

# The Danish Air Quality Monitoring Programme

Annual Report for 1997

NERI Technical Report No. 245

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### **Summary**

The programme

The Danish Air Quality Monitoring Programme (LMP) was started in 1982 as the first nation-wide urban air pollution monitoring programme in Denmark. The programme has been adjusted to the pollution pattern by two revisions. The present phase (LMP III) was started in 1992. This report presents the results from 1997 and updates the trends from the start of the programme in 1982. Measurements are performed at twin sites in the cities of Copenhagen, Odense and Aalborg. One of the sites is at kerb side at a street with heavy traffic and the other is on the roof of a building a couple of hundreds meters from the street site. Two rural sites, one outside Copenhagen and one at Keldsnor in the southern part of the country, are also included. NO, NO,, SO,, total suspended particulate matter (TSP) and elements in the aerosols are measured at the street sites. O, and the meteorological parameters, wind direction, wind speed, temperature, relative humidity and global radiation are measured at the roof sites. Additional measurements of CO at street and NO and NO, at roof sites are now performed continuously in order to improve the knowledge about the NO, NO, and O, problem complex. At the rural site outside Copenhagen the same program is conducted as at the street stations with the inclusion of O<sub>3</sub>. Only NO, NO, and O, are reported from the other rural site.

Limit values

Air quality limit values have been implemented in Denmark for NO<sub>2</sub>, SO<sub>2</sub>, TSP in order to protect human health. All limit values are based on EU limit values, which also include a limit value for Pb. A set of threshold values for O<sub>3</sub> came into force in March 1994. They were laid down with consideration of the protection of both human health and plants. The EU Commission has proposed new limit values. They are expected to be adapted in 1998 or 1999 and will then be valid from 2005 or 2010. The new values shall protect human health and ecosystems. They are based on the present knowledge about the toxicity of the species.

Nitrogen oxides

The measured NO<sub>2</sub> concentrations were about a factor of two lower than the limit value, while they are close to the new values proposed by the EU Commission. The trend for NO<sub>2</sub> since 1982 indicates a weak decrease. The introduction of three way catalytic converters (TWC) on all new petrol driven cars from October 1990 will reduce mainly the NO emission. As a result of this the observed NO concentrations are significantly decreasing. O<sub>3</sub> is at present a limiting factor for the formation of NO<sub>2</sub> at street level and it remains to be seen to what extent the NO<sub>2</sub> concentrations will be reduced at highly polluted places as result of the TWC's.

Ozone

Some of the threshold values for O<sub>3</sub> were frequently exceeded. The average O<sub>3</sub> concentrations are almost the same at all sites. The average levels are, especially during the winter, lowest at winds from south-easterly directions. The peak concentrations were also observed at south-easterly winds. While O<sub>3</sub> is the limiting factor for

formation of NO<sub>2</sub> at street level, NO is the limiting factor at roof level and in background areas.

Sulphur dioxide and TSP

The  $SO_2$  concentrations have been continuously decreasing since 1982. They were in 1997 only about 1/10 of the limit values. They are also far below the new values proposed by the EU commission. The amount of TSP shows a slightly decreasing trend as a result of less windblown dust due to an increased number of fields with "winter crops" and better combustion control. The concentrations of TSP were approximately 1/3 of the limit value. The measured values are not directly comparable with the EU Commissions new proposed limit values, which is based on  $PM_{10}$ . However, the  $PM_{10}$  concentration at the traffic sites exceeds probably the proposed limit values. It is estimated that the  $PM_{10}$  concentrations are roughly 60% of the TSP.

Lead

The lead pollution has been reduced with about a factor of 20 since 1982 as a result of the reduction of the lead content in petrol. All petrol sold in Denmark is now in practice lead free. The development has outdated the limit value, which is more than a factor of 100 higher than the measured concentrations. Also the proposed new limit value is far above the measured concentrations in Denmark.

### 1 Introduction

LMP III

The third Danish Air Quality Monitoring Programme (LMP III) was started in 1992. The programme comprises an urban monitoring network with stations in three Danish cities. The results are used for assessment of the air pollution in urban areas. The programme is carried out in co-operation between the National Environmental Research Institute (NERI), the Danish Environmental Protection Agency, the Greater Copenhagen Air Monitoring Unit and the municipal authorities in the cities of Odense and Aalborg. NERI is responsible for the practical programme in co-operation with the Agency of Environmental Protection for the City of Copenhagen, the Environmental and Food Control Agency, Funen, and the Department for the Environment and Urban Affairs, Aalborg. The results are currently published in quarterly reports in Danish and they are summarised in annual reports in English. Statistical parameters are accessible at the internet at the address www.dmu.dk/ AtmosphericEnvironment/netw.htm.

Previous programme

The programme was revised considerably during 1992 compared to the previous phase (LMP II) (Palmgren, Kemp, Manscher 1992). The installation of the new equipment took place during 1992 and the beginning of 1993. All instruments were updated as planned during 1993 (Kemp 1993) and are now running continuously except for short interruptions due to technical problems.



Figure 1.1 Cities and the background sites in the LMP network

Table 1.1 LMP III stations in 1997. TSP is the total suspended particulate matter collected on a filter and determined by weighing. The station type refers to the classification given in Kemp, 1993. BTX is measurements of benzene, toluene and xylene with a monitor. The meteorological measurements comprise wind direction, wind speed, ambient temperature, relative humidity and global radiation.

		Measuring Programme				
	Station type	½ hour average	24 hour average			
Copenhagen/1257	Main (Traffic)	NO, NO <sub>2</sub> , SO <sub>2</sub> , CO, O <sub>3</sub> , BTX	SO <sub>2</sub> , TSP, Elements			
Copenhagen/1259	Roof (Urban background)	O <sub>3</sub> , meteorology,NO,NO <sub>2</sub>	-			
Odense/9155	Main (Traffic)	NO, NO <sub>2</sub> , SO <sub>2</sub> , CO	SO <sub>2</sub> , TSP, Elements			
Odense/9154	Additional (Traffic)	-	SO <sub>2</sub> , TSP, Elements			
Odense/9159	Roof (Urban background)	O <sub>3</sub> , meteorology, NO,NO <sub>2</sub>	-			
Aalborg/8151	Main (Traffic)	NO, NO <sub>2</sub> , SO <sub>2</sub> , CO	SO <sub>2</sub> , TSP, Elements			
Aalborg/8159	Roof (Urban background)	O <sub>3</sub> , meteorology, NO,NO <sub>2</sub>	-			
Lille Valby/2090	Rural background	NO, NO <sub>2</sub> , SO <sub>2</sub> , O <sub>3</sub>	SO <sub>2</sub> , TSP, Elements			
Keldsnor/9055	Rural background	NO, NO <sub>2</sub> , (O <sub>3</sub> )	-			

### Measurement programme

The measurement programmes at stations in operation during the major part of 1997 are shown in table 1.1. The map (figure 1.1) shows where the sites are located. All sites and measurement methods are described in Kemp, 1993 and NERI, 1998.

### Campaigns

The campaign measurements that have been performed the previous years have been extended to cover the whole year. This has been possible by contribution from the TOV programme for an intensive study of the pollution from traffic (Berkowicz et al. 1996). Beside NO/NO<sub>2</sub> and CO, O<sub>3</sub> and the VOC's benzene, toluene and xylene have been measured at Copenhagen/1257 (table 1.1).

## Annual statistics, trends, phenomenology

The annual statistics and episodes are summarised for all groups of species. The results are compared with Danish limit and guide values and WHO guideline values. At present limit values are set for SO<sub>2</sub>, suspended particulate matter, NO<sub>2</sub> and Pb in Denmark. A set of threshold values for O<sub>3</sub> was introduced in 1994 by the implementation of an EU directive (EEC 1992). The trends since the start of the first LMP programme in 1982 are illustrated using results from Aalborg/8151 and Odense/9154. These are the only stations, which have been in operation since 1982.

New limit values propose by the EU commission

The present Danish limit values are almost identical with the values laid down in the EU directives (EEC, 1982, 1985, 1989, 1992). These values and the principles behind are under revision. The structure will be a framework directive (EC 1996), giving general rules for network design and limit value strategies, and a number of daughter directives for specific pollutants. The limit values will primarily be based on the known health effects of the species. The framework directive has already been adapted. The EU Commission has prepared a proposal for the first daughter directive covering  $NO_2$ , particulate matter  $(PM_{10})$ ,  $SO_2$ , and Pb (EC 1997). It is expected to be adapted late in 1998 or at the beginning of 1999. The proposed limit

values in relation to the measured concentrations are discussed for the single species in the following chapters.

Smog warning

A permanent smog warning system including  $NO_2$ ,  $SO_2$  and  $O_3$  was introduced from the beginning of 1994. For  $NO_2$  and  $SO_2$  warnings will be transmitted, if the concentrations exceed 350  $\mu g/m^3$  for more than three consecutive hours and no immediate decrease is expected. According to the ozone directive (EEC 1992) information will be broadcasted, if the hourly average concentration of  $O_3$  exceeds 180  $\mu g/m^3$ . An alarm will be broadcasted, if the hourly average concentration exceeds 360  $\mu g/m^3$ .

1997 reports

The 1997 results are found in quarterly reports (Danmarks Miljø-undersøgelser 1997a, 1997b, 1998a 1998b). The results obtained during 1997 are summarised in the present report in form of annual statistics and trends. Results for CO and benzene, toluene and xylene, which cover a whole years measurement, has been included. A overview of results from the LMP programmes together with a description of model calculations and an evaluation of the health aspects is found in Palmgren et al., 1997. A description of the Danish air quality monitoring programmes and selected results are shown on the internet (NERI 1998).

Other air quality networks in Denmark

Beside the LMP two other air quality monitoring networks are in operation in Denmark. The Greater Copenhagen Air Monitoring Unit is responsible for a network in the Greater Copenhagen area. A number of pollutants are measures at five sites. The measurements are comparable with the LMP measurements and the two programmes supplement each other in Copenhagen (HLU 1997). A network in rural areas (the Danish Background Monitoring Program) was established in 1978. At present gas and aerosol measurements are performed at six stations while various ions are determined in precipitation collected at 12 sites. The aim is i.a. to study acidification and eutrofication of the forests farmland, Danish sea and freshwater areas (Ellermann et al. 1997).

### 2 Nitrogen oxides

Source

The term  $NO_x$  denotes usually the sum of NO and  $NO_2$ .  $NO_x$  is emitted from combustion processes. The main part of the direct emission consists of NO (more than 90%). The most important sources in Denmark are motor vehicles and power plants. The emitted NO is oxidised in the atmosphere to  $NO_2$  and further to  $HNO_3/NO_3$  (nitrate), or e.g. PAN. If the  $O_3$  concentration is sufficiently high the conversion of NO takes place almost instantaneously, whereas the reaction time for the formation of  $HNO_3/NO_3$  is of the order of several hours. The exact reaction rates depend very much on the actual concentrations, the photochemical activity and the temperature.

Measurements

During 1997 continuous measurements of NO and NO<sub>2</sub> were performed at all stations except Odense/9154. More than 90% of the possible results are valid for all stations except the two in Aalborg, where only about 70% are available (see table 2.1).

### 2.1 Annual statistics

Limit values

The limit value for Denmark is 200  $\mu g/m^3$  for the 98-percentile of hourly average values of  $NO_2$  measured over one year. The guide values are  $135\mu g/m^3$  for the 98-percentile and  $50~\mu g/m^3$  for the median (Miljøministeriet 1987, EEC 1985). At least 75% of the possible measurements have to be available for a valid comparison with the limit and the guide values. The 98-percentiles and the medians of NO and  $NO_2$  since 1988 are found in figure 2.1 and 2.2. The statistical parameters corresponding to the limit and guide values are found in table 2.1 together with the annual averages. The 99.9-percentile represents the seventh or eighth largest value. It may be representative for the peak concentration, with exception of a few extremes.

The limit values were not exceeded in 1997, but the results from Copenhagen exceeded the WHO guide value (40  $\mu$ g/m³) and was close to the Danish guide values for the median.

Proposed new limit values

It is proposed that the new limit values shall be met in January 2010. The values in table 2.1 are for protection of human health. Beside these values the annual average concentration of  $\mathrm{NO+NO_2}$  in rural areas shall be below 30 equivalent  $\mathrm{NO_2}~\mu\mathrm{g/m^3}$  for protection of vegetation. The annual average for protection of health is the only of the proposed limit values, which are exceeded at present. It is expected that the ambient concentrations will decrease in the coming years due to already taken measures, e.g. introduction of TWC.

Increase of NO at Aalborg/8151

The NO concentration was higher in 1997 than the previous years at Aalborg/8151. The reason is probably higher traffic density and queuing on the bridge over Limfjorden in connection with repair work in the tunnel, which ordinarily takes a major part of the traffic

crossing the fjord. No effect is seen on the  $NO_2$  concentrations, because  $O_3$  is the limiting factor.

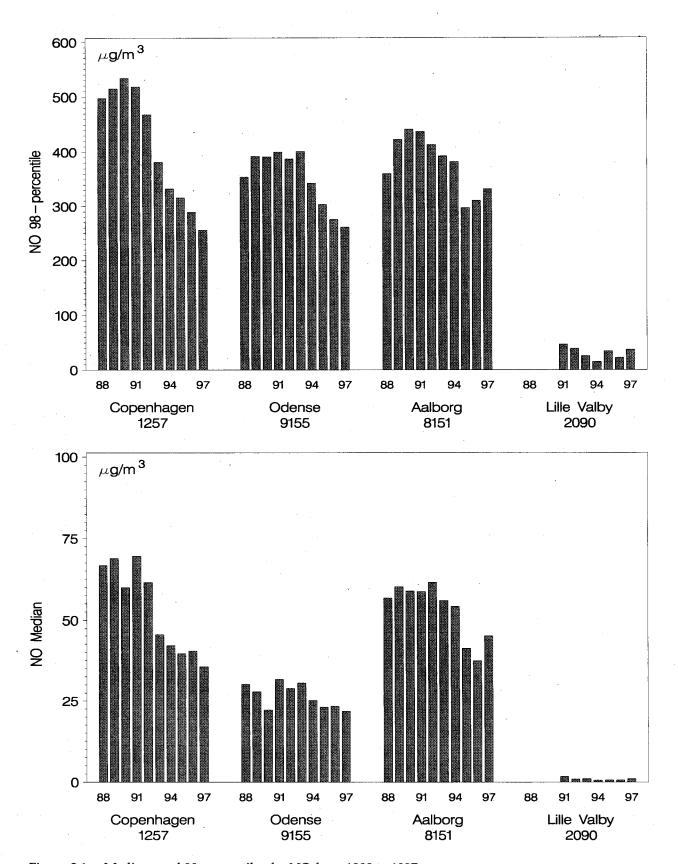


Figure 2.1 Medians and 98-percentiles for NO from 1988 to 1997

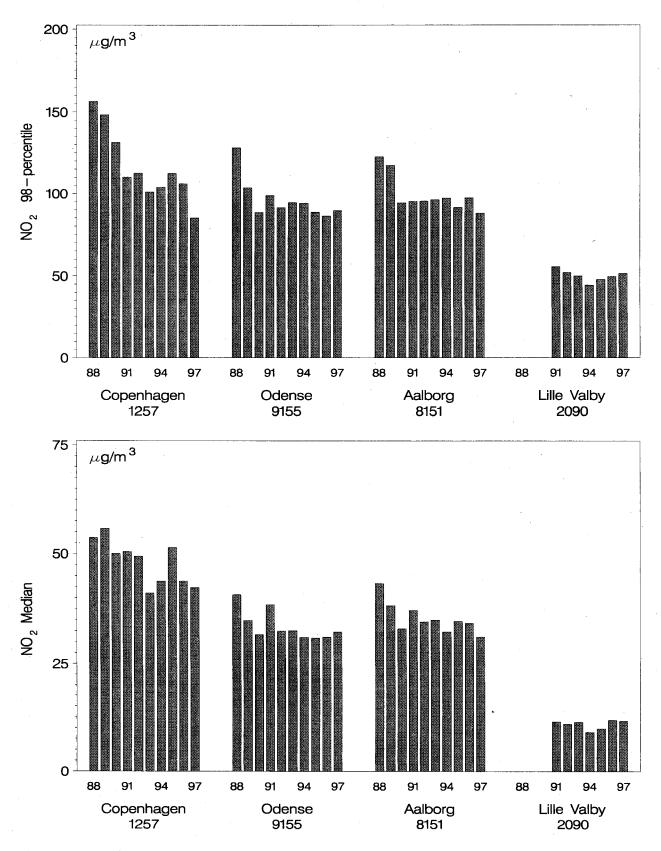


Figure 2.2 Medians and 98-percentiles for NO<sub>2</sub> from 1988 to 1997

Table 2.1 The values are calculated for all measurements from 1997 and based on hourly average values. Values below the detection limit are included as one half of the detection limit (more than half of the NO values from Lille Valby/2090 and Keldsnor/9055 are below the detection limit). Note that Aalborg/8151 and Aalborg/8159 did not yield sufficient results for a valid comparison with the limit and guide values. The number of measurements is listed in the second column. The limit and Danish guide values are found in Miljøministeriet, 1987, the proposed value in EC, 1997 and the WHO guide value is given in WHO (1998).

		NO (μg(NO)/m³)			ΝΟ₂ (μο	NO₂ (μg(NO₂)/m³)				
Station	Num- ber		Ave- rage	Me- dian	98- perc	99.9- perc	Ave- rage	Me- dian	98- perc	99.9 perc
Traffic sites:			·							
Copenhagen/1257	8308	60	35	256	501	43	42	84	123	
Odense/9155	8648	48	23	263	471	36	32	88	134	
Aalborg/8151	6386	78	47	341	596	34	31	85	128	
Urban background:										
Copenhagen/1259	8614	7	2	52	191	28	24	72	97	
Odense/9159	8524	8	<b>, 4</b> ,	56	203	23	20	64	92	
Aalborg/8159	6421	8	3	65	280	19	16	58	111	
Rural:									٠	
Lille Valby/2090	8580	3	(1)	37	182	15	11	51	78	
Keldsnor/9055	8713	2	(1)	13	59	12	8	47	92	
Limit value	>6570	-			-		-	200	-	
Proposed limit value		-	-	-	-	40	-	· -	200	
Guide value (DK)		-	-	-	-	-	50	135	-	
Guide value (WHO)		_	-	-	•	40	-	-	-	

NO vs. NO,

The high concentration of NO compared to NO<sub>2</sub> at traffic stations illustrates that the NO is not a limiting factor for the formation of NO<sub>2</sub> at streets. Under ordinary conditions almost all NO has been oxidised a few hundred meters away at the urban background sites.

Low No in Odense

It has been observed every year that the average and median concentrations for NO at Odense/9155 is relatively low. It is a result of the location of the station on the north-east side of the street, which is perpendicular to the prevailing south-western wind direction. Due to the street canyon effect the station will not be exposed directly to the pollution from the passing traffic during the prevailing south-westerly winds (Kemp, Palmgren, Manscher 1996a).

### 2.2 Episodes

Smog warning

 $NO_2$  is included in the national smog warning system. A warning will be issued if the concentration exceeds 350  $\mu g(NO_2)/m^3$  for more than three consecutive hours, and if an immediate improvement is not expected.

Table 2.2 shows the highest values measured at the four stations. NO is included for comparison. The values are calculated according to

the provisions in the warning system. Neither the WHO guide line value nor the warning limit were exceeded in 1997.

The highest concentrations of NO are usually seen in the winter month at all stations, however local road or building construction may influence the maximum values. The peak concentrations of NO<sub>2</sub> are most frequent in spring or summer due to the higher background values of O<sub>3</sub>.

Long range transport episode

In January a long range transport episode brought air with high concentrations of  $NO_x$  from South to Denmark. Increased levels were observed at all stations. The episode is illustrated in Figure 2.3 for the urban station Odense/9155 and the two rural stations. Lille Valby/2090 and Keldsnor/9055. Almost all  $O_3$  was depleted before the air mass crossed the border. This limits the formation of more  $NO_2$  by the reaction  $NO+O_3$  and the only additional contribution is the directly emitted  $NO_2$  from e.g. traffic and power plants. It is seen that the  $O_3$  is close to zero during the episode and  $NO_2$  concentrations are almost at the same level at all stations.

Table 2.2 Maximum concentrations of NO (not included in the smog warning system) and  $NO_2$  in 1997. For comparison with the warning limit the lowest 1 hour values are identified for every consecutive three hours. (The warning criteria: that the concentration should exceed 350  $\mu g/m^3$  for consecutive three hour is the same as that the lowest hourly value within the three hour period exceeds 350  $\mu g/m^3$ ). The highest of these values during the whole year are listed under "max. 3 hour". The values under "max. hour" are the absolute one hour maximum values. The indication of time is the beginning of the periods.

	NO							
	Max. 3 hour (µg(NO)/m³)	Day hour	Max. hour (μg(NO)/m³)	Day hour				
Traffic sites:				1974				
Copenhagen/1257	489	971124: 6	708	971124: 7				
Odense/9155	527	970110: 8	692	970110: 8				
Aalborg/8151	585	970108:14	729	970108:15				
Urban background:								
Copenhagen/1259	191	971202: 8	310	970106:19				
Odense/9159	166	970925: 6	258	970110: 8				
Aalborg/8159	259	971202: 8	559	971202: 9				
Rural:								
Lille Valby/2090	236	970110:19	312	971124: 9				
Keldsnor/9055	70	970116:21	75	970116:23				
Warning limit	-	-	<u>.</u>	_				

		NO	D <sub>2</sub>	
,	Max. 3 hour	Day hour	Max. hour	Day hour
	(µg(NO <sub>2</sub> )/m³)		(µg(NO <sub>2</sub> )/m³)	
Traffic sites:			•	
Copenhagen/1257	124	970814:19	140	970814:19
Odense/9155	134	970814:13	146	970814:16
Aalborg/8151	125	970820: 7	137	970820: 7
Urban background:				
Copenhagen/1259	95	970117: 6	128	970814:21
Odense/9159	92	970115:15	126	970814: 8
Aalborg/8159	99	970321: 6	130	971104: 2
Rural:				
Lille Valby/2090	85	970117: 5	89	970117: 5
Keldsnor/9055	94	970116:17	99	970116:18
Warning limit	350	-	-	-
Guide value(WHO 1998)	-	-	200	

### 2.3 Trends

Percentiles

The annual percentiles and average values for NO and NO<sub>2</sub> measured at Aalborg/8151 are shown in figure 2.4. The level of NO was almost constant in the period from 1982 to 1991, but decreased during the following years synchronously with the increasing number of cars with TWC. The level seems however to be stabilised in 1996 and 1997, which may be surprising since still more cars have TWC. It is probably a result of local changes in the traffic near the site (see section 2.1). The same pattern is not observed at the other stations (cf. figure 2.1).

The NO<sub>2</sub> level may have be been slightly decreasing, but the change is not significant and almost obscured by the meteorological variations from year to year.

The skewness of the distributions is obviously much greater for NO than for NO<sub>2</sub>. The ratios between the 98-percentile and the median are approximately 7 for NO, whereas they are only 2-3 for NO<sub>2</sub>. This indicates that at least at high NO concentrations the NO<sub>2</sub> formation is limited – probably by the O<sub>3</sub> concentrations.

Averages

The trend of the monthly average values and the annual variation are shown in figure 2.5. The variation for NO and NO<sub>2</sub> seems to be (to some extent) opposite in the sense that years with high NO concentrations correspond to years with low NO<sub>2</sub> concentrations and vice versa. There is a distinct annual variation for NO with low concentrations during the summer, when the emissions are lower and the oxidation rate is higher. The variation is much less pronounced for NO<sub>2</sub>.

Copenhagen vs. other cities

Figure 2.1 indicate that the NO concentrations have been decreasing more in Copenhagen than in the two smaller cities Odense and Aalborg. The reason for this is not obvious, but it may be caused by a reduction of the urban background levels, which are higher in Copenhagen than in the two other cities.

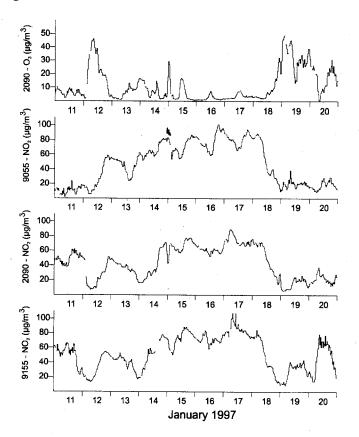


Figure 2.3 The January  $NO_2$  episode recorded at Odense/9155, Lille Valby/2090 and Keldsnor/9055.  $O_3$  measured at Lille Valby/2090 is shown for comparison.

General explanation to the figures: 2.4, 4.4 and 5.2

- The bars represent annual percentiles measured at Aalborg 8151.
- The bar sections are from the top defined by the 98-, 95-, 75-, 25- and 5-percentiles.
- The horizontal line in the middle section is the median and the bottom represents the minimum value.
- The interconnected points are the average values.
- The area of each bar-section is proportional to the number of measurements between the two percentiles defining the section. A skew frequency distribution results in a "Humpty-Dumpty" shape of the bars.

General explanation to the figures: 2.5, 4.5-6, 5.3 and 6.2

- The crosses joined by the full drawn line are the measured monthly average values.
- The dotted curve represents a moving average over 12 month. The straight line is the linear regression, considering the auto-correlation between the monthly values indicating the long term trend

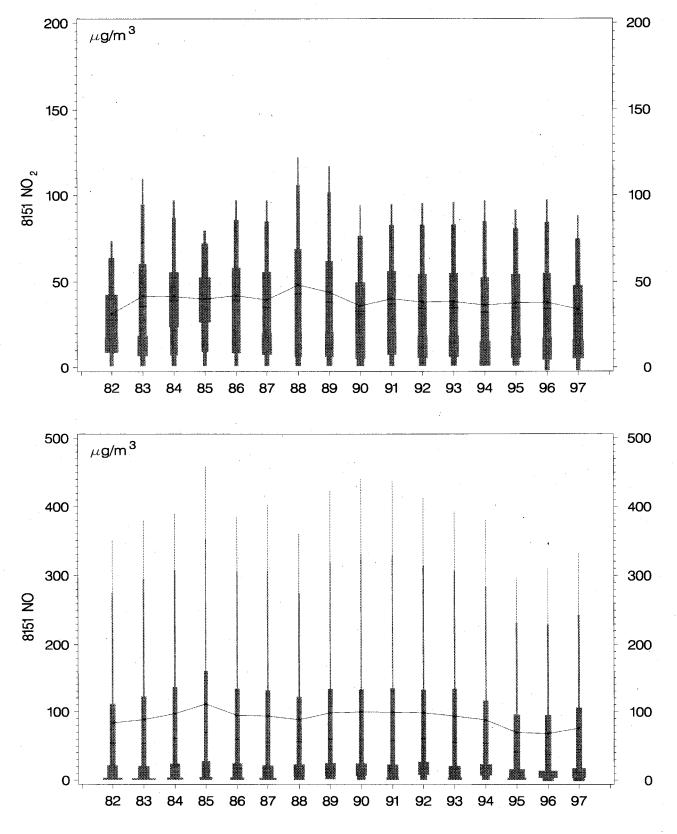


Figure 2.4 Trends for annual 98-, 95-, 75-, 50-, 25- and 5-percentiles, average and minimum value based on hourly average concentrations of  $NO_2$  and NO measured at Aalborg/8151. (See explanation on p. 16).

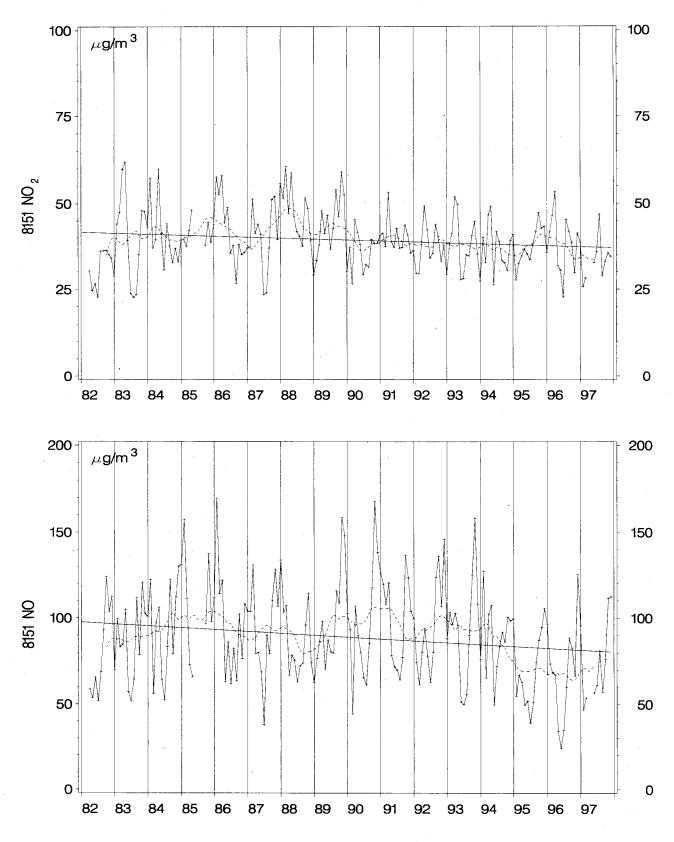


Figure 2.5 Trend for NO and NO<sub>2</sub> measured at Aalborg/8151. The points are measured monthly averages, the dotted curve is a moving average over 12 month and the straight line is a linear regression line. (see explanation p. 16).

### 3 Ozone

Measurements in 1997

Measurement of O<sub>3</sub> was started mid 1991 at the rural station (Lille Valby/2090). At the end of 1992 the urban background stations (Kemp 1993) were equipped with monitors. The measurements started at Odense/9159 in August 1992 and at Aalborg/8159 in December 1992. At Copenhagen/1259 continuous measurements started in February 1993 with a DOAS instrument and a monitor was installed in April 1993. The O<sub>3</sub> measurements at Keldsnor/9055 began in January 1995 (see table 1.1). Further O<sub>3</sub> measurements were performed from April 1994 at the street station Copenhagen/1257 in connection with the TOV programme (Berkowicz et al. 1996). Almost complete series of results are available from all stations except Keldsnor/9055. Due to technical problems with a monitor it has been necessary to discard 10 month of measurements from Keldsnor/9055.

Sources and formation

The  $O_3$  in the lower troposphere is formed as a secondary pollutant mainly by photochemical reactions involving i.a. volatile organic compounds (VOC) and NO<sub>2</sub>. An important parameter for the reaction velocity is the ambient temperature. The VOC may either be of anthropogenic or natural origin. Oxidation of NO is the main reaction for the reduction of  $O_3$  in urban areas. The climatic conditions and the emission patterns in Denmark result in a net decomposition in urban areas due to the high NO emissions from combustion processes, whereas the presence of  $O_3$  in background areas, especially during the summer, exceeds the levels of reducing compounds.

### 3.1 Annual statistics

Threshold values

The EEC directive on air pollution by  $O_3$  (EEC 1992) is implemented in Denmark through a governmental regulation (Miljøministeriet, 1994). It obligates the member states i.a. to perform measurements of  $O_3$  at localities where the threshold values given in the directive are likely to be exceeded, and where it is possible that human individuals or vegetation are exposed to  $O_3$  pollution.

Concentrations depending on site type

The levels at the rural and the urban background stations are almost the same. The concentrations in street level are, as could be expected considerably lower. This confirms that the  $\mathrm{NO}_{\mathrm{x}}$  concentrations in general are lower than the  $\mathrm{O}_{\mathrm{3}}$  concentrations away from the busy streets. There will only be NO enough to remove a significant part of the  $\mathrm{O}_{\mathrm{3}}$  close to trafficked streets.

Exceedings

The measured values are compared to the threshold values in table 3.1. In August the meteorological conditions were favourable for O<sub>3</sub> formation and transport. The temperature was relatively high and the air was in periods coming from Central Europe. Otherwise there were only few occasions with high concentrations. The values in 1997, were generally slightly lower than the corresponding 1996 value. The max. 24 hour and the max. 8 hour threshold values were exceeded on many occasions in 1997 at all stations. There were

several exceedances as early as February and they continued up to and including August. It is always the 24 hour threshold that is exceeded in the winter. The threshold at 65  $\mu$ g/m³ is very close to the background of the northern hemisphere. As shown previously (Kemp; Palmgren and Manscher, 1996a) the O<sub>3</sub> concentrations always reach this level at wind speeds above 10 m/s.

Table 3.1 Annual average values, percentiles and maximum values for  $O_3$  measured in 1997 compared with threshold values. (Miljøministeriet 1994, EEC 1992). The eight hour values are calculated in accordance with the EEC directive, as a non-overlapping moving average; they are calculated four times a day from the eight hourly values between 0 and 9, 8 and 17, 16 and 1, 12 and 21. (The results from Keldsnor/9055 are missing due to monitor problems).

Ο <sub>3</sub> (μg/m³)	Average	Median (hour)	98-perc. (hour)	99.9- perc. (hour)	max. 24 hours	max. 8 hours	max. 1 hour
Urban Background:					· <u>·</u>	<u> </u>	
Copenhagen/1259	43	44	95	149	95	146	164
Odense/9159	48	48	105	140	108	138	150
Aalborg/8159	49	53	90	117	84	112	124
Rural:							
Lille Valby/2090	47	49	101	155	104	155	182
Keldsnor/9055	-	-	-	-	-	-	-
Traffic:							
Copenhagen/1257	26	23	66	122	68	110	149
Threshold value	÷ .	-	-		65	110	200
Average number of exceedances per station (excl. Copenhagen/1257)	-	-	-		84	12	0

AOT40

UN-ECE uses the concept of critical levels to assess the effects of  $O_3$  to agricultural crops and ecosystems (UN-ECE 1996). The effect parameter is calculated as the accumulated  $O_3$  exposure above a threshold values of 40 ppb ( $\approx 80~\mu g/m^3$ ), the so-called AOT40. The excess is expressed as the number of ppb·h above 40 ppb. The guideline for crops is based on an integration over all daylight hours during May-June, while the guideline for forest is based on the whole period April-September

The results for the two background stations Lille Valby/2090 and Keldsnor/9055 show that the measured values were close to the guide values and that they may vary considerably from year to year and within the country (Table 3.2).

### 3.2 Episodes

Threshold values

The EEC directive makes it mandatory to inform the population, if the hourly average concentration of the  $O_3$  exceeds  $180 \,\mu\text{g/m}^3$  and to issue a warning, if the hourly average concentration exceeds  $360 \,\mu\text{g/m}^3$ . The information or warning shall include the following information:

 Date, hour and place of the occurrence of concentrations in excess of the above mentioned threshold values.

- Reference to the type(s) of community values exceeded (information or warning).
- Forecasts of the change of concentrations, geographical area concerned and the duration.
- Population concerned.
- Precautions to be taken by the population concerned.

Table 3.2 AOT40 values (UN-ECE 1996). Unit ppb·h

		The second secon	
Station	1995	1996	1997
AOT40 (crops)			
Lille Valby/2090	4700	1513	2848
Keldsnor/9055	2850	2540	•
Guide v. UN-ECE		3000	·
AOT40 (forest)			
Lille Valby/2090	8850	5510	10332
Keldsnor/9055	6800	8020	. ·
Guide v. UN-ECE		10000	

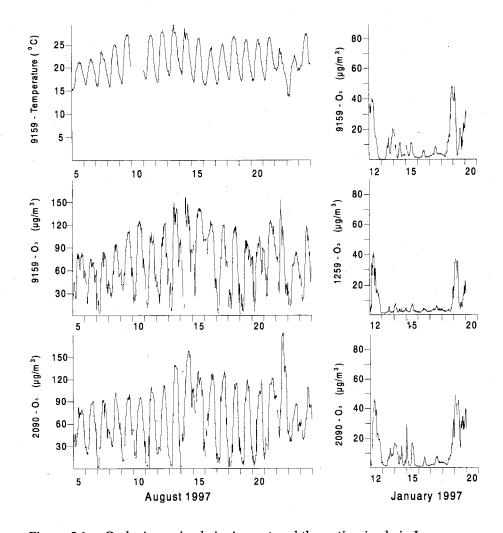


Figure 3.1  $O_3$  during episode in August and the anti-episode in January.

Press releases

At August 22, 1997 the hourly  $O_3$  concentration exceeded slightly 180  $\mu g/m^3$  at Lille Valby/2090. However, no press release was sent out because the raw (before final QA/QC) concentration was measured to only 179  $\mu g/m^3$ . The opposite situation occurred in 1996, where information was given based on a raw value above 180  $\mu g/m^3$ . The concentrations in 1997 were at several occasions above 150  $\mu g/m^3$ . But, as mentioned above, the concentration did not exceed 180  $\mu g/m^3$  during either of these periods. This illustrates that 180  $\mu g/m^3$  is about the highest concentration that is reached in Denmark.

Episode in August, anti-episode in January

The results from Lille Valby/2090 and Odense/9159 during the episode in August are shown in figure 3.1. The episodes had the typical meteorological behaviour with a day to day increase in temperature and a more and more stable air transport from south. Quite the opposite situation occurred in January. Polluted air was transported from south-western Europe. All O<sub>3</sub> was removed from the air by i.e. NO<sub>x</sub> and no new O<sub>3</sub> could be created under the winter conditions.

Wind direction distribution

There is a strong wind direction dependency of the frequency of the high concentrations. Figure 3.2 shows the frequency of ½-hourly concentrations above the 98-percentile relative to the total number of events in each 20° wind sector. In most cases concentrations above the 98-percentile were found at winds between east and south, but they may occur in all wind sectors. The pattern in Copenhagen is somewhat different. When the wind is from south-east the air has to pass the centre of the city before it reaches the measuring station which will reduce the O<sub>3</sub> concentrations.

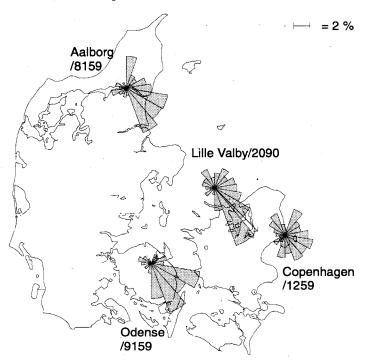
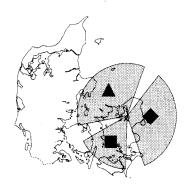


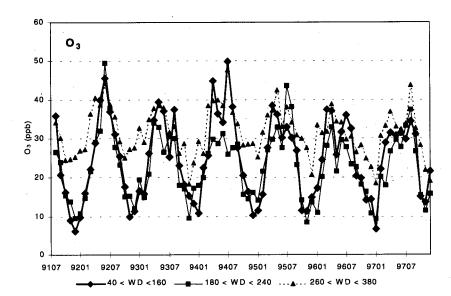
Figure 3.2 Distribution with wind direction of the upper 2% of the  $O_3$  concentrations (above the 98-percentile). The radii of the circle sections are proportional to the ratio between the number of measurements above the 98-percentile in the corresponding wind sector and the total number of measurements in the sector.

### 3.3 Trend

Trend for O, and O,

More than six years of data are now available from Lille Valby/2090. The development is illustrated by means of the monthly average values in figure 3.3. The results are divided according to wind direction sectors. The sector from 40 to  $160^{\circ}$  represent the continental contribution with an addition of some regional contribution from the Copenhagen area, the sector from 180 to  $240^{\circ}$  represents the western part of Continental Europe, while the background contribution is assumed to be found in the sector from 260 to  $20^{\circ}$ . No significant trend is observed in the period, but the seasonal variation is a factor of 1.5 to 3.





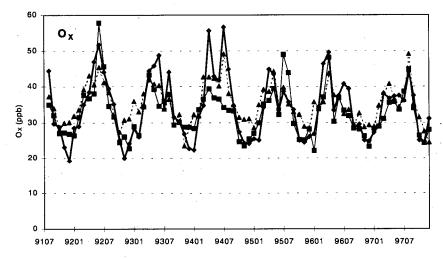


Figure 3.3 Monthly average values measured at Lille Valby/2090 for  $O_3$  and  $O_x$  ( $O_3$ +N $O_2$ ). The wind sectors for the single curves are shown on the map. The signatures on the map correspond to the points on the curves.

The relatively low winter concentrations in the background sector illustrate the lower  $O_3$  production in the dark winter periods. The yearly variation is enhanced in the sectors with anthropogenic pollution by the lower conversion rate of the anthropogenic precursors to  $O_3$ , i.e. nitrogen oxides and VOC's during the winter.  $O_x$  (=  $O_3$  +  $NO_2$ ) is, as shown by other examples in the previous annual

reports (Kemp, Palmgren, Manscher 1997), remarkably alike for all three sectors. Both the absolute concentrations and the seasonal variation for the sectors with anthropogenic contribution were close to the  $\rm O_3$  background.

### 4 Sulphur compounds

Sources

Sulphur is determined in gas phase as SO<sub>2</sub> and as the elemental content in particulate matter. The main source of SO<sub>2</sub> is combustion of heavy oil and coal. Sulphur in particulate matter is expected to be sulphate (either HSO<sub>4</sub> or SO<sub>4</sub><sup>2</sup>). The two main sources of the sulphate are the oxidation of SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub> and sulphate directly emitted from the sea. Sea spray will only contribute significantly to the sulphate at the stations in the Danish Air Quality Monitoring Programme during strong wind from west and north-west. The oxidation time for SO<sub>2</sub> in the atmosphere is of the order of one day meaning that the collected particulate sulphur to a large extent has been emitted from sources several hundred km from the stations, while the SO<sub>2</sub> may be of local origin as well as long range transported.

Measurements

In 1997 the concentration of SO<sub>2</sub> was determined as ½-hour average values at the three main stations (Copenhagen/1257, Odense/9155 and Aalborg/8151) and the background station (Lille Valby/2090). SO<sub>2</sub> and particulate sulphur were determined as 24-hour values at the same stations and at the additional station Odense/9154.

### 4.1 Annual statistics

Limit values

The limit values for SO<sub>2</sub> concentrations are listed in table 4.1 together with the measured concentrations in Denmark (Miljøministeriet 1986). The set of limit values is a simplified, but more stringent, version of those laid down by EEC (EEC 1980, 1989). The medians and 98 percentiles are shown in figure 4.1. At all stations the measured values were well below the limit and guide values. The winter concentrations were somewhat higher than the values for the whole year.

Table 4.1 SO<sub>2</sub> and particulate sulphur pollution in Danish cities. The values are calculated for all valid 24 hour results from 1997. The winter is defined as the three first and three last months of the year. The number of measurements for SO<sub>2</sub> is given for the whole year/as well as for the winter.

Station				SO2				Parti	culate S
		(µg(SO <sub>2</sub> )/m³)							
	Number	Median year	Median winter	max. 3 days	98-perc.	max. day	Average	Numbe	r Average
Copenhagen/1257	350/179	3.6	4.1	20	18	27	4.6	350	1.18
Odense/9155	363/182	1.7	1.8	17	12	27	2.6	363	1.25
Odense/9154	361/179	1.6	1.7	17	14	26	2.5	362	1.24
Aalborg/8151	348/173	1.8	1.9	5	13	21	2.7	348	1.15
Lille Valby/2090	351/175	1.0	1.2	4.0	10.9	12	1.5	357	0.94
Limit value	-	80	130	250	250	-	-	<u>-</u>	-
Guide - (EEC 1980)	· •		-	-		-	40-60	-	-
Guide - (WHO 1998)	-	-	=	-	-	125	50	-	-

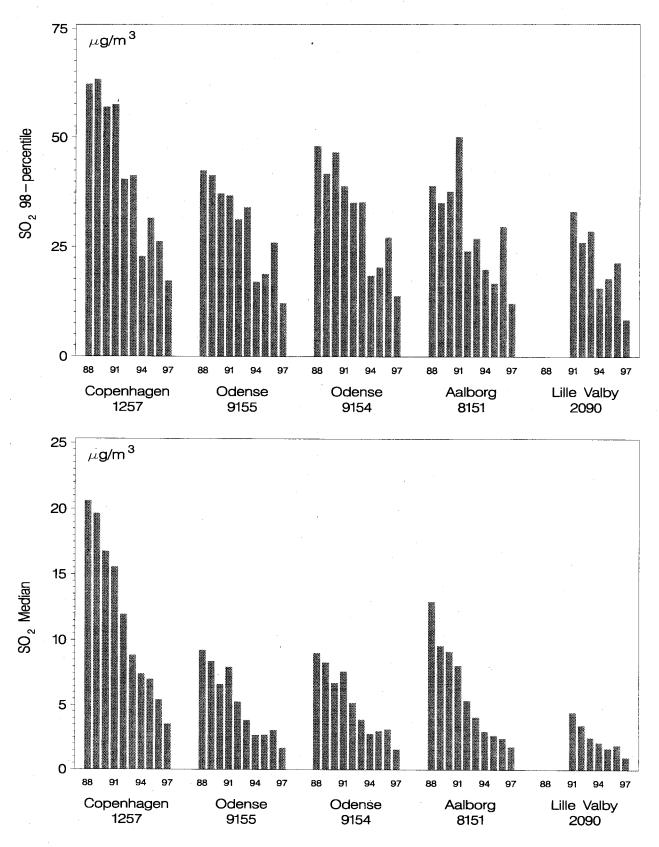


Figure 4.1 Medians and 98-percentiles for SO<sub>2</sub> from 1988 to 1997.

Proposed new limit values

The EU commissions proposal for new limit values for SO<sub>2</sub> are found in table 4.2 together with the measurement results. The limit values shall be met January 1, 2005. All measured values are far below the proposed values.

Table 4.2 Limit values proposed by the EU commission and the corresponding measured results from 1997. The 98 percentile and the daily limit value are for protection of human health, while the yearly and winter averages are for protection of ecosystems.

SO₂ µg/m³	98-percent. hour	Max. day	Yearly average	Winter average
Copenhagen/1257	25	27	4.6	5.4
Odense/9155	20	27	2.6	3.1
Odense/9154	<u>-</u> ,	26	2.5	3.0
Aalborg/8151	18	21	2.7	2.6
Lille Valby/2090	15	12	1.5	1.9
Proposed limit value	350	125	20	20

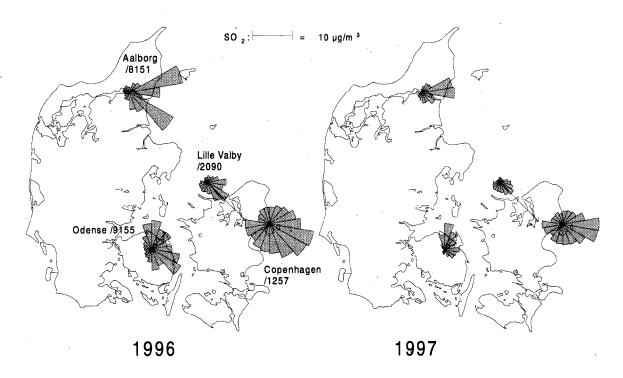


Figure 4.2 Wind direction distributions for SO, in 1996 and 1997.

Drastic decrease in sulphur in 1997

The measured values were considerably lower in 1997 than in 1996. The difference is mainly due to a much smaller contribution from eastern Europe. This is illustrated on figure 4.2, which shows that the average concentrations when the wind is coming from south-east were reduced by a factor of 5 from 1996 to 1997, while the contributions from other wind directions were almost the same. The effect is observed for both  $SO_2$  and particulate S. Whether it is due to change in emission pattern or meteorological conditions is not clear. The concentration of particulate S was only about  $3 \, \mu g/m^3$  during the august episode, while concentrations up 7-10  $\, \mu g/m^3$  have been observed the previous years under similar conditions.

### 4.2 Episodes

### Smog warning

A smog warning system for  $NO_2$ ,  $SO_2$  and  $O_3$  was implemented in Denmark in April 1994. A warning will be issued for  $SO_2$ , if the concentration exceeds 350  $\mu g(SO_2)/m^3$  for more than three consecutive hours and an immediate improvement is not expected.

### *Episode types*

The SO<sub>2</sub> episodes may occur during one of three different types of meteorological conditions:

- Long range transport: A stable transport from directions between east and south may be established, i.e. often in connection with a warm front passage.
- Inversion: An inversion layer may prevent the dispersion of the local emitted pollution.
- Hot-spot: Local eddies may bring down the plume from a high stack to a spot within a few km from the stack. The plume will under ordinary conditions be transported much farther.

#### Measured maxima

Table 4.3 shows the highest concentrations, calculated according to the provisions in the warning system, at the three main stations and the background station. The  $SO_2$  concentrations were far below the warning limit at 350  $\mu$ g/m³. The highest concentrations of particulate S were found New Year's day at all urban sites. This is of cause a result of the traditional new year fireworks. The effect was enhanced by calm wind conditions. The incident is discussed further in chapter 6.

Table 4.3 Maximum concentrations of  $SO_2$ . For comparison with the warning limit the lowest 1 hour values are identified for every consecutive three hours. (The warning criteria that the concentration should exceed 350  $\mu$ g/m³ for consecutive three hour is the same as the lowest hourly value within the three hour period exceeds 350  $\mu$ g/m³). The highest of these values during the whole year are listed under "max. 3 hour". The values under "max. hour" are the absolute one hour maximum values. The time is the beginning of the periods. The number of hot spot episodes are given in the sixth column.

			s	$D_{\!\scriptscriptstyle 2}$		Parti	culate S
				(µg	(S)/m³)		
Station	Max. 3 hour	Day hour	Max hour	Day hour	"Hot-spot" episodes	Max. day	Day
Copenhagen/1257	50	970820:11	113	970808:14	10	6.3	970101
Odense/9155	53	971220:3	110	970710:9	5	11.2	970101
Odense/9154	-	_	- ,	· •	-	14.3	970101
Aalborg/8151	82	970927:11	147	970927:13	8	13.7	970101
Lille Valby/2090	29	971219:3	47	970126:13	0	3.9	970326
Warning limit	350		-		-	-	

### Long range episode

The only major episode in 1997 occurred in August. The episode is also observed in O<sub>3</sub> (cf. figure 3.1). Hot polluted air was driven from central and eastern Europe to Denmark. Figure 4.3 shows that there is a close similarity between the particulate S, which may be regarded

as indicator for long range transport, and the daily hourly maxima for  $O_3$  corrected for the hemispheric or "natural" background (cf. chapter 3).

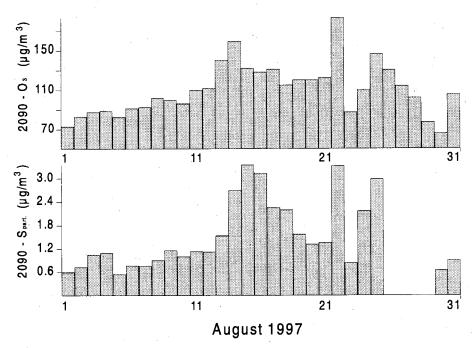


Figure 4.3 Daily maxima for  $O_3$  and daily averages for particulate S measured at Lille Valby/2090. Note that the scale for  $O_3$  is shifted 50  $\mu g/m^3$  corresponding to the hemispheric background.

Hot-spot episodes

Hot-spot episodes are observed at irregular intervals in all three cities. We define hot-spot episodes as a more than  $50 \,\mu\text{g/m}^3$  increase and decrease of the  $SO_2$  concentration within a period of less than 8 hours. The number of observed episodes are listed in table 4.3. The number of hot-spot episodes was somewhat lower in 1997 than in 1996. As in the previous years the hot-spot episodes in Odense were most frequent at northerly winds, pointing at the power plant north of Odense as the most likely source. In Aalborg the hot-spots occurred mainly when the wind was from north-east, indicating that the cement plant was the most likely source. No single source could be identified as the main contributor in Copenhagen.

#### 4.3 Trends

*Percentiles for SO,* 

The annual percentiles and average values based on daily average SO<sub>2</sub> concentrations measured at Aalborg/8151 are shown in figure 4.4. The level of SO<sub>2</sub> has been decreasing since 1982. The reduction is most evident for the "long term" values (median and average values), which are determined by the contributions from a number of local sources, while the long range transport episodes contribute very much to the 95- and 98-percentile. After a couple of years with stagnation or even increase of the short term parameters the values for 1997 were drastically reduced. The results for all parameters were the lowest ever recorded.

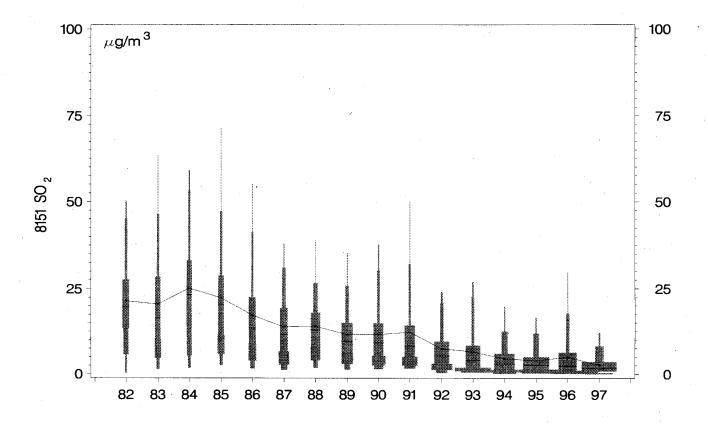


Figure 4.4 Trends for annual 98-, 95-, 75-, 50-, 25- and 5-percentiles, average and minimum value based on hourly average concentrations of SO<sub>2</sub> measured at Aalborg/8151. (See explanation on p. 16).

Avarage SO<sub>2</sub> and S concentrations

The trends for the monthly average values at Aalborg/8151 and Odense/9154 are shown in figure 4.5 for SO<sub>2</sub> and in figure 4.6 for particulate sulphur. The average SO<sub>2</sub> concentrations have been reduced with almost a factor of five, since it peaked around 1984. The steep decrease in 1985-86 was caused by a compulsory reduction of the sulphur content in fossil fuel from January 1986. Better combustion control and increased use of natural gas for domestic and district heating and introduction of lighter diesel oil are the main reasons.

Average SO<sub>2</sub> and S concentrations

Up to 1996 particulate S has, in contrast to SO<sub>2</sub>, shown only a slightly downward trend. This is probably because the sulphur emission has been reduced more in Denmark than in our neighbouring countries. The amount of particulate S may also be limited by the amount of compounds in the atmosphere that are able to oxidate SO<sub>2</sub>. From 1996 to 1997 the concentrations of particulate S were reduced with more than 30 %. This is, as for SO<sub>2</sub>, mainly caused by a reduction of the contribution from south-east (cf. figure 4.2). It will be interesting to follow the development the following years to see to what extent the decrease in concentrations is a result of reduced sulphur emissions.

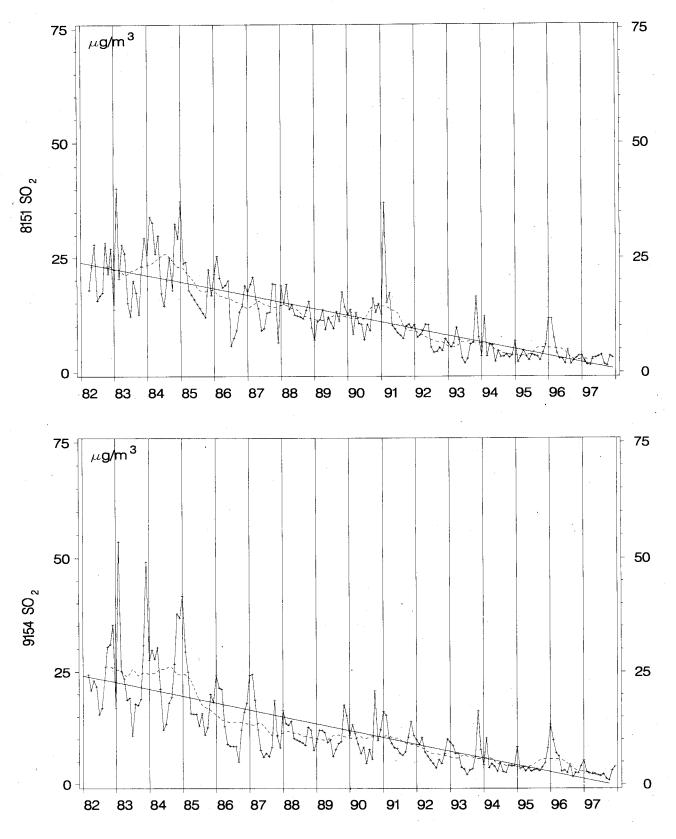


Figure 4.5 Trend for  $SO_2$  measured at Aalborg/8151 and Odense/9154. The points are measured monthly averages, the dotted curve is a moving average over 12 month and the straight line is a linear regression line (see explanation on p. 16).

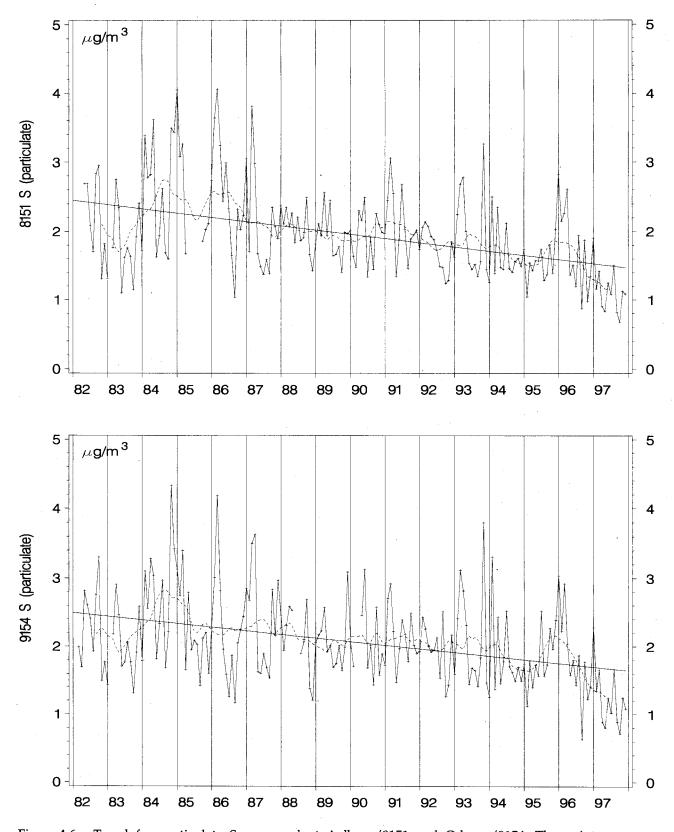


Figure 4.6 Trend for particulate S measured at Aalborg/8151 and Odense/9154. The points are measured monthly averages, the dotted curve is a moving average over 12 month and the straight line is a linear regression line (see explanation on p. 16).

### 5 Total suspended particulate matter

Particle size

The total suspended particulate matter (TSP) is determined by weighing of the aerosol filters. The samplers collect particles up to an aerodynamical diameter of around 25  $\mu$ m, but this cut-off varies from about 10 to 50  $\mu$ m depending on the wind speed (Kemp 1993).

Sources

The particles are a mixture from the different source types, but the coarse particles (> 2  $\mu$ m) of windblown dust of local origin are expected to dominate. The fine particle fraction include contributions of long range transported soil dust and particles from combustion processes.

Sites

TSP was in 1997 measured as 24 hour average values at Copenhagen/1257, Odense/9155, Odense/9154, Aalborg/8151 and Lille Valby/2090. The measurements at Lille Valby started in the beginning of 1995.

### 5.1 Annual statistics

Limit values

The limit values in force in Denmark (Miljøministeriet 1986) are based on EEC directive (EEC 1980). The limit values and the relevant statistical parameters for 1997 are given in table 5.1. The annual 95-percentiles and average values are shown for 1988-1997 in figure 5.1, see next page.

Table 5.1 Average values, 95-percentiles and maximum values for TSP in 1997. The numbers are calculated for 24 hour average values.

		TSP (μg/m³)							
Station	Number	Average - whole year	95-perc.	Max. value	Day				
Copenhagen/1257	350	. 47	86	140	970216				
Odense/9155	363	61	127	316	971027				
Odense/9154	362	45	82	154	970101				
Aalborg/8151	348	54	100	148	970101				
Lille Valby/2090	354	26	52	72	971106				
Limit value	min. 100	150	300	<u>-</u>					

Measured values

The measured values at the urban stations were between 1/4 and 1/2 of the limit values. The 1997 results were somewhat lower than in 1996. The reason may, as for the sulphur components, be a reduced long range contribution. The general trend has been slightly decreasing since 1988 (figure 5.1, next page) and there is no reason to believe that it will change much within the coming years. A major part of the collected particles are windblown dust and may be considered to be either of "natural" origin or resuspended particles from the roads. The particles from combustion processes are in the fine particle fraction, and it is expected to decrease in the future due

to reduction of the emission as a result of i.e. better cleaning of the smoke from power plants, obligatory TWC on petrol cars and restrictions on the diesel exhaust.

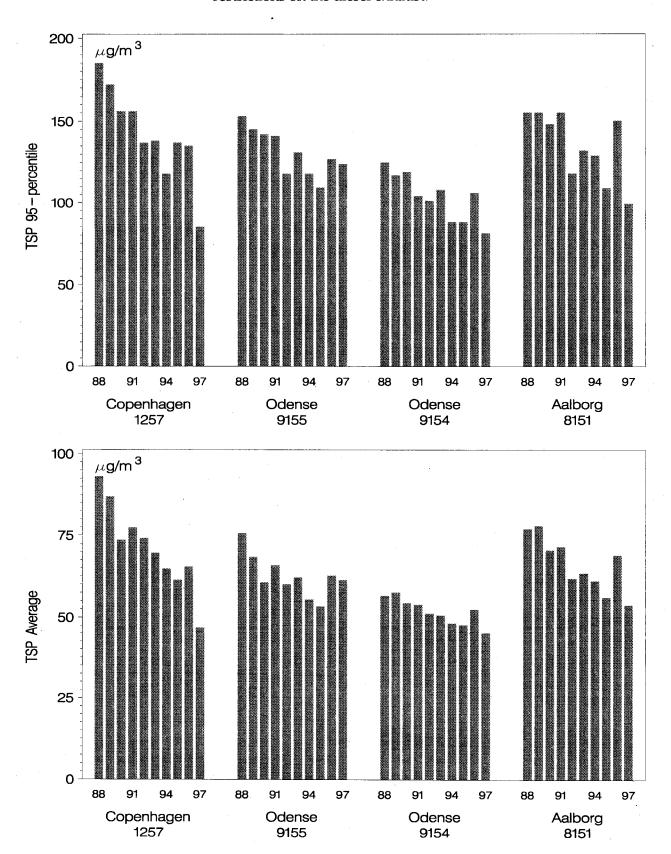


Figure 5.1 Average values and 95-percentiles for TSP from 1988 to 1997.

TSP has been measured at the rural station Lille Valby/2090 for almost 2 years. The results are between on third and one half of the results from the urban street stations.

#### Proposed new limit values

The EU Commissions proposal for new limit values are based on  $PM_{10}$ , i.e. particles having an aerodynamical diameter <10 µm. The values shall be implemented in two stages (see table 5.2). These values are not directly comparable with the LMP results, which are based on TSP. It may however be estimated that the  $PM_{10}$  values are about 60% of the measured TSP concentrations. Having that in mind it seems like the concentrations at the traffic sites are somewhat higher than the proposed values.

Table 5.2 Limit values for  $PM_{10}$  proposed by the EU commission (EC, 1997). All values are for protection of human health

		Averaging	Limit value	Date by which limit value is to be met
Stage 1	24 hour limit value	24 hours	50 μg/m³ not to be exceeded more than 25 times per year (93 percentile)	January 1, 2005
	Annual Limit value	calendar year	30 μg/m³	January 1, 2005
Stage 2	24 hour limit value	24 hours	50 µg/m³ not to be exceeded more than 7 times per year (98 percentile)	January 1, 2010
	Annual Limit value	calendar year	20 μg/m³	January 1, 2010

### 5.2 Episodes

The measured maxima of the daily average values are given in table 5.1, on page 33. There were no pronounced episodes in 1997. The concentrations during the August episode, which is discussed for O<sub>3</sub> and S in chapters 3 and 4, were only slightly higher than the average values. The highest values represent single incidents at the single stations. New Years day high values were recorded at all urban stations.

#### 5.3 Trends

Percentiles

The annual percentiles and average values based on daily average TSP concentrations measured at Aalborg/8151 are shown in figure 5.2. The level of TSP seems to be slightly decreasing since 1986. The ratio between the "short term" values (95- and 98-percentiles) and the "long term" values (median and average) are almost constant in contrast to the case for SO<sub>2</sub> where the decrease was steeper for the long term than for the short term values.

Annual average

After relatively high concentrations from 1984-1986 there has been a continuous decrease since 1986 (figure 5.3, page 37). This may be a result of better emission control at power plants and other large combustion installations and the substitution of oil with natural gas for domestic heating. Other factors like the obligatory demand for "winter crops" from 1987 may, as discussed in the annual report for 1993 (Kemp, Palmgren, Manscher 1994), also play an important role.

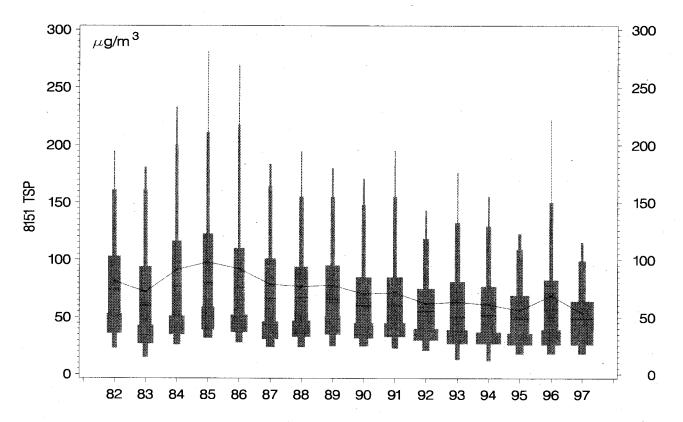


Figure 5.2 Trends for annual 98-, 95-, 75-, 50-, 25- and 5-percentiles, average and minimum value based on daily average concentrations of TSP measured at Aalborg/8151. (See explanation on p. 16).

### Annual variation

The highest concentrations were found in the early spring and in the autumn. The low summer concentrations were a result of generally lower wind velocities during the summer and a lower level of activity in the city areas in the holiday period around July, while occasional snow periods kept the dust grounded in the winter months.

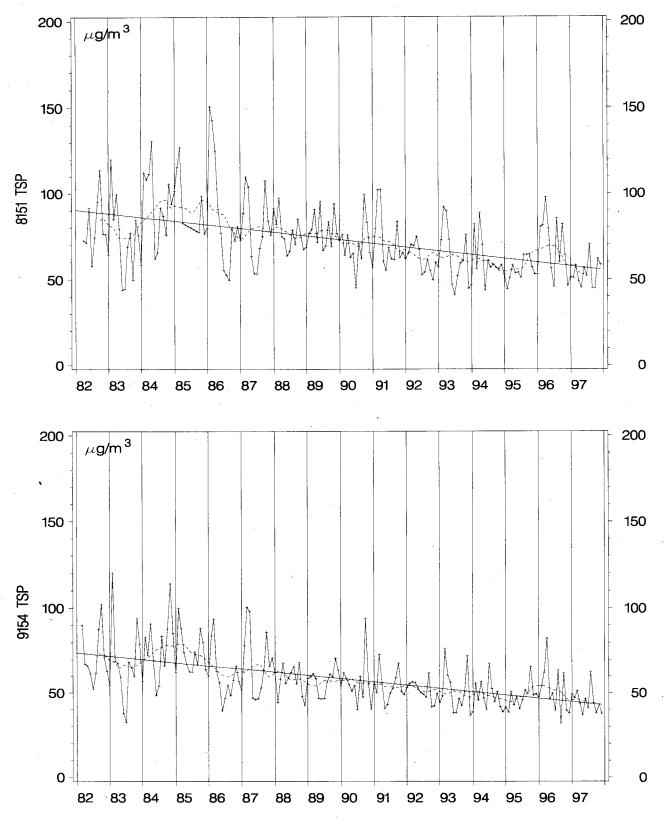


Figure 5.3 Trend for TSP measured at Aalborg/8151 and Odense/9154. The points are measured monthly averages, the dotted curve is a moving average over 12 month and the straight line is a linear regression line (see explanation on p. 16).

### 6 Elements

The aerosol samples are analysed by means of a true multi-element method (PIXE) (Kemp 1993). About 20 elements are found in concentrations above the detection limit in almost all samples, while about 5 more elements are found frequently. The elemental composition of the aerosols was in 1997 measured at all five stations in operation. In addition to monitoring purposes the measurement of the elements may be used for evaluation of the different source types that contribute to the pollution, because many of the elements mainly come from a single source type. For instance combustion of heavy oil is the main source of V and Ni, wind blown dust of Si, and particulate S is mainly caused by long range transport.

#### 6.1 Annual statistics

The average values for the elements are listed in table 6.1.

Pb is the only element with a EU limit value. The annual average concentration must not exceed 2  $\mu g/m^3$  (EEC 1982). The limit value was laid down when the petrol was heavily leaded, app. 0.6 g/l. At present in practice all petrol sold in Denmark is unleaded. The EU commission has proposed a new limit value of 0.5  $\mu g/m^3$ . The measured annual averages in 1997 were below 1 % of the present limit value and 2-3 % of the proposed value at the traffic sites in streets with heavy traffic (figure 6.1, on page 40 and table 6.1).

The concentrations of several species are increased New Year's day due to the traditional launching of fireworks and in some cases bonfires are started in the streets. It was calm weather the first hours of 1997. This limited the dispersion of the smoke from the New Year activities in the streets. Data for some species are shown in table 6.2 on page 40. Some of the concentrations at January 1 have a significant influence on the yearly average. At Aalborg/8151 the annual average for Pb would be more than 15 % lower if the single day was excluded and the average for K would be reduced with almost 30%.

The elements in table 6.2 are known constituents in fireworks. Pb is however only present in imported, i.e. mainly Chinese, fireworks as it is illegal to use Pb in fireworks produced in Denmark (Barfod, 1998).

#### 6.2 Trends

Pb exhibits the most interesting and encouraging trend. Since the start of the LMP programmes in 1982 the average Pb concentrations in the air have been reduced with more than a factor of 40 (see figure 6.2, page 41). The present level in urban areas is only about twice the background level in Denmark.

Lead

New Years day

Table 6.1 Average values for 1997. All concentrations are given as  $ng/m^3$  (1  $\mu g/m^3 = 1000 \ ng/m^3$ ).  $N_{tot}$  is the number of measurements in 1997.  $N_0$  is the number of measurements above the detection limit. The arithmetic mean value are calculated for the measured concentrations, if more than 90% of the measurements were above the detection limit. If less than 90% of the measurements were above the detection limit, a fit to a log-normal distribution is calculated based on the values above the detection limit. The values in the tables represent in these cases the arithmetic mean value for the fitted distribution. The method is under normal conditions reliable if less than half of the measurements are below the detection limit and may in any case give an impression of the average values even if it is based on a few values only.

	Copenh	nagen/1257	Odense/9155		Odense/9154		Aalborg/8151		Lille Valby/2090	
Element	N <sub>o</sub>	Average	N <sub>o</sub>	Average	N <sub>o</sub>	Average	N <sub>o</sub>	Average	N <sub>o</sub>	Average
Al	236	209.0*	277	597.0*	255	220.0*	232	316.0*	80	45.8*
Si	349	837.0	359	1860.0	354	886.0	346	1160.0	299	238.0*
S	350	1180.0	363	1250.0	362	1240.0	348	1150.0	357	941.0
CI	350	1500.0	363	2560.0	361	1660.0	348	2480.0	324	648.0
K	350	210.0	363	314.0	362	261.0	348	275.0	357	142.0
Ca	350	515.0	362	1050.0	360	458.0	348	696.0	338	158.0
Ti	350	35.0	362	69.7	360	37.3	346	38.8	278	6.3*
V	322	5.5	320	5.3*	314	4.1*	279	3.5*	281	3.0*
Cr	345	3.7	350	4.2	344	3.0	339	2.8	171	0.6*
Mn	350	13.9	363	28.2	362	17.7	348	17.0	357	3.7
Fe	350	856.0	363	1080.0	362	628.0	348	842.0	357	103.0
Ni ·	348	3.4	361	3.1	360	2.7	340	2.7	350	1.8
Cu	350	41.1	363	32.6	362	19.7	348	30.9	302	2.0*
Zn	349	46.2	362	68.3	360	50.7	348	52.0	317	15.7*
As	233	1.2*	249	1.6*	249	1.1*	195	1.0*	252	0.9*
Se	246	0.5*	254	0.5*	315	0.6*	252	0.4*	315	0.5*
Br	350	3.5	363	4.2	362	3.9	348	4.2	357	2.7
Sr	350	3.3	361	5.4	359	3.3	347	4.6	325	1.5
Zr	339	3.0	340	4.1	340	2.4	338	2.7	94	0.3*
Мо	285	2.4*	232	1.9*	202	1.2*	250	1.9*	21	0.2*
Cd	21	0.4*	20	0.3*	21	0.5*	13	0.3*	22	0.4*
Sb	320	12.7	284	9.4*	274	5.9*	295	8.3*	61	1.4*
Ва	309	26.1*	303	32.5*	295	18.8*	295	22.1*	31	2.8*
Pb	350	16.6	361	14.9	361	14.5	348	13.9	352	7.6
N <sub>tot</sub>	350		363		362		348		357	

<sup>\*</sup> Calculated from a fit to a log-normal distribution.

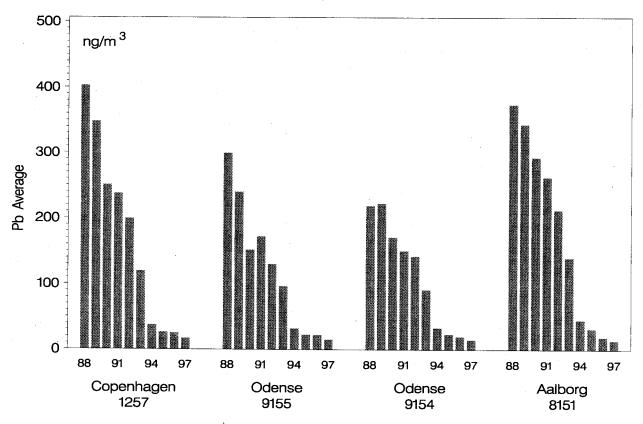


Figure 6.1 Annual average values for Pb from 1988 to 1997.

Table 6.2 Concentrations new years day 1997 for species showing very high concentrations. The "normal" values represent a rough average over all urban station for the whole year 1997

Specie	Copenhagen/	Odense/9155	Aalborg/8151	"Normal" 1997	
Unit: ng/m³	1257				
TSP (µg/m³)	109	138	148	50	
S	6300	11200	13700	1200	
Κ .	9600	21000	24100	250	
Sr	141	218	255	5	
Sb	37	43	61	10	
Ва	690	1640	1560	20	
Pb	380	530	800	15	

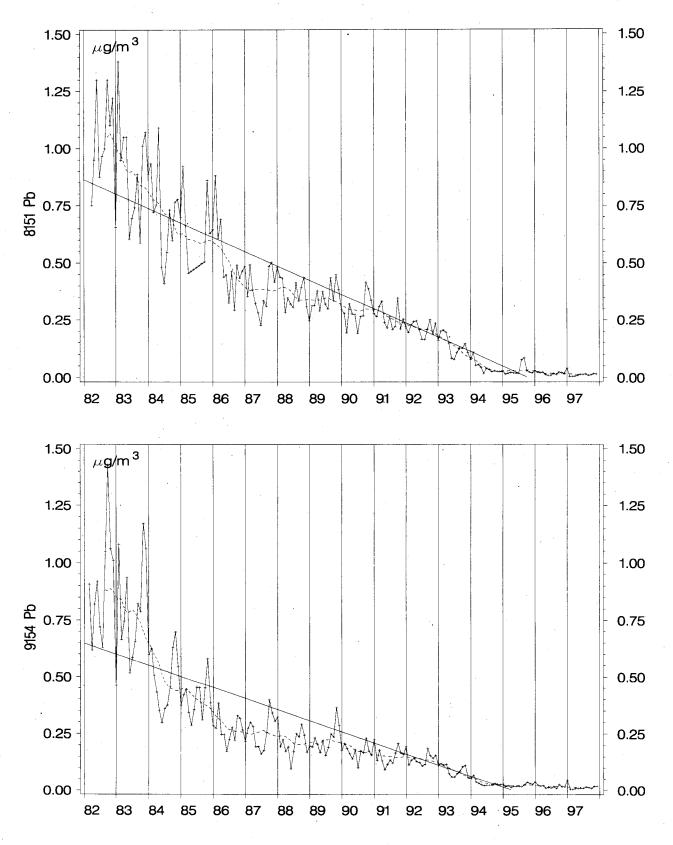


Figure 6.2 Trend for Pb measured at Aalborg/8151 and Odense/9154. The points are measured monthly averages, the dotted curve is a moving average over 12 month and the straight line is a linear regression line (see explanation on p. 16).

### 6.3 Heavy metals in urban and rural areas

Several of the elements are toxic heavy metals. WHO has assessed the toxic effects of some heavy metals (WHO 1987, WHO 1998). These are Cr, V, Mn, Ni, As, Cd, Hg and Pb. Guidelines are suggested for V, Mn, Cd, Hg and Pb. Cr, Ni, and As are carcinogenic in certain compounds and only life time cancer risks are estimated.

Non-carcinogenic heavy metals

Table 6.3 shows the WHO guidelines for yearly averages for the non-carcinogenic elements together with the corresponding measured values at Aalborg in 1982 and 1995 and at Copenhagen/1257, where in most cases the highest values are measured. Apart from Pb, 10 years ago, all measured values are more than a factor of 10 below the guideline values. Hg is not measured within the LMP programme, but estimates of the Hg pollution in the air in Europe indicates that the concentrations are between 0.001 and 20 ng/m³ (Lahmann et al. 1986). The amount of V in urban air has decreased by a factor of 3-5 since 1982. It followed the reduction in the SO<sub>2</sub> concentrations and it is expected to decrease further in the future. Mn does only show a slightly decreasing trend.

Table 6.3 WHO guidelines (WHO 1987 and 1997) for non-carcinogenic heavy metals compared to measured annual average concentrations at street level. N.M. = not measured.

ng/m³	WHO guideline	Aalborg/8151 Aalborg/8151		Copenhagen/1257	
		1982	1997	1997	
V	1000	22	4	6	
Mn	150	20	17	14	
Cd	5	<2	0.3	0.4	
Hg	~1000	N.M.	N.M.	N.M	
Pb	500	1100	. 14	17	

Carcinogenic heavy metals

The estimated human lifetime risks are estimated for air concentrations of 1  $\mu g/m^3$ . These values and the corresponding urban concentrations are shown in table 6.4. The evaluation of the lifetime risks is very uncertain and assessment of acceptable risks is debatable. The risks of concentrations at the measured levels are calculated assuming the dose-response curve can be extrapolated linearly towards zero (see below). Fig. 6.3 shows the trends for the LMP stations and the stations in the Danish Background Monitoring Program with long time records.

Table 6.4 Estimated lifetime risks (WHO 1998) for carcinogenic heavy metals compared to measured concentrations.

	Lifetime risk at 1 µg/m³	Aalborg/8151 1982 µg/m³	Aalborg/8151 1997 μg/m³	Copenhagen/1257 1997 µg/m³	
Cr ·	1)	0.0029	0.0028	0.0037	
Ni	3.8×10 <sup>-4</sup>	0.0070	0.0027	0.0034	
As	1.5×10 <sup>-3</sup>	<0.02	0.0010	0.0012	

<sup>&</sup>lt;sup>1</sup>) the WHO estimated life time risk for Cr(VI) is  $4\times10^{-2}$ , while the measurements are total Cr (see text).

#### Chromium

Only hexavalent Chromium (Cr(VI)) is carcinogenic, while the most abundant trivalent Chromium (Cr(III)) is relatively harmless. Little is known about the fraction of Cr(VI) in the ambient atmosphere, but it is expected to amount to a very small part of the total Cr because Cr(VI) is easily reduced to Cr(III). A downward trend at the background stations and an almost constant level at the urban stations indicates that the sources for Cr are mainly urban. The difference between the levels in Copenhagen and the other cities shows that other sources than the local traffic contribute considerable. The traffic pollution at the street stations are almost equal (see chapter 2).

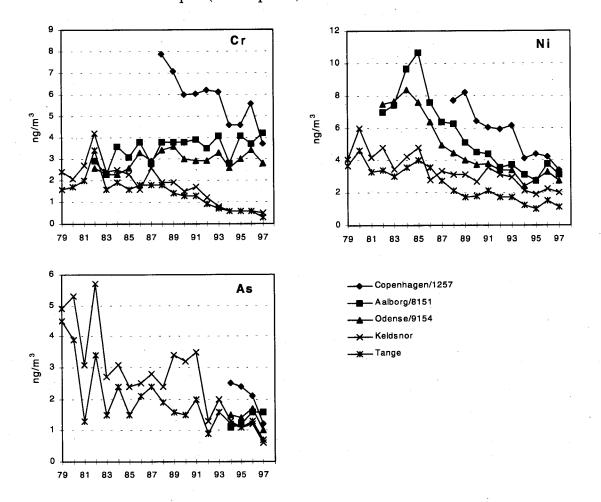


Figure 6.3 Yearly average values for the potential carcinogenic heavy metals. Results from the stations in the Danish Background Monitoring Program at Tange and Keldsnor are included for the comparison.

Nickel

A linear extrapolation indicates that the measured Ni concentrations correspond to a life time risk above 10°. The estimate becomes however further uncertain because the carcinogenic effect of various Ni compounds is very different and the partitioning between the different compounds in the air is not known. The WHO estimate is based on epidemiological data for workers at Ni refineries. The Ni pollution has been decreasing at all stations and it is expected to be further reduced. The major part of the Ni is emitted from oil burning and the trend is following that of SO<sub>2</sub> (see chapter 4). The difference between the concentrations at urban and background stations is

decreasing, which indicates that the major part is long range transport.

Arsenic

The detection limit for determining As has unfortunately previously been too high to give reliable estimates of the yearly average values at the urban stations. However, data from 1994 and on are available due to the decreasing Pb concentrations (Pb interferes with the determination of As) and an improved data treatment method. The records go back to 1979 at the background stations and shows that the concentration has been reduced by a factor of 3 since 1979. The values for 1997 are almost equal at the background stations and the street stations in Odense and Aalborg, while the values in Copenhagen are somewhat higher. At present the concentrations correspond to a lifetime risk above 10<sup>-6</sup>. It can, as for Ni, be concluded that a major part of As is long range transported.

Summary

If the risks for the three elements are added the total lifetime risk may be estimated to more than 10°. The variation of the concentration from station to station indicates that the occurrence of Cr is widespread over urban areas and Ni and As over the whole country.

# 7 CO and VOC

Continuous measurements of CO have been performed since the beginning of 1996 at the three traffic stations Copenhagen/1257, Odense/9155 and Aalborg/8151 together with the urban background station Copenhagen/1259. The first whole year of measurements of the VOC's benzene, toluene and xylene (BTX) has been performed at the traffic station Copenhagen/1257. The measurements have been possible by integration of the LMP and TOV (Berkowicz et al. 1996) measurements partly funded by the Ministry of Traffic. In addition the BTX measurements are partly funded by the Danish Environmental Protection Agency. The behaviour of the three VOC's is very much alike. Only benzene and toluene will be discussed in the following. Benzene is carcinogenic, while the most severe effect of toluene is damage to the central nervous system.

Sources

The main source of CO, benzene and toluene is petrol vehicles. The CO is emitted due to incomplete combustion of the petrol. The TWC will retain the major part of the CO. There is practically no CO in the exhaust from diesel vehicles. It has been estimated that of the total hydrocarbon emission from motor vehicles in Denmark only about 9% came from diesel vehicles while petrol fuelled vehicles accounted for the remaining 91%; of the latter, about 59% came from the exhaust while 41% was released by evaporative emission (Danmarks Statistik 1993). The hydrocarbon content of vehicle exhausts are influenced by several factors related to driving mode and speed, ambient temperature, vehicle conditions (e.g. age and performance), fuel to air ratio and fuel type. A limit of 5% content of benzene has been introduced in 1986 in all EU-countries. The petrol in Denmark was produced with a benzene content between 3 and 5% depending on the content in the crude oil and the production processes. From 1995 petrol with app. 2 % of benzene has been sold in the eastern part of Denmark (east of the Great Belt). The total content of aromatic compounds is 40-45 %. The emission of benzene depends on the content in petrol, but the emission is also linked to the total content of aromatic compounds in petrol, because it is formed during the combustion process.

#### 7.1 Annual statistics

Statistics

A number of statistical parameters are shown in table 7.1 and 7.2. Compared with the 1996 (Kemp, Palmgren and Manscher, 1997) the CO levels are lower at all stations except Aalborg/8151. As was the case for NO (see discussion in chapter 2) the CO concentrations were about 15 % higher in 1997. Still all parameters are below the WHO guidelines. For benzene the risk of cancer can be estimated to about  $4\cdot10^5$  at an life time exposure to the average value. The concentration of toluene seems not to be critical compared to the WHO guideline value.

Table 7.1 Statistical parameters based on hourly results for CO in 1997. All values are given in μg/m³. \*) The 8 hours values are calculated as a moving average based on hourly results.

,							
Station	Average	Median (hour)	98-perc. (hour)	99.9-perc. (hour)	Max. 24 hour	Max. 8 hour	Max. 1 hour
Copenhagen/1257	1277	1015	3985	7073	3883	5784	10190
Odense/9155	929	672	3396	5925	3953	556	8821
Aalborg/8151	1191	858	4112	7153	3778	6113	9348
Copenhagen/1259	376	301	1074	2277	1348	2314	3954
WHO guideline value	-	-	-	-		10000	30000

Table 7.2 Statistical parameters based on hourly results for benzene and Toluene in 1997 measured at Copenhagen/1257. All values are given in  $\mu g/m^3$ . The lifetime risk and guideline value are from WHO, 1998. The 7 days maximum is calculated as a moving average based on 24 hour averages.

Specie	Average	Median (hour)	98-perc. (hour)	99.9-perc. (hour)	Max. 7 days	Lifetime risk at 1 µg/m³	Guideline for 7 days average
Benzene	7.8	6.0	24.8	46.6	-	4.4-7.5·10 <sup>-6</sup>	-
Toluene	27.7	21.3	89.9	169	54	-	260

#### 7.2 Trends

The aromatic compounds showed very high correlation with CO (e.g. between benzene and CO, Figure 7.1), confirming that they were emitted from petrol powered vehicles. This was expected since the contribution of CO from diesel vehicles was relatively low at Jagtvej and the emission of aromatic VOCs from diesel powered vehicles were expected to be unimportant. The main emission of aromatic compounds from diesel vehicles is expected to be heavier hydrocarbons and PAHs. The correlation between CO, benzene, toluene, ethylbenzene, n-, o- and p-xylene were generally high indicating that they have been emitted from the same type of sources. Examples are given in Figure 7.1, which shows a very high correlation of benzene with both CO and toluene, all three are emitted from petrol engines.

**Emission** 

The emissions and the meteorological conditions influence the trends of the air pollution concentrations. A technique to determine the emission from road traffic has been developed at NERI (Palmgren et al. 1998) based on inverse model calculations by the OSPM model (Berkowicz et al., 1997). The technique has been applied on CO, benzene and NO<sub>x</sub> data from Jagtvej in Copenhagen. In figure 7.2 are shown the measured concentrations of NO, benzene and CO from 1994 to 1997. In addition, the calculated daily emissions are shown based on the inverse model calculation. Fluctuations in the concentrations of NO, and CO were observed due to the meteorological conditions, e. g. the concentrations were higher in 1996 than in 1995. However, the emissions decreased continuously from 1994 to 1997 due to the increasing number of TWC cars and nearly constant traffic flow at Jagtvej. For benzene more steep negative trends were observed for the concentration as well as for the emission. This is due to the reduced content of benzene in petrol from 1995 from approx. 3.5% to approx. 2%. This reduction dominated over the unfavourable dispersion conditions in 1996.

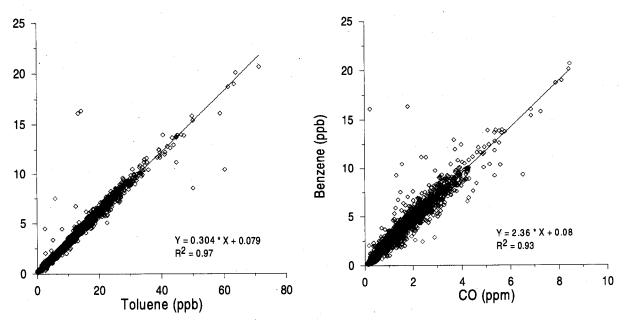


Figure 7.1 The concentrations of benzene versus CO and the concentrations of benzene versus toluene measured as 1 h averages measured at Copenhagen/1257 May-December 1996.

Ratio Benzene/CO

The ratio between benzene (ppb) and CO (ppm) in 1994 -95 was 4.3. In the period 1996 - 97 the ratio was 2.4, see Figure 7.3. The reduction in this ratio corresponds to the relative reduction in the benzene content of approx. 40%. In figure 7.3 is shown the ratios toluene/CO and benzene/CO. The reduction in the toluene/CO ratio was much less, because the total content of aromatic compounds was not reduced.

Emission factors

The above technique also made it possible to estimate the emission factors for different car categories, if good and detailed traffic statistics exist. This is the case at Jagtvej and the estimated emission factors for  $NO_x$ , benzene and CO are listed for petrol and diesel (other cars) cars in table 7.3. The emission factors are for the "average" cars, it means that the fraction of TWC cars is imbedded in the numbers. It is demonstrated that the benzene emission from diesel cars is negligible.

Table 7.3 Estimated emission factors (g/km) for the different vehicle categories. Vans, buses and trucks are included in one category for benzene and CO.

	N	O <sub>x</sub>		Ве	nzene	CO		
Year	Cars	Vans	Trucks and buses	Cars	Other vehicles	Cars	Other vehicles	
1993	1.6±0.2	5.4±4.5	20.7±5.4	-	-	-	-	
1994	1.8±0.1	3.9±2.5	18.0±3.0	0.38± 0.04	0.10± 0.21	25.2±1.1	11.2±6	
1995	1.5±0.2	3.8±3.3	18.0±4.0	0.27±0.03	0.09± 0.15	22.9±1.0	12.7 <u>±</u> 6	
1996	1.2±0.1	3.9±2.6	18.6±3.2	0.15±0.01	0.04±0.07	19.4± 0.8	10.8±5	
1997	0.9±0.1	6.3±2.5	12.5±3.0	0.11±0.01	0.05±0.05	17.3±0.7	9.6±4	

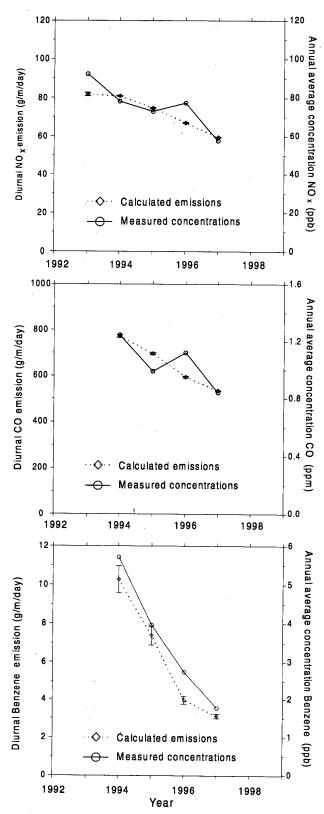


Figure 7.2 Evolution in annual (background subtracted) mean  $NO_x$ , CO and benzene concentrations and calculated traffic emissions in Jagtvej at Copenhagen/1257.

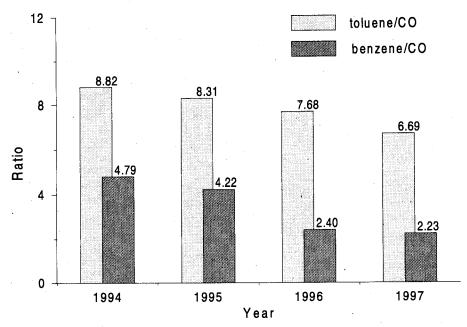


Figure 7.3 Annual ratios toluene/CO and benzene/CO (ppb/ppm), determined as the slopes of the linear regression lines.

# 8 Conclusion

Nitrogen dioxide

The measured 98-percentiles for  $NO_2$  were about half the limit value (200  $\mu g/m^3$ ), whereas medians were approximately equal to the guide value (50  $\mu g/m^3$ ). The measured values were in 1997 almost the same as in the previous years. A trend analysis covering the last 16 years showed that the  $NO_2$  level have been only slightly decreasing, while a significant decrease is observed for NO since 1993 as a result of the increasing number of cars with three way catalytic converters. The measured concentrations are close to the limit values proposed by the EU Commission.

Ozone

A set of threshold values for O<sub>3</sub> has been implemented in Denmark in 1994. The values are based on an EEC directive for protection of human health and vegetation. During 1997 some of the threshold values were exceeded frequently. The reduction of O<sub>3</sub> concentrations can only be obtained in an international co-operation, because the precursors to a large extent are emitted in other countries and because O<sub>3</sub> in the lower troposphere is a secondary pollutant. The precursors are NO<sub>x</sub> and organic gases which may be of either natural or anthropogenic origin.

Sulphur dioxide

The actual measured values at all stations were more than a factor of 10 lower than the limit values for SO<sub>2</sub>. The measured values were more than a factor of 5 below the EEC guide values. There is a marked decrease of the SO<sub>2</sub> levels since 1982. The most pronounced reduction was observed in 1986 as a result of the decrease of the sulphur content in the fossil fuel products used in Denmark. But even in the recent years the concentrations have been decreasing due to better emission control on larger installations and the introduction of natural gas for i.e. domestic heating. The negotiation of international protocols for a further reduction of the SO, emission in the European countries will probably lead to a continuation of the downward going trend. The 1997 results were considerably lower than the previous years. The decrease is mainly due to lower concentrations under winds from south-east. It is not clear to what extent the results reflects lower emissions in eastern Europe or how much they are influence by the meteorological conditions.

Particles (TSP)

The collected TSP is a mixture of "natural" wind blown dust (the particles may be raised by the influence of the traffic) in form of coarse particles and anthropogenic derived fine particles. The measured concentrations were lower than half the limit values. A slightly decreasing trend has been observed for the last 10 years. This may be a result of the "winter crops" during the winter and of better control with the combustion processes. The decrease can thus be expected to continue in the future, due to the introduction of catalysts on all new gasoline driven cars, and as expected limitations on the particle emission from diesel vehicles become more stringent. The TSP values were slightly lower in 1997 than in the previous years. The measured TSP concentrations are not directly comparable with the limit values for PM<sub>10</sub> proposed by the EU Commission. But

they strongly indicate that the PM<sub>10</sub> values at the traffic sites are about twice the limit values.

Elements

Both the actual limit value for Pb of 2  $\mu g/m^3$  and the 0.5  $\mu g/m^3$  proposed by the EU commission are obviously irrelevant in Denmark after lead has been removed from gasoline. At present values less than 1% of the limit value are found at street level in the Danish cities. In practice all petrol sold in Denmark is now un-leaded. Lead in the atmosphere over Denmark will probably in a few years originate mainly from industrial sources outside the country. Other heavy metals are found in rather low concentrations, but at least the trend should be followed for those having carcinogenic properties.

CO and benzene

CO was found in concentrations below the WHO guideline values; while the average concentration of benzene was approx. 6  $\mu g/m^3$ . Petrol cars are the dominating source for both compounds at street level. The concentration of benzene decreased significantly from 1995 to 1997 due to less benzene in petrol.

Smog warning

A smog warning system was implemented from April 1994. It is for SO, and NO, a continuation of the provisional system, which was started in 1987. The population is warned through the public broadcast stations, if the concentration of either SO, or NO, exceeds 350 µg/m³ in more than three consecutive hours and an immediate improvement is not expected. No warnings have been issued since the start in 1987 and, taking the measured concentrations and the expected development into account, it can with almost certainty be excluded that the warning limits will be exceeded in Denmark. O<sub>3</sub> has been included in the new system: The population is informed immediately if the hourly average concentration exceeds 180 µg/m³ and if the hourly concentration exceeds 360 µg/m³ a warning is issued to the population. The information threshold was not exceeded in 1997, but final quality assurance of the results showed that the concentration at one occasion actually was 181 µg/m<sup>3</sup>. The information threshold will statistically be exceeded once every year. It is not realistic to assume that the warning threshold will be exceeded.

Ultra short summary

The results from the Danish Air Quality Program in 1997 showed that the concentrations found in the Danish cities were below the existing limit values. The O<sub>3</sub> threshold values, which were implemented in 1994, are however frequently exceeded. The NO<sub>2</sub> concentrations were around half the limit value and no clear trend was observed. The measurements in LMP III program aims i.a. at a description of the O<sub>3</sub>-NO<sub>x</sub> interaction in order to reveal the effect of actions already taken to reduce the NO<sub>x</sub> emissions (obligatory three way catalysts on new gasoline driven cars and reduction of the emission from power plants) and the effect of future reductions, which hopefully will be realised through international protocols within the ECE-LRTAP convention and the coming EU acidification strategy for the emission of the O<sub>3</sub> precursors.

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# Danish Summary - Dansk resumé

Det Landsdækkende Luftkvalitets Måleprogram Årsrapport for 1997

Faglig rapport fra DMU nr. 245

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**LMP** 

Luftkvaliteten i de danske byer overvåges gennem Det Landsdækkende Luftkvalitets Måleprogram (LMP). LMP startede i 1982 og er ændret med henblik på belysning af de aktuelle forureningsproblemer ved revisioner i 1987 og 1992. I det nuværende program (LMP III) foretages målinger i København, Odense og Aalborg i et samarbejde mellem Danmarks Miljøundersøgelser (DMU), Miljøstyrelsen, Hovedstadsregionens Luftovervågningsenhed (HLU) og Odense og Ålborg kommuner. Det praktiske arbejde udføres af DMU sammen med Miljøkontrollen i København, Miljø- og Levnedsmiddelkontrollen på Fyn og Erhvervs- og Miljøforvaltningen i Aalborg.

Måleprogram

I hver af de tre byer er opstillet et par af målestationer. En basisstation i gadeniveau på en trafikeret gade og en tagstation nogle hundrede meter fra basisstationen (Kemp, K. 1993). Som noget nyt i 1997 er de hidtil foretagne kampagnemålinger blevet udvidet så de foregår kontinuert gennem hele året. På basisstationen foretages således kontinuert måling af NO, NO2, SO2, CO, svævestøv samt grundstofindholdet i svævestøvet. På tagstationerne måles NO, NO, og O, koncentrationen i "taghøjde" samt følgende meteorologiske parametre: vindretning, vindhastighed, relativ fugtighed, temperatur og global stråling. I København måles desuden CO på tagstationen og O<sub>3</sub> samt benzen og toluen i gadeniveau. Baggrundsforureningen måles på en station ved Lille Valby ca. 25 km vest for København og på Keldsnor på sydspidsen af Langeland. Ud over den generelle overvågning af luftkvaliteten er et væsentlig formål med LMP III programmet at give mulighed for at beskrive vekselvirkningen mellem og dannelsen af NO<sub>2</sub> og O<sub>3</sub>.

Specialprogrammer

LMP målingerne giver kontinuerte flerårige måleserier, som er nødvendige for at vurdere de systematiske variationer og sammenhængen mellem forekomsten af forskellige forurenende stoffer i atmosfæren. Flere mere forskningsorienterede projekter udnytter den umådelige fond af viden, som LMP programmerne har bragt til veje. Disse projekter har bl.a. til formål at beskrive omdannelsen af kvælstofoxider, som udsendes fra trafikken, forekomst og kilder til PAH aromatiske hydrocarboner) (polycykliske. som kræftfremkaldende stoffer, og VOC (flygtige organiske hydrocarboner) af hvilke nogle er kræftfremkaldende og som i øvrigt er af stor betydning ved dannelsen af  $O_3$  i atmosfæren.

Det følgende resumé er inddelt i afsnit efter kapitlerne i selve rapporten. Relevante tabeller og figurer kan findes i de pågældende kapitler.

Nitrogenoxider

For NO<sub>2</sub> (kapitel 2) er de målte koncentrationer i alle tilfælde under den gældende grænseværdi på 200 μg/m³ for 98-percentilen og de vejledende værdier på 135 μg/m³ for 98-percentilen og 50 μg/m³ for medianen. Afstanden til de vejledende værdier er ikke ret stor. WHO's vejledende værdi på 40 μg/m³ for årgennemsnittet er overskredet i København. Emissionen af NO<sub>x</sub> fra benzindrevne bliver reduceret efterhånden som der kommer katalysatorer på flere og flere biler. Det er nu tydeligt at niveauet for NO er blevet reduceret; mens der ikke kan påvises nogen ændring for NO<sub>2</sub>. Emissionen fra de øvrige hovedkilder, dieselbiler og kraftværker, vil ikke blive ændret ret meget de første par år. EU Kommissionen har foreslået nye grænseværdier, som skal være gældende fra 2010. De målte koncentrationer ligger i enkelte tilfælde tæt på de foreslåede værdier.

Ozon

De målte O<sub>3</sub> værdier (kapitel 3) var som tidligere næsten ens over hele landet. Med gennemførelsen af et EU direktiv om O<sub>3</sub> er der i 1994 fastsat en række tærskelværdier i Danmark i forbindelse med beskyttelse af både plantevæksten og sundheden. Flere af disse tærskelværdier blev overskredet i løbet af 1997. O<sub>3</sub> i den nedre del af atmosfæren dannes ved fotokemiske reaktioner. VOC og kvælstofoxider er af stor betydning for dannelse af O<sub>3</sub>. Da en stor del af den VOC der findes i luften i Danmark stammer fra andre lande, kan en effektiv nedsættelse af O<sub>3</sub> forureningen kun ske gennem et internationalt samarbejde. De største koncentrationer findes i sommerhalvåret i perioder med varmt og solrigt vejr. Der er indført en tærskelværdi på 180 μg/m³. Hvis timemiddelværdien overskrider denne værdi, skal befolkningen underrettes. Det skete ikke i 1997. (Den efterfølgende kvalitetskontrol viste dog, at koncentrationen i et enkelt tilfælde var 181 μg/m³).

Svovldioxid

Forureningen med SO<sub>2</sub> (kapitel 4) er klart faldende i Danmark. De målte koncentrationer var mere end en faktor 10 under grænseværdierne og mere end en faktor 5 under den i EU gældende vejledende værdi. De målte koncentrationer ligger også langt under de nye grænseværdier, som er foreslået af EU Kommissionen. Det største fald skete omkring 1985-86, hvor svovlindholdet i fossile brændsler blev begrænset som følge af et lovindgreb, men bedre røgrensning, indførelse af naturgas og en fortsat reduktion af svovlindholdet i bl.a. olieprodukter har fortsat den positive udvikling i svovlforureningen. Der kan dog fortsat episodisk findes høje koncentrationer. De største værdier findes oftest under de såkaldte hot-spot episoder, hvor røgfanen fra en nærliggende industri eller kraftværk "slår ned" ved målestationen. Antallet af hotspot episoder er gået ned i de seneste år. Der var et markant fald i 98 percentilen for SO<sub>2</sub> og gennemsnitskoncentratioen af partikulært svovl. Begge dele kan bruges som indikatorer for forurening transporteret over lange afstande. Det er ikke klart i hvor høj grad

nedgangen skyldes mindre emissioner i Østeuropa, idet forskellige meteorologiske faktorer også kan have været afgørende.

Svævestøv

Den totale partikelkoncentration i luften, TSP (=Total Suspended Particulate matter) (kapitel 5) findes i byerne i koncentrationer på mellem 1/2 og 1/4 af grænseværdierne. TSP består af en blanding af bidrag fra flere kilder, hvoraf ophvirvlet jordstøv er den væsentligste. Der er generelt en svagt nedadgående tendens for TSP. Den kan til dels forklares ved bedre kontrol med partikeludslippet ved forbrændingsprocesser (især kraftværker og trafik); men ikke mindst de "grønne marker" om vinteren, som er blevet mere og mere udbredt, synes at have haft en virkning. EU Kommissionen har foreslået nye grænseværdier baseret på måling af PM, (dvs partikler med en aerodynamisk diameter mindre end 10 µm). De målte TSP værdier er derfor ikke umiddelbart sammenlignelige med de foreslåede grænseværdier. Men det kan skønnes at PM<sub>10</sub> koncentrationerne på gadestationerne i nogle tilfælde er omkring dobbelt så store som de grænseværdier, som efter forslaget skal gælde fra 2010.

Bly

Nedgangen af blyforureningen i atmosfæren (kapitel 6) er helt enestående i luftforureningens historie. I takt med at blyet er fjernet fra benzinen er blyforureningen i de danske byer faldet fra et niveau, der sandsynligvis medførte skadevirkning på de mest udsatte befolkningsgrupper, til næsten ingenting. Middelværdierne for 1997 var mere end en faktor 50 lavere end ved LMP-programmernes start i 1982. Der er i praksis ikke mere bly i benzin. Blyforurening er nu på niveau med flere andre tungmetaller.

Kulmonoxid, benzen og toluen

Der er gennemført målinger af CO på alle gadestationer samt på tagstationen i København. Der er målt flere organiske forbindelser, bl.a. benzen og toluen på gadestationen i København (kapitel 7). CO-koncentrationerne var i 1997 under WHO's vejledende værdier. Benzenkoncentrationerne er faldet klart siden 1994 som følge af katalysatorerne og en nedsættelse af benzenindholdet i benzin. Målingerne bekræfter, at såvel CO som benzen hovedsageligt stammer fra benzin biler.

Resumé

LMP resultaterne fra 1997 viser, at den forurening, der findes i de danske byer, var under de gældende grænseværdier, men tærskelværdierne for O<sub>3</sub> blev overskredet jævnligt. Selv om NO<sub>2</sub> koncentrationerne var under grænseværdien, var de dog ret tæt på. LMP III programmet har bl.a. til hensigt at give grundlag for en beskrivelse af O<sub>3</sub>-NO<sub>x</sub> vekselvirkningen i byatmosfæren, så virkningen af emissionsbegrænsende foranstaltninger (katalysatorer på nye biler og reduktion af udslippet fra kraftværker) kan dokumenters. På længere sigt vil konsekvenserne af internationale protokoller for reduktion af udslippet af udgangsstofferne for O<sub>3</sub> forhåbentlig også slå igennem.

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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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