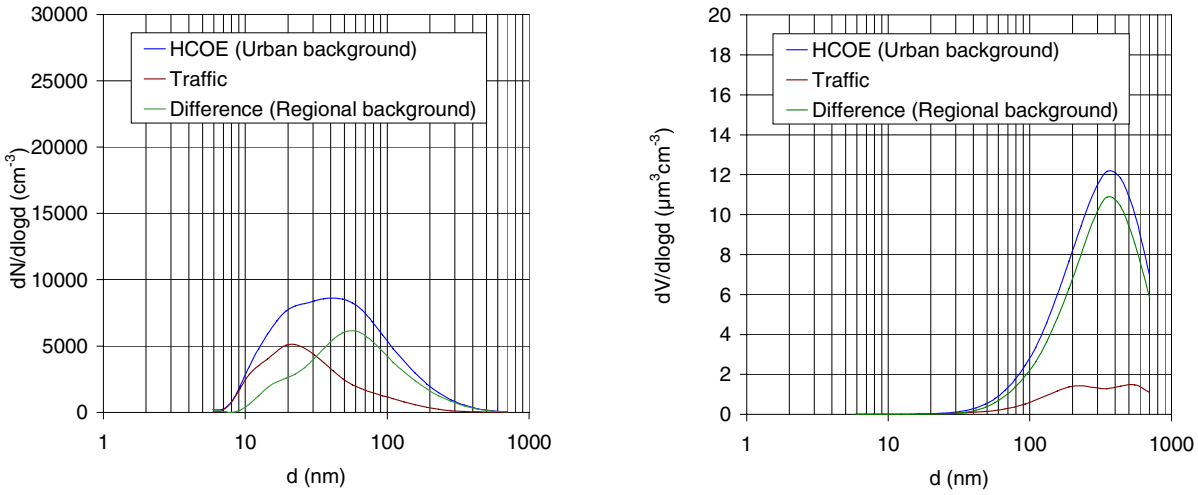

Figure 30 The traffic contribution of particle size distributions at urban background under the simplified assumption that the particle/NO_x ratio is the same as at Jagtvej.

Table 13 Measured particle concentrations (N: number, V: volume), NO_x and CO at Jagtvej and HCØ. The regional background is calculated as the difference by simple down scaling to the regional NO_x concentration (3.5 ppb).

	N (cm^{-3})	V ($\mu m^3 cm^{-3}$)	NO_x (ppb)	CO (ppm)
JGTV	22900	12.3	44.8	0.74
HCOE	8800	7.8	12.2	0.27
Regional background (calculated)	5000	6.6	3.5	0.14

Different size distributions during the week

The average difference between the street and the urban background of the size distributions of particles can be separated in three lognormal distributions ('modes' with median at 12 nm, 23 nm and 57 nm respectively), also for single half-hour distributions. In *Figure 31* it is shown that the relative size of the three modes can vary significantly during the days/week, and can be very different from the average *Figure 29*.

Saturday and Sunday nights are different from the rest of the week

The most significant deviations occur at nights after Fridays and Saturdays, when the smallest mode (12 nm) dominates. These are periods with many taxies at Jagtvej, and it is assumed that they emit many nano-particles. Because the taxies are generally new diesel cars with oxidising catalysts, and different from most other diesel vehicles in Denmark, it is obvious that they emit special types of particles, i.e. the nano-particles. A simple physical explanation is the following: We know from emission measurements on dynamometers that the larger diesel particles (> 50 nm) are solid soot particles generated in the engine. The smaller particles are volatile particles, which are formed by condensation of material on condensation nuclei during cooling in the exhaust system or immediately after the tailpipe. The oxidising catalyst removes the major fraction of the volatile compound, doing this it prevents growth of the 12 nm mode particles. The diesel cars with oxidising catalysts produce particles in the 12 nm and 57 nm modes, whereas other diesel vehicles produce the 23 nm and 57 nm modes.

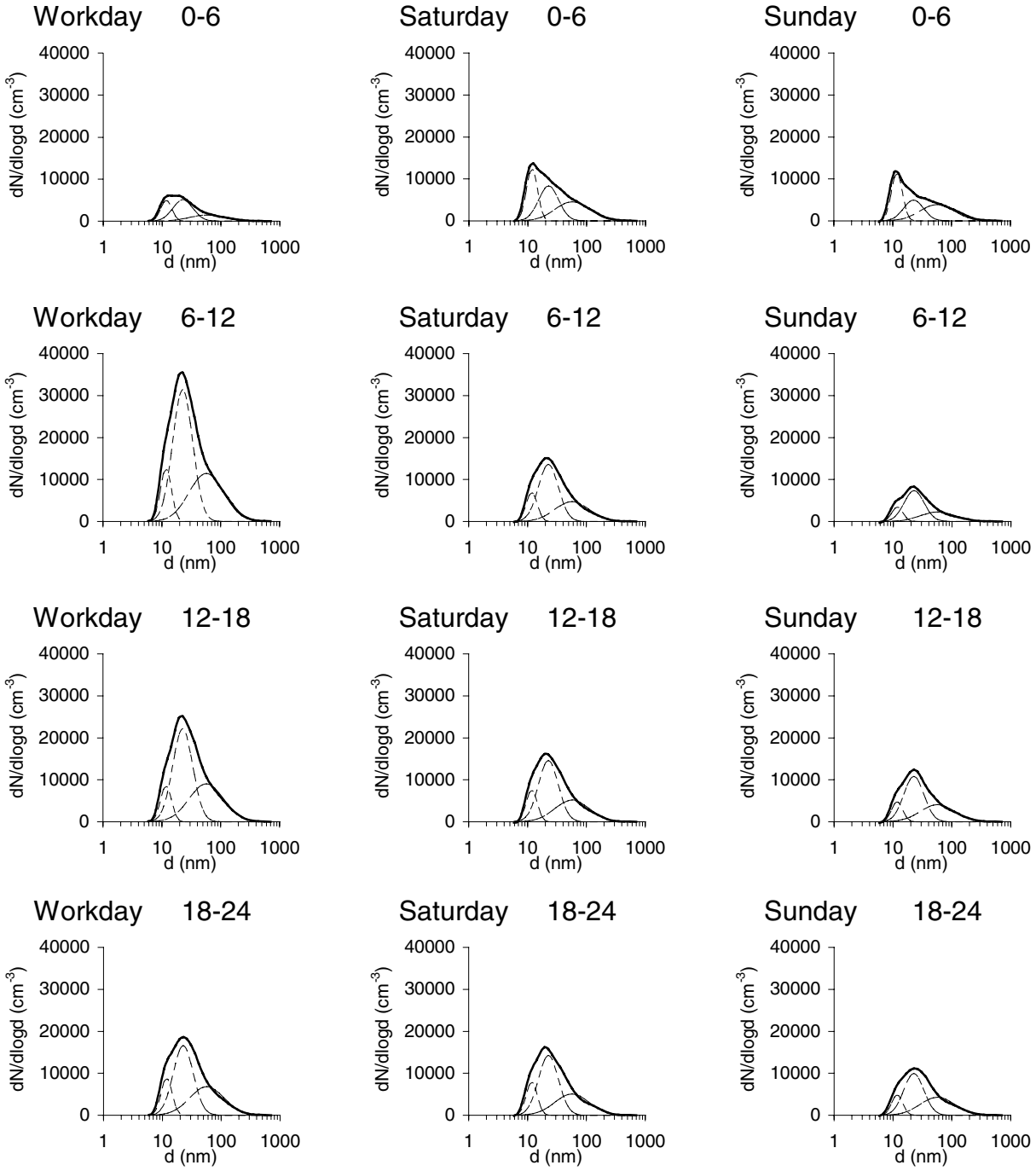

Figure 31. The difference between size distributions at street and urban background can be estimated as the sum of three modes with the medians 12 nm, 23 nm and 57 nm, respectively. The average size distributions and the three modes are shown for representative 6-hour periods during an average week.

Improved receptor modelling by three modes

The existence of two distinct traffic sources has earlier been demonstrated by a statistical analysis of particle size distributions in relation to NO_x and CO (Wåhlin et al. 2001a). It was assumed that the two sources were diesel and petrol traffic. However, the calculated contribution from petrol cars appeared to be very large compared to results from emission measurements at a dynamometer. The new receptor model with three traffic sources, one petrol source and two diesel sources, has lead to a much better agreement between measurements and the model. The analysis also shows that the two diesel sources alone can explain the variations of the size distributions, and

the three sources are necessary to explain the NO_x variations. For the moment it is not possible to draw a more precise conclusion, and it is most likely that the petrol cars contributes only a little to the concentration of ultrafine particles in urban areas.

The ultrafine particles mainly from traffic

The ultrafine particles (diameter < 0.1 µm) in a busy street like HCAB mainly originate from the traffic. This is clearly demonstrated by comparison of measurement results of ultrafine particles at the street Jagtvej, the urban background HCØ and the rural background Lille Valby. *Figure 32* shows the average size distributions at HCAB, Jagtvej and HCØ in the period July-September 2001. Data from Lille Valby are unfortunately missing from this period, but data are available from a short period (only 5 days) in November 1999 (*Figure 32*). The concentrations at HCAB are much higher than at Lille Valby, where the contribution from traffic is small. The concentrations are also almost twice as high at HCAB compared to Jagtvej. This corresponds to similar higher NO_x (approx. 1.6 times) concentrations at HCAB than at Jagtvej. The concentration of ultrafine particles at HCØ are only moderately higher than at Lille Valby, in accordance with the observation that the NO_x concentration is much lower than in the street (6 times less at HCØ than at Jagtvej).

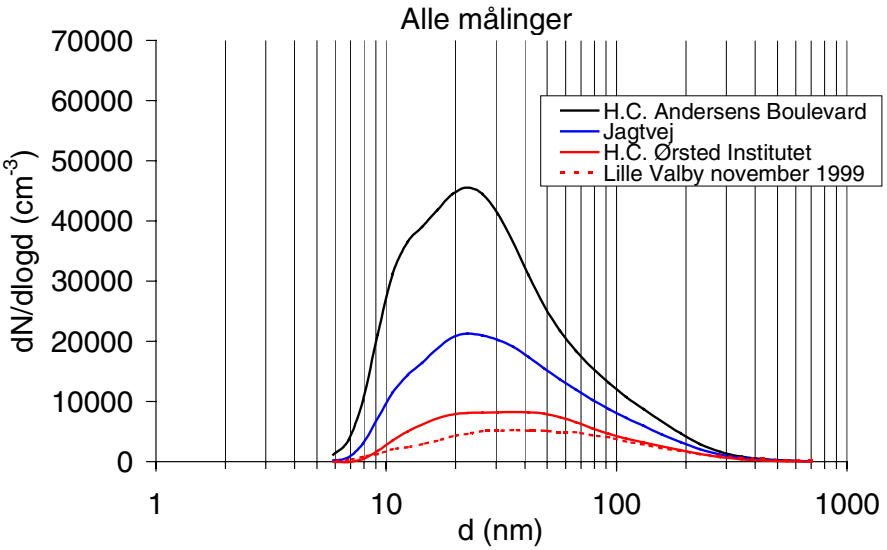

Figure 32 The average particle size distributions from HCAB (street), Jagtvej (street) and HCØ (urban background) from the period July-September 2001. Data from Lille Valby (rural background) are unfortunately only available for a short period (5 days) in November 1999.

Reduced sulphur in diesel fuel

The size distributions in *Figure 32* include at least 3 modes of log-normal distributions. The left is the little "shoulder" 12 nm. It has been demonstrated earlier (Wåhlin et al., 2001b) that this mode most likely is due to the sulphur content in the diesel fuel, because it was much more conspicuous before reduction of the sulphur content in diesel fuel from 500 ppm to 50 ppm in July 1999, *Figure 33*. The 23 nm mode is the most dominating mode, which most probably is unburned hydrocarbons and other volatile compounds (fuel and lubricants), which condenses in or after the exhaust system. To the right is the third mode (50-100 nm) with a tail of larger particles (>100 nm). This mode is soot particles formed especially in the diesel engines. This mode is dominating in a mass plot. There is an overlap between

this mode and the long range transported secondary particles formed by oxidation of gaseous pollutants, i.e. SO_2 and NO_x to ammonium nitrate and sulphate.

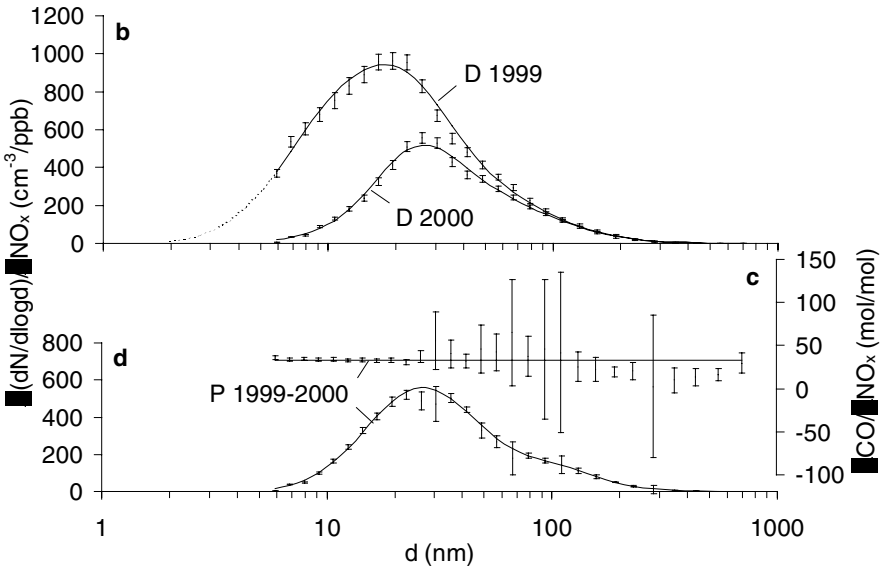

Figure 33 Linear relations between the concentrations of particles (per decade of diameter, dN/dlogd), CO, and NO_x, for average weeks corresponding to the two campaigns in 1999 and 2000. The calculated particle/NO_x ratios, •(dN/dlogd)/•NO_x, of 'D 1999' and 'D 2000' are plotted with standard deviations and fitted with smooth size functions (b). The calculated ratio, •CO/•NOx, of 'P 1999-2000' is constant in the nano-size range, but the uncertainty of 'P 1999-2000' increases rapidly in the size range > 30 nm. The horizontal line indicates the weighted average, 33.1±0.6 mol/mol, of all values in the whole size range (c). The calculated particle/NO_x ratio, •(dN/dlogd)/•NO_x, of 'P 1999-2000' is plotted with standard deviations and fitted function (d).

Comparison between average weekly variations at HCAB of NO_x, CO, EC, total particle number (N) and total volume (V) in *Figure 34* demonstrates strong correlation except for CO. CO has a strong daily variation with distinct morning and afternoon peak correspond to the rush hours. This is probably because the petrol cars emit most of the CO and less NO_x, EC and particles. A statistical analysis (principal component analysis) has confirmed earlier findings (Wåhlin et al., 2001a), but hat also indicated that two different diesel sources are present.

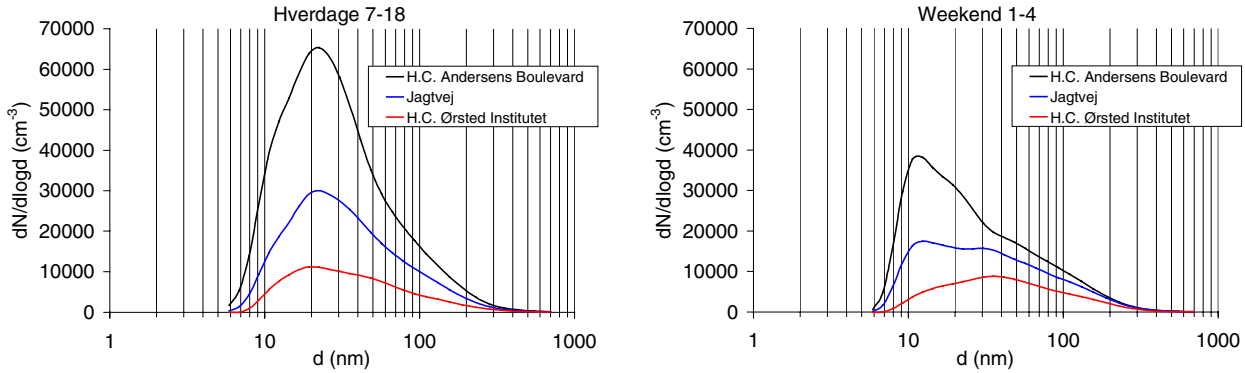

Figure 34 Comparison of particle size distributions on weekdays during the working hours and on weekends during night hours, when the taxi (diesel) traffic is pronounced. It is obvious that the taxies emit less particles around 25 nm that the vehicles during working hours.

Two types of diesel sources

Figure 34 shows that two diesel sources can be identified, one is normal diesel traffic (perhaps including a small contribution from petrol cars), and the other diesel source consists of taxies, which are modern diesel cars with oxidising catalysts. The catalysts oxidise the volatile and semi-volatile compounds (the smell of diesel), of which the semi-volatile compounds are the most important source for formation of ultrafine particles by condensation. An example of the difference between measured size distributions on a dynamometer is shown in *Figure 35*. Results from a VW Lupo with catalyst and a VW Golf without catalyst is shown normalised by the NO_x emission. The particle distribution for the Lupo peaks at around 100nm, typically soot particles. The size distribution for the Golf peaks around 25 nm, where the liquid particles are, e.g. condensed hydrocarbons.

Dependence on temperature

Concentration size profiles (normalised by NO_x) are calculated based on data from HCAB (*Figure 36*). The calculations were carried out at different ambient temperature intervals by regression analysis of measured particle and NO_x data. NO_x was used as an indicator of the general traffic pollution. The shape of the size distribution depends on the ambient temperature, showing that condensation is more pronounced at low ambient temperatures.

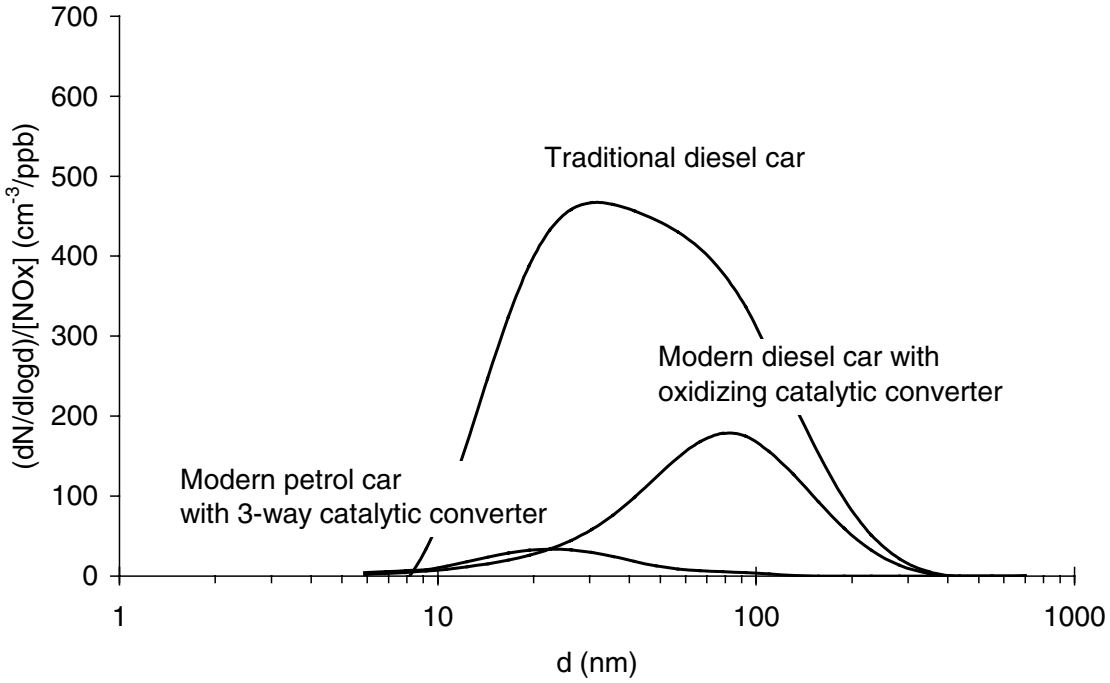

Figure 35 The emission profiles (normalise with NO_x) of an older diesel car (VW Golf diesel), a newer (VW Lupo 3L TDI with oxidising catalyst) and a modern petrol car with TWC measured at a dynamometer under transient driving cycles like the driving pattern at Jagtvej in Copenhagen. The measurements were carried out in a co-operation between NERI and the Technological Institute in Århus.

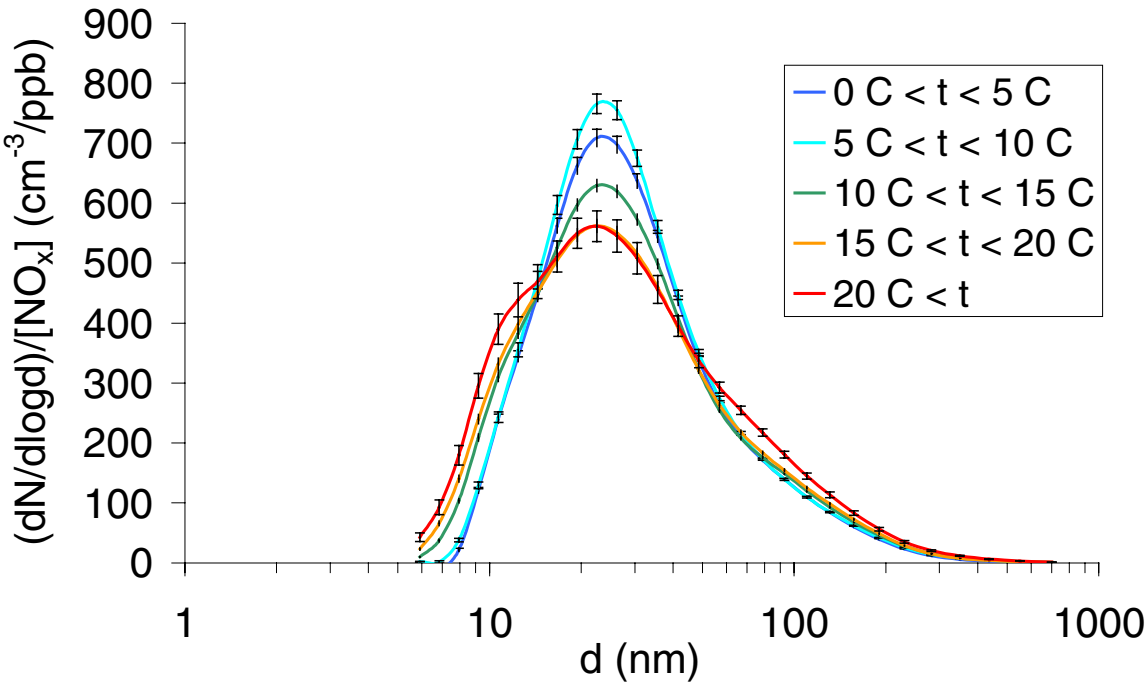

Figure 36 The ratios between particle number concentration (versus size) and the NO_x concentration at HCAB. The analysis was carried out by regression analysis in groups of ambient temperatures

6.10 Emission factors

The measurements of ultrafine particles, NO_x and CO at Jagtvej and HCOE in combination with the traffic statistics from the traffic count monitor at Jagtvej have been used to estimate emission factors from the traffic (Ketzel et al. 2003).

Inverse use of models

The concentrations measured at the monitoring station inside the street canyon are a function of both dilution conditions and the emissions. This relationship was studied in detail at the Jagtvej station and led to the development of the Operational Street Pollution Model (OSPM) by Berkowicz et al. (1997) and Berkowicz (1999). The OSPM has been validated against several sets of field data and is able to describe the source receptor relationship in a street canyon. The usual purpose of a dispersion model is to calculate the concentration based on a given emission strength and meteorology. On the other hand it is possible to calculate the in-situ emissions based on available measurements, this method is often referred as inverse modelling (Palmgren et al., 1999) and can be described by:

$$C_{diff} = C_{total} - C_{background} = C_{street} - C_{roof} = Q \cdot F(meteorology, traffic) \qquad \text{Eq. 1}$$

where

$C_{total}, C_{backgr.}$: measured total / urban background conc. [g/ m^3] (e.g. in the street / at roof level)

C_{diff}: difference (street-roof) gives the contribution of the particular street to the measured total concentrations

Q: emission density [g/(m s)] caused by the sum of all vehicles in the street

F: function describing the dilution, calculated by OSPM, [s/m^2].

The function, *F*, is equal to the concentration calculated by OSPM using unit emissions [=1g/(m s)]. It depends on meteorology (wind direction, wind speed) and traffic flow (speed and number of vehicles), since the turbulence induced by the vehicles is a crucial dispersion mechanism especially for low wind speeds. Using the measured meteorology and the information about traffic flow we calculated for each half-hour of our measuring period. The inverse modelling method will lead to a high uncertainty if the emission *Q* is calculated for a short time interval. The inverse modelling for a short time interval results in a high uncertainty of Q, because many measured components - each with uncertainties - are used for calculation of the concentration differences and divided by *F*. This is especially true for situations with low emissions (night-time) or high dilution (high wind speeds, or wind from Northwest for our case). The method is better suited for longer time series of measurements, when data may be grouped according to similar situations (e.g. particular hours of the weeks). There are several ways to calculate the hourly emissions. Either one can use a regression method on the data set C_{diff} versus F and use the slope as an estimate for the emission density Q or simply the ratio of the means of C_{diff} and *F*. Both ways were initially tested for our data set and only minor differences were observed for the NO_x

emissions. However the second method (ratio of the means) turned out to be more reliable for cases with low emissions and high scatter in the values of C_{diff} and was therefor used for all estimates of emissions.

Emission factors at Jagtvej

The averaged diurnal variations in measured street contribution C_{diff} for NO_x, CO and ToN were calculated for working days, Saturdays and Sundays (*Figure 37*). Using *Eq. 1* and the modelled concentrations with unit emissions *F* based on the measured meteorology we calculate the emission density *Q* for the different compounds for each hour of the average week.

Using the relationship:

$$Q\left[\frac{\#}{km \cdot s}\right] = N\left[\frac{veh}{s}\right] \cdot q\left[\frac{\#}{km \cdot veh}\right] \qquad \text{Eq. 2}$$

we calculate an average emission factor *q* by dividing the emission density *Q* and the traffic volume *N* for each hour of the weekly profile. Traffic counts were available from the automated video counts at Jagtvej for parts of the measuring period up to August 2002 and for comparison from detailed traffic counts in 1994/95 (*Figure 38*a). The traffic counts from the different years showed a very good agreement with minor changes towards more traffic in recent years. Since the traffic counts parallel to the measuring period in 2001 were incomplete we used counts from 2002 during a similar period for the emission factor estimation. The average traffic speed in Jagtvej (*Figure 38*a) changes between 40 and 50 km/h depending on the time of day and traffic volume with lower speeds during the working day rush hours and weekend afternoon hours and generally higher speeds at nighttime. During all days a drop in the traffic speed of about 10 km/h is observed during night hours 1-4. This is connected with a change in the traffic light control to a night regime during these hours, which lets especially the north going traffic at Jagtvej encounter more frequently red light and decelerate (Andreasen, H.D. Copenhagen Road Administration, Personal Information, 2002).

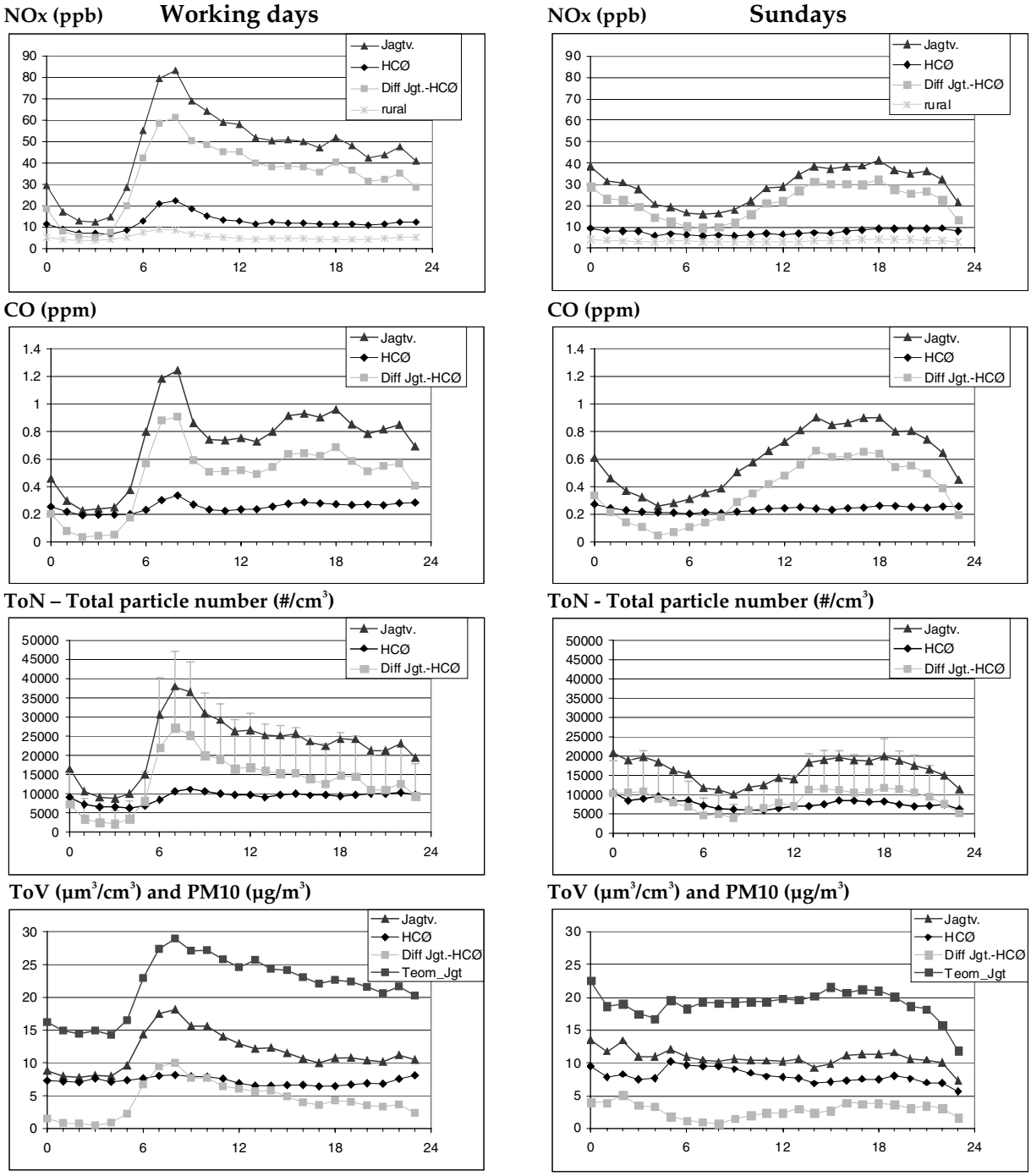

Figure 37 Average diurnal variation of NOx, CO, particle number and particle volume, working days (left column) and Sundays (right column).

The average emission factors

The average emission factors grouped in one-hour increments for working days, Saturdays and Sundays are shown in *Figure 38*b. For the day time hours 7 to 18 the emission factors per average vehicle are found in the range 1-1.6 gNO_x/(veh km), 10-16 gCO/(veh km) and 2-4*10^{14} #/(veh km). In the early morning hours on all days we observe substantially higher NO_x and particle emissions and lower CO emissions. Since CO is mainly emitted by petrol cars, the CO emission factors or the CO/NO_x ratio (see *Figure 38*c) is an indicator of the percentage of petrol cars on the road. The CO/NO_x ratio is decreasing with time from the evening after hours 20-21 toward 4:00 in the morning, i.e. smaller number of petrol cars. At the same time particle and NOx emissions increase, that can be attributed to a progressive domination of the traffic by diesel taxis. The early morning traffic in hours 5-7 is accompanied with an increase of CO emissions to the daytime levels and above average NO_x and particle emissions. These relatively high emissions might be caused by the higher traffic speeds during the first hours. In the evening hours 18-23 all emissions are slightly increasing. This again could be caused by an increase in the traffic speed. For the working days we estimated average emission factors for conditions at Jagtvej to be (1.45±0.2) gNO_x/(veh km), (12.4±2) gCO/(veh km) and (3±0.5) *10^{14} #/(veh km).

Comparison with the literature

In *Figure 39* the estimated number emission factors in this study are compared with values estimated in other atmospheric studies. The studies from Minnesota (Kittelson et al., 2001), and Queensland (Jamriska and Morawska, 2001) are performed on suburban/urban highways while the studies in California (Kirchstetter et al., 1999), in Stockholm (Kristensson et al., 2002) and in Pennsylvania (Abu-Allaban et al., 2002) use an urban/interstate highway tunnel. The driving pattern in all the studies corresponds to highway conditions, i.e. constant speed 70-100 km/h. No studies under urban driving conditions were found in the literature so far. The Stockholm study reports data with lower vehicle speeds during rush hours (average 60km/h) with similar emission factors for LDV (Light Duty Vehicles) and reduced emissions by a factor 4 for HDV (Heavy Duty Vehicles) compared to speeds of 70-80km/h.

All studies had a HDV share of ca. 5-10%, comparable to conditions in Copenhagen, except for the Tuscarora tunnel with a HDV share between 13-80%.

Our emission range of the average fleet (3±0.5)*10^{14} #/(veh km) is comparable to the upper values reported from Minnesota, Queensland and Tuscaroa tunnel. The reason our data tend to be slightly higher could be related to a higher share of diesel cars and vans present at Jagtvej and the urban unsteady driving conditions. The emission data reported from Stockholm are slightly higher than in Copenhagen. The Stockholm study was performed under winter conditions with temperatures around –8 ºC outside the tunnel. That may have favoured the production of 'nuclei mode particles' (Kittelson et al., 1999 and Kittelson, 1998 and 2002). Laboratory experiments that estimate the emission factors of single vehicles using different techniques to dilute the raw exhaust show a wide range of emission factors. They are for LDV from 3*10^{11} #/(veh km) for modern gasoline port fuel injection (PFI) engines to 3*10^{14} #/(veh km) for diesel cars or

gasoline direct injection (Graskow et al., 1998, 1999 and 2000). The upper values are comparable to our estimate for Jagtvej.

Using multiple regression and the weekly traffic pattern of different vehicle categories, it is in principle possible to estimate category specific emission factors. This would under optimal conditions require weekly traffic profiles

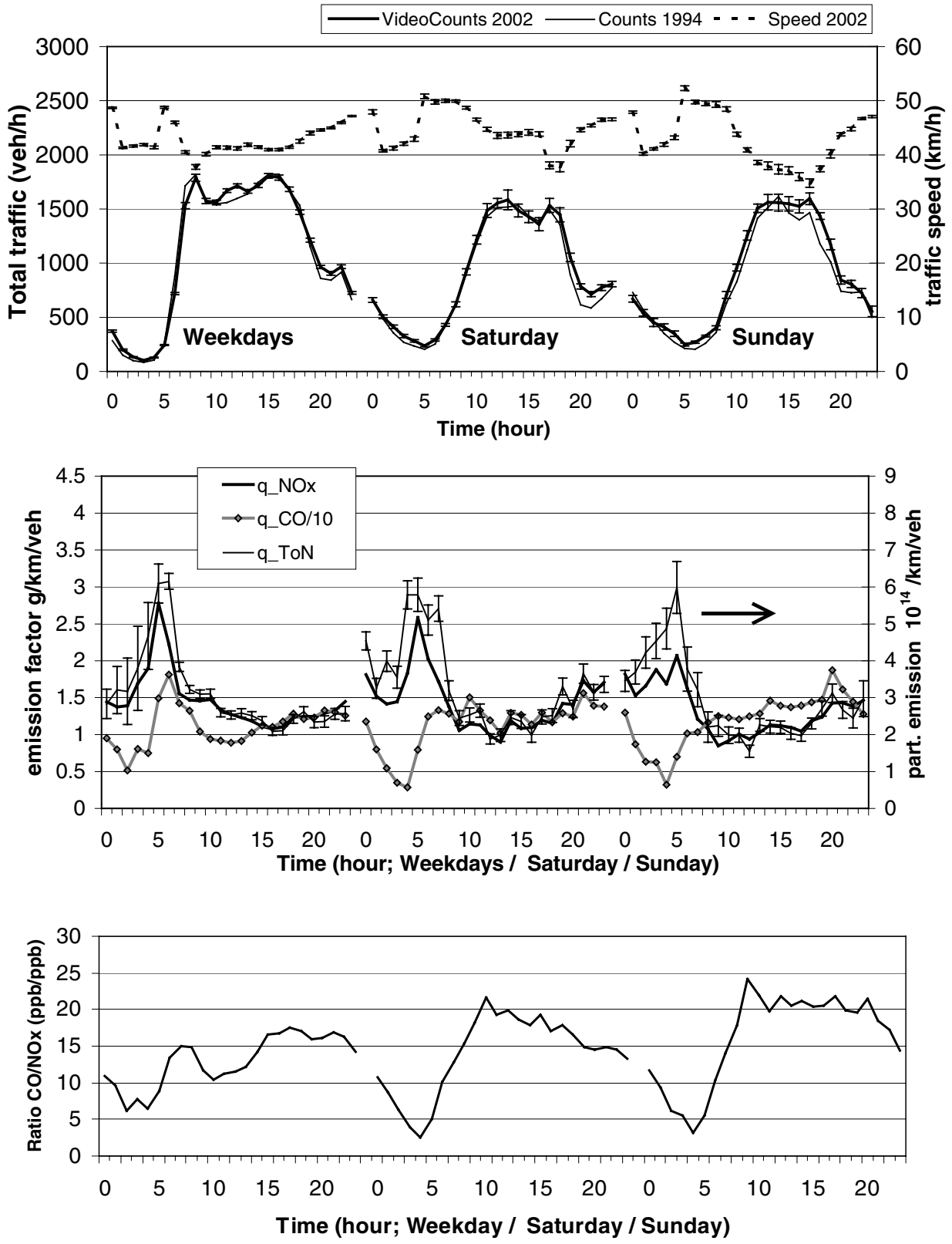

Figure 38 Traffic volume and traffic speed measured by the automated traffic counts in 2002 and traffic volume from 1994 counts for a weekly profile working days/ Saturday/ Sunday (a). Emission factors for NOx, CO and ToN plotted with uncertainty of ToN emission factors (b).

separately for all relevant categories with different emission characteristic, e.g. buses, heavy duty vehicles, light duty diesel (vans + cars),

diesel-taxi and gasoline-cars. As an additional parameter the variations in the traffic speed will influence the emission factors. Unfortunately the present size of our database and our limited knowledge on the traffic profiles does not allow for such a differentiation of emission factors at the moment.

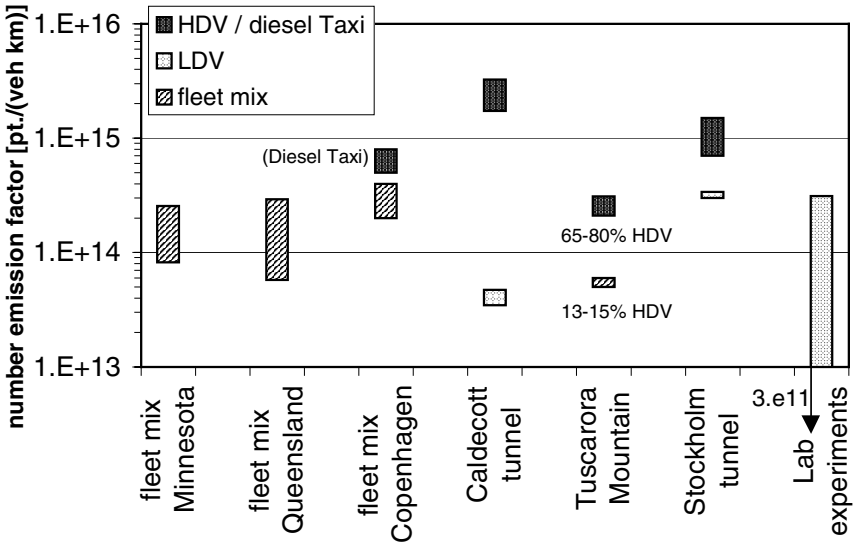

Figure 39 Comparison of number emission factors (particle diameter larger than approximately 10 nm) published in the open literature. Values for Minnesota (Kittelson et al., 2001), Queensland (Jamriska and Morawska, 2001) and Copenhagen (this study) were measured near urban/suburban roads or highways and represent the average vehicle fleet. The studies at the Caldecott tunnel (Kirchstetter et al., 1999), Tuscarora Mountain tunnel (Abu-Allaban et al., 2002) and in a Stockholm road tunnel (Kristensson et al., 2002) are able to separate emission factors for light duty vehicles (LDV) and heavy duty vehicles (HDV). The range of emission factors for LDV from lab experiments extents over several orders of magnitude depending on the engine technology (Graskow et al., 1998).

6.11 Indoor/outdoor PM

Introduction

Several institutions in the Copenhagen region have initiated collaboration on the study of the indoor-outdoor relation of particles from traffic. The objective of the work is to develop and validate a model capable of predicting indoor particle pollution from traffic, based on information about outdoor particle pollution together with construction details about the building envelope and ventilation system. Important parameters in the model are the penetration efficiency and the deposition rate, which can be quantified for different particle size fractions by the study of indoor/outdoor time series (Long et al., 2001). The model will be developed by analysis of data obtained from outdoor and indoor monitoring of concentrations together with information about the air exchange rate. Methods and some preliminary results concerning ventilation and indoor/outdoor particle number concentrations are presented (Le Bihan et al., 2002, Wåhlin et al. 2002 and Wåhlin et al. 2003).

Methods

The apartment used in the present study is located in a residential building in a street canyon, Jagtvej, in central Copenhagen, Denmark. The uninhabited, but fully furnished, apartment is on the fourth floor

of a five-floor building, approximately 300 m from an existing monitoring station on the other side of the street. The kitchen was used for operation of most of the instruments during 4 measuring campaigns in 2001/2002, one 5-weeks campaign for each of the seasons summer, autumn, winter and spring. The kitchen was sealed from the rest of the apartment by an airtight door with holes for the tubes and the wires connecting the instruments. They are located in the kitchen with sampling points and sampling devices in the living room and right outside a window of the living room facing the street. The intention was to ensure that most of the ventilation air should be supplied via ventilation slits in this window. A mechanical exhaust system is installed with an exhaust opening in the bathroom. This is the dominant exit route of ventilation air. During the first campaign the air exchange rate of approximately 0.8 h^{-1} in the daytime was reduced automatically to approximate 0.4 h^{-1} during late night and early morning (h = 3600 s). During the three other campaigns the ventilation rate was changed manually once a week between high (approximately 1.1 h^{-1}) and low ventilation (approximately 0.5 h^{-1}) with the ventilation running constantly for one week in each state at a time.

Outdoor measurements have been provided from the routine monitoring of street level air quality at Jagtvej, Copenhagen, and the air quality and meteorological observations from the urban background station located on the roof of the HCOE.

The measurement programme

A variety of instruments and techniques was used, including condensation particles counters (CPC) measuring total particle concentrations or in combination with a differential mobility analyser (DMA) scanning particle number size distributions, an Aerosol Particle Sizer (APS), PM_{10} monitors (TEOM), a pressure gauge for the indoor/outdoor pressure difference, monitors for nitrogen oxides (NO_x), ozone and carbon monoxide, cascade impactors (BLPI and MOUDI), and constant concentration tracer gas technique for the air exchange rate (the incoming airflow divided by the apartment volume). For the comparison, all data with high time resolution are averaged on a half-hour basis. The PM_{10} measured by the TEOM monitors was collected at a temperature of 50°C.

Estimates of the particle concentrations outdoors

Half-hour averages of particle number size distributions (particle spectra) were measured in the living room, at the street station (JGTV), and at the urban background station (HCOE). Particles outside the window of the living room (JGTV83_EXT) were not measured directly. Instead, using a simple model, the particle concentrations were calculated on the basis of measured NO_x concentrations outside the window, in the street, and in the urban background. The air outside the window is considered as a mix of the background air and of air at the street station corrected for background contributions:

$$[Particles]_{JGTV83\_EXT} \approx [Particles]_{HCOE} + \alpha\left([Particles]_{JGTV} - [Particles]_{HCOE}\right) \quad \text{Eq. 3}$$

where

$$\alpha = \frac{\left[NO_x\right]_{JGTV83\_EXT} - \left[NO_x\right]_{HCOE}}{\left[NO_x\right]_{JGTV} - \left[NO_x\right]_{HCOE}} \qquad \textit{Eq. 4}$$

The variable α is a measure of the relative contribution from traffic polluted air in the street canyon. The apartment is in the lee side of the street relative to the predominant westerly wind direction, while the street station is in the wind side. For that reason the NO_x concentration outside the window was in most cases higher than the concentration at the street station ($\alpha > 1$).

In cases with low NO_x concentrations measured at the street station ($[NO_x]_{JGTV}$-$[NO_x]_{HCOE}$ < 25 ppb, ppb = 10^{-9} mol/mol) an even simpler model is used:

$$[Particles]_{JGTV83\_EXT} \approx [Particles]_{HCOE} + \beta\left(\left[NO_x\right]_{JGTV83\_EXT} - \left[NO_x\right]_{HCOE}\right) \qquad \textit{Eq. 5}$$

$$\beta = \frac{[Particles]_{JGTV} - [Particles]_{HCOE}}{\left[NO_x\right]_{JGTV} - \left[NO_x\right]_{HCOE}} \qquad \textit{Eq. 6}$$

where the coefficient is used as a constant factor (the average particle/NO_x traffic emission ratio). *Eq. 5* is essentially the same as eq. (1), but in the simplified model the factor, β, is determined by regression analysis using the data of all half-hour occasions. The particle concentrations are measured as a derived function of diameter, dN/dlogd (number concentration per decade of particle diameter). The corresponding derived β-function is shown in *Figure 40*. The error bars indicate the standard deviation due to scatter, determined by the regression analysis.

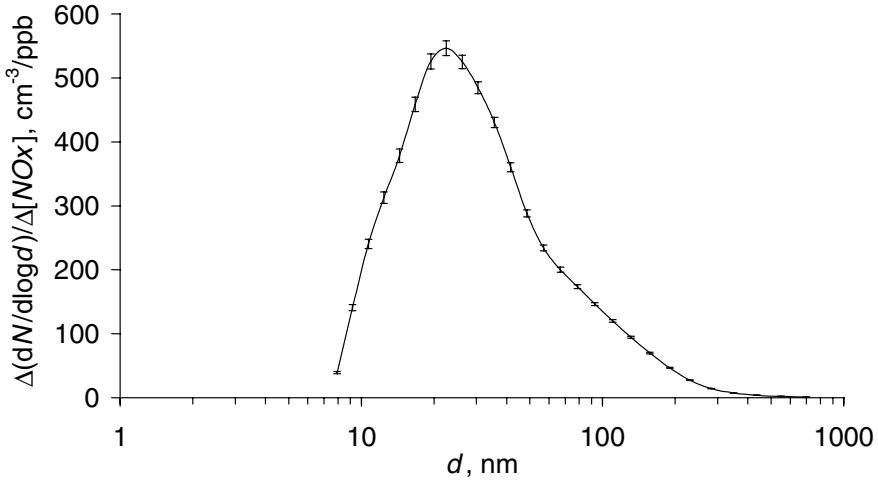

Figure 40 Average particle/NO_x traffic emission ratios (•) determined for Jagtvej in Copenhagen by regression analysis (ppb = 10^{-9} mol/mol).

The incoming airflow was measured independently in the three connecting rooms (living room, bedroom and hall) by the amounts of the tracer gas emissions necessary for the maintenance of a constant tracer gas concentration in each room. The detected distribution of the incoming airflow between the different rooms might be only approximately true, because the doors between the rooms were wide open. Except for the sealed kitchen the apartment consists of these three rooms and a bathroom. The open door between the hall and the bathroom acts as the exit route of the forced ventilation air. The contributions to the total air exchange rate in each of the three rooms (a_x) were monitored continuously along with the indoor/outdoor pressure difference (dP). Using a simple Bernoulli description valid for holes and larger cracks, an 'air exchange conductance' for each room can be defined as

$$I_x = \frac{a_x}{\sqrt{dP}} \qquad \text{Eq. 7}$$

Under calm wind conditions (wind speed < 2 ms^{-1}) a relation between the air exchange rates and the indoor/outdoor pressure difference was found consistent with eq. 5. In periods with 'low' ventilation only one ventilation slit in the living room was opened, while two slits were opened in the periods of 'high' ventilation. This was far from sufficient for a doubling of the ventilation rate in the periods of 'high' ventilation. To achieve a doubling it was required also to increase the gap of the vent hole in the bathroom. This immediately shows that the ventilation slits in the living room only delivered a minor part of the total 'air exchange conductance' $I = I_{Iliving\ room} + I_{bedroom} + I_{hall}$ of the apartment. A calculation based on the measurements under the two different ventilation regimes results in the conductance values shown in *Figure 41*. The analysis indicates that most of the ventilation air was supplied to the living room, but only a minor part coming through the slits in the window. It was the intention that most of the ventilation air should be supplied from the street through the slits, but the conclusion is that this condition could not be achieved. Thus, unfortunately, the actual pathway of most of the incoming ventilation air cannot be mapped out exactly. The possibility exists that a considerable part of the air was coming from neighbour (occupied) apartments.

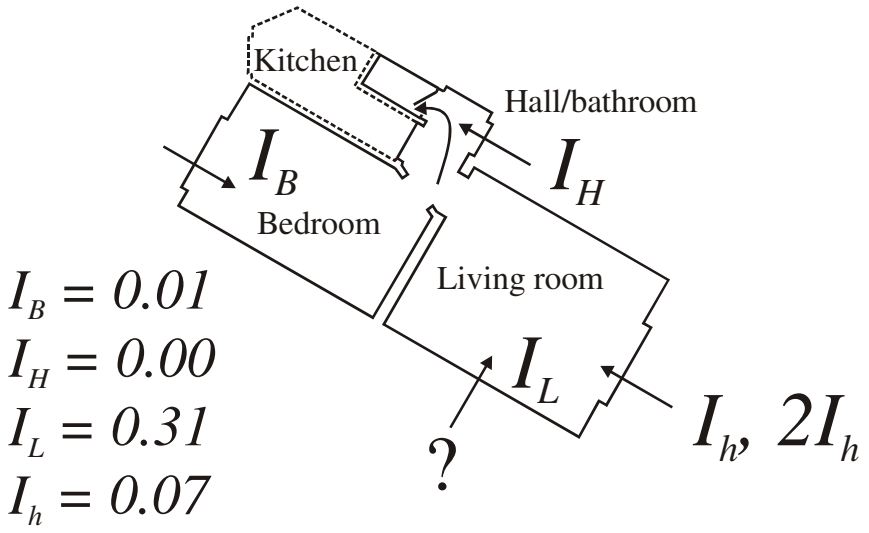

Figure 41 Measured air exchange conductance for the different rooms. In the 'low' ventilation periods (one slit) the value for the living room was 0.38 (= I_L+I_h), in the 'high' ventilation periods (two slits) 0.45 (= I_L+2I_h). Direct measurements of the flows (in units of the apartment volume of 76 m^3) and the pressure drops with the slits mounted on a small box exposed to suction gave the result I_h = 0.05 in good agreement with the indirectly measured value I_h = 0.07. The question mark symbolises that the actual pathway of I_L to the living room is unknown. Unit: $h^{-1}/\sqrt{(Pa)}$.

The average particle distributions for the apartment ('JGTV83_INT'), for urban background ('HCOE'), and outside the window of the living room ('JGTV83_EXT', calculated) are shown in *Figure 42*. The averages are based on simultaneous measurements during the last three campaigns. The first campaign was excluded, because the ventilation was different during this campaign. The single half-hour particle spectra could be well fitted with lognormal modes with geometric mean diameters of 11 nm, 23 nm, 56 nm, and 186 nm. The average contributions due to these modes are shown in *Figure 42*. By comparing the average spectrum from outside the window ('JGTV83_EXT') with the average spectrum from urban background ('HCOE') it is evident that the traffic in the street contributes to the 11 nm, 23 nm, and 56 nm modes. It is also clear that the 186 nm mode is mostly found in the indoor environment ('JGTV83_INT'), where, on the other hand, the influence of the 11 nm and 23 nm traffic modes is very weak. In urban background the contributions of the 11 nm and 23 nm modes, respectively, are 4.5 and 4.1 times smaller that in the street. Roughly the same ratio (3.8) is found for the traffic generated NO_x, which indicates that these modes in urban background are mostly due to the traffic. On the other hand the 56 nm mode is only 1.9 times higher in the street, which indicates that approximately 1/3 of this mode in urban background is due to the traffic. The rest comes from other sources, probably mostly as long-range transported secondary particles. The 56 nm mode from the traffic consists mainly of soot particles. The 11 nm and the 23 nm mode are due to nucleation and condensation of volatile material. These modes disappear indoors, probably by coagulation and evaporation. The dominant indoor 56 nm mode can be considered as a combination of long-range transported secondary particles and solid soot particles penetrating

from outside the building, but probably also indoor generated particles from neighbour (occupied) apartments contribute.

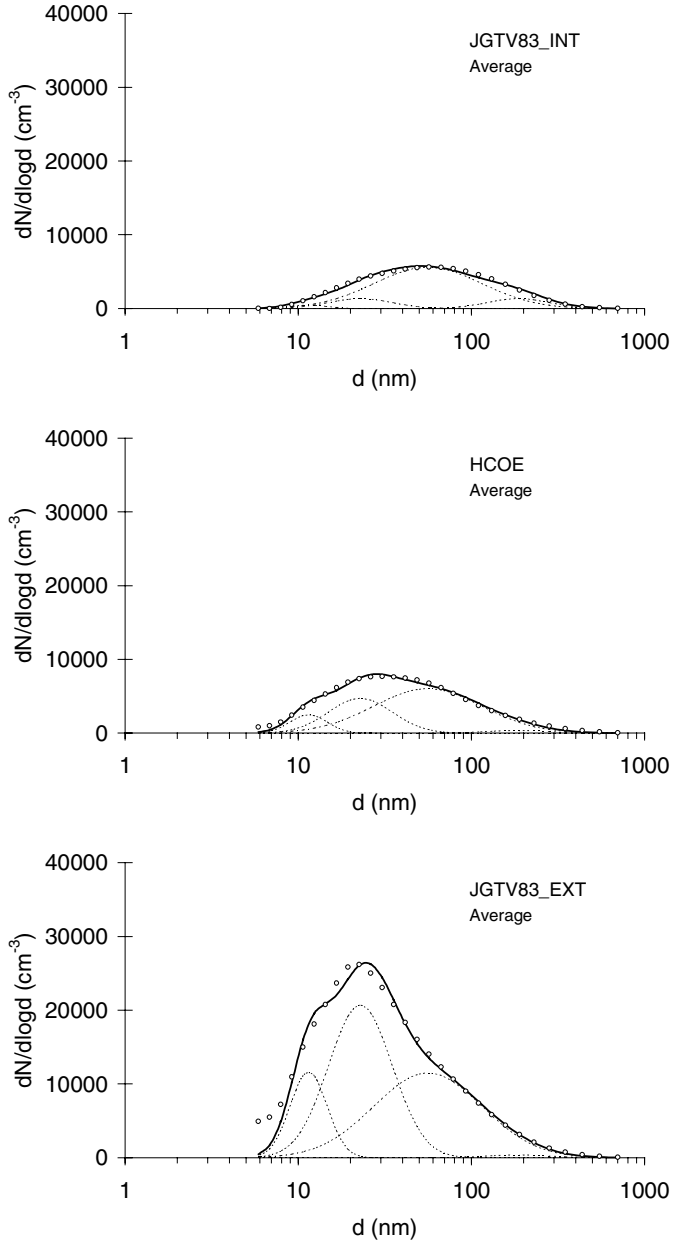

Figure 42 Averages of simultaneous particle distributions in the apartment ('JGTV83_INT'), in urban background ('HCOE'), and outside the window of the living room ('JGTV83_EXT'). The two first were measured directly; the last one calculated using the simultaneous measurements at the Jagtvej street station ('JGTV') as described above. The size distributions are fitted using four log-normal distributions at 11 nm, 23 nm, 56 nm, and 186 nm.

The average magnitudes of the 56 nm mode in *Figure 42* are approximately equal in the apartment and in the urban background. This might indicate that the indoor particles in this mode have penetrated from urban background. To investigate the relation between the 56 nm mode outside the window, in urban background and in the apartment in more details the time series for an average week are shown in *Figure 43*. By inspection it can be seen that there are some similarity between the time variation indoor and in urban background ('JGTV83_INT' and 'HCOE', respectively), but unmistakable differences are also apparent. The most prominent discrepancies are seen in the early evenings where indoor peaks appear without counterparts in the urban background air or in the street outside the window (JGTV83_EXT'). The positions of the peaks in the average week time series indicates that cooking and tobacco smoking in neighbour apartments are the responsible indoor source.

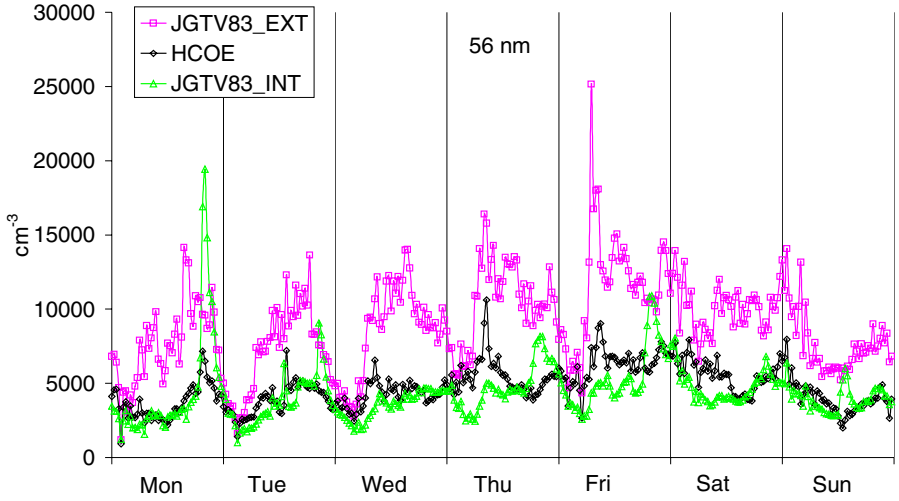

Figure 43 T he variation during an average week of the 56 nm particle mode. Same data as in *Figure 42*.

The variation of the 186 nm particle mode during an average week is shown in *Figure 44*. This mode originates clearly from indoor sources. Several peaks in late night and some co-variation with indoor carbon monoxide (r = 0.4) indicate that tobacco smoking might be a source.

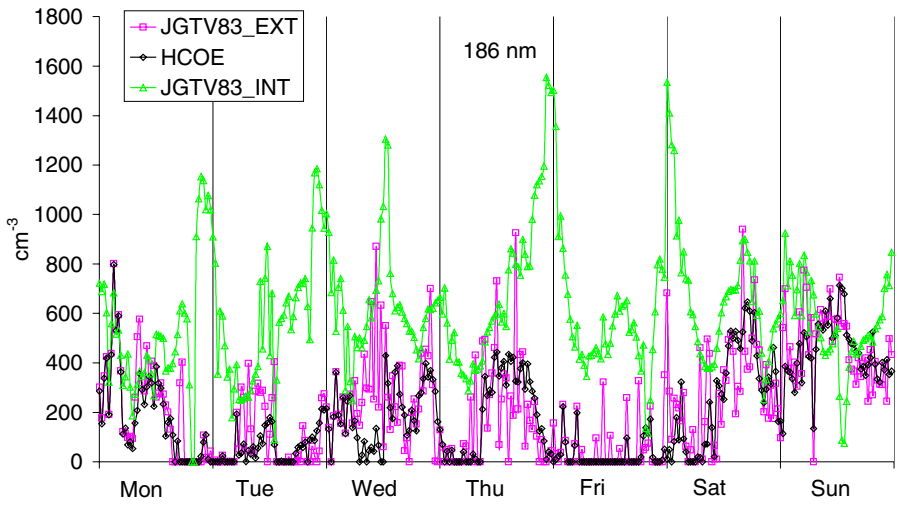

Figure 44 The variation in an average week of the 186 nm particle mode. Same data as in *Figure 42*

The analysis of the airflow to the apartment has shown that the ventilation slits connecting the living room with the street outside the living room delivered only a minor part of the total air exchange of the apartment. The analysis indicates that most of the ventilation air was supplied to the living room and not to the connecting rooms, but the possibility exists that a considerable part of this air was supplied from neighbour apartments. This assumption is confirmed by the observation of frequent indoor particle episodes without counterparts in urban background air or in the street outside the window. The position of the particle peaks in the average week time series indicates that cooking and smoking in neighbour apartments were important indoor sources.

The original idea was to perform a 'clean' experiment in an unoccupied apartment with no indoor sources and with the major part of the ventilation air coming from the street. A disappointing conclusion is that this ideal situation was not achieved. It is evident that significant indoor sources were present during the measurements, and that the main ventilation pathway probably was not from the street. Unfortunately, direct quantification of the traffic particle penetration efficiencies and deposition rates is not possible under such conditions.

Nevertheless, one important conclusion about the penetration of traffic particles can be readily drawn. The very low indoor levels of the 11 nm and 23 nm traffic particles modes compared with the levels in urban background show that these particles are not stable in the indoor environment. They either evaporate or deposit quickly.

A huge amount of air quality data and meteorological data have been collected during the four campaigns of the experiment. Only a minor part of these data have been studied up till now. Further work is demanded doing analysis of the data using statistical and other indirect mathematical methods.

7 Air Quality Models for Particles

NERI's models

NERI has a long tradition and experience in development and application of air quality models. Models are available for all scales, from global, to European, regional, urban and local scales. The local scale models include street pollution models and point and area source models. The models are able to describe the dispersion of pollutants, some chemical processes and deposition. The models are originally developed for gaseous pollutant and stable pollutants, but now expanded also to include more complicated chemical processes and dispersion and transformation of particles is in process.

Important inputs to the models are emission data, meteorological data and data about the topography.

Different scales and processes

Specifics of the urban pollution modelling are mainly related to the geographical and time scale of the relevant physical and chemical processes considered. For the regional scale models we need to take into consideration transport as well as physical and chemical transformation processes that have a scale of hundreds to thousands kilometres. The scale of an urban domain is normally only few to tens of kilometres, and when dealing with single streets, the relevant scale is only few metres. The urban environment is characterised by a very short distance to main pollution sources. Actually, when dealing with street level pollution, the modelling domain is practically identical with the source domain. From the modelling point of view this implies that such processes as dilution by turbulent dispersion are much more important than chemical or physical transformations and deposition, which are crucial for the regional scale modelling. In this respect, the particle pollution modelling is not especially different from modelling of traditional gaseous pollutants on the local scale.

The first part of this chapter describes the modelling of the stable pollutants or the rather simple and well-known chemical processes. At the end of the chapter is given a short description of the more complicated particle processes.

7.1 The long-range transported air pollution

The long-range transport air pollution model, the Danish Eulerian Hemispheric Model, DEHM for background scale (e.g. the greater European scale) calculates transport, dispersion, deposition and chemistry (including photo chemistry) of 56 chemical compounds. Furthermore, the model can be used to describe and forecast sand/dust storms. The emission data used in DEHM are derived from a combination of information provided by the European Monitoring and Evaluation Programme (EMEP) and global emission databases. The left map at *Figure 45* shows the calculated PM_{10} for Europe based on the EMEP emission data of primary particles and of the gases NO_x, SO_2 and NH_3 leading to the secondary inorganic particles NH_4NO_3 and $(NH_4)_2SO_4$. The contributions from sea salt and secondary organic particles are not included at the moment. The calculated

values are for a single hour, but calculations can be made for longer time periods, e.g. in relation to the limit values for 24 hours or a full year. The right map at *Figure 45* shows the calculated NO_2 concentration at a certain hour over Denmark. This could also be done for particles, if data on spatial emissions are available. The models are described in Brandt et al., 2003 and Brandt et al., 2001.

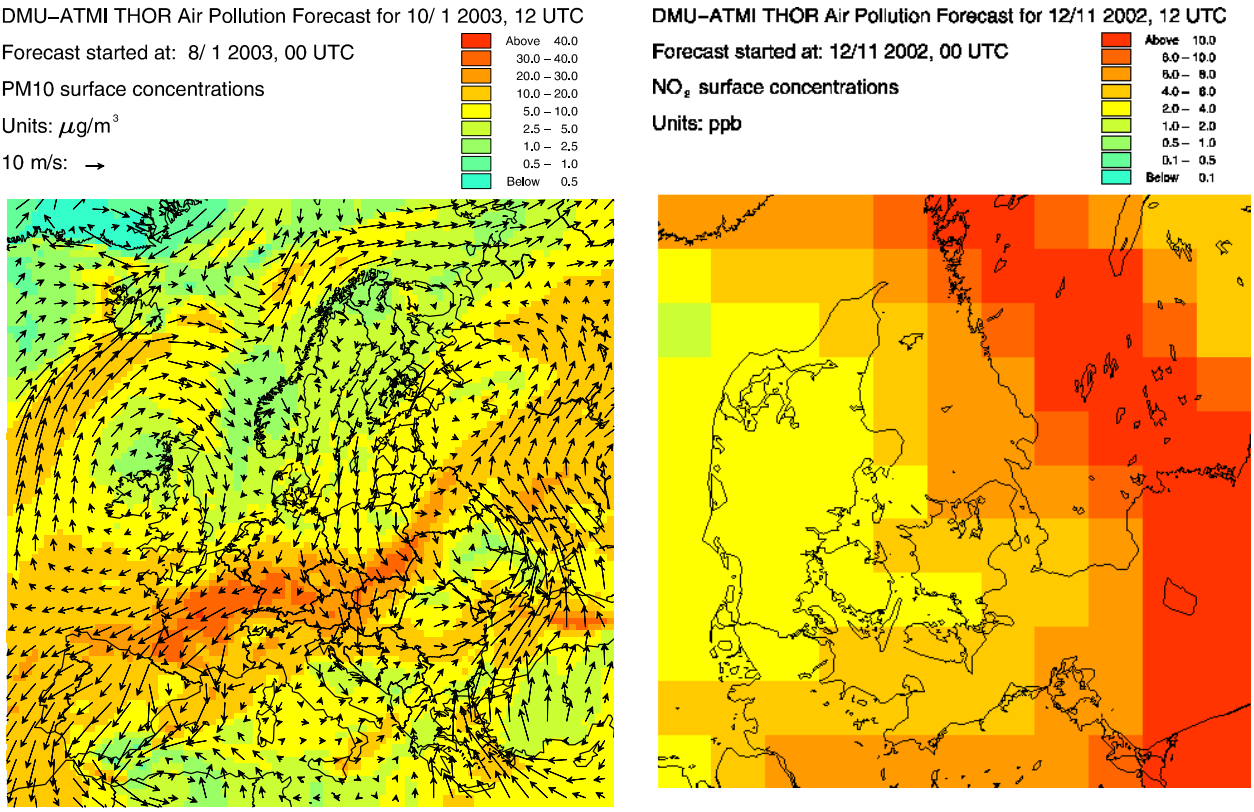

Figure 45 To the left modelled PM_{10} concentrations in Europe (39 km x39 km) 8 January 2003 at 1200 UCT based on the EMEP emission data of primary particles and of the gases NO_x, SO_2 and NH_3 leading to the secondary inorganic particles NH_4NO_3 and $(NH_4)_2SO_4$. To the right modelled NO_2 concentrations in Denmark (10 km x10 km) based on emission data from EMEP.

7.2 Air pollution in the urban background

Meteorological data and air pollution concentrations from the long-range transport model are subsequently used as input to the Urban Background Model, UBM, (Berkowicz, 2000) calculating the urban background air pollution based on emission inventories with a spatial resolution down to one kilometre. The UBM model, in the version presently applied in Denmark, is suitable for calculations of urban background concentrations when the dominating source is the road traffic and/or large point sources. *Figure 46* shows the emissions and concentrations of PM_{10} in the city of Copenhagen based on a special emission inventory for PM_{10} from traffic. The emission inventories for the traffic will be further improved during this project

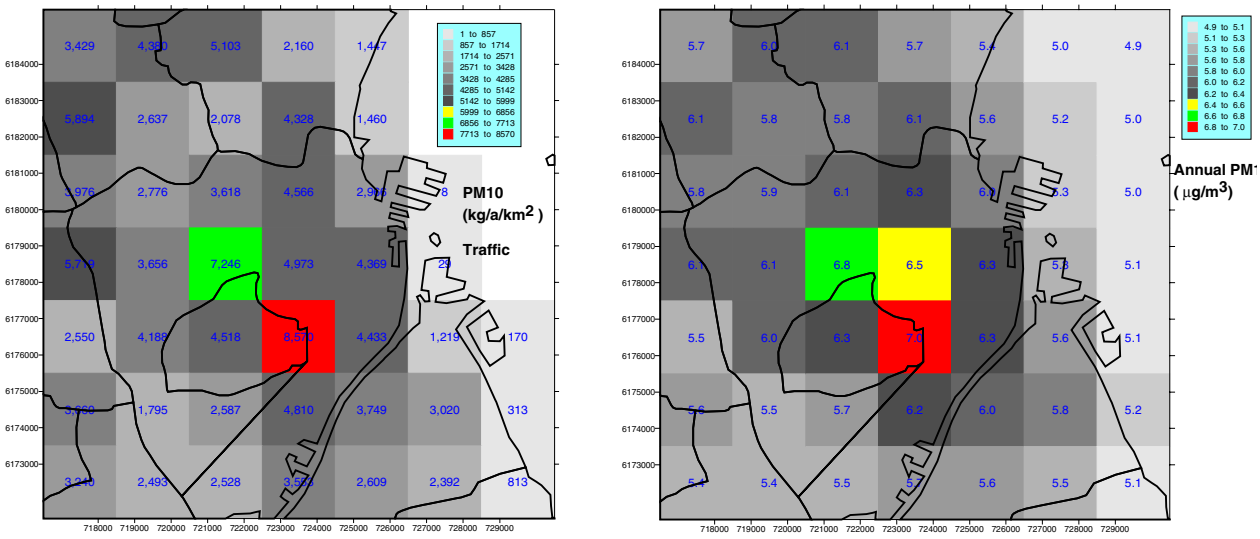

Figure 46 The figure shows the emissions from traffic (left) and the PM_{10} concentrations (right) as annual average in Copenhagen.

7.3 Air pollution in street canyons

The output from the urban background model is used as input to the Operational Street Pollution Model, OSPM, (Berkowicz et al. 1999) producing the air pollution concentrations at street level at both sides of the streets in cities, *Figure 47*. The model calculates air concentrations of NO, NO_2, NO_x, O_3, CO and benzene in the street canyon at both sides of the street. Particles will be included in the model in the near future. The OSPM has been successfully tested under specific European field campaigns in a variety of different climatic and air quality conditions in, e.g., Copenhagen, Gothenburg, Helsinki, Oslo, Brussels, Berlin, Hanover, and Milan. Due to the circulation of air in street canyons, the air pollution concentrations can be very different at the two sides of a street, *Figure 47*.

Until now standard emission data are used, based on traffic density and standard emission factors. The present project will produce much better emission data, not only for PM_{10}, but also for other parameters, e.g. number of ultrafine particles. The non-exhaust emission factors are very uncertain at the moment, and the present project will produced better emission data also for this part of the emission.

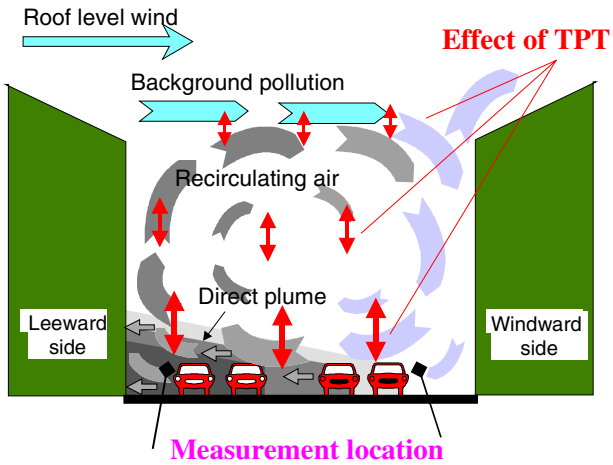

Figure 47 Principal flow pattern inside a street canyon for near perpendicular roof level wind direction and schematic picture of the main processes assumed in the empirical OSPM, adopted from (Berkowicz et al., 1997).

7.4 Particle processes

Particle processes include nucleation, condensation and evaporation, coagulation, cloud processes, deposition, primary emissions, re-emissions, atmospheric chemistry and meteorology.

In order to be able to understand the formation and growth processes of atmospheric aerosols and cloud droplets their thermodynamic properties should be known. For example, in the condensation process, the driving force is the vapour pressure difference between gas phase and surface. However, in the atmosphere where there are multi-component, multiphase mixtures, their thermodynamic state and phase diagrams are typically very complex.

The formation of particles in the atmosphere can be kinetically limited by some of the intermediate steps of its formation processes. Condensation growth increases aerosol mass and changes composition. It is important particularly for nucleation and Aitken modes. The observed growth rate for these modes is 1-20 nm/h (Kulmala *et al.*, 2001). In practise, sulphuric acid cannot explain this alone and other condensable vapours are needed. Different non-volatile or less volatile organics are very good candidates. When investigating multi-component condensation of sulphuric acid, ammonia, organics and water very complex thermodynamics is involved. Therefore parameterisations are needed also for thermodynamic point of view. The mass accommodation coefficient affects condensation rates, particularly in kinetic and transition regime. The driving force in condensation is the vapour concentration, which is related to vapour sources and to atmospheric chemistry. An open key question is how charged particles with polar condensing molecules will enhance condensation growth.

The chemistry due to the ageing by nucleation, coagulation and condensation determines if the particles will activate as cloud droplets. The mass transfer from gas to cloud droplets will increase aerosol

mass and change composition. This will end up with changes in size distribution.

Dry and wet deposition investigations including continuous measurements of aerosol fluxes (Buzorius *et al*., 1998, 2000) are very important in aerosol life cycle point of view. The number of measurements is increasing and new information on deposition velocity as a function of boundary layer conditions is obtained.

Direct emissions and re-emissions of aerosol particles as well as direct emissions of precursor gases are needed to obtain as good as possible initial and boundary conditions for aerosol dynamic models. However, more detailed emission inventories are needed

Taking into account that the particle concentrations in an urban environment are usually much higher than in the rural environment (especially considering the particle number) one could expect that the non-linear aerosol dynamics processes could be of importance here. However, at the same time one should also take into account the relatively short residence time of pollutants in an urban environment. For the street scale, the residence time is normally less than 1 min, while for a city it is of the order of some hours at most. Numerical model calculations show that processes such as e.g. coagulation, are quite negligible when considering aerosol dynamics in a car exhaust plume (Vignati et al., 1999). The rapid dilution and the short travelling time prevents the coagulation process to take place efficiently.

The processes acting on atmospheric aerosols are listed and briefly explained in their impact on the particle number and volume in the following table.

Table 14 Processes that alter the particle size distribution in the atmosphere and their effect on the particle number dN and particle volume dV. '+' means increase, '–' means decrease, while '0' stands for no change.

process	sink/source	dN	dV
nucleation	source of new, very small particles	+	((+))
condensation	gas to particle conversion	0	+
evaporation	caused particle to shrink and eventually disappear totally	0 or –	–
coagulation	particles collide with each other and stick together	–	0
deposition and gravitational settling	sink of particles	–	–
emission	source	+	+
dilution, mixing	source or sink depending on the concentration of the diluting air mass	+ or –	+ or –

Similar to dispersion modelling a great variety of aerosol dynamic models exists with a wide range in degrees of complexity. The models differ e.g. in the size of the modelling domain, the description of the aerosol size distribution, the mixing state (externally or internally mixed) and chemical composition and the number and accuracy of the aerosol dynamical and chemical processes included. The range

begins with e.g. a simple box model describing the development of a mono-disperse aerosol in time and extends to regional or global Lagrangian models with a representation of single particles each with a different composition and size (Kleeman).

The aerosol dynamic model AERO3 (Vignati et al. 1999) is able to model the processes listed in *Table 14* for 3 classes of aerosol, i.e. soluble, insoluble and mixed particles. The size distribution is represented in a sectional form, i.e. 46 size classes with a logarithmic width dlogDp=0.1 and the model assumes in the present version one mixed volume (box model). The model is applied for episode calculations to evaluate the relevance of aerosol dynamic at street and urban level. The subroutines of AERO3 are planned to be incorporated in urban dispersion models.

A powerful way to compare different source, sink and transformation processes acting on compounds in the atmosphere is the evaluation of the time scale of each process (e.g. Wexler et al., 1994). The process with the smallest time scale has most relevance in changing the concentrations of the compound. The often-used term residence time is based on the same concept.

The time scale for dilution of the particle and gaseous traffic emissions with background air depends on the ambient wind speed. Using typical values under low wind speed conditions e.g. for Jagtvej in Copenhagen we estimate a dilution time scale of ca. 110 s. This value presents and upper estimate since the dilution time scale will decrease for higher wind speeds.

Other processes (see *Table 14*) will be able to alter the particle size distribution of they have a time scale smaller or comparable to dilution time scale.

In order to estimate the time scale for coagulation we calculated the time development of the size distribution (half-hourly mean) measured in Jagtvej during a morning rush hour with AERO3. Results are shown in *Figure 48*. Both the total number concentration of about 1.1 × 105 # cm^{-3} and the total particle volume of ca. 37 μm^3 cm^{-3} during this particular situation lie in the upper most range of observed values during the 2001 measuring period and coagulation should be fastest in this case. Coagulation is efficient in removing smallest particles (diameter smaller than ca. 30 nm) and it takes about 10 min to let 10% of the particles coagulate. From this simulations we evaluate a coagulation time scale for the initial distribution of ca. 4500 s (75 min). Comparing this value with the previous estimated dilution time scale we find that dilution is by far the dominating process at street level with a 40 times smaller time scale.

We can conclude that both in a vehicle exhaust plume and inside street canyons the dilution with the ambient air is the dominating process and coagulation is not expected to alter the size distribution significantly.

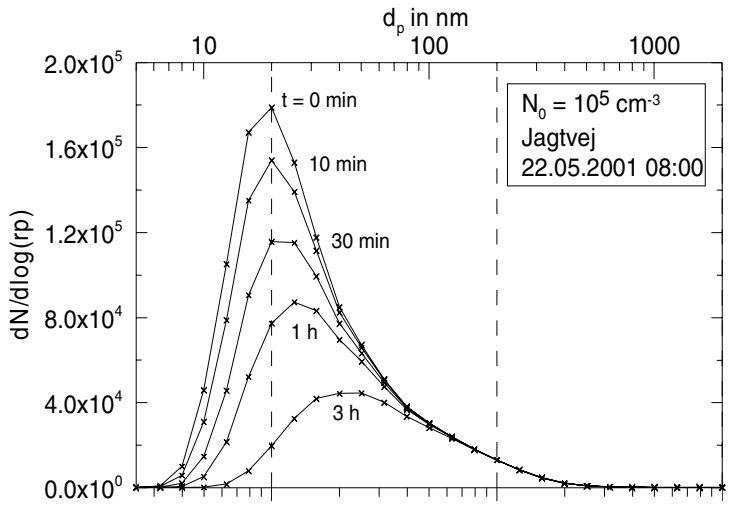

Figure 48 Development of a particle size distribution due to coagulation alone calculated with AERO3. No dilution is assumed.

We can conclude that both in a vehicle exhaust plume and inside street canyons the dilution with the ambient air is by far the dominating process and coagulation is not expected to alter the size distribution significantly.

8 Summary and future work

This report gives a mid-term status of NERI's contribution to the four-year project "Air pollution with fine particles", which was initiated by the Danish Ministry of the Environment in 2001.

The overall objective of the PM programme is to establish better knowledge on the health effects of atmospheric particles in Denmark in order to develop strategies to reduce the adverse health effects of man-made and natural sources. The activities at NERI should be closely related to other investigations of emissions and health effects of particles in Denmark. Specifically, NERI shall investigate emissions, size distributions, chemical composition, transformation and dispersion of particles. Human exposure and socio-economic aspects shall also be included in the activities. Establishment and further development of international co-operation should also be prioritised.

The midterm status of NERI's contributions given in this report is a summary of the results, which are described in more details in papers in international journals, presentations at international and Danish conferences and workshops and different more informal meeting and seminars. In addition, the project team has contributed to items in newspapers, radio and television.

Most of the results were obtained under this project supported by the funding from the Ministry, but NERI has also contributed by own resources, especially during start-up. In addition, funding was also given from the Danish Strategic Environmental Programme (SMP), especially for the studies of the relationship between indoor and ambient PM pollution.

A summary of the research activities and the obtained results at NERI are more specifically given in the following.

8.1 Obtained results

Characterisation of particles

Characterisation of particles includes size distributions, other physical properties and chemical composition of particles. The studies on size distributions and chemical composition of the particles are based on field studies at streets, urban background and rural sites. The field studies exploited the logistics and the data from the national air quality monitoring programmes, i.e. the nation-wide monitoring programmes (Kemp & Palmgren, 2003) and the special additional monitoring activities under the Municipality of Copenhagen. The data include air quality data, traffic density data and meteorological data. The special measurements under this project were typically carried out in or near the permanent monitoring stations.

Source apportionment of ultrafine particles

Size distribution measurements in the size range 0.006 to 0.7 µm were carried out at streets, urban background and rural background by DMPS monitors with high time resolution. Receptor modelling and

other data analyses were used for determination contributions in size fractions from traditional diesel vehicles, small modern diesel vehicles with oxidising catalysts and petrol vehicles (Wåhlin et al. 2001a). Diesel vehicles are the dominating source – given as particle number – to nano-particles and ultrafine particles in urban air in Denmark. The petrol vehicles contribute less. The long-range transported particles contribute significantly compared to the traffic, especially to the particle mass.

The effect of reduced sulphur in diesel

Field studies in streets in Copenhagen have demonstrated the effect of the reduction of the sulphur content in Danish diesel fuel from 500 ppm to 50 ppm during the summer 1999 (Wåhlin et al. 2001b). The method was the receptor modelling technique developed at NERI. The reduced particle emission from the diesel vehicles was pronounced among the smallest particles below 0.05 µm. These particles are partly liquid and semi-volatile, and they consist of fuel, lubricant oil – pure or partly combusted. The phenomenon has been further investigated and related to studies in other countries. A clear relationship to ambient temperature was proved. Further reduction of the sulphur content will probably not reduce the particle emission further, but advantage could be taken in relation to engine technology and lifetime and maintenance of filters and catalysts.

Emission factors of ultrafine particles from road traffic

The emission factors of ultrafine particle from road traffic were estimated using DMPS data from streets and urban background in Copenhagen and application of NERI's street pollution model, OSPM and automatic traffic counting (Ketzel et al., 2003). The found emission factors are comparable with data from field studies in USA and Sweden. However, they deviate significantly from the laboratory measurements on dynamometers. This is probably mainly due to artefacts during the laboratory measurements, i.e. non-realistic dilution of exhaust gases and driving cycles during the measurements in the laboratory.

PM_{10} and $PM_{2.5}$ from road traffic

Longer time series of PM_{10} and $PM_{2.5}$ were measured with high time resolution (½ hour) by TEOM in streets and urban background. The data analysis showed a large contribution from road traffic in Copenhagen. The PM is both direct exhaust and non-exhaust from wear of road surface, tires, brakes etc. and re-suspension of dust cause by the turbulence from the traffic. The non-exhaust part of PM_{10} and $PM_{2.5}$ is at present determined with rather high uncertainty, but the first estimates are made for Copenhagen (Wåhlin & Palmgren, 2003b).

Supplementary measurements by a mobile station

A mobile measurement container has been established under the project. In addition to the special particle measurement equipment, e.g. DMPS, TEOM, EC/OC analyser, MOUDI impactors and high volume impactors, traditional analysers for traffic-related gaseous pollutant were installed in order to relate the measurements to routine monitoring data. The plan is to use the mobile station for special measurements.

Is urban background stations representative?

The urban background stations are often located at rooftops in the urban areas. One urban background station is located at a roof at the University of Copenhagen, approx. 25 m above ground. In order to demonstrate the representativity of the station supplementary meas-

urements were carried out close to the station but at ground level. The agreement was very good.

Wood stoves

Wood stoves are known to emit large amounts of particles. A specific measurement campaign was therefore carried out using the mobile station in a town with many wood stoves. The data are in process of analysis.

Elemental and organic carbon, EC/OC

Measurements of Elemental and organic carbon (EC/OC) were carried out with high time resolution in a street in central Copenhagen. EC was strongly correlated with NO_x, and the diesel traffic. EC is therefore believed to be a good indicator for black carbon (soot) or the solid carbonaceous from diesel vehicles (Le Bihan et al., 2001).

PIXE analysis of size fractionated particles

Measurement campaigns were carried out in streets by the so-called MOUDI impactor in 10 size fractions from 0,056 to 10 µm and analysed by PIXE. The data were used for analysis of the origin of the different size fractions (Glasius et al., 2002 and Le Bihan et al. 2002).

PAH analysis of size fractionated particles

A high volume impactor (800 l/min) during the wood stove campaign and campaigns in a street and rural background collected large samples. The PAH (and other organics) analyses are ongoing. The intention is to quantify the contributions from different source types and make the basis for better assessment of the adverse health effect of the particles.

Transformations of traffic particles in streets

The physical and chemical transformations of particle in street canyons can be disregarded due the very short residence time of the air in the street, typically less than a minute. Some transformations take place in the urban scale, but quantification of these transformations is still very uncertain. More detailed analysis of the chemical composition – especially in relation to organic substances - and size distributions will be applied for this issue.

Indoor PM pollution

Investigations of penetration and deposition of traffic particles in an apartment in a street canyon were carried out under a special project funded by the National Environmental Research Program (SMP). The measurement showed high penetration and low deposition of fine particles - 50 to 700 nm (Palmgren et al., 2001a and Wåhlin et al 2002). The nano particles disappeared indoors probably due to low penetration rate and high deposition (high mobility) and losses by evaporation indoor.

Modelling of particles

NERI's air quality and exposure models now include particles to some extend. The very limited transformations of particles in street canyons allow inclusion of particles, if good emission factors can be obtained. The emission factors for PM from traffic are still rather uncertain, especially the non-exhaust part. The urban background model can probably also by used for cities like Copenhagen, but better data for validation are needed. The regional and large scale models (NERI's so-called air quality management and forecast system) include now some of the secondary particles, i.e. nitrate and sulphate particles formed by oxidation of SO_2 and NO_x, and also some primary particles emitted at the European continent. The models will be further developed in relation to PM pollution. The project delivers data for development and validation of the modelling systems.

Future activities

The activities under this issue will be continued and expanded during the last two years of the project, especially on determination of emission factors and chemical characterisation of particles in different size fractions.

Inventories of emissions from different sources and determination of emission factors.

Detailed emission inventories are routinely carried out by NERI (SYS) based on CORINAIR. The preparation of the emission inventories are supplemented with more detailed investigations of specific source types. They are prepared for stationary as well as for mobile sources.

Traffic and wood stoves are large emitters

The largest emissions takes place from road traffic (diesel vans and trucks), from other mobile sources (machinery for farming, constructions and industry) and individual house heating (89% of this from wood stoves). The road traffic and the wood stoves give most probably rise to the highest human exposure, because the emissions are high, the release height is low and the emissions take place in urban areas where the population lives, works and goes about.

Emission factors

Better and more detailed emission factors are determined, especially for the road traffic including exhaust as well as non-exhaust. Validation of the emission factors is still not completed and will be supported by this project. The above mentioned receptor models also support determination of the emission factors. High quality and high-resolution emission factors are crucial input for air quality and exposure models.

Future activities

The development of emission factors will be continued, especially on traffic and wood stoves.

Particle emissions from road traffic (fuel, engine types etc.).

A co-operation between NERI and the Danish Technological Institute (TI) was established and series of emission measurements of ultrafine particles by DMPS during different driving cycles and on different vehicles were performed. The measurement programme included buses as well as petrol and diesel passenger cars, with different filters and catalysts.

Large variations in emissions of PM

The measurements showed extremely large variations between different types of cars. The largest emissions were observed from traditional diesel vehicles without filters. The oxidising catalysts remove most of the semi-volatile particles, which are condensates formed in or immediately behind the tailpipe. The PM emissions from modern petrol cars with catalysts are very low.

Effective particle filters

The particles filters for large diesel vehicles are in general very efficient (> 95%) also for ultrafine particles. However, not all technologies work; test or type approval is necessary.

Driving cycles or transients

TI has developed the measurement technique in the laboratory to more real life conditions. It includes possibilities for large and more realistic dilution and transient emissions measurements, which corresponds more to real driving conditions. Better agreement has been

obtained between field and laboratory measurements and by this better emission factors.

The effect of reduction measures.

Selection and preparation of scenario calculations is in process. A few selected scenarios will be used for demonstration of the methods.

Filter on heavy-duty vehicles in Denmark

An assessment of the health effect of installation of particle filters on all heavy-duty vehicles in Denmark has been carried out (Palmgren et al., 2001a and Palmgren et al., 2002). The assessment should be carried out very fast and very early in the project and only few Danish data and some data from other countries were available. The results are rather uncertain, like similar assessments in other countries. An update has been made recently, resulting in a lower uncertainty. They were used for cost-benefit analysis carried out by the Traffic Agency and the Institute for Environmental Assessment.

Air quality and exposure models

As mentioned above the air quality and exposure models are under development to include PM in connection with this project.

Socio-economic assessment, incl. cost-benefit analyses

The pricing of premature deaths and increased morbidity in relation to human exposure with PM will be assessed. The results will be part of the above scenario calculations and other cost-benefit calculations.

International activities/co-operation

EU directive

Participation in the EU working group on the air quality directive for PM has taken place.

International networks

The project is included in the EUROTRAC-2 sub-project SATURN about urban air pollution (Palmgren et al. 2001b) and results will be given in the final SATURN report. The project is also a part of CITY-DELTA under CAFE (EU activity Clean Air For Europe) in relation to assessment of pollution with ozone and particles in European cities. A EU project, SAPPHIRE under the 5th Framework Programme has been funded. The project includes characterisation of particles and source apportionment in 5 European cities.

The project group is involved in a consortium concerning PM pollution undet the 6th Framework Programme.

Co-operation has been established with Danish and foreign scientists. A Ph.D. study under the project has been established in a co-operation with the University of Lund in Sweden. The study is concentrated on development of models for PM. Another Ph.D. study has been initiated in a co-operation with the Municipality of Copenhagen the Oil refineries in Denmark, JRC Ispra Italy and the University of Copenhagen. The main issue is PAHs and other organics in the air from the road traffic.

8.2 Main conclusions

The road traffic and wood stoves are the particle sources, which cause the highest outdoor human exposure due to high emissions, at low release heights and in urban areas, where the population lives, works and goes about.

Diesel vehicles are the dominating source of nano-particles and ultra-fine particles. Modern petrol cars do only contribute a little the PM pollution. In addition to the tailpipe, the non-exhaust emissions from wear of road surfaces, tires, brakes etc contributes significantly to the PM_{10} pollution from diesel as well as from petrol vehicles. The non-exhaust emission depends on many factors, e.g. wind speed, salting and sanding of roads in winter, precipitation and properties of the road surface.

The highest emissions of particles take place from traditional diesel vehicles without filters or catalysts. The particle filters are generally very efficient (>95%) for all particles including nano particles and ultrafine particles. The oxidising catalysts on diesel vehicles remove a significant part of the semi-volatile particles (condensates, which are fuel, lubricants or reaction products).

Long-range transported particles, i.e. primary particles and secondary particles formed by oxidation of SO_2 and NO_x emitted at the European continent, are dominating in urban background and comparable with the traffic contribution in busy streets (mass concentration, $PM_{10}/PM_{2.5}$).

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Danish Summary – Dansk resumé

Fireårigt Project

I 2000 vedtog Folketinget at støtte et fireårigt forskningsprojekt om luftforurening med partikler i Danmark. Det skulle omfatte karakterisering partiklernes fysiske og kemiske egenskaber og deres kilder samt en vurdering af de helbredsskadelige effekter samt en vurdering af den samfundsøkonomiske betydning for Danmark. En styringsgruppe, hvor Miljøstyrelsen har formandsskabet koordinerer programmet, og Danmarks Miljøundersøgelser udfører opgaverne, karakterisering af partikler og deres kilder samt samfundsøkonomiske vurderinger. Studier af helbredseffekter gennemføres af forskellige institutioner og universiteter, fx. Kræftens Bekæmpelse og Københavns Universitet, afd. for Folkesundhedsvidenskab.).

Formål

Det generelle formål med partikelprogrammet er at fremskaffe ny og bredere viden i Danmark om helbredseffekter af partikler i luften med det mål at udvikle strategier til reduktion af negative helbredseffekter af menneskeskabte og naturlige kilder til partikler. Forskningen skal koordineres med andre studier i Danmark og internationalt.

Specielt skal Danmarks Miljøundersøgelser (DMU) undersøge emissioner, størrelsesfordelinger, kemisk sammensætning, omdannelser og spredning af partikler i luften.

Nærværende rapport er midtvejsrapport for DMU's aktiviteter.

Metode

Det danske overvågningsprogram for luftkvalitet, som udføres af DMU (Kemp & Palmgren, 2003) danner basis for de eksperimentelle studier. Det omfatter løbende målinger i lange tidsserier af de væsentligste luftforureninger relateret til de væsentligste kilder i Danmark. Overvågningsprogrammet suppleres i disse studier med specielle målinger af partikler i kortere eller længere kampagner. Denne kombination af lange tidsserier af traditionelle forureninger og specielle partikelmålinger i kampagner gør det muligt at konstatere en sammenhæng mellem kilder og partiklernes egenskaber (størrelse og fysiske/kemiske egenskaber).

Kort om undersøgelserne

Undersøgelserne omfatter emissionsopgørelser af danske stationære og mobile (trafik) kilder, eksperimentelle studier af PM_{10}, $PM_{2.5}$ og ultrafine partikler i Danmark i trafikerede gader, bybaggrund og ude på landet. Studierne omfatter kemisk sammensætning, herunder indhold af kulstof, og størrelsefordelinger. Emissions faktorer af partikler er blevet beregnet under aktuelle kørselsbetingelser ved hjælp af luftkvalitetsmålinger. Desuden er der foretaget målinger af partiklers (PM_{10}, $PM_{2.5}$ og ultrafine partikler) indtrængen og afsætning i en lejlighed med vinduer i facaden til en trafikeret gade. Resultaterne anvendes til udvikling og validering af DMU's luftkvalitets- og eksponeringsmodeller for partikler.

Hovekonklusioner

Vejtrafik og brændeovne er de partikelkilder, som bidrager til den største udendørs befolkningseksponering, fordi disse kilder emitterer store mængder af partikler i lav højde og i byområder, hvor mennesker bor, arbejder og færdes.

Dieselkøretøjer er den dominerende kilde til nanopartikler og ultrafine partikler. Moderne benzinbiler bidrager kun lidt til partikelforureningen. Udover emissionen via udstødningsrøret bidrager trafikken i væsentligt omfang til PM_{10} med partikler fra slid på kørebane, dæk, bremser m.v., og det gælder både diesel- og benzinkøretøjer. Omfanget af denne del af partikelforureningen afhænger af en række forhold, fx. vindhastighed, saltning og grusning om vinteren, nedbør og kørebanens beskaffenhed m.v.

De højeste emissioner af partikler finder sted fra traditionelle dieselkøretøjer uden filtre og katalysatorer. Partikelfiltre er generelt effektive (>95%) for alle partikler fra udstødning, inklusiv nanopartikler og ultrafine partikler. Oxiderende katalysatorer på dieselkøretøjer fjerner effektivt de flygtige partikler (kondensater, som er brændstof, smøreolie og omdannelsesprodukter).

Fjerntransporterede partikler, som er både primære partikler og sekundære partikler dannet ved oxidation af SO_2 and NO_x, som er emitteret på det Europæiske Kontinent, er dominerende i bybaggrund og bidrager væsentligt i trafikerede gader (massekoncentration, $PM_{10}/PM_{2.5}$).

Flere resultater findes i nærværende rapport, samt en række rapporter og artikler i internationale tidsskrifter, se referencelisten under denne rapports forfattere.

National Environmental Research Institute

The National Environmental Research Institute, NERI, is a research institute of the Ministry of the Environment. In Danish, NERI is called *Danmarks Miljøundersøgelser (DMU)*.
NERI's tasks are primarily to conduct research, collect data, and give advice on problems related to the environment and nature.

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Publications:
NERI publishes professional reports, technical instructions, and the annual report. A R&D projects' catalogue is available in an electronic version on the World Wide Web.
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