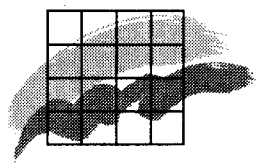

The Danish Air Quality Monitoring Programme

Annual Report for 1996

NERI Technical Report No. 216

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Data Sheet

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Contents

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 1996 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 at 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_2, SO_2, total suspended particulate matter (TSP) and elements in the aerosols are measured at the street sites. O_3 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_2 at roof sites are performed in campaigns in order to improve the knowledge about the NO, NO_2 and O_3 problem complex. At the rural site outside Copenhagen the same program is conducted as at the street stations with the inclusion of O_3. Only NO, NO_2 and O_3 are reported from the other rural site.

Limit values

Air quality limit values have been implemented in Denmark for NO_2, SO_2, 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_3 came into force in March 1994. They were laid down with consideration of the protection of both human health and plants.

Nitrogen oxides

The measured NO_2 concentrations were about a factor of two lower than the limit value. The trend for NO_2 since 1982 shows no significant changes. 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_3 is at present a limiting factor for the formation of NO_2 at street level and it remains to be seen to what extent the NO_2 concentrations will be reduced at highly polluted places as result of the TWC's.

Ozone

Some of the threshold values for O_3 were frequently exceeded. The average O_3 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_3 is the limiting factor for formation of NO_2 at street level, NO is at roof level and in background areas.

Sulphur dioxide and TSP

The SO_2 concentrations have been continuously decreasing since 1982. They were in 1996 only about 1/10 of the limit values. 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.

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 50 higher than the measured concentrations.

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 http://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.

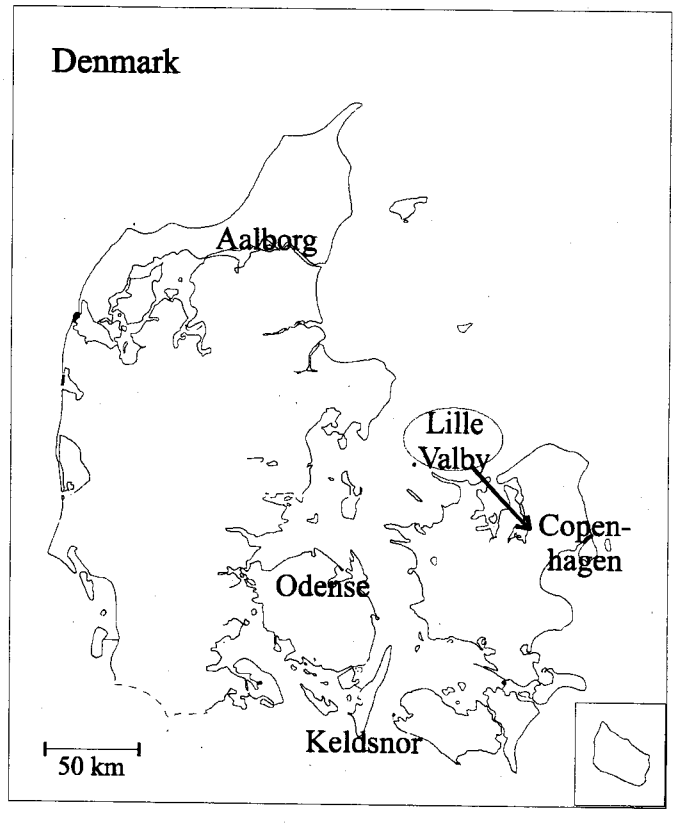


Figure 1.1 Cities and the background sites in the LMP network.

Table 1.1 LMP III stations in 1996. 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. 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_2, SO_2	SO_2, TSP, Elements
Copenhagen/1259	Roof (Urban background)	O_3, meteorology	-
Odense/9155	Main (Traffic)	NO, NO_2, SO_2	SO_2, TSP, Elements
Odense/9154	Additional (Traffic)	-	SO_2, TSP, Elements
Odense/9159	Roof (Urban background)	O_3, meteorology	-
Aalborg/8151	Main (Traffic)	NO, NO_2, SO_2	SO_2, TSP, Elements
Aalborg/8159	Roof (Urban background)	O_3, meteorology	-
Lille Valby/2090	Rural background	NO, NO_2, SO_2, O_3	SO_2, TSP, Elements
Keldsnor/9055	Rural background	NO, NO_2, O_3	-

Measurement programme

The measurement programmes at stations in operation during the major part of 1996 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 (1997).

Campaigns

The continuous measurements in the programme are supplemented with campaign measurements in periods of 4 months or more. During the campaigns additional measurements of CO, O_3, NO and NO_2 are i.e. carried out in order to get a better understanding of the NO_2 in the urban background and the NO - NO_2 - O_3 interaction in the atmosphere in urban areas.

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 Denmark has limit values for SO_2, suspended particulate matter, NO_2 and Pb. A set of threshold values for O_3 was introduced in 1994 by the implementation of an EEC 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.

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 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 $\mu g/m^3$.

1996 reports

The 1996 results are found in quarterly reports (Danmarks Miljøundersøgelser 1996a, 1996b, 1997a 1997b). The results obtained during 1996 are summarised in the present report in form of annual

statistics and trends. The phenomenology of O_3 is again in 1996 treated as a special topic since O_3 is a key species in the present studies of the atmospheric chemistry of i.e. transformation of nitrogen oxides and VOC compounds. Further, the programme for campaigns with intensive measurements was continued in 1996. The results of a campaign in Aalborg and Odense are summarised in chapter 7. The campaign measurements in Copenhagen are still an integrated part of an intensive programme for studying the pollution from traffic (Berkowicz et al. 1996). A description of the Danish air quality monitoring programmes and selected results are shown on the internet (NERI 1997).

2 Nitrogen oxides

Sources

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 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 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 1996 continuous measurements of NO and NO_2 were performed at five stations: Copenhagen/1257, Odense/9155, Aalborg/8151, Lille Valby/2090 and Keldsnor/9055. The first three stations are located in urban areas at kerbside on streets with heavy traffic, whereas the last two are located in rural surroundings, without nearby sources of importance. Results are missing from September to December due to technical problems at Copenhagen/1257. More than 90% of the possible results for the whole year are available from the other stations. (see table 1.1).

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 1996, but the results from Copenhagen exceeded the WHO guide value (40 $\mu g/m^3$) and was close to the DK guide values for the median. The very low values for NO at Lille Valby/2090 and Keldsnor/9055 illustrate the fast conversion of NO to NO_2.

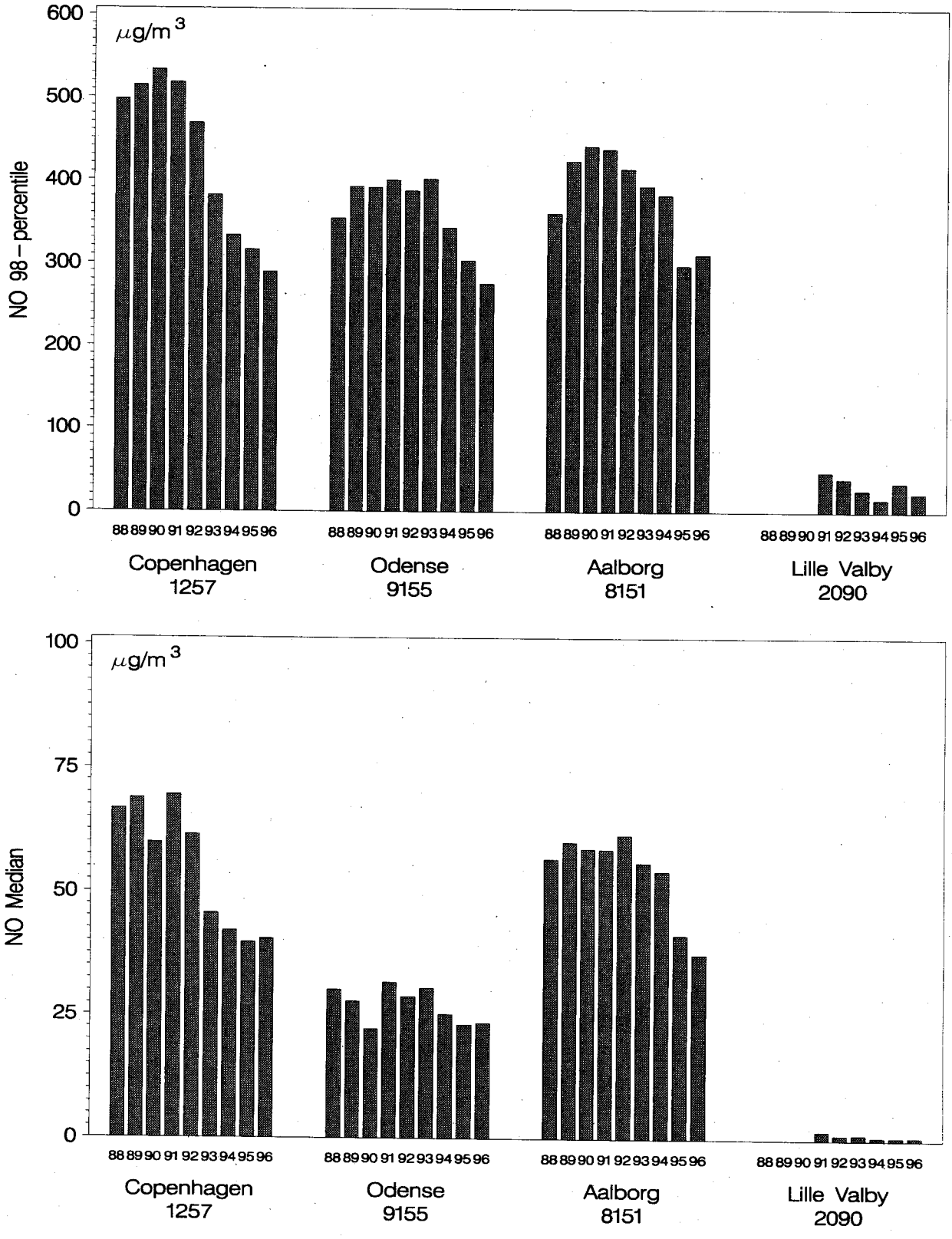


Figure 2.1 Medians and 98-percentiles for NO from 1988 to 1996

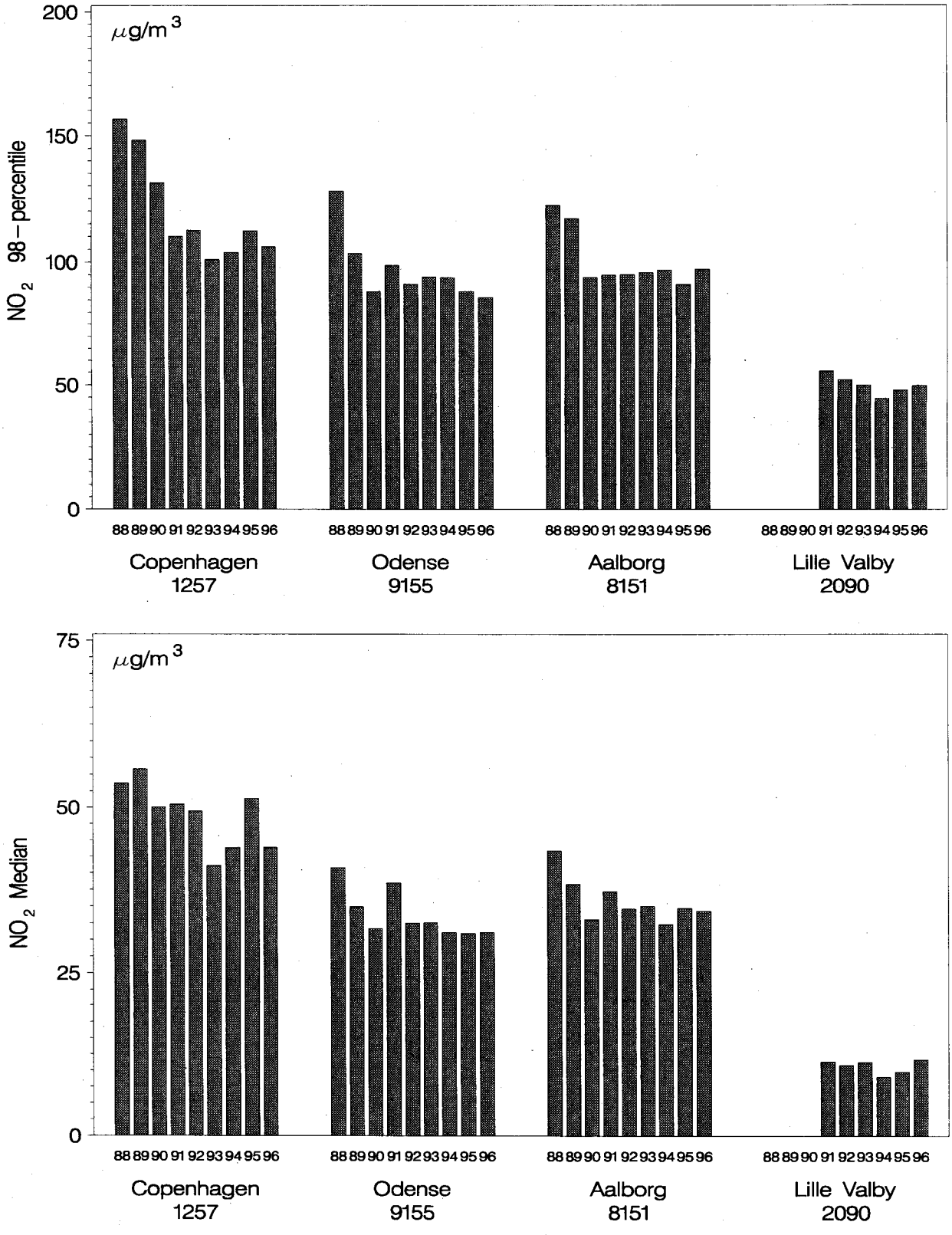


Figure 2.2 Medians and 98-percentiles for NO_2 from 1988 to 1996.

Table 2.1 The values are calculated for all measurements from 1996 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 Copenhagen/1257 and Keldsnor/9055 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 DK guide values are found in Miljøministeriet, 1987, while the WHO guide value is given in WHO (1997).

		NO (µg(NO)/m^3)				NO_2 (µg(NO_2)/m^3)			
Station	Number	Average	Median	98-perc	99.9-perc	Average	Median	98-perc	99.9-perc
Copenhagen/1257	5808	72	45	298	509	45	43	104	189
Odense/9155	8106	54	25	275	535	34	31	85	133
Aalborg/8151	8220	69	38	312	604	38	34	96	131
Lille Valby/2090	7949	(2)	(1)	23	115	15	12	49	84
Keldsnor/9055	5800	(2)	(1)	10	79	13	10	42	74
Limit value	>6570	-	-	-	-	-	-	200	-
Guide value (DK)		-	-	-	-	-	50	135	-
Guide value (WHO)		-	-	-	-	40	-	-	-

NO vs. NO_2

The high concentration of NO compared to NO_2 at urban stations illustrates that the NO is not a limiting factor for the formation of NO_2 at streets, whereas almost all NO has been oxidised at the rural sites.

Low NO in Odense

The relative low values for the average and median concentrations for NO in Odense may be 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 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. The WHO guide values was exceeded one hour at Copenhagen/1257 .

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_2 are most frequent in spring or summer due to the higher background values of O_3.

Table 2.2 Maximum concentrations of NO (not included in the smog warning system) and NO_2 in 1996. 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 ($\mu g(NO)/m^3$)	Day:hour	Max. hour ($\mu g(NO)/m^3$)	Day:hour
Copenhagen/1257	590	960607:10	799	960607: 7
Odense/9155	516	961114:16	843	960925: 7
Aalborg/8151	583	961217: 8	673	961023:10
Lille Valby/2090	125	960129:12	141	960126:12
Keldsnor/9055	180	961024:13	406	961024:13
Warning limit	-	-	-	-

	NO_2			
	Max. 3 hour ($\mu g(NO_2)/m^3$)	Day:hour	Max. hour ($\mu g(NO_2)/m^3$)	Day:hour
Copenhagen/1257	189	960607:10	218	960607: 7
Odense/9155	141	960421:19	150	960421:21
Aalborg/8151	132	960417:13	148	960422:20
Lille Valby/2090	90	960421:21	116	960421: 1
Keldsnor/9055	77	960410:20	91	960410:23
Warning limit	350	-	-	-
Guide value (WHO 1997)	-	-	200	-

Episode due to local construction

Figure 2.3 shows a local episode due to building construction work close to the station. The work took place June 6 and 7 in the periods marked on the figure. The two days were quite hot with low wind speed and high background concentrations of O_3. The extra amount of NO_2 related to the construction work is limited by the available O_3. This can be seen in the morning of June 7, where the O_3 concentration was very low and the increase in the NO_2 was delayed compared to NO. The wind velocity was below 1 m/s, but increased slowly and brought new O_3 to street level. It can be concluded that only a small fraction of the NO_x was emitted as NO_2. The WHO guide value was exceeded one hour during the work.

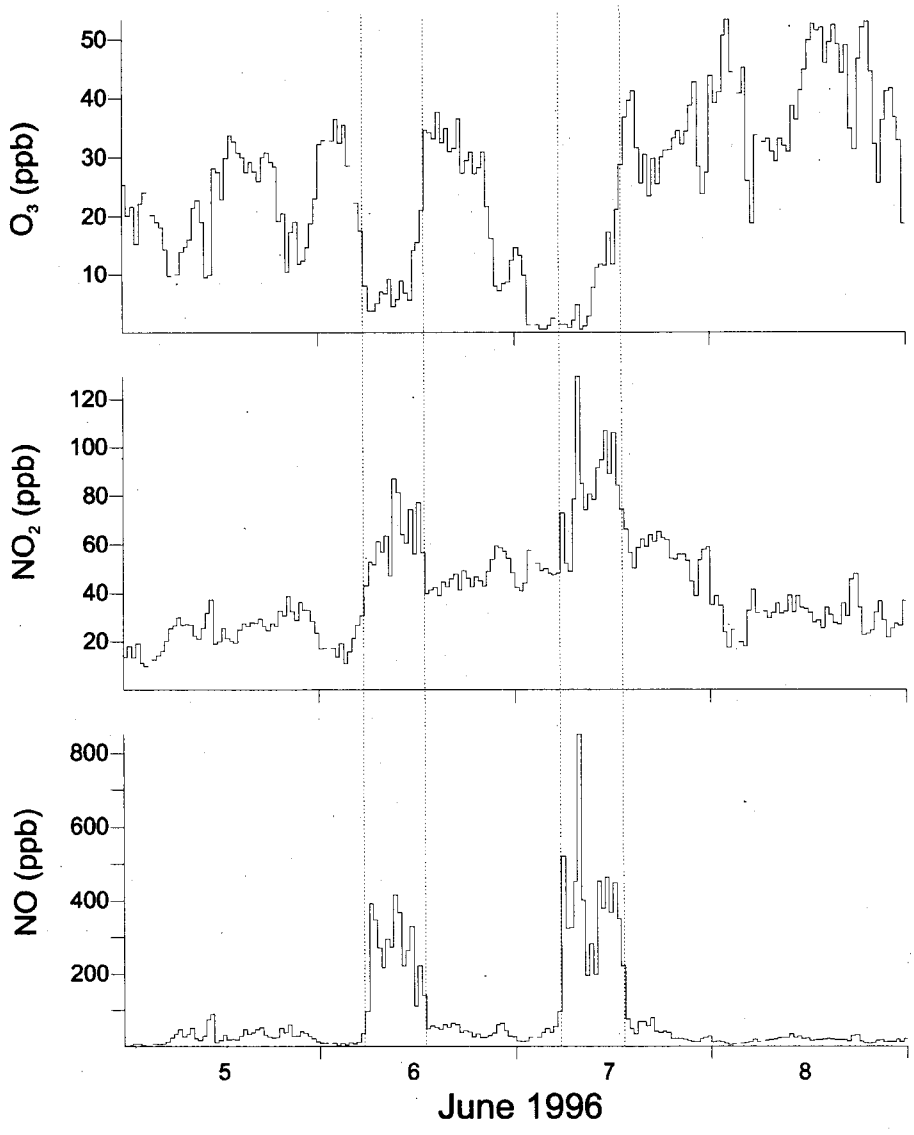


Figure 2.3 The episode recorded at Jagtvej/1257. The vertical dotted lines include the hours when the construction work took place.

Long range transport episode

In April a long range transport episode brought air with high concentrations of NO_x and O_3 from South to Denmark. Increased levels were observed at all stations. The course is illustrated in figure 2.4 for the two stations Jagtvej/1257 and Lille Valby/2090 together with the wind directions and temperatures measured at Copenhagen/1259. The concentrations were remarkably high. At Lille Valby/2090 it seems like the NO_2 was removed during the day, maybe due to formation of HNO_3 as a result of photochemical formation of OH radicals.

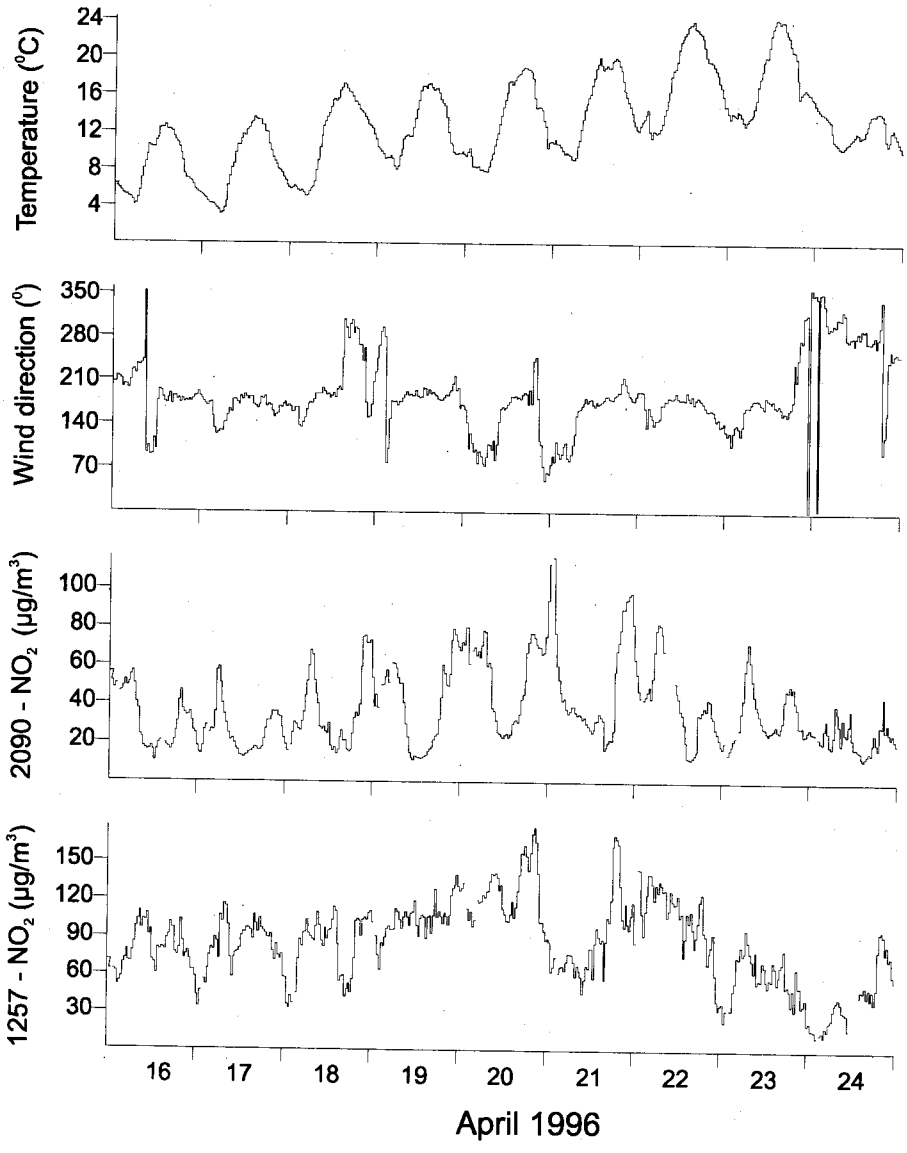


Figure 2.4 The NO_2 episode at Copenhagen/1257 and Lille Valby/2090. The meteorological parameters were measured at Copenhagen/1259.

2.3 Trends

Percentiles

The annual percentiles and average values for NO and NO_2 measured at Aalborg/8151 are shown in figure 2.5. The level of NO was almost constant in years synchronously with the increasing number of cars with TWC. The NO_2 level has, within the uncertainty due to meteorological variations, been constant the period from 1982 to 1991, but decreased apparently during the last few since the start of the measurements in 1982. The skewness of the distributions is obviously much greater for NO than for NO_2. The ratios between the 98-percentile and the median are approximately 7 for NO, whereas they are only 2-3 for NO_2. This indicates that at least at high NO concentrations some other factor limits the NO_2 formation. This is most likely the O_3 concentrations.

Averages

The trend of the monthly average values and the annual variation are shown in figure 2.6. Except for the decrease in NO from 1994 a possible trend is obviously hidden by the year to year variations for both NO and NO_2. The variation for NO and NO_2 seems to be (to some extent) opposite in the sense that years with high NO concentrations correspond to years with low NO_2 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_2.

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.

General explanation to the figures: 2.5, 4.3 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: 2.6, 4.4-5, 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.*

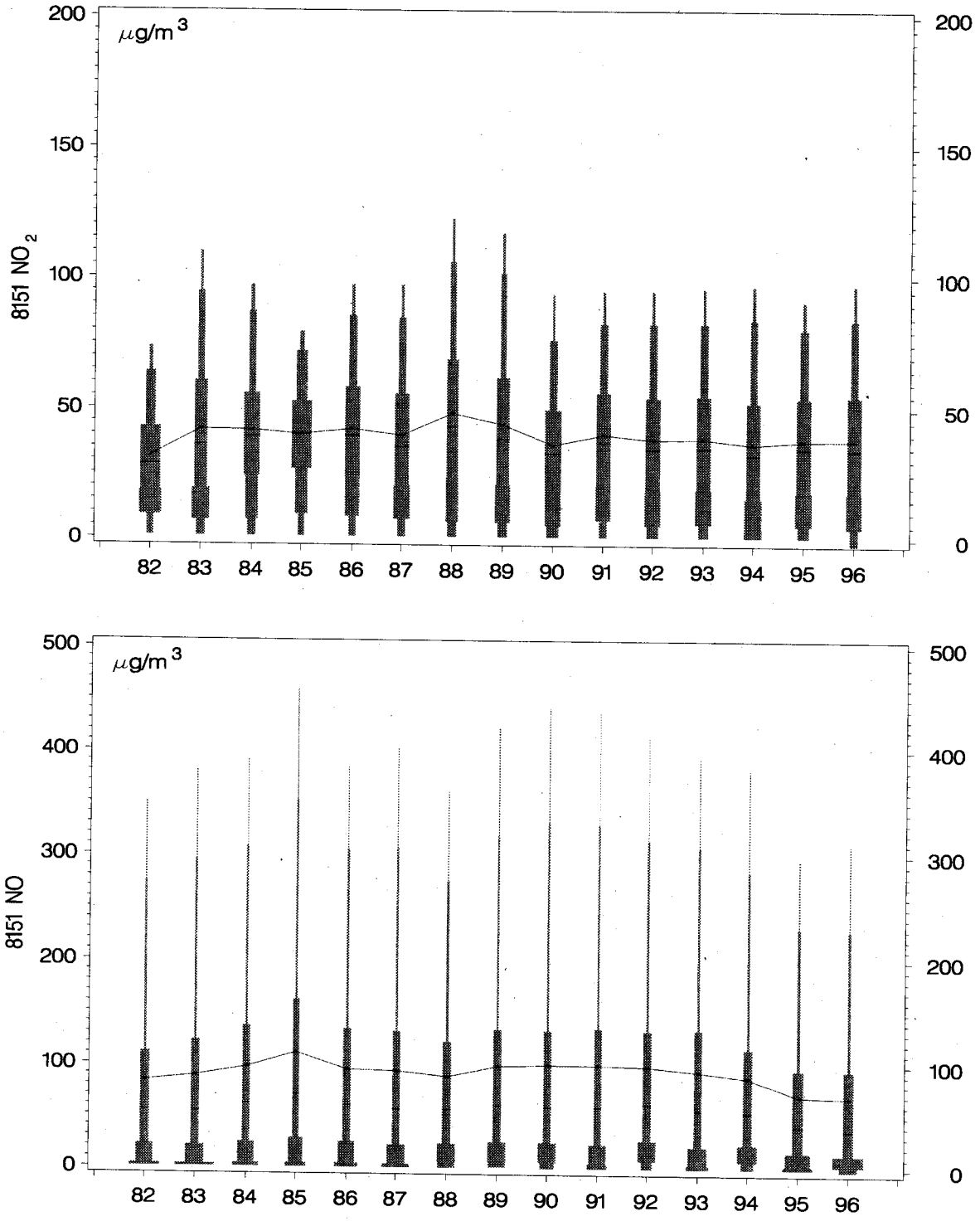


Figure 2.5 Trends for annual 98-, 95-, 75-, 50-, 25- and 5-percentiles, average and minimum value based on hourly average concentrations of NO_2 and NO measured at Aalborg/8151. (See explanation on p. 17).

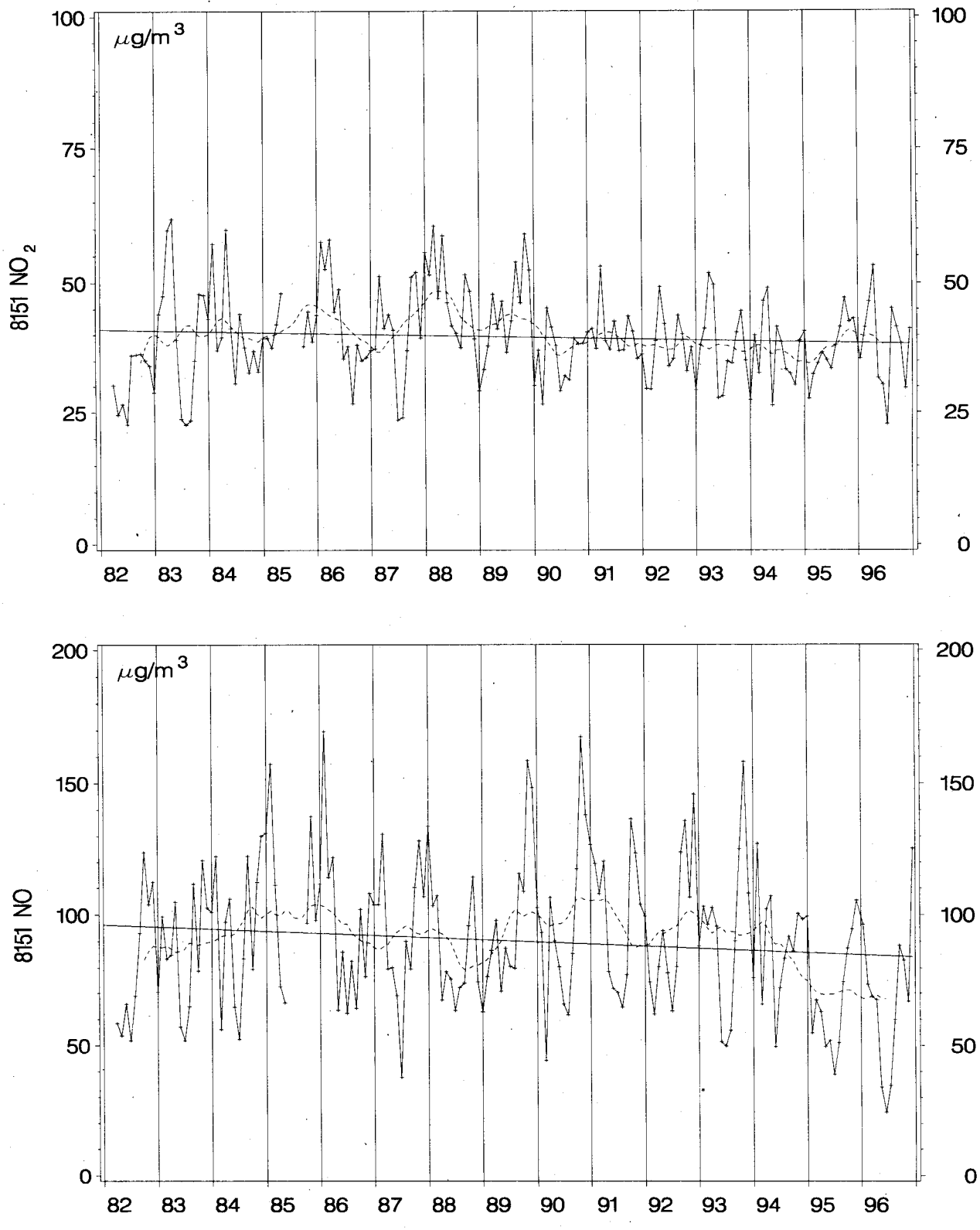


Figure 2.6 Trend for NO and NO_2 measured at Aalborg/8151. The points are measured monthly averages, the dotted curve is a moving average over 12 month and the straight line is a linear regression line. (see explanation p. 17).

3 Ozone

Measurements in 1996

Measurement of O_3 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_3 measurements at Keldsnor/9055 began in January 1995 (see table 1.1). Further O_3 measurements were performed from April 1994 at the street station Copenhagen/1257 in connection with the intensive traffic programme (Berkowicz et al. 1996). Almost all results are available for the whole year 1996 from all the stations, where it was planned to measure O_3, i.e. Copenhagen/1259, Odense/9159, Aalborg/8159, Lille Valby/2090 and Keldsnor/9055. However, all results from October to December from Aalborg 8159 were lost due to technical problems.

Sources and formation

The O_3 in the lower troposphere is formed as a secondary pollutant mainly by photochemical reactions involving i.e. volatile organic compounds (VOC) and NO_2. 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.e. 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.

Exceedings

The measured values are compared to the threshold values in table 3.1. The meteorological conditions were at the end of April and the beginning of June 1996 favourable for O_3 formation and transport. The temperature was relatively high and the air was in periods coming from Central Europe. The values in 1996, see table 3.1, were generally lower than the corresponding 1995 values. Especially the max. values and 99.9 percentiles were considerably lower. Both the max. 24 hour and the max. 8 hour threshold values were exceeded in many occasions in 1996 at all stations. The events occurred only from March to September. There were no exceedances during the winter month as have been the case the previous years.

Table 3.1 Annual average values, percentiles and maximum values for O3 measured in 1996 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.

O_3 (µg/m³)	Ave-rage	Median (hour)	98-perc. (hour)	99.9-perc (hour)	max. 24 hours	max. 8 hours	max. 1 hour
Copenhagen/1259	47	47	105	144	117	137	167
Odense/9159	44	45	104	146	122	147	166
Aalborg/8159	53	55	104	149	93	134	157
Lille Valby/2090	50	50	105	144	104	132	151
Keldsnor/9055	58	59	113	148	120	141	173
Threshold value	-	-	-	-	65	110	200
Average number of exceedances per station	-	-	-	-	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 (≈ 80 µg/m³), 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 AOT40 values (UN-ECE 1996). Unit ppb·h.

Station	AOT40 (crops)		AOT40 (forest)	
	1995	1996	1995	1996
Lille Valby/2090	4700	1513	8850	5510
Keldsnor/9055	2850	2540	6800	8020
Guide v. UN- ECE	3000		10 000	

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 µg/m³ and to issue a warning, if the hourly average concentration exceeds 360 µg/m³. 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.

Press releases

At one occasion in 1996 it was recorded that the concentrations exceeded the threshold for information of the population. A press release was broadcasted by the nation-wide radio in the news at June 7. The final quality control of the data showed however that the concentration was slightly below 180 $\mu g/m^3$. At two occasions, from April 18 to 23 and from June 5 to 10, a stable high pressure near Denmark gave frequent air transport from Central Europe to Denmark. The concentrations 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.

The episodes in April and June

Figure 3.1 shows the results from Keldsnor/9055 during the episodes in April and June. The temperature during the episode in April was unusual high for that time of year - up to 25°C. The air was probably coming from far south. High concentrations of NO_2 were observed in the same period together with the O_3 (see chapter 2.2).

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 until the conditions changed drastically by a cold front passing the country.

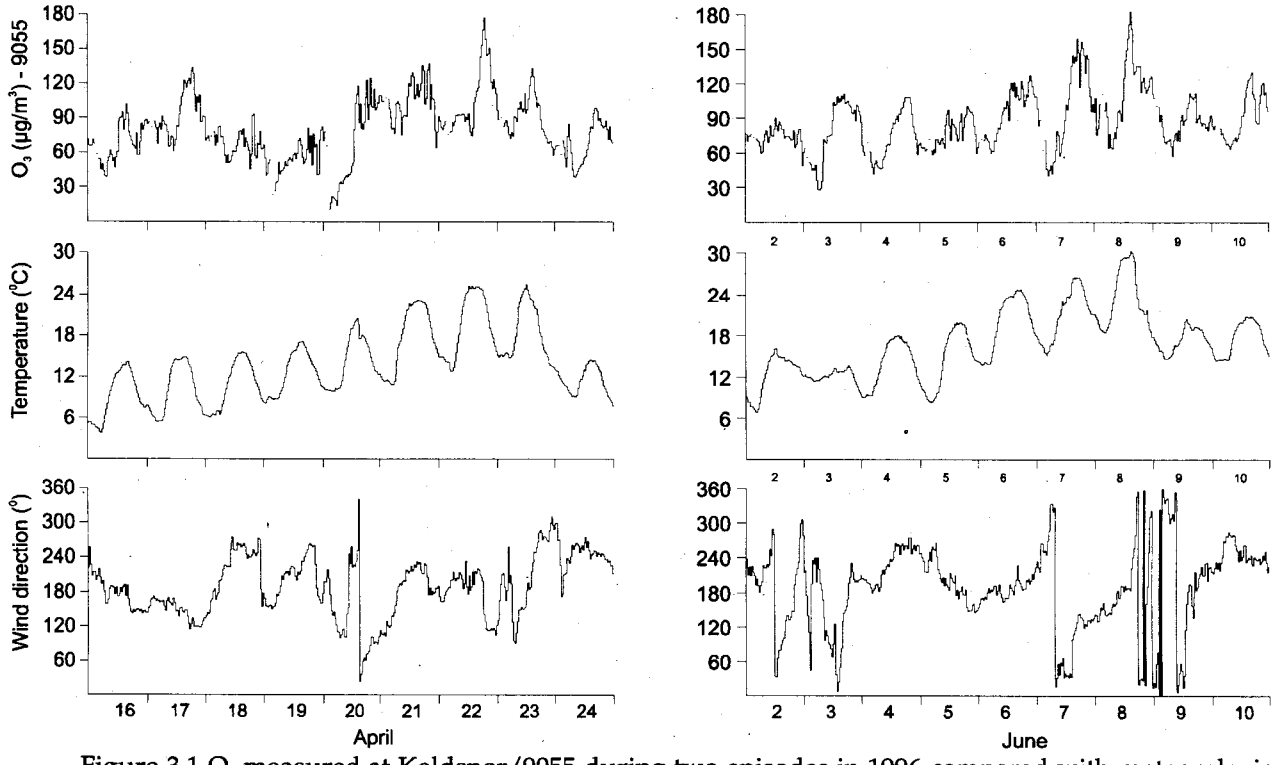


Figure 3.1 O_3 measured at Keldsnor/9055 during two episodes in 1996 compared with meteorological results from Odense/9159.

3.3 Phenomenology

Wind direction dependency

The reaction mechanisms for formation and decomposition of O_3, as described in the first part of this chapter, are illustrated in the following by different extracts of the results.

The average concentrations corresponding to different wind directions are shown in figure 3.2. The results from 1995 and 1996 are divided on summer (May-August) and winter (November-February) periods. Concentrations of 50-80 $\mu g/m^3$ in average were found for winds from NW both summer and winter. This represents probably the hemispheric background concentrations. At winds from south and south east the concentration exceeded the background level in the summer period, while it was lower during winter. This indicates a net production of O_3 during summer, when the photochemical activity is high, and a net depletion during winter in the polluted air coming from Central Europe. The pattern at all stations was very similar but the levels were slightly reduced at the urban stations (Copenhagen/1259, Odense/9159 and Aalborg/8159) as a result of the presence of i.a. NO.

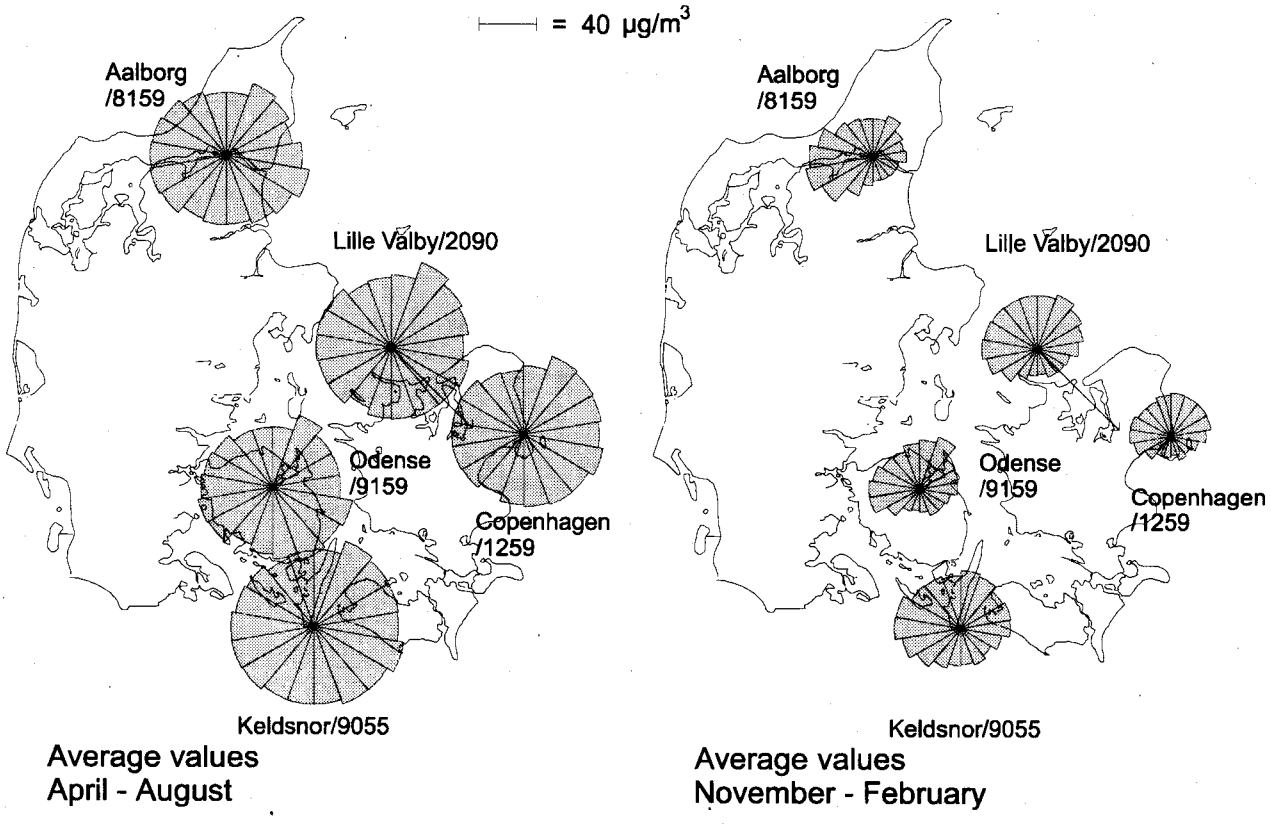


Figure 3.2 Wind direction distribution for O_3 for results from 1995-1996. The radii of the circle sections are proportional to the average concentrations for winds coming from the direction the section points towards.

There is a strong wind direction dependency of the frequency of the high concentrations. Figure 3.3 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 from ESE, but they may occur in all wind sectors.

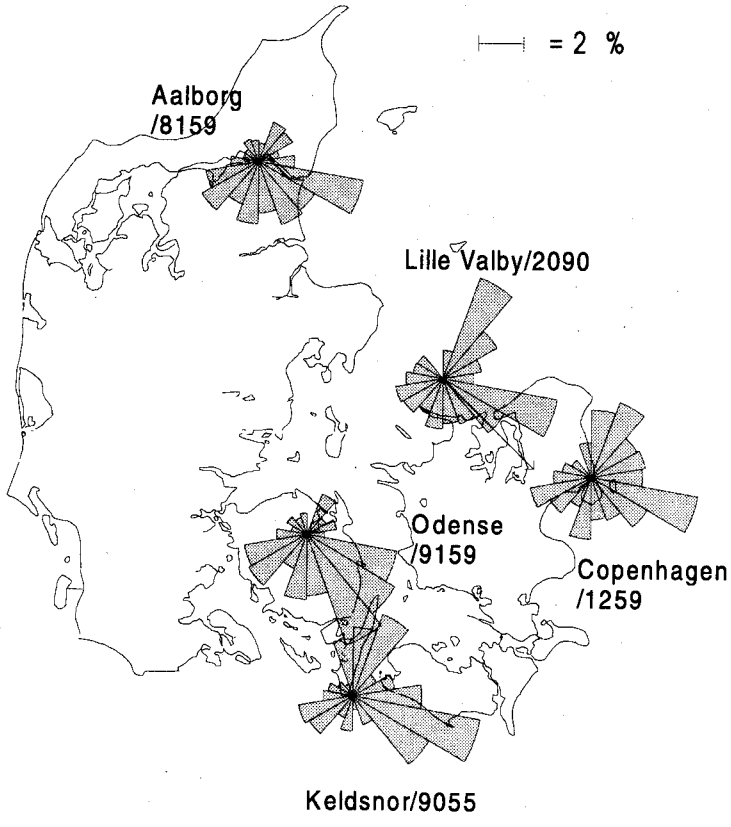
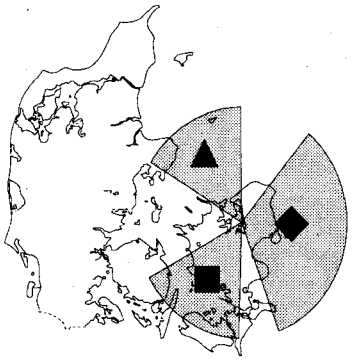


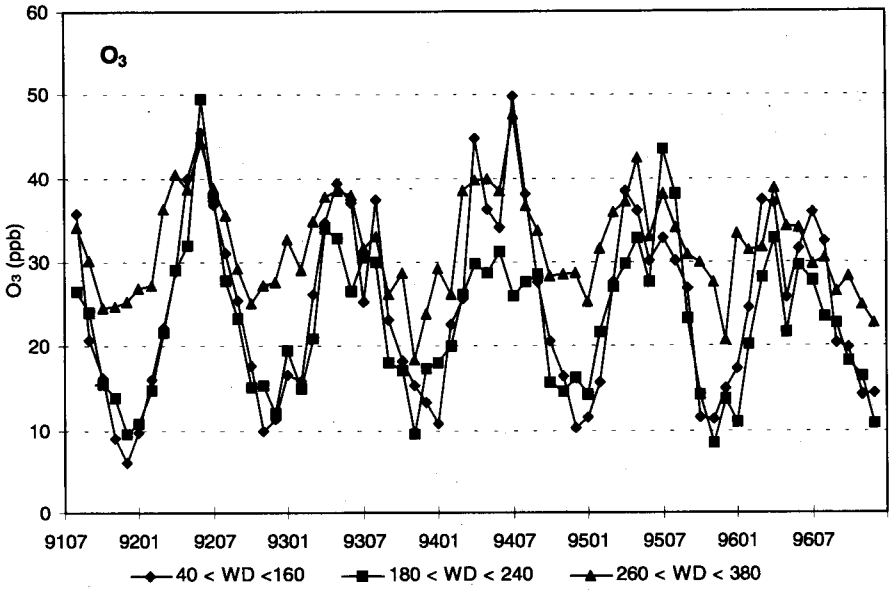
Figure 3.3 Distribution with wind direction of the upper 2 % of the O_3 concentrations (above the 98-percentile) drawn as frequency in the wind sectors compared to the number of measurements in the same sectors. Results from 1995 and 1996 are included. The radii of the circle sections are proportional to the relative frequency for winds coming from the direction the section points towards.

Trend for O_3 and O_x

More than five years of data are now available from Lille Valby/2090. The development is illustrated by means of the monthly average values in figure 3.4. The results are divided according to wind direction sectors. The sector from 40 to 160° represent the continental contribution with an addition of some regional contribution from the Copenhagen area, the sector from 180 to 240° represents the western part of Continental Europe, while the background contribution is assumed to be found in the sector from 260 to 20°. No significant trend is observed in the period, but the seasonal variation is a factor of 1.5 to 3. The relatively low winter concentrations in the background sector illustrates 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 1993, 1994, 1996a, 1996b), remarkably alike for all three sectors. Both the absolute concentrations and the seasonal variation for the sectors with anthropogenic contribution were close to the O_3 background.





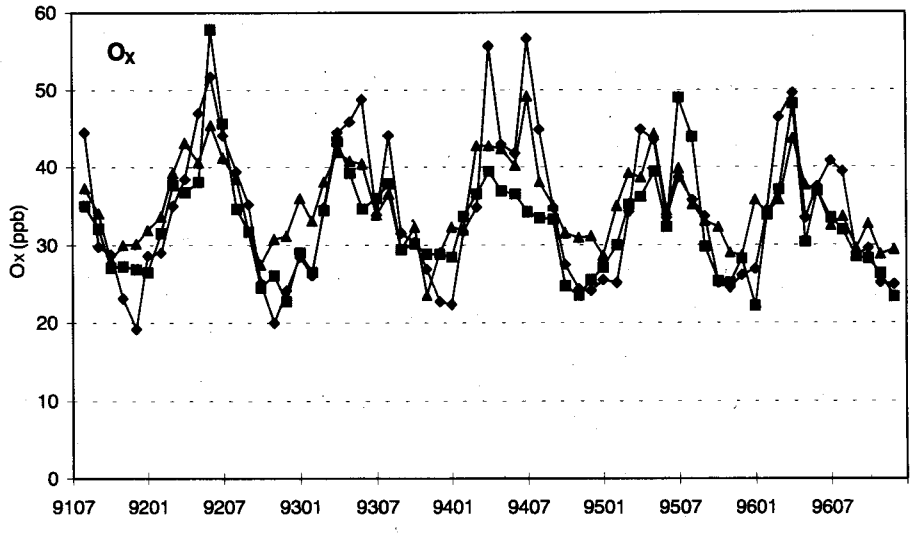


Figure 3.4 Monthly average values measured at Lille Valby/2090 for O_3 and O_x (O_3+NO_2). The wind sectors for the single curves are shown on the map. The signatures on the map correspond to the points on the curves.

Correlation between stations

The correlation between simultaneous measurements is high at all stations (table 3.2). The parameters in the table are very close to the corresponding results from previous years (Kemp, Palmgren and Manscher 1996b). The correlation seems to be more related to the geographical distance between the stations (figure 1.1) than to the direct surroundings i.e. urban or rural. The slope of the regression lines (a) are in all cases close to one. There are small differences for the cut-off values (b), which may be related to the NO_x concentrations at the stations.

Table 3.2 Correlation between O_3 concentrations for measurements from 1996. The parameters for the orthogonal regression line $y = a \cdot x + b$ and the correlation coefficient, ρ, are given for all combinations of stations.

x \ y	Keldsnor/9055			Lille Valby/2090			Aalborg/8159			Odense/9159		
	a	b	ρ	a	b	ρ	a	b	ρ	a	b	ρ
		µg/m³			µg/m³			µg/m³			µg/m³	
1259	0.93	15	0.71	0.95	5.6	0.83	0.98	-0.2	0.69	0.98	-1.2	0.71
9159	0.97	15	0.76	0.98	6.5	0.80	1.02	0.7	0.73			
8159	0.95	14	0.61	0.99	2.6	0.72						
2090	0.99	8.4	0.68									

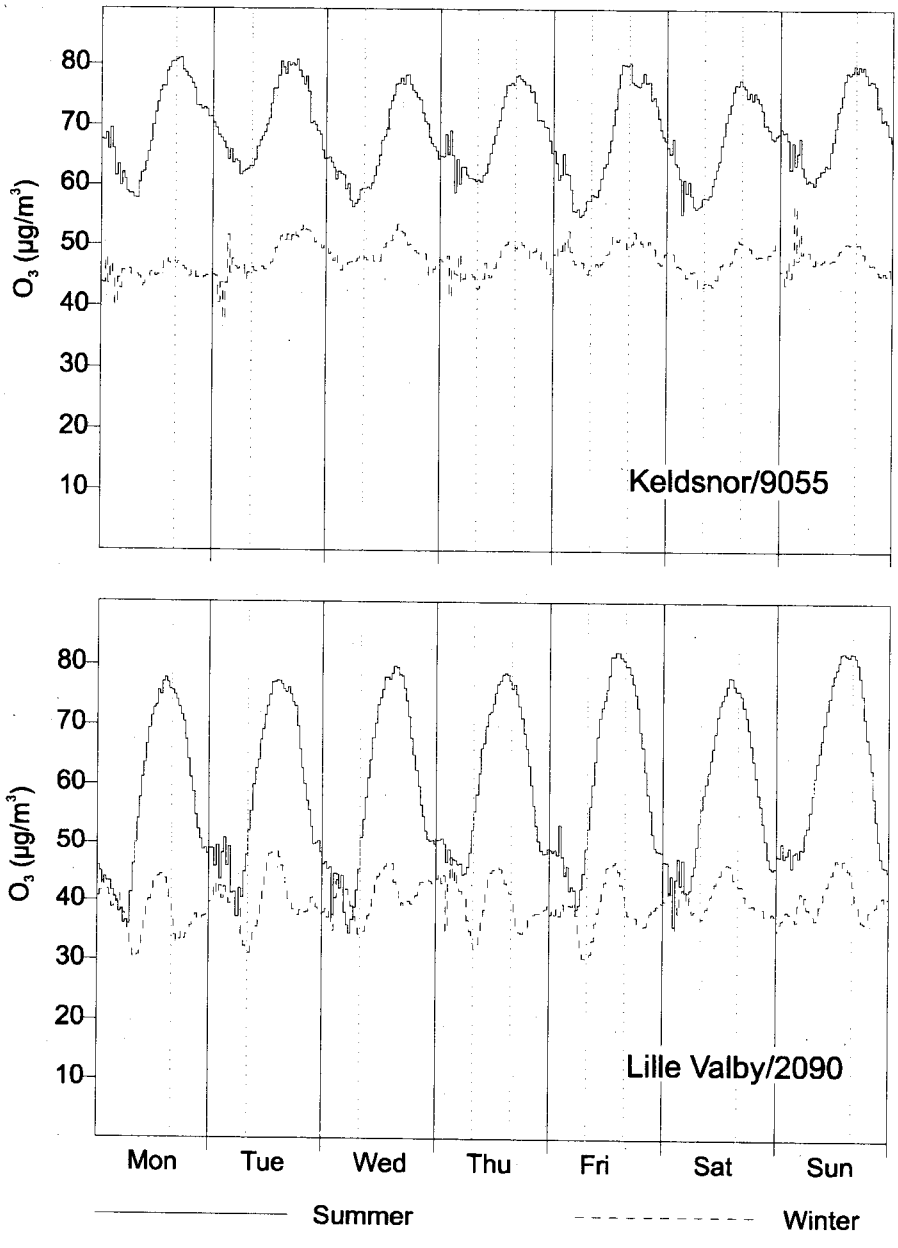


Figure 3.5 Weekly average variation for O_3 at Keldsnor/9055 and Lille Valby/2090 during 1995 and 1996. The summer is defined as the period daylight saving time is used. The time on the graphs is Danish standard time (i.e. wintertime).

Coastal vs. inland site

Keldsnor/9055 is located near the coast, which makes the micro-meteorological conditions quite different from the location for the other rural site Lille Valby/2090. In periods with warm and stable meteorological conditions the mixing layer will become very low at the inland site in the nights. There will be very low admission of new O_3 from aloft and the old will deposit or react with the nitrogen oxides. At the coastal station the mixing layer will be higher and the available O_3 will not be depleted or deposited so much. This difference is illustrated by the variation during the week in figure 3.5. While the average summer maxima are approximately the same at the two stations the night minima are about 50 % higher at Keldsnor/9055 than at Lille Valby/2090. The average concentrations peaks at around 3 p.m. at Lille Valby; but is delayed until 5 p.m. at Keldsnor. During the winter the average concentrations are almost constant during the week at both stations.

4 Sulphur compounds

Sources

Sulphur is determined in gas phase as SO_2 and as the elemental content in particulate matter. The main source of SO_2 is combustion of heavy oil and coal. Sulphur in particulate matter is expected to be sulphate (either HSO_4^- or SO_4^{2-}). The two main sources of the sulphate are the oxidation of SO_2 to H_2SO_4 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_2 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_2 may be of local origin as well as long range transported.

Measurements

In 1996 the concentration of SO_2 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_2 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

There are several limit values for SO_2 concentrations in Denmark (Miljøministeriet 1986). They are listed in table 4.1 together with the measured concentrations. The limit values are 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_2 and particulate sulphur pollution in Danish cities. The values are calculated for all valid 24 hour results from 1996. The winter is defined as the three first and three last month of the year. The number of measurements for SO_2 is given for the whole year/as well as for the winter.

Station	SO_2 ($\mu g(SO_2)/m^3$)							Particulate S ($\mu g(S)/m^3$)	
	Number	Median year	Median winter	max. 3 days	98-perc.	max day	Average	Number	Average
Copenhagen/1257	349/177	5.4	6.8	27	28	38	7.1	351	2.0
Odense/9155	363/181	3.2	4.1	28	26	52	4.9	363	1.9
Odense/9154	322/164	3.2	4.3	27	30	47	5.1	322	1.9
Aalborg/8151	300/147	2.5	3.3	47	39	62	5.0	300	1.8
Lille Valby/2090	359/179	2.0	3.0	26	24	43	3.7	360	1.5
Limit value	-	80	130	250	250	-	-	-	-
Guide - (EEC 1980)	-	-	-	-	-	-	40-60	-	-
Guide - (WHO 1997)	-	-	-	-	-	125	50	-	-

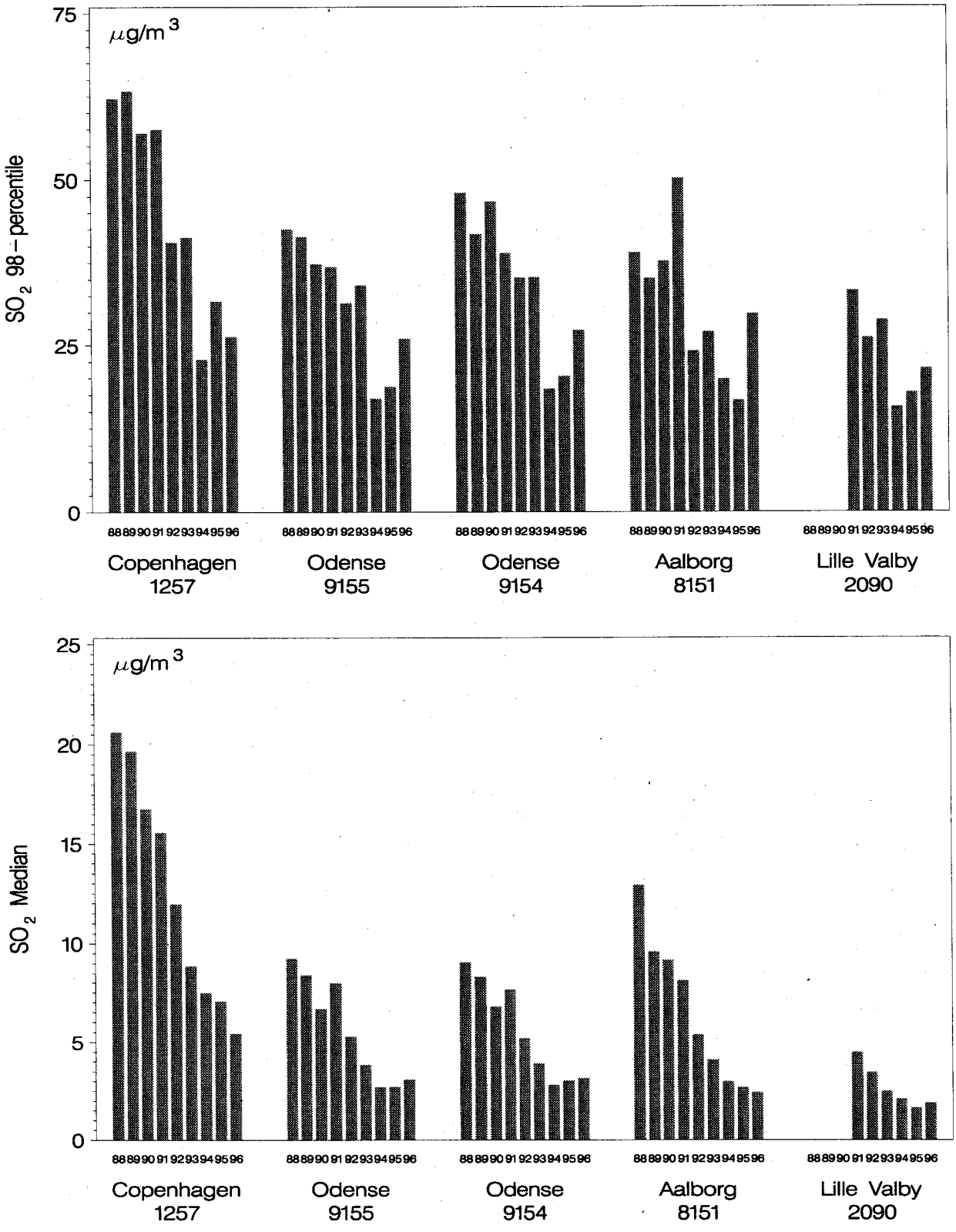


Figure 4.1 Medians and 98-percentiles for SO_2 from 1988 to 1996.

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_2 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 4.2 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 $\mu g/m^3$.

Table 4.2 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 $\mu g/m^3$ for consecutive three hour is the same as 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 time is the beginning of the periods. The number of hot spot episodes are given in the sixth column.

	SO_2 ($\mu g(SO_2)/m^3$)					Particulate S ($\mu g(S)/m^3$)	
Station	Max. 3 hour	Day:hour	Max hour	Day:hour	"Hot-spot" episodes	Max. day	Day
Copenhagen/1257	103	960410:13	261	960325:12	13	7.8	960116
Odense/9155	104	960817:10	183	960817:11	13	8.1	960213
Odense/9154	-		-	-	-	6.5	960617
Aalborg/8151	91	960210:12	163	960512:17	16	7.3	961015
Lille Valby/2090	65	960116:18	78	960116:19	0	7.0	960213
Warning limit	350		-		-	-	

Long range episode

The concentrations of both SO_2 and particulate S were high during the winter months January to March 1996. The period was rather cold, which gave rise to relatively high domestic emissions. The wind was coming from South-east most of time, which in periods opened for long range transported pollution. These conditions are reflected in i.e. the 98-percentiles for 1996 (table 4.1 and figure 4.1), which for most stations were considerably higher than the previous

years. The most pronounced long range episode occurred in February (figure 4.2). The wind direction was very stable and the wind was brisk from February 9 to 13. Both SO_2 and particulate sulphate was found in high concentrations at all stations. As seen in figure 4.2 the SO_2 concentration was highest the 11th and 12th, while the particulate sulphate peaked the 13th indicating that the air came from other source areas, while the front, which passed between the 13th and 14th, was approaching.

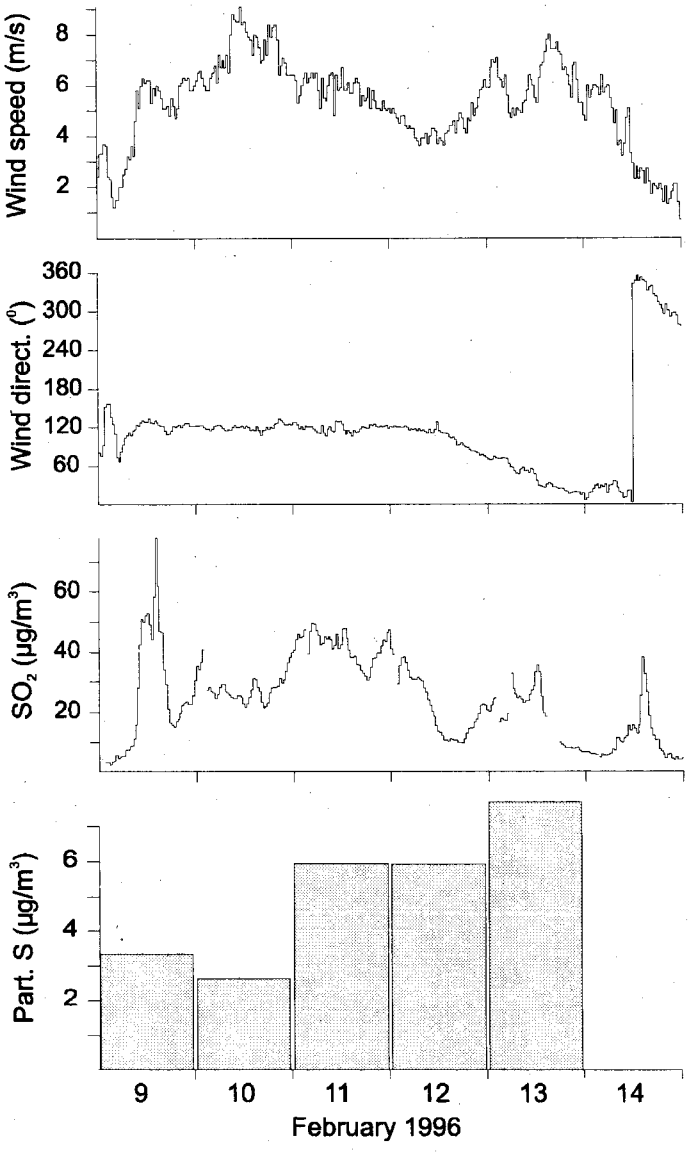


Figure 4.2 The SO_2 episode in February 1996 at Odense/9155.

Hot-spot episodes

Hot-spot episodes are observed at irregular intervals in all three cities. We identify hot-spot episodes as a more than 50 µg/m³ 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 4.2. The number of hot-spot episodes was somewhat higher in 1996 than in 1995. As in the previous years the hot-spot episodes in Odense was

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 appointed as main contributor in Copenhagen.

4.3 Trends

Percentiles for SO_2

The annual percentiles and average values based on daily average SO_2 concentrations measured at Aalborg/8151 are shown in figure 4.3. The level of SO_2 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 several mild winters the winter 94/95 and 95/96 were close to normal. The results from 1996 show an increase of especially the short term parameters compared to the previous years (cf figure 4.1).

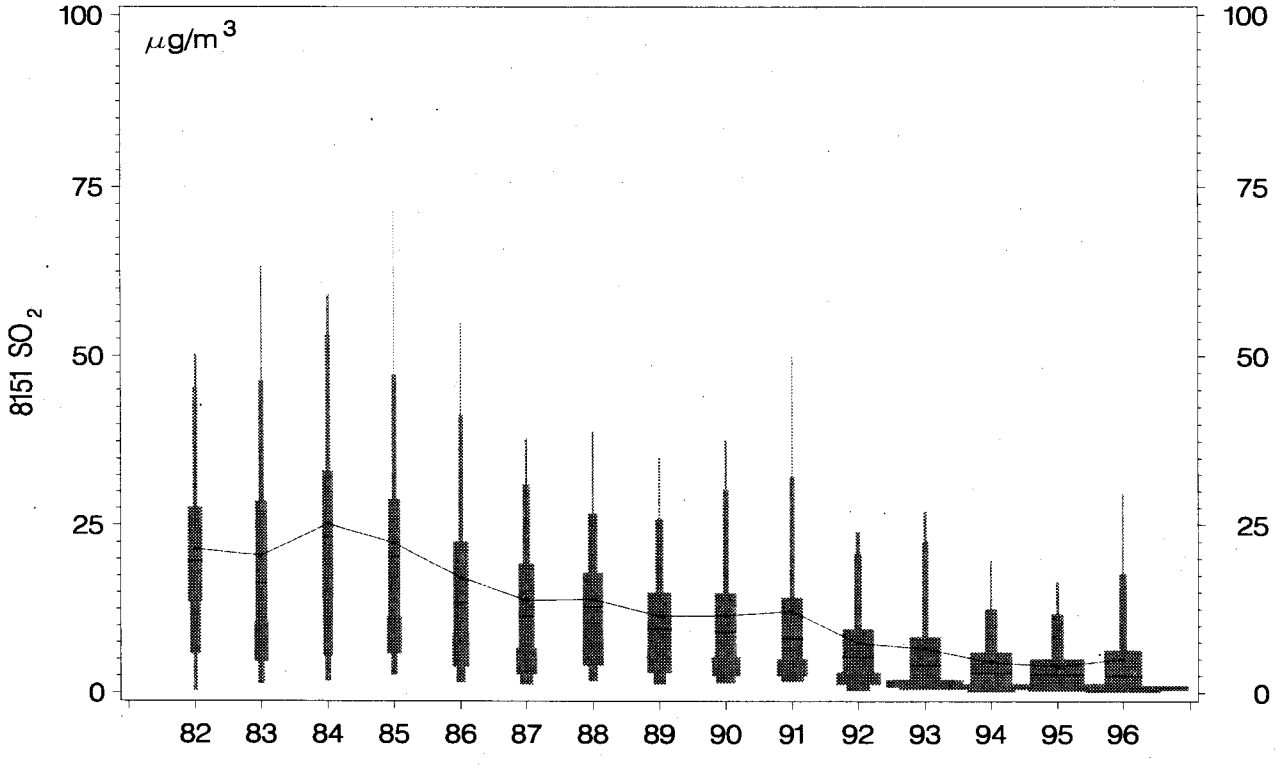


Figure 4.3 Trends for annual 98-, 95-, 75-, 50-, 25- and 5-percentiles, average and minimum value based on hourly average concentrations of SO_2 measured at Aalborg/8151. (See explanation on p. 17).

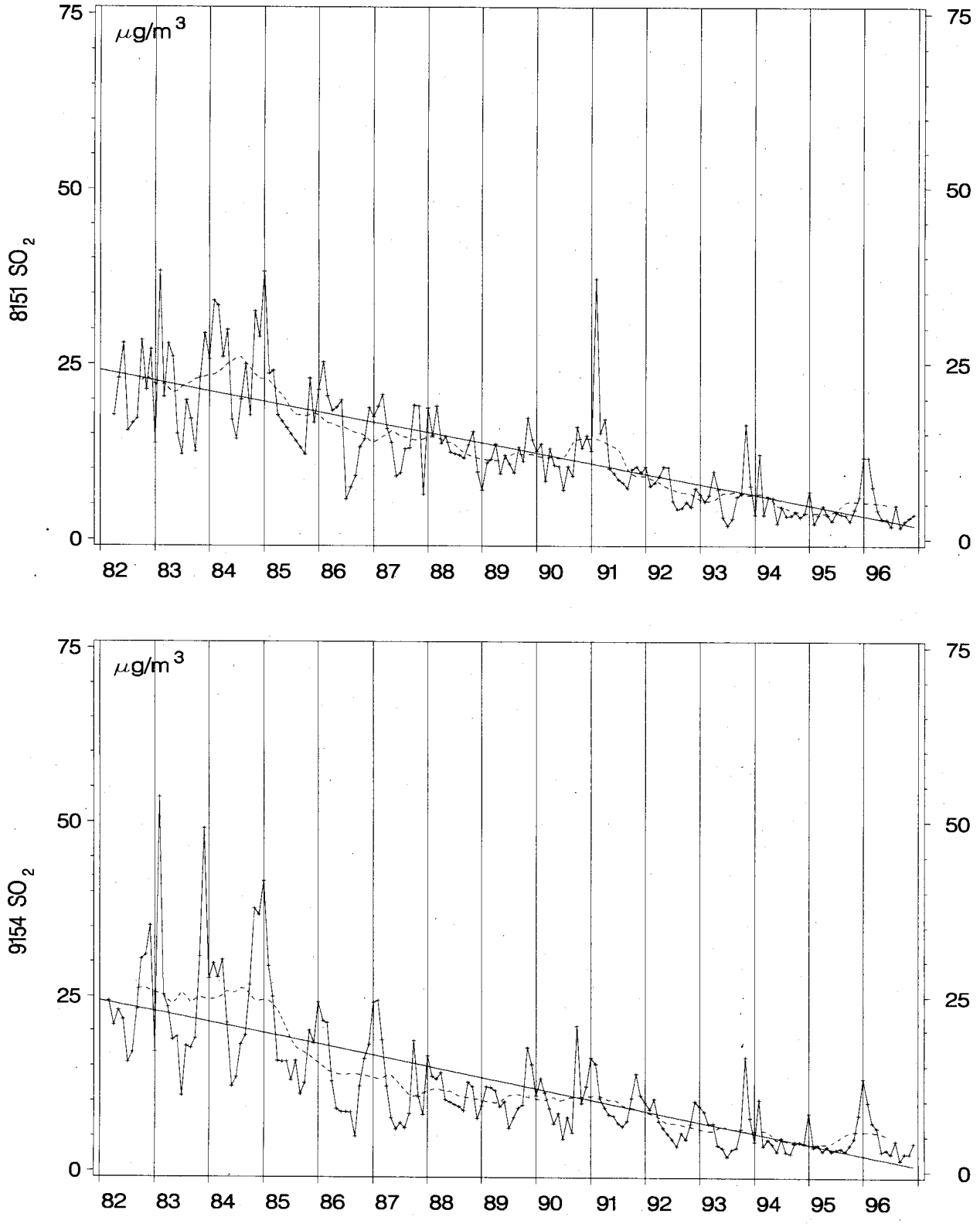


Figure 4.4 Trend for SO_2 measured at Aalborg/8151 and Odense/9154. The points are measured monthly averages, the dotted curve is a moving average over 12 month and the straight line is a linear regression line (see explanation on p. 17).

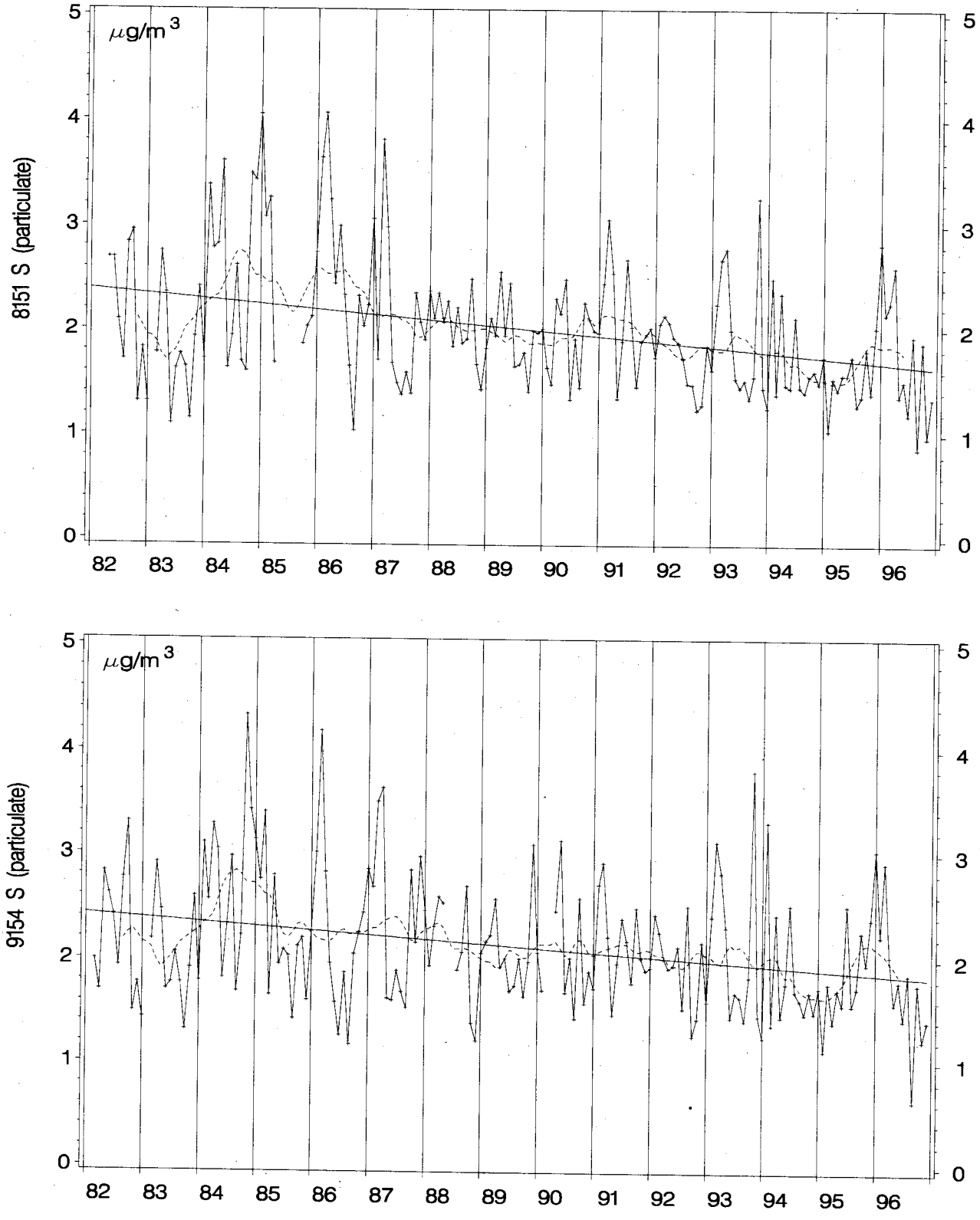


Figure 4.5 Trend for particulate S measured at Aalborg/8151 and Odense/9154. The points are measured monthly averages, the dotted curve is a moving average over 12 month and the straight line is a linear regression line (see explanation on p. 17).

Average SO_2 and S concentrations

The trends for the monthly average values at Aalborg/8151 and Odense/9154 are shown in figure 4.4 for SO_2 and in figure 4.5 for particulate sulphur. The average SO_2 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. The concentrations have been almost stable at the present level since 1994. Particulate S shows, in contrast to SO_2, only a slightly downward trend. This shows probably that 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_2.

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 µm, but this cut-off varies from about 10 to 50 µm depending on the wind speed (Kemp 1993).

Sources

The particles are a mixture from the different source types, but the coarse particles (> 2 µm) 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 1996 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 1996 are given in table 5.1. The annual 95-percentiles and average values are shown for 1988-1996 in figure 5.1.

Table 5.1 Average values, 95-percentiles and maximum values for TSP in 1996. The numbers are calculated for 24 hour average values.

		TSP (µg/m³)			
Station	Number	Average - whole year	95-perc.	Max.value	Day
Copenhagen/1257	351	65	149	366	960208
Odense/9155	363	63	129	261	961114
Odense/9154	322	52	103	186	960422
Aalborg/8151	300	69	151	287	960205
Lille Valby/2090	359	28	59	174	960420
Limit value	min. 100	150	300	-	-

Measured values

The measured values at the urban stations were between 1/4 and 1/2 of the limit values. The 1996 results were somewhat higher than in 1995. The main reason is the cold and windy conditions in the first months of 1996. The general trend has been slightly decreasing since 1988 (figure 5.1) 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. obligatory three way catalysts on gasoline cars and restrictions on the diesel exhaust.

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

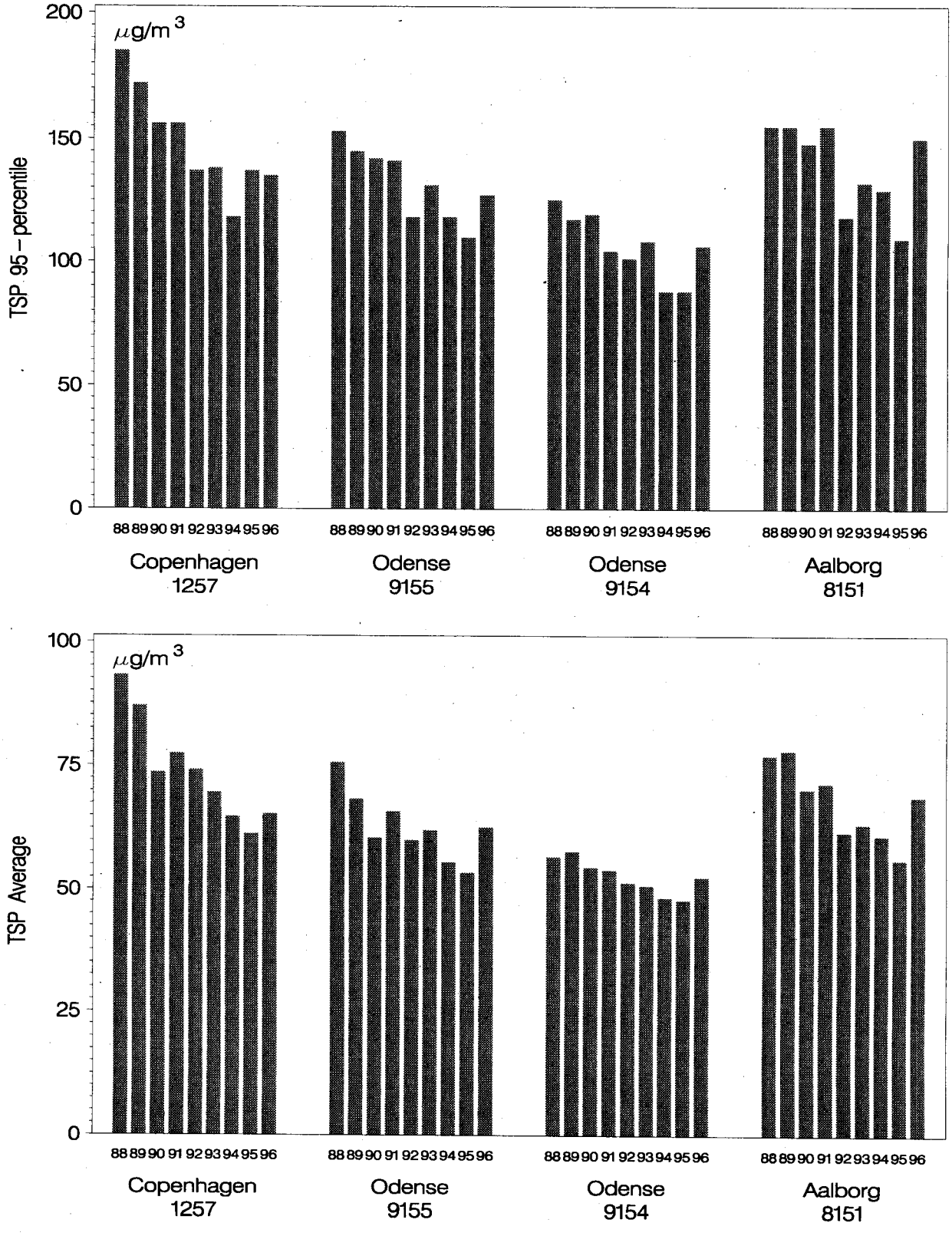


Figure 5.1 Average values and 95-percentiles for TSP from 1988 to 1996.

5.2 Episodes

The measured maxima of the daily average values are given in table 5.1. There were several episodes in 1996. The highest value was recorded February 8 at Copenhagen/1257 during a cold and dry period. The concentration (366 µg/m^3) was the highest value measured in the program since 1991. High values were also recorded during the episodes in April and June (see chapter 3.2).

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 seem 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_2 where the decrease was steeper for the long term than for the short term values.

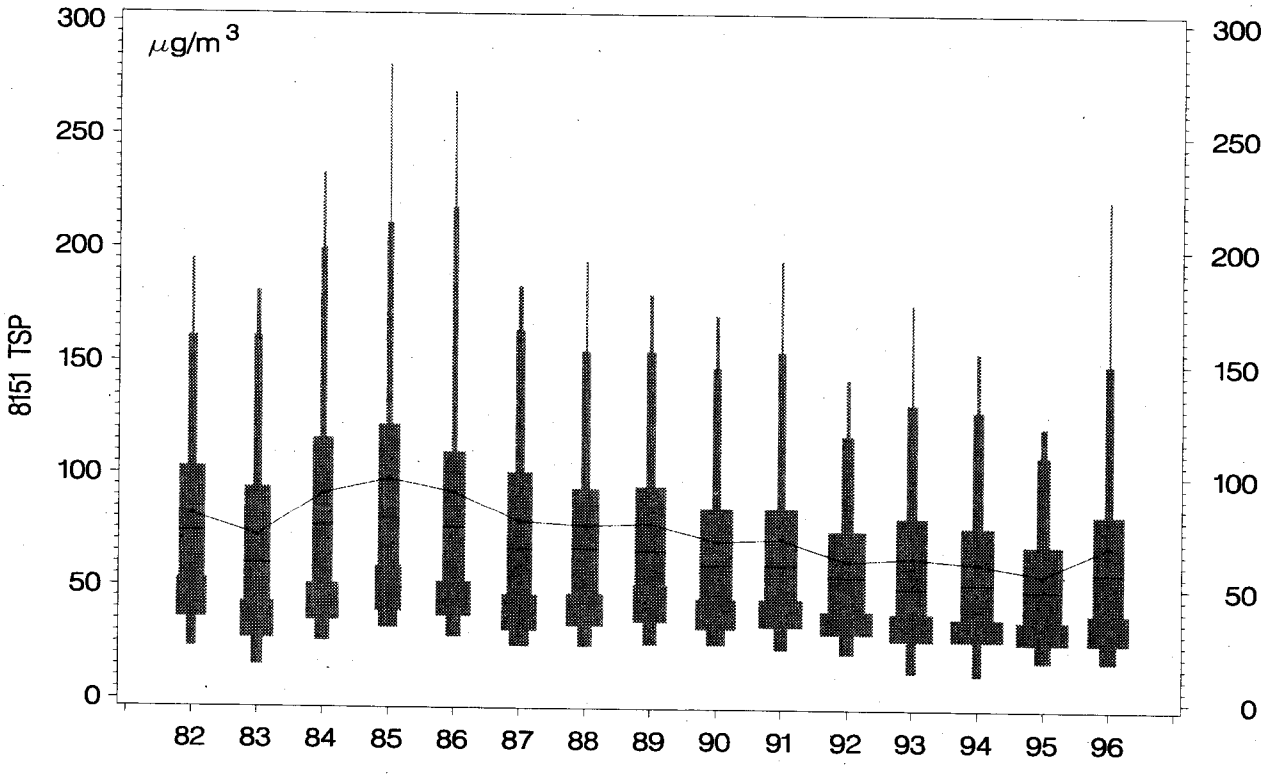


Figure 5.2 Trends for annual 98-, 95-, 75-, 50-, 25- and 5-percentiles, average and minimum value based on daily average concentrations of TSP measured at Aalborg/8151. (See explanation on p. 17).

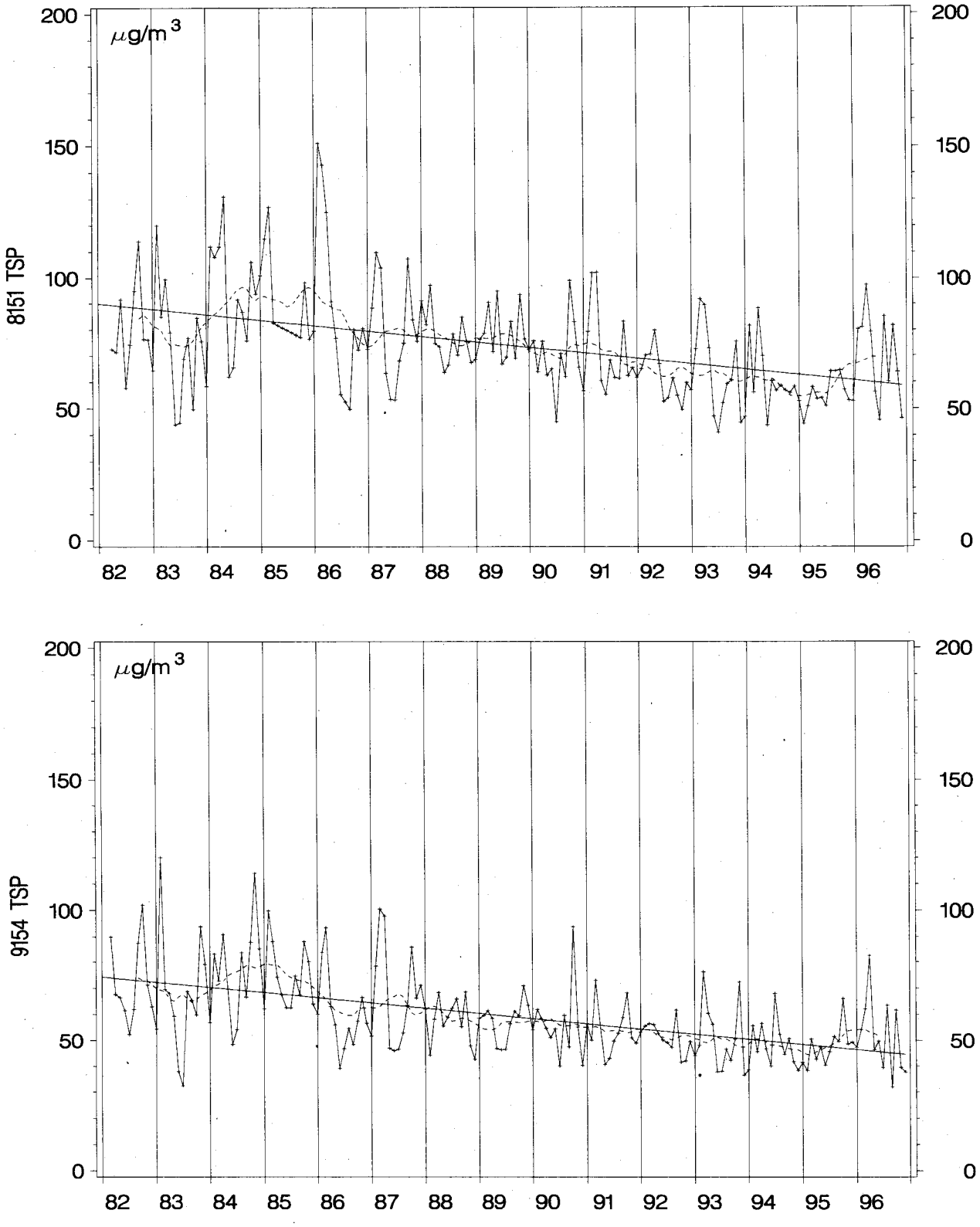


Figure 5.3 Trend for TSP measured at Aalborg/8151 and Odense/9154. The points are measured monthly averages, the dotted curve is a moving average over 12 month and the straight line is a linear regression line (see explanation on p. 17).

Annual average

After relatively high concentrations from 1984-1986 there has been a continuous decrease since 1986 (figure 5.3). 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.

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.

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 1993 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 is combustion of heavy oil the main source of V and Ni, wind blown dust of Si, and the main origin of particulate S is 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 measured annual averages in 1996 were just above 1 % of the limit value at the traffic sites in streets with heavy traffic (figure 6.1 and table 6.1).

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 then a factor of 40 (see figure 6.2) . The present level in urban areas is only about twice the background level in Denmark.

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 1997). 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.

Table 6.1 Average values for 1996. All concentrations are given as ng/m^3 (1 µg/m^3 = 1000 ng/m^3). N_{tot} is the number of measurements in 1996. 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.

	Copenhagen/1257		Odense/9155		Odense/9154		Aalborg/8151		Lille Valby/2090	
Element	N_0	Average	N_0	Average	N_0	Average	N_0	Average	N_0	Average
Al	308	605.0*	311	672.0*	267	354.0*	261	748.0*	133	123.0*
Si	351	1520.0	363	1740.0	322	994.0	300	2320.0	351	370.0
S	351	2000.0	363	1890.0	322	1880.0	300	1800.0	360	1500.0
Cl	351	4530.0	363	3450.0	322	1840.0	300	4020.0	360	421.0
K	351	281.0	363	308.0	322	258.0	300	318.0	360	183.0
Ca	351	1110.0	363	1160.0	322	564.0	300	1580.0	360	191.0
Ti	351	58.7	363	70.7	322	43.5	300	58.1	318	11.1*
V	346	7.2	336	6.0	304	5.1	277	5.7	319	4.4*
Cr	351	5.6	363	5.4	319	3.4	299	3.7	324	1.1
Mn	351	21.6	363	32.6	322	18.5	300	17.5	360	4.8
Fe	351	1200.0	363	1110.0	322	691.0	300	982.0	360	143.0
Ni	351	4.2	363	3.5	322	3.3	298	3.8	360	2.3
Cu	351	48.2	363	31.6	322	20.4	300	26.0	334	2.1
Zn	351	66.8	363	92.3	322	48.8	300	67.2	330	18.5
As	313	2.1*	310	2.0*	281	1.7*	246	1.6*	324	1.5
Se	312	0.6*	328	0.8	310	0.8	253	0.6*	355	0.6
Br	351	5.3	363	5.0	322	4.9	300	6.0	360	3.6
Sr	351	5.3	363	5.1	322	3.2	300	7.7	357	1.5
Zr	350	4.3	358	4.3	320	2.6	298	3.3	235	0.4*
Mo	332	3.1	307	2.2*	279	1.5*	232	1.7*	134	0.4*
Cd	94	0.9*	93	0.8*	94	0.8*	53	0.7*	99	0.6*
Sb	336	13.3	337	9.9	279	5.8*	253	6.7*	181	1.5*
Ba	348	36.8	342	34.1	304	22.0	265	23.7*	132	3.8*
Pb	351	24.8	363	21.9	322	19.4	300	18.6	360	11.0
N_{tot}	351		363		322		300		360	

* Calculated from a fit to a log-normal distribution.

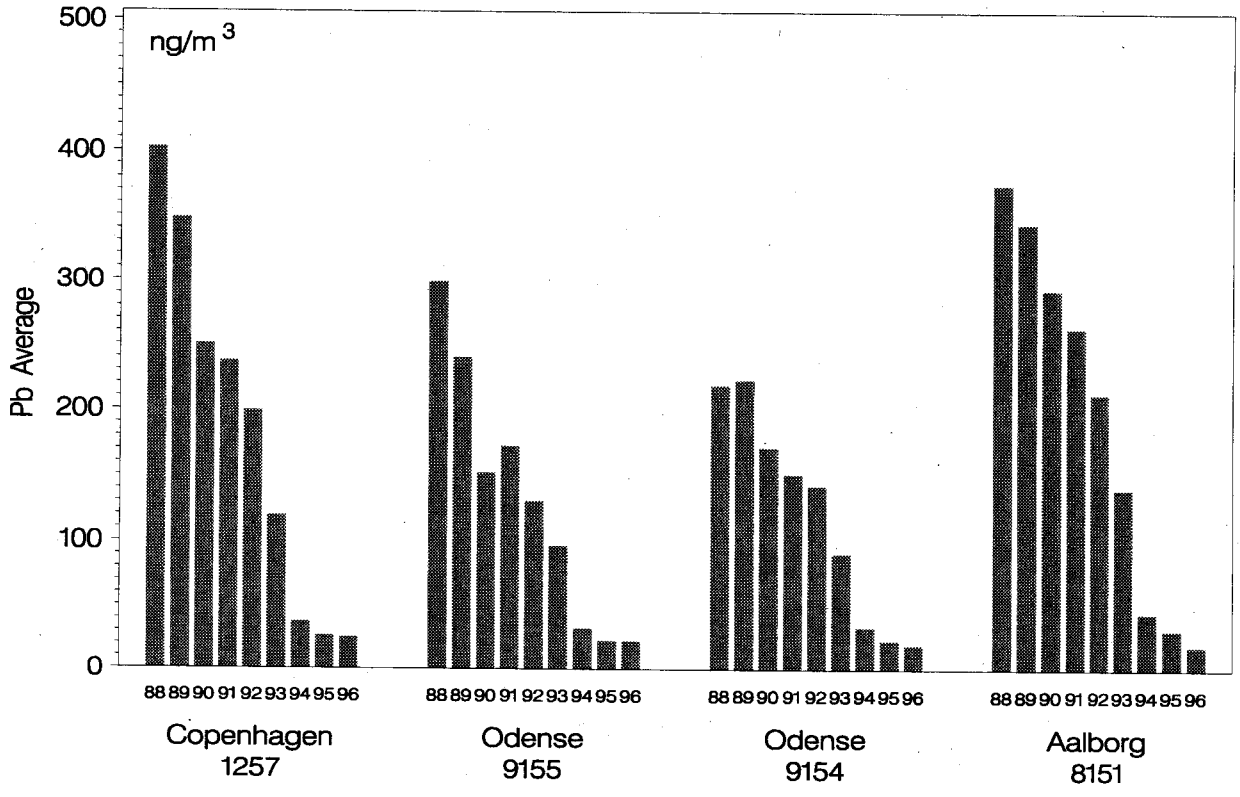


Figure 6.1 Annual average values for Pb from 1988 to 1996.

Non-carcinogenic heavy metals

Table 6.2 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 lead 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/m^3 (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_2 concentrations and it is expected to decrease further in the future. Mn do only show a slightly decreasing trend.

Table 6.2 WHO guidelines (WHO 1987 and 1997) for non-carcinogenic heavy metals compared to measured annual average concentrations at street level. N.D. = not determined.

ng/m^3	WHO guide-line	Aalborg/8151 1982	Aalborg/8151 1996	Copenhagen/1257 1996
V	1000	22	6	7
Mn	150	20	18	22
Cd	5	<2	0.9	0.7
Hg	~1000	N.D.	N.D.	N.D.
Pb	500	1100	19	25

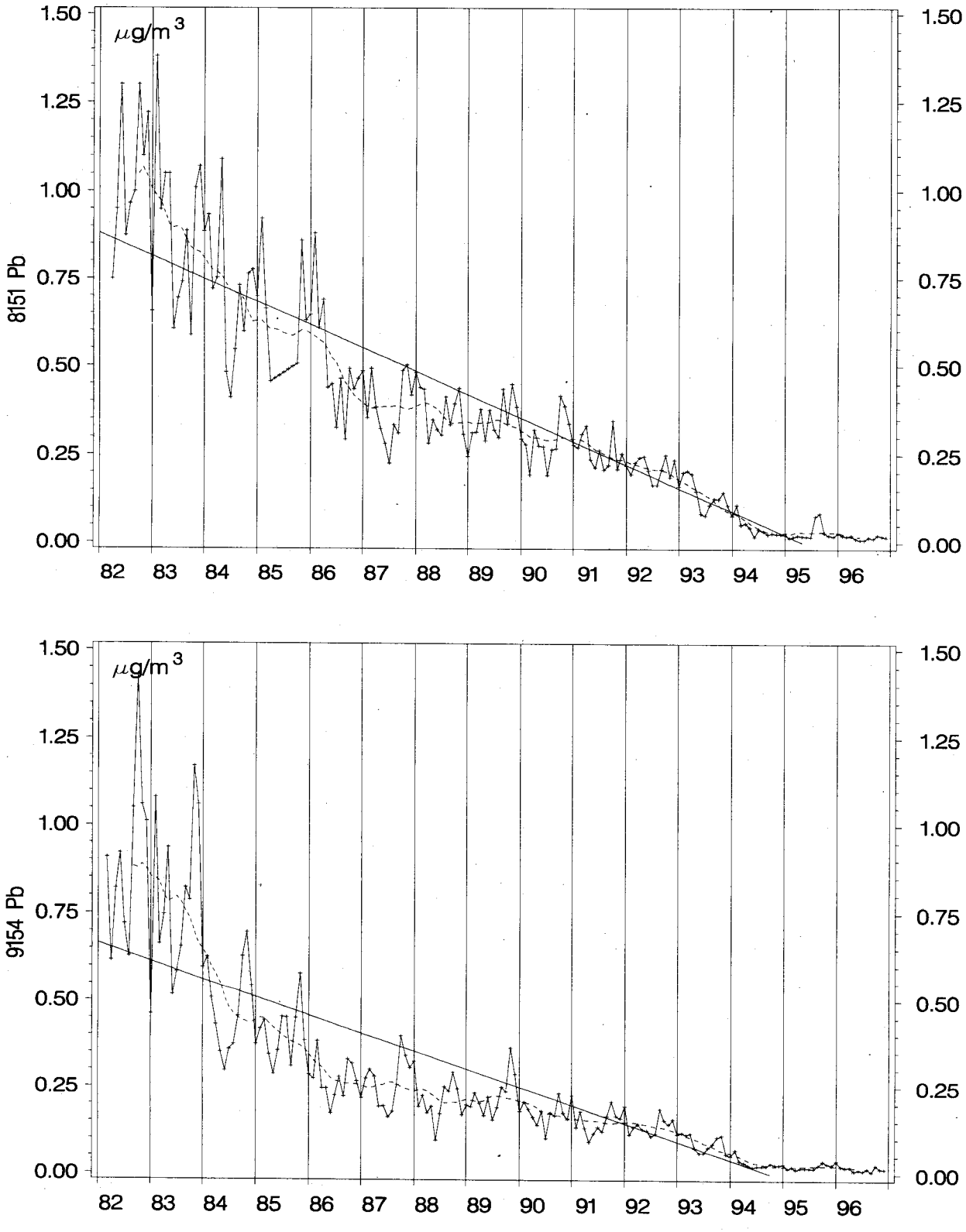


Figure 6.2 Trend for Pb measured at Aalborg/8151 and Odense/9154. The points are measured monthly averages, the dotted curve is a moving average over 12 month and the straight line is a linear regression line (see explanation on p. 17).

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 6.3. The evaluation of the lifetime risks are very uncertain and assessment of acceptable risks are 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 6.3 Estimated lifetime risks (WHO 1997) for carcinogenic heavy metals compared to measured concentrations. D.L. = below detection limit.

	Lifetime risk at 1 $\mu g/m^3$	Aalborg/8151 1982 $\mu g/m^3$	Aalborg/8151 1996 $\mu g/m^3$	Copenhagen/12571996 $\mu g/m^3$
Cr	1)	0.0029	0.0037	0.0056
Ni	3.8×10^{-4}	0.0070	0.0038	0.0042
As	1.5×10^{-3}	D.L.	0.0016	0.0021

1) the WHO estimated life time risk for Cr(VI) is 4×10^{-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).

Nickel

A linear extrapolation indicates that the measured Ni concentrations correspond to a life time risk above 10^{-6}. 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_2 (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.

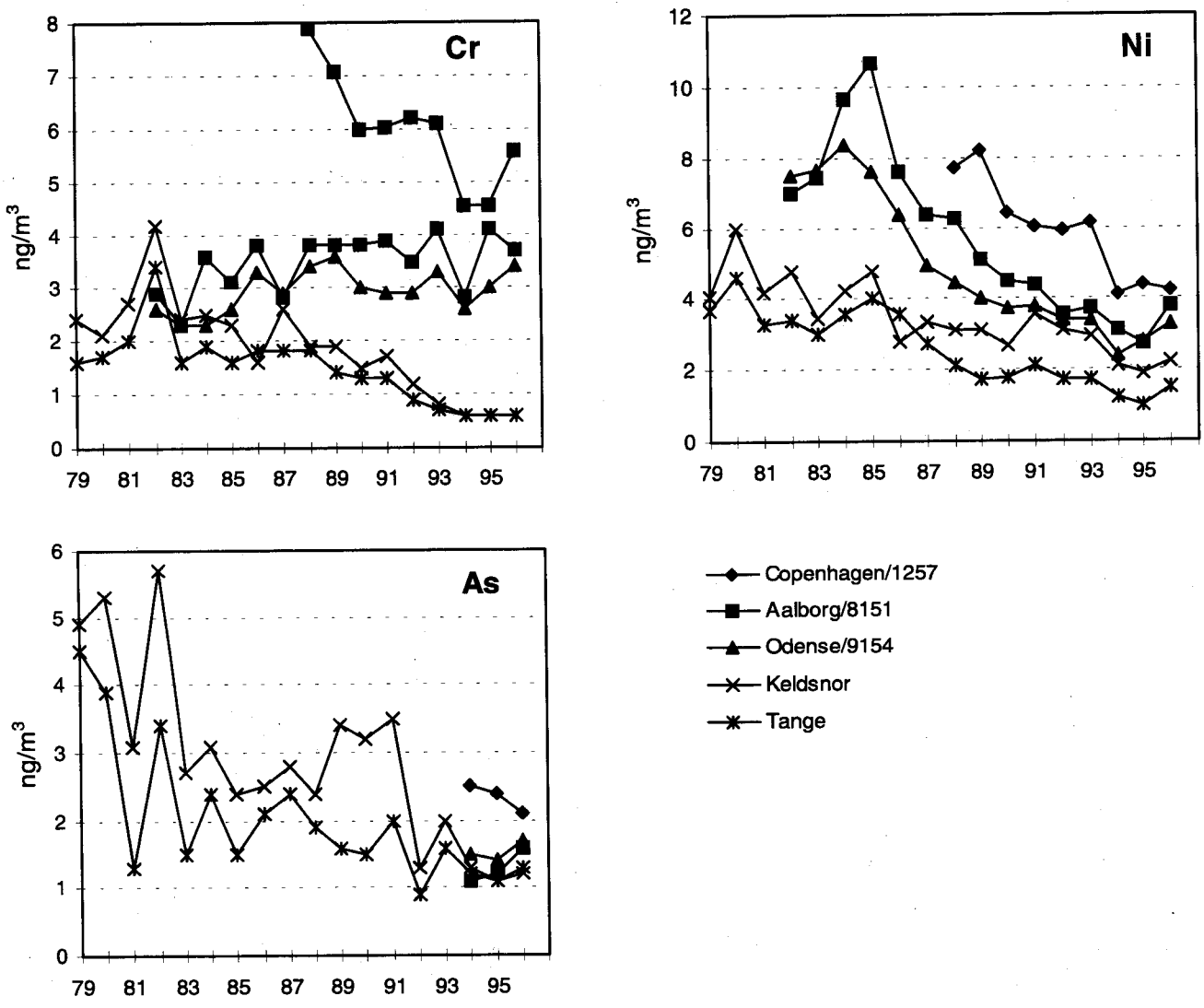


Figure 6.3 Yearly average values for the potential carcinogenic heavy metals. Results from the stations in the Danish Background Monitoring Program at Tange and Keldsnor are included for the comparison.

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 have been reduced by a factor of 3 since 1979. The values for 1996 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^{-6}. 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^{-6}. 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 Campaigns

Components

In addition to the continuous measurements under the monitoring programme campaigns have been carried out. The campaigns include more detailed measurements of the conventional components, i.e. $NO/NO_2/NO_x$ and CO. Petrol vehicles are the main source of CO. Both petrol and diesel vehicles are main sources of NO_x in urban areas. Considerable differences exist in the emission factors depending i.e. of the type of vehicles (Miljøstyrelsen 1991).

7.1 NO_x and CO

1996 results

It has been possible to extend the "campaigns" with CO at the street stations and NO_x at the roof stations to continuos measurements in all 1996 in the three cities, due to contributions from the projects SMP (Berkowicz 1996) and TOV (Hertel 1997). Further, CO have been measured at the roof station Copenhagen/1259. The results are briefly summarised in the following.

Table 7.1 Statistical parameters based on hourly results for campaign results from 1996 . All values are given in $\mu g/m^3$.

Compound	City	Street station				Roof station			
		Ave-rage	Medi-an	98-perc.	99.9-perc.	Ave-rage	Medi-an	98-perc.	99.9-perc.
NO	Copenhagen	72	45	298	509	6.3	2.3	50	151
	Odense	54	25	275	535	8.2	3.6	50	200
	Aalborg	69	38	312	604	6.4	1.8	44	234
NO_2	Copenhagen	45	43	104	189	30	26	77	123
	Odense	34	31	85	133	23	21	62	99
	Aalborg	38	34	96	131	20	17	59	102
CO	Copenhagen	1470	1230	4380	7840	407	322	1230	3270
	Odense	1060	790	3530	8260	-	-	-	-
	Aalborg	1070	795	3950	6910	-	-	-	-

Statistics

Statistical parameters are shown in table 7.1 The ratios between the average values at the street and at roof stations are around a factor of 10 for NO, while it is only around a factor of 1.5-3 for NO_2. The NO_2 concentrations at the roof stations are several times higher than the NO concentrations. This illustrates that the conversion of NO to NO_2 is almost complete after the transport, which normally takes a few minutes, to the roof level. The NO concentrations at the roof stations were extremely skew. The ratios between the 99.9 and 98 percentiles were around a factor 4. The highest NO concentrations were greater than the corresponding NO_2 concentrations. The conversion of NO was at these occasions limited by the amount of O_3. The ratio for CO at street and roof level was about a factor of 5 for all parameters. As

the traffic (especially petrol cars) is supposed to be the main source of CO in urban areas the difference may be taken as a measure of the dilution of the traffic pollution. The great difference between the 1995 (Kemp, Palmgren, Manscher 1996) and 1996 results from Aalborg may be ascribed to the short measuring periods in 1995.

Guide values for CO

The concentrations of NO_2 in relation to limit and guide values are discussed in chapter 2. There are no limit values for CO in Denmark, but WHO (WHO 1997) have recommended a set of guide values based on different averaging times. The measured values are well below the guide values (table 7.2).

Table 7.2 Measured maximum values for CO compared with WHO guide values (WHO 1997). The measurements are performed on a half hourly basis. Besides the values in the table, WHO gives 100 mg/m^3 as guide value for 15 min.

Station	CO (mg/m^3)		
	max ½ hour	max 1 hour	max 8 hour
Copenhagen/1257	14.3	9.7	5.5
Odense/9155	10.6	9.8	6.0
Aalborg/8151	13.3	9.5	5.5
Guide value (WHO 1987)	60	30	10

CO and NO_x at street

NO_x ($NO+NO_2$) is emitted from both diesel and petrol vehicles, while CO is found mainly in the exhaust from petrol cars. It may be expected that the ratio between the two types of cars on a given street will be almost the same and thus that there is a linear relation between CO and NO_x. Figure 7.1 show that this generally is true at Copenhagen/1257. The same pattern is seen both in Odense and Aalborg. A few outliers (marked with crosses in figure 7.1) are from the "local construction episode" June 6 and 7 (cf. figure 2.3) where the diesel powered machinery gave increased levels of NO_x but not CO.

Daily variation of CO/NO_x

The relative number of diesel to petrol cars will change during the day and thus the ratio between CO and NO_x will vary. Figure 7.2 shows the average variation during the week. The ratio is lowest at all street stations during work hours, when a great number of lorries and busses pass the stations. It is highest in evenings and week-ends The ratios at Copenhagen/1257 are low in nights compared to the other two stations. This may be a result of the 24 hours bus service in Copenhagen.

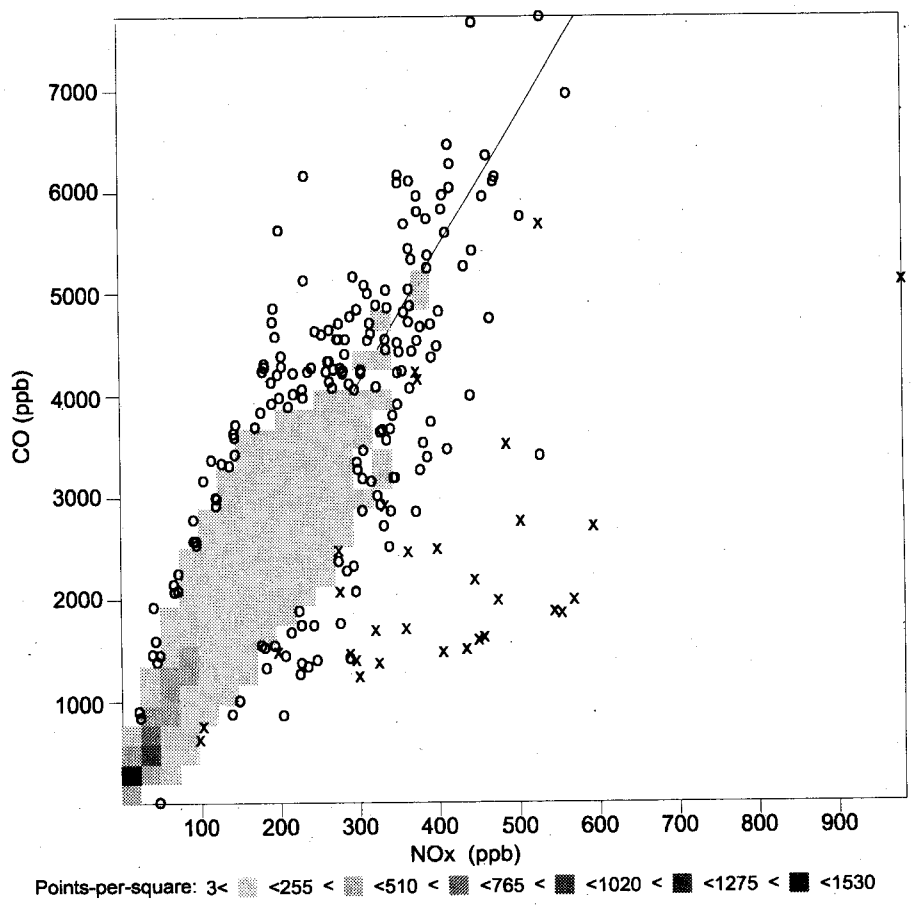


Figure 7.1 Scatterplot of ½-hourly results for NO_x and CO measured at Copenhagen in 1996. The plot area is divided in 40×40 squares. Squares including more than three points are shaded according the scale below the figure. Results from June 6 between 5.30 and 12.30 and June 7 between 5.30 and 13 are drawn as **x**.

7.2 Volatile organic air pollutants from road traffic

VOC's

Volatile organic air pollutants (VOC) has been measured in campaigns in Copenhagen at the traffic station Copenhagen/1257 since 1994 by an automatic gas chromatograph. The pollutants determined as ½ hour averages were benzene, toluene, ethylbenzene, p-xylene, m-xylene and m-xylene.

Earlier measurements have shown a very close correlation between these pollutants and also with CO (Palmgren et al. 1995). It is well known that these pollutants mainly originate from petrol fuelled vehicles.

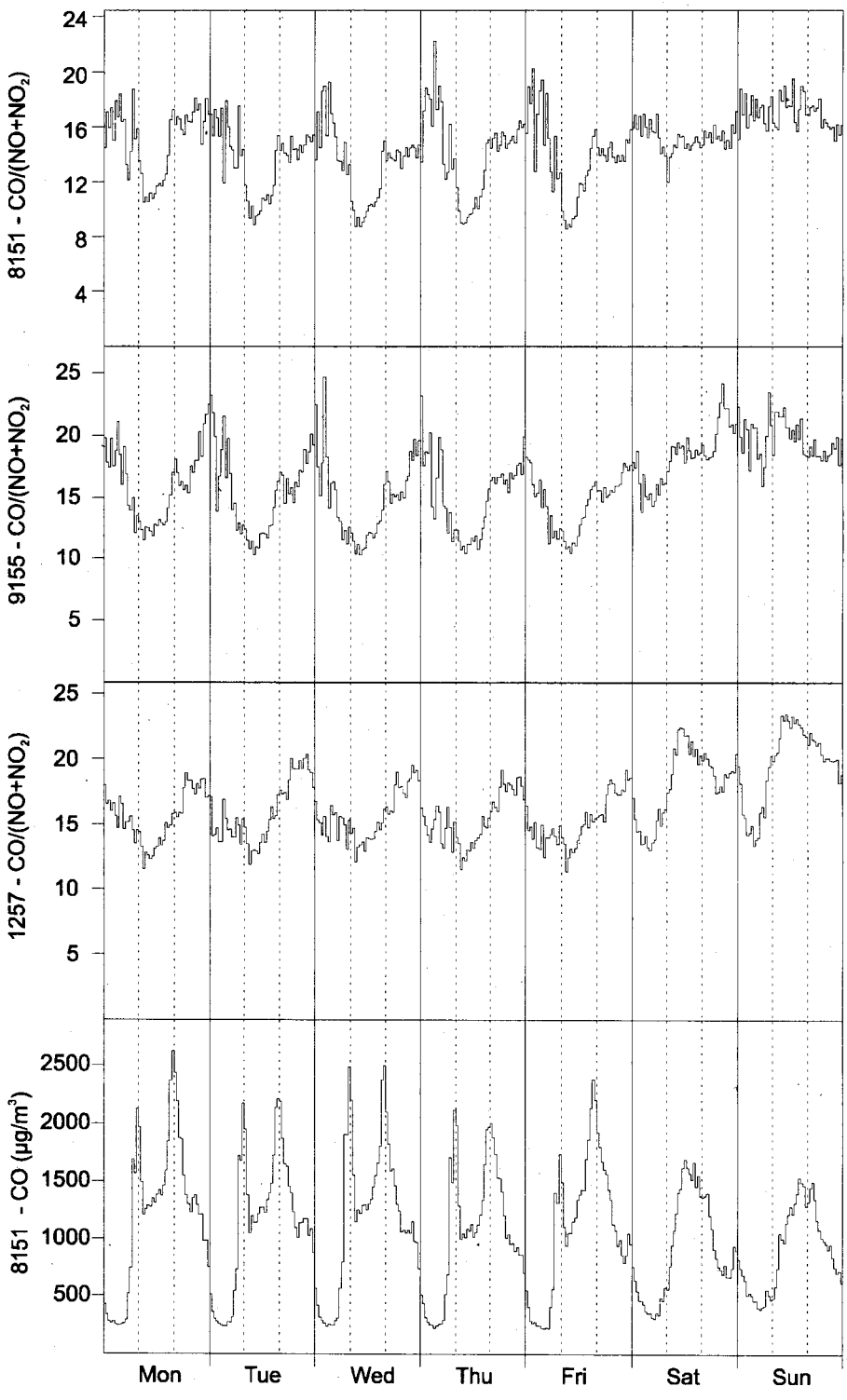


Figure 7.2 Average weekly variation at Copenhagen/1257, Odense/9155 and Aalborg/8151 for the ratio CO(ppb)/(NO(ppb)+NO_2(ppb)). The corresponding averages of CO concentrations at Aalborg/8151 are shown for comparison. All results from 1996 are included in the calculations.

VOC from traffic

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.

Benzene

Introduction of lead-free petrol in connection with installation of three way catalysts (TWC) in all new cars after October 1990 and the total removal of lead from most of the petrol sold in Denmark may have lead to a higher content of aromatic VOCs in petrol. However 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 approx. 40 %. The emission of benzene depends of 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.

TWC

To day lower emission factors will be expected due to higher percentage of TWC vehicles - the traffic work with TWC vehicles is estimated to approx. 50% in 1996. In addition, the lower content of benzene will lead to a relatively lower emission factor for benzene.

Results

Figure 7.3 shows the concentrations of benzene and toluene measured at Copenhagen/1257 May-December 1996 (Palmgren, Berkowicz 1997). The slope of the regression line is 0.32. For measurements in 1994 the slope was determined to 0.45 (Palmgren et al. 1995). Figure 7.4 shows the corresponding plot for benzene and CO. In this case the slope decreased from $3.6 \cdot 10^{-3}$ in 1994 to $2.3 \cdot 10^{-3}$ in 1996. The change since 1994 is a result of the lower benzene content in petrol. The average concentrations of benzene and toluene measured from May to December 1996 are shown in figure 7.5.

The average concentration of benzene from May to December 1996 was approx. 3 ppb. It should be compared with the expected new EU limit value, which is expected to be 3 ppb or lower.

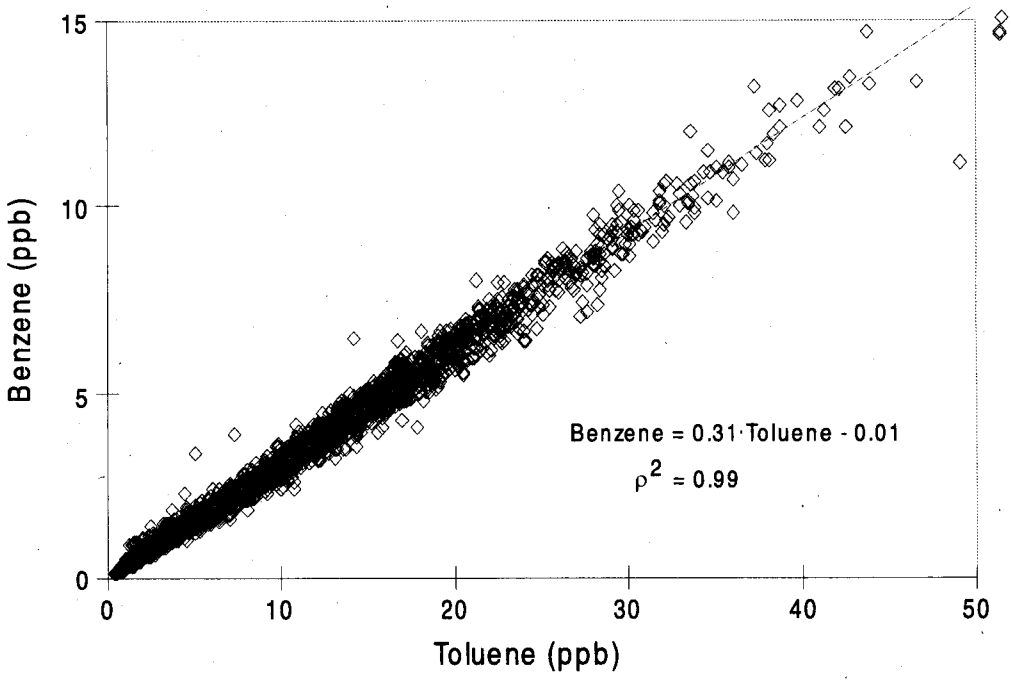


Figure 7.3 Hourly values of Benzene and toluene measured at Copenhagen/1257 May-December 1996.

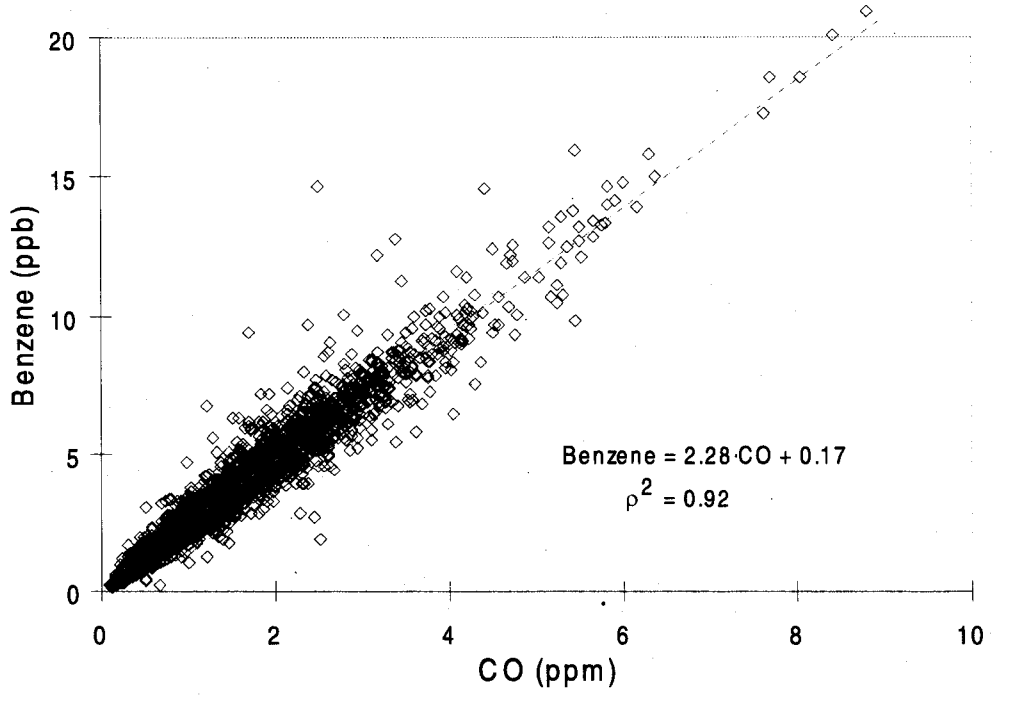


Figure 7.4 Hourly values of Benzene and CO measured at Copenhagen/1257 May-December 1996.

Conclusion

The conclusion is that a decrease in the benzene (and toluene) has been observed compared to 1994, caused by relatively more TWC vehicles and reduction in the content of benzene in petrol. However, the expected new limit value will be exceeded at some streets in Danish cities at Zealand. West of the Great Belt, the benzene concentration may still be higher due to higher content of benzene in petrol.

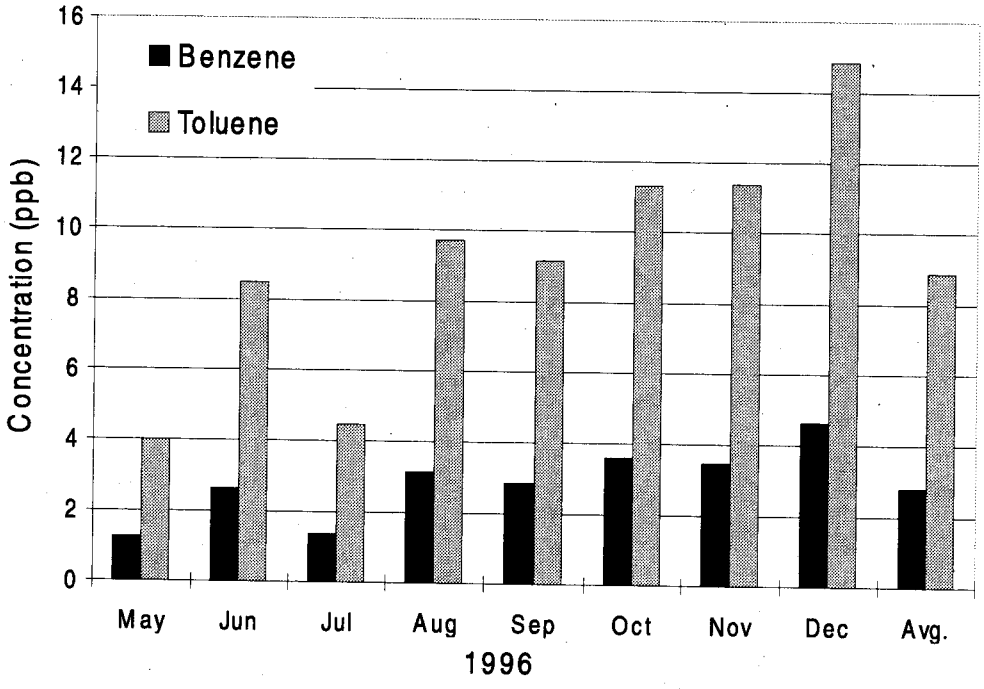


Figure 7.5 Monthly average concentrations of benzene and toluene measured at Copenhagen/1257. The relatively high average concentrations in December represents only a week of measurements the week before Christmas, which may be untypical.

8 Conclusion

Nitrogendioxid

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 1996 almost the same as in the previous years. A trend analysis covering the last 15 years showed that the NO_2 level have been almost constant, while a significant decrease is observed for NO since 1993 as a result of the increasing number of cars with three way catalytic converters.

Ozone

A set of threshold values for O_3 has been implemented in Denmark in 1994. The values are based on an EEC directive for protection of human health and vegetation. During 1996 some of the threshold values were exceeded frequently. The reduction of O_3 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_3 in the lower troposphere is a secondary pollutant. The precursors are NO_x and organic gases which may be of either natural or anthropogenic origin. While the average O_3 concentrations during winter are much lower than the background contribution the sum of O_3 and NO_2 is almost independent of the origin air mass.

Sulphurdioxide

The actual measured values at all stations were more than a factor of 10 lower than the limit values for SO_2. The EEC guide value were more than a factor of 5 above the measured values. There is a marked decrease of the SO_2 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_2 emission in the European countries will probably lead to a continuation of the downward going trend. The 1996 values were nevertheless slightly higher than the previous years. This may however be ascribed to the winter conditions the first 3-4 month of 1996.

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 higher in 1996 than the previous years, which may be explained by the meteorological conditions the first months of 1996.

Elements

The limit value for Pb of 2 $\mu g/m^3$ has obviously been outdated by the gradual removal of lead from gasoline. At present values around 2% 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. 3 ppb, which is the same as the expected EU limit value. Petrol cars are the dominating source for both compounds at street level.

Smog warning

A smog warning system was implemented from April 1994. It is for SO_2 and NO_2 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_2 or NO_2 exceeds 350 $\mu g/m^3$ 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_3 has been included in the new system: The population is informed immediately if the hourly average concentration exceeds 180 $\mu g/m^3$ and if the hourly concentration exceeds 360 $\mu g/m^3$ a warning is issued to the population. Information was send to the population once in 1996, due to an apparent exceedance of the 180 $\mu g/m^3$ level. The final quality control showed however that the concentration actually was slightly below the threshold. 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 1996 showed that the concentrations found in the Danish cities were below the existing limit values. The O_3 threshold values, which were implemented in 1994, are however frequently exceeded. The NO_2 concentrations were around half the limit value and no clear trend was observed. The measurements in LMP III program aims i.e. at a description of the O_3-NO_x interaction in order to reveal the effect of actions already taken to reduce the NO_x 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_3 precursors.

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Danish Summary - Dansk resumé

Det Landsdækkende Luftkvalitets Måleprogram Årsrapport for 1996

Faglig rapport fra DMU nr. 216

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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). På basisstationen foretages kontinuert måling af NO, NO_2, SO_2, svævestøv samt grundstofindholdet i svævestøvet. På tagstationerne måles O_3 koncentrationen i "taghøjde" samt følgende meteorologiske parametre: vindretning, vindhastighed, relativ fugtighed, temperatur og globalstråling. Desuden måles baggrundsforureningen 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_x og O_3. Der foretages desuden kampagnemålinger med udvidet program på stationerne. Ved at kombinere kampagnemålingerne i LMP med målinger i tilknyttede forskningsprojekter (se nedenfor) har det været muligt at bestemme CO på gadestationerne samt NO og NO_2 på tagstationerne i hele 1996.

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 (polycykliske aromatiske hydrocarboner) som er 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_2 (kapitel 2) er de målte koncentrationer i alle tilfælde under den gældende grænseværdi på 200 µg/m^3 for 98-percentilen og de vejledende værdier på 135 µg/m^3 for 98-percentilen og 50 µg/m^3 for medianen. Afstanden til de vejledende værdier er ikke ret stor. WHO's vejledende værdi på 40 µg/m^3 for årgennemsnittet er overskredet i København. Emissionen af NO_x 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_2. Emissionen fra de øvrige hovedkilder, dieselbiler og kraftværker, vil ikke blive ændret ret meget de første par år.

Ozon

De målte O_3 værdier (kapitel 3) var som tidligere næsten ens over hele landet. Der var god korrelation mellem ½-times middelværdierne på alle stationer. Med gennemførelsen af et EU direktiv om O_3 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 1996. O_3 i den nedre del af atmosfæren dannes ved fotokemiske reaktioner. VOC og kvælstofoxider er af stor betydning for dannelse af O_3. Da en stor del af den VOC der findes i luften i Danmark stammer fra andre lande, kan en effektiv nedsættelse af O_3 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 mg/m^3. Hvis timemiddelværdien overskrider denne værdi skal befolkningen underrettes. Det skete én gang i 1996. (Den efterfølgende kvalitetskontrol viste dog, at koncentrationen var lidt under 180 µg/m^3).

Svovldioxid

Forureningen med SO_2 (kapitel 4) er for nedadgående 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. 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 hot-spot episoder er gået ned i de seneste år. Nedgangen for partikulært svovl, som især er forurening transporteret over lange afstande, har ikke været nær så markant som for SO_2.

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 væsentlig-

ste. De målte koncentrationer var lidt højere i 1996 end i 1995. Det skyldes især forskellen mellem de meteorologiske forhold de to år. På trods heraf er der 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.

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 1996 var mere end en faktor 40 lavere end ved LMP programmerne start i 1982. Der er i praksis ikke mere bly i benzin. Blyforurening er nu på niveau med flere andre tungmetaller.

Kampagner

Der er gennemført målinger af CO på alle gadestationer samt NO og NO_2 på alle tagstationer hele året 1996. Der er desuden foretaget målinger af flere organiske forbindelser, bl.a. benzen på gadestationen i København (kapitel 7). CO koncentrationerne var i 1996 under WHO's vejledende værdier. Gennemsnitskoncentrationerne for benzen var omkring den forventede EU grænseværdi på 3 ppb. Benzen koncentrationerne er faldet siden 1996 som følge af katalysatorerne og en nedsættelse af benzen indholdet i benzin. Målingerne bekræfter, at såvel CO som benzen hovedsageligt stammer fra benzin biler; mens NO_x kommer fra såvel diesel som benzin køretøjer.

Resumé

LMP resultaterne fra 1996 viser at den forurening, der findes i de danske byer, var under de gældende grænseværdier, men tærskelværdierne for O_3 blev overskredet jævnligt. Selv om NO_2 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_3-NO_x 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_3 forhåbentlig også slå igennem.

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The National Environmental Research Institute, NERI, is a research institute of the Ministry of Environment and Energy. 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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