The Danish Air Quality Monitoring Programme

Annual Report for 1995

NERI Technical Report No. 180

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Data Sheet

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Content

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 change in the pollution pattern by two revisions. The present phase (LMPIII) was started in 1992. This report presents the results from 1995 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 regional background 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 level and NO and NO_2 at roof level are performed in campaigns in order to improve the knowledge about the NO, NO_2 and O_3 problem complex. At the background site outside Copenhagen the same program as at the street stations was conducted with the inclusion of O_3. While only NO, NO_2 and O_3 were measured at the other background 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 corresponding 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 are 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. The amount of O_3 is at present a limiting factor for the formation of NO_2 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.

Sulphur dioxide

The SO_2 concentrations have been continuously decreasing since 1982. They were in 1995 only about 1/10 of the limit values. The amount of TSP is slightly downwards going as a result of "winter crops" during the winter period and better combustion control. The concentrations of TSP are 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. Almost all petrol sold in Denmark is now lead free. The development has outdated the limit value, which is more than a factor of 50 higher than the measured

concentrations. The lead emission from road traffic will be negligible within a few years.

Ozone

Some of the threshold values for O_3 are frequently exceeded. O_3 is remarkable because the average 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 are oddly enough also observed at south-easterly winds. The levels of O_3 are of the same order as the highest levels of NO_2, which means that both O_3 and NO can be limiting factors for the formation of NO_2.

1 Introduction

LMPIII

The third Danish Air Quality monitoring Programme (LMPIII) 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 a 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 together with the Agency of Environmental Protection 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 summarized in annual reports in English. Statistical parameters are accessible on 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 (LMPII) (*Palmgren, Kemp and Manscher, 1992*). The installation of the new equipment took place during 1992 and the beginning of 1993. Except for short interruptions due to technical problems, all instruments were operated as planned during 1995 (*Kemp, 1993)*.

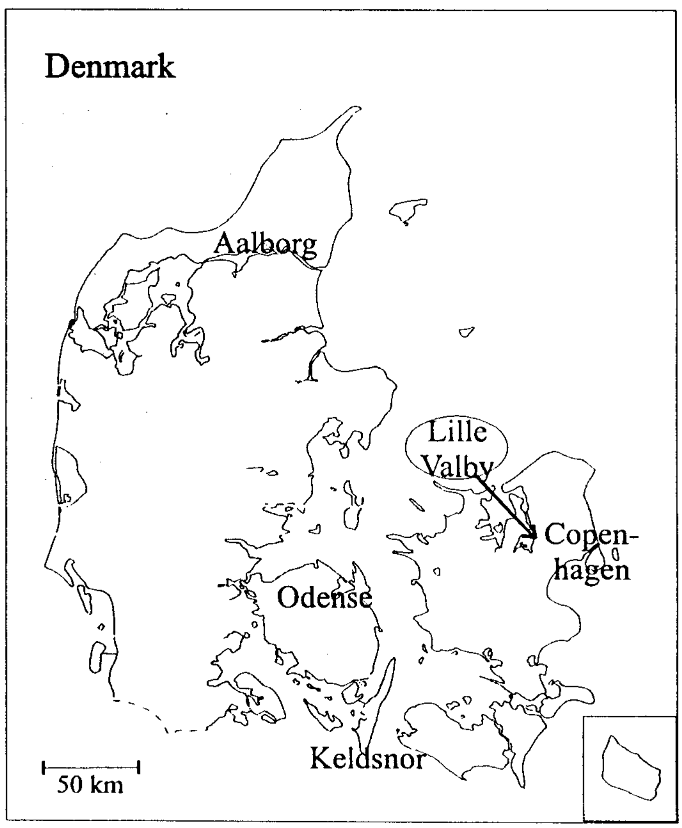


Figure 1.1 Cities and the background sites in the LMP network.

Table 1.1 LMPIII stations in 1995. TSP is the total suspended particulate matter 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[1])	Main	NO, NO_2, SO_2	SO_2, TSP, Elements
Copenhagen/1259	Roof	O_3, meteorology	-
Odense/9155	Main	NO, NO_2, SO_2	SO_2, TSP, Elements
Odense/9154	Additional	-	SO_2, TSP, Elements
Odense/9159	Roof	O_3, meteorology	-
Aalborg/8151	Main	NO, NO_2, SO_2	SO_2, TSP, Elements
Aalborg/8159	Roof	O_3, meteorology	-
Lille Valby/2090	Background	NO, NO_2, SO_2, O_3	SO_2, TSP, Elements
Keldsnor/9055 [2])	Background	NO, NO_2, O_3	-

[1]) The station was closed from medio June to medio August, due to intensive road repair close to the station.
[2]) There are no valid results from September to medio December due to technical problems at the station..

Measuring programme

The measuring programmes at stations in operation during the major part of 1995 are shown in *table 1.1*. The map (*figure 1.1*) shows where the sites are located. All sites and measuring methods are described in *Kemp, 1993* and *NERI, 1996.*

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 and NO_x are i.a. carried out in order to get a better understanding of the NO_2 in the urban background and the NO_x - 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 a new 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 is introduced from the beginning of 1994. For NO_2 and SO_2 warnings are given if the concentrations exceed 350 $\mu g/m^3$ for more than three consecutive hours and no immediate decrease is expected. In addition to NO_2 and SO_2 O_3 is included in the system. According to the directive *EEC, 1992* information will be broadcasted if the hourly average concentration exceeds 180 $\mu g/m^3$, while an alarm is sent to the population, if the hourly average concentration exceeds 360 $\mu g/m^3$.

1995 reports

The 1995 results are found in quarterly reports *(Danmarks Miljøundersøgelser, 1995a, 1995b, 1996a 1996b)*. The results obtained during 1995 are summarized in the present report in form of annual statistics and trends. The phenomenology of O_3 is again in 1995 treated as a special topic since O_3 is a key species in the present studies of the atmospheric chemistry of i.a. transformation of nitrogen oxides and VOC compounds. Further the programme for campaigns with intensive measurements was continued in 1995. The results of a campaign in Aalborg and Odense are summarized 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, 1996*).

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 oxidized 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 and the temperature.

Measurements

During 1995 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 three first 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. More than 90% of the possible results for the whole year are available at Odense/9155, Aalborg/8151 and Lille Valby/2090, while only about 2/3 of the possible results are available at Copenhagen/1257 and Keldsnor/9055 (see table 1.1).

2.1 Annual statistics

Limit values

The limit value for Denmark is 200 µg/m^3 for the 98-percentile of hourly average values of NO_2 measured over one year. The guide values are 130 µg/m^3 for the 98-percentile and 50 µg/m^3 for the median (*Miljøministeriet, 1987 and 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 since 1988 are found on *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 highest concentration, with exception of a few extremes.

The limit value and guide values were not exceeded in 1995 apart from the the median value at 50 µg/m^3, which was touched in Copenhagen. The very low values for NO at Lille Valby/2090 and Keldsnor/9055 illustrate the fast conversion of NO to NO_2.

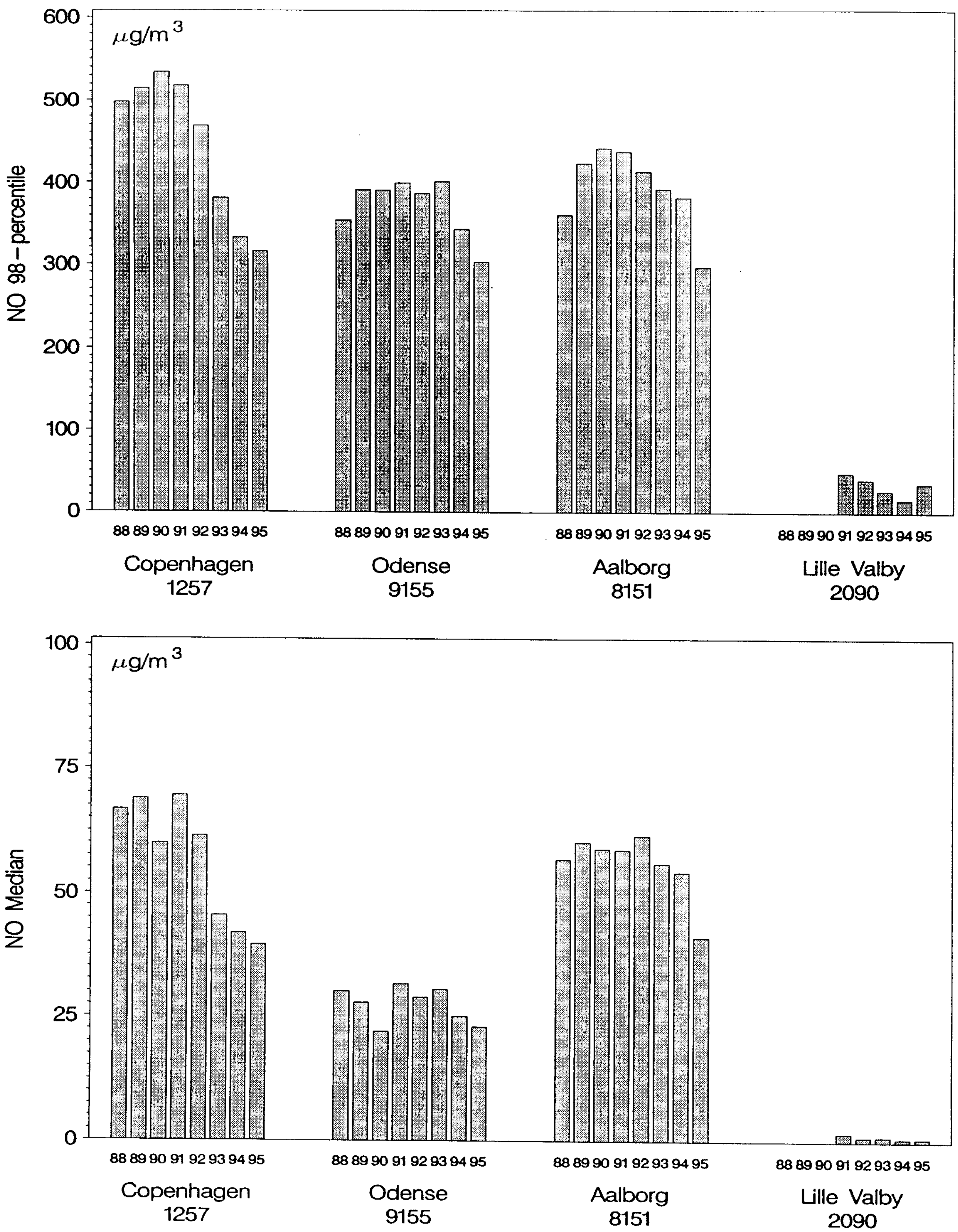


Figure 2.1 Medians and 98-percentiles for NO from 1988 to 1995

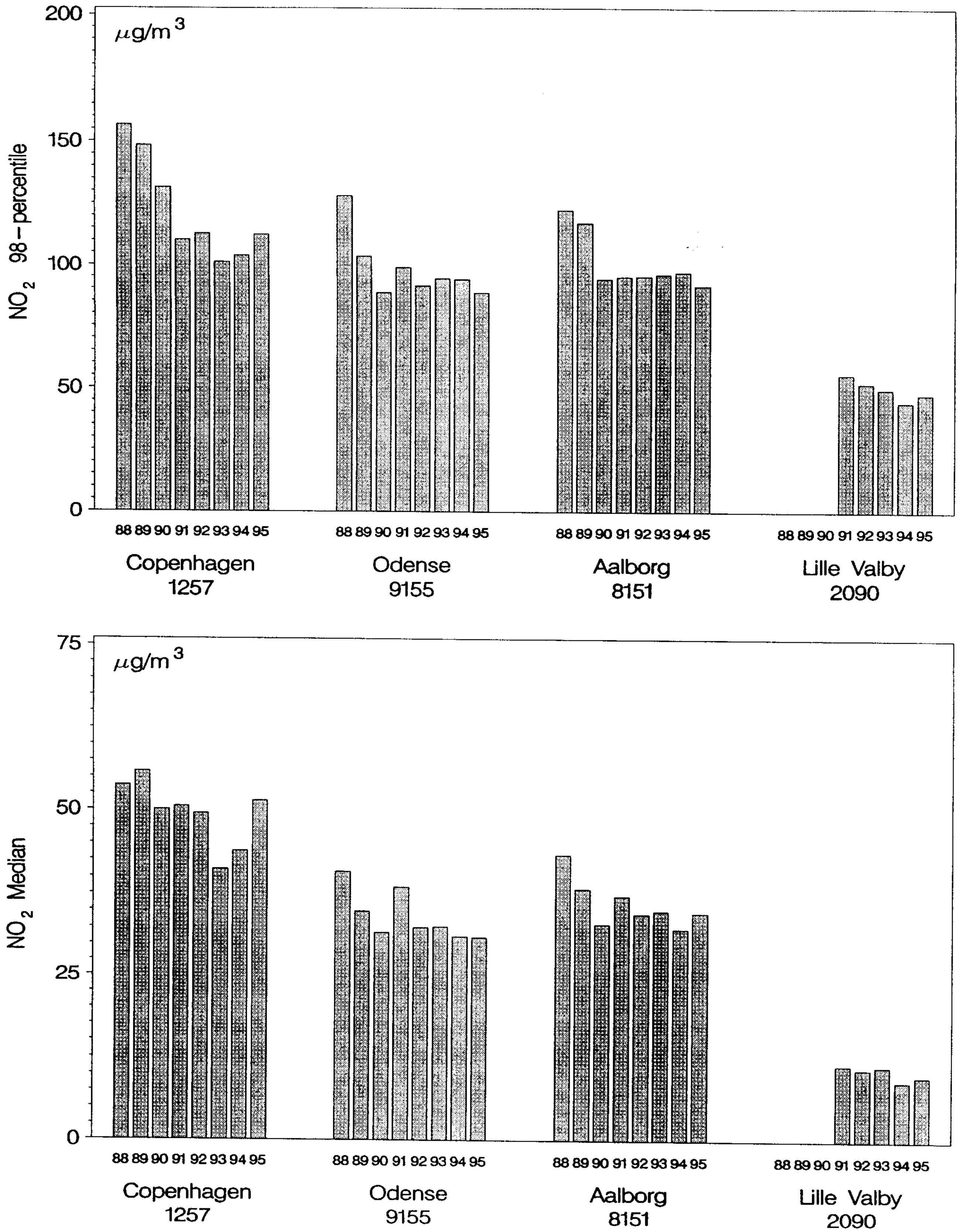


Figure 2.2 Medians and 98-percentiles for NO_2 from 1988 to 1995.

Table 2.1 The values are calculated for all measurements from 1995 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 formal comparison with the limit and guide values. The number of measurements is listed in the second column.

		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	75	43	317	656	52	51	102	169
Odense/9155	8106	55	25	306	505	35	31	88	117
Aalborg/8151	8220	73	44	301	564	38	35	90	121
Lille Valby/2090	7949	(3)	(0)	36	178	14	10	47	66
Keldsnor/9055	5800	(1)	(0)	6	36	9	7	34	55
Limit value	>6570	-	-	-	-	-	-	200	-
Guide -		-	-	-	-	-	50	135	-

NO vs. NO_2

The high concentration of NO compared to NO_2 at urban stations illustrates that the NO not is a limiting factor for the formation of NO_2 at streets, whereas almost all NO has been oxidized at the background 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 goes 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 south-westerly winds (*Kemp, Palmgren and Manscher, 1996*).

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 μg(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 highest concentrations of NO were with a single exception measured in the winter month at all stations, whereas NO_2 may peak any time of the year, due to the higher background values of O_3 in summer.

Table 2.2 Maximum concentrations of NO (not included in the smog warning system) and NO_2 in 1995. 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 µg/m³ for consecutive three hour is the same as the lowest hourly value within the three hour period exceeds 350 µg/m³). The highest of these 1 hour 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
Copenhagen/1257	505	951201:09	728	951201:07
Odense/9155	434	951107:19	573	950711:17
Aalborg/8151	479	951215:22	632	951215:17
Lille Valby/2090	134	951108:03	258	951201:11
Keldsnor/9055	38	950114:11	42	950114:10
Warning limit	-	-	-	-

	NO_2			
	Max. 3 hour (µg(NO_2)/m³)	Day:hour	Max. hour (µg(NO_2)/m³)	Day:hour
Copenhagen/1257	163	950116:10	182	950116:10
Odense/9155	101	950531:13	135	950818:17
Aalborg/8151	117	950731:13	132	950731:11
Lille Valby/2090	64	951225:08	73	950913:09
Keldsnor/9055	49	951227:22	62	951227:211
Warning limit	350	-	-	-

Single episodes

There were no major nation-wide episodes in 1995. The results in table 2.2 show that the maximum concentrations were relatively low and they did not occur at the same days at the different locations. The NO_2 levels were generally high in the cities around August 1, when the O_3 concentrations were high, while transboundary transport of NO_x gave the highest concentrations at the rural stations.

2.3 Trends

Percentiles

The annual percentiles and average values for NO and NO_2 measured at Aalborg/8151 are shown on *figure 2.3.* The level of NO was almost constant in the period from 1982 to 1991, but has apparently been decreasing during the last few years synchronously with the increasing number of cars having TWC. The NO_2 level has, within the statistical uncertainty, been constant since the start of the measurements in 1982.

The skewness of the distributions are 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 at *figure 2.4*. Except for the decrease in NO in 1994 and 1995 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 and *2.2* 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.

Explanation to the trend figures: 2.3, 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. The Humpty-Dumpty shape of the bars is a result of a skew frequency distributions.

Explanation to the trend figures: 2.4, 4.4-5, 5.3 and 6.2

The figures are intended to illustrate these properties

- *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, showing the long term trend.*

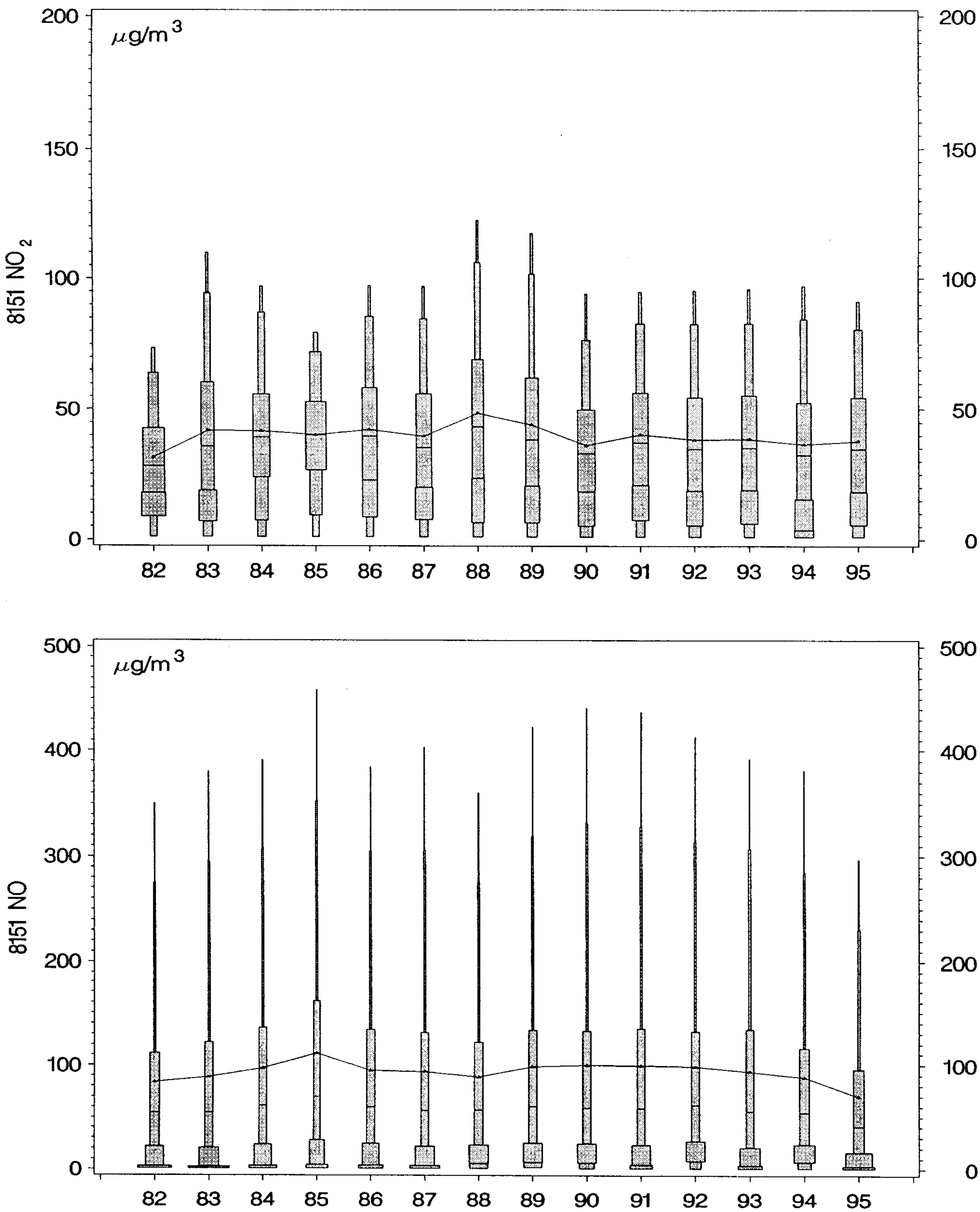
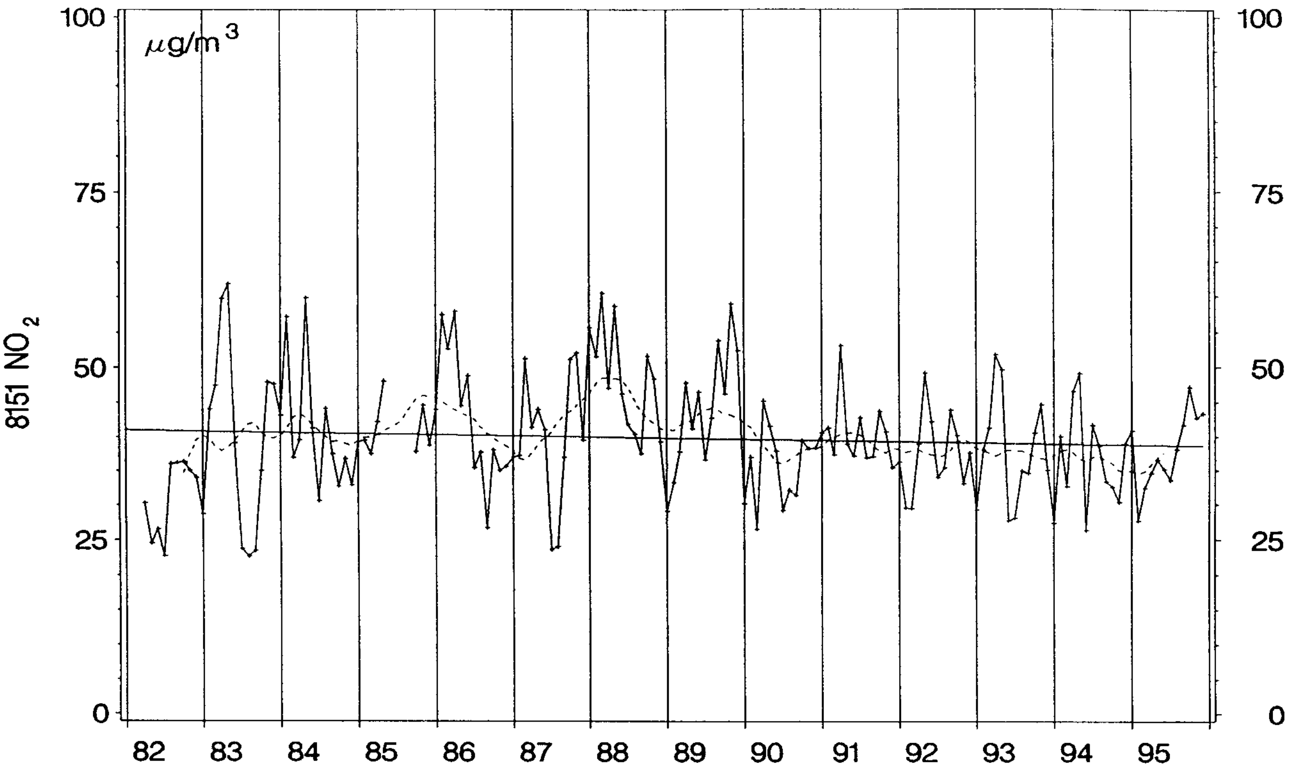


Figure 2.3 Trends for annual 98-, 95-, 75-, 50-, 25- and 5-percentiles, average and minimum value based on hourly average concentrations of NO_2 and NO measured at Aalborg/8151. (See explanation on p. 15).



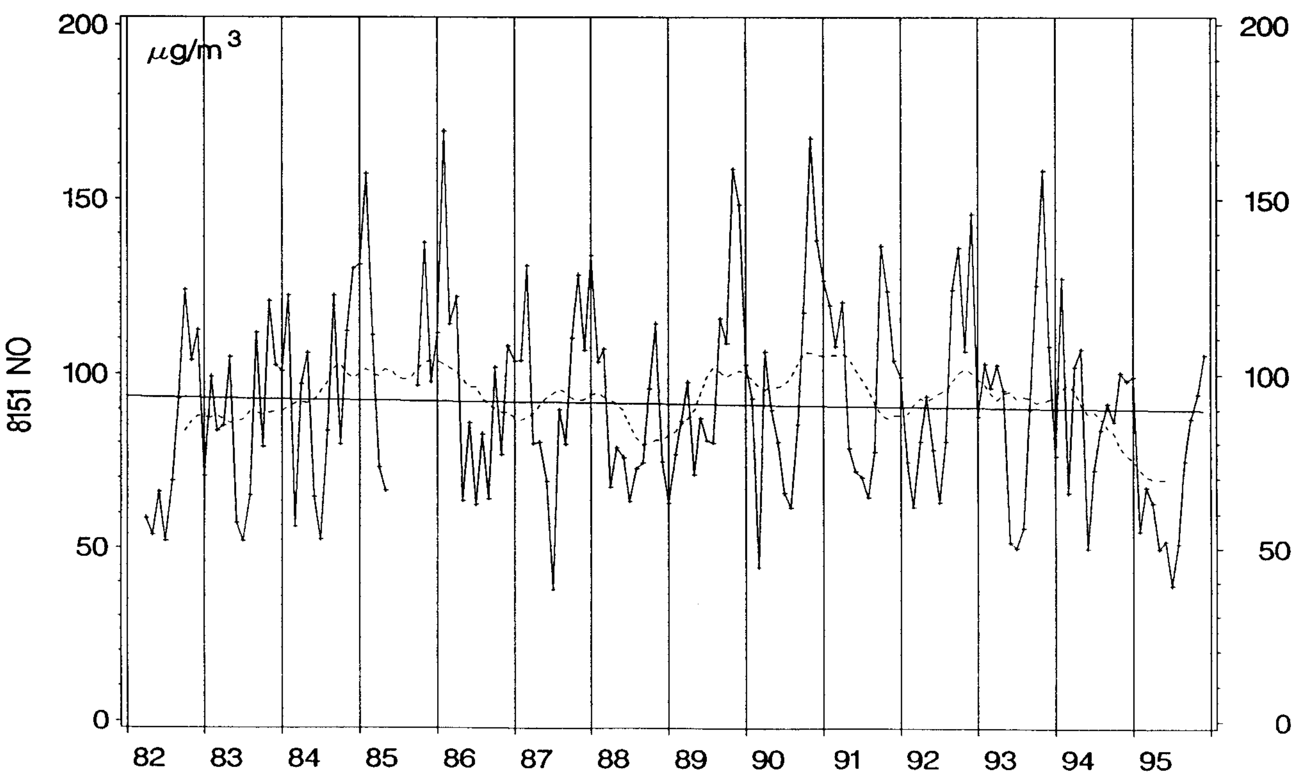


Figure 2.4 Trend for NO and NO_2 measured at Aalborg/8151. The points are measured monthly averages, the dotted curve is a moving average over 12 month and the straight line is a linear regression line. (see explanation p. 15).

3 Ozone

Measurements in 1995

Measurement of O_3 was started mid 1991 at the background station (Lille Valby/2090). The roof stations (*Kemp, 1993)* were equipped with monitors at the end of 1992. 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, but there is no valid results from August to November (see table 1.1) due to technical problems at the stations. Almost all results are thus available from 1995 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. 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).*

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_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 and NO_2 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.

Exceeding

The measured values are compared to the threshold values in the directive in *table 3.1*. The meteorological conditions were at the end of July and the beginning of August 1995 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 *table 3.1* are generally higher than the corresponding 1993 results, but very close to the 1994 results. Both the max. 24 hour and the max. 8 hour threshold values were exceeded in many occasions in 1995 at all stations. The events were of course most frequent in the summer, but it is worth noting that they also occurred in the winter months January and February.

Table 3.1 Annual average values, percentiles and maximum values for O_3 measured in 1995 compared with threshold values. (*Miljøministeriet, 1994* and *EEC, 1992*).

O_3 ($\mu g/m^3$)	Average	Median (hour)	98-perc. (hour)	99.9-perc (hour)	max. 24 hours	max. 8 hours[1)]	max. 1 hour
Copenhagen/1259	46	46	105	185	128	183	197
Odense/9159	48	48	106	177	149	182	201
Aalborg/8159	52	54	104	155	134	147	181
Lille Valby/2090	52	53	110	183	130	186	202
Keldsnor/9055	63	65	109	159	124	146	173
Threshold value	-	-	-	-	65	110	200
Average number of exceedances per station	-	-	-	-	94	7	0.4

1) 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 0.00 and 9.00, 8.00 and 17.00, 16.00 and 1.00, 12 and 21.

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 $\mu g/m^3$ and to issue a warning, if the hourly average concentration exceeds 360 $\mu g/m^3$. 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.

Press releases

The concentrations exceeded threshold for information of the population at one occasion in 1995. A Press releases were transmitted by the nation wide radio at May 5 in the news broadcasts. An almost stable high pressure over the eastern part of Scandinavia in last part of July and the beginning of in the August gave frequent air transport from Central Europe to Denmark. The concentrations were at several occasions above 150 $\mu g/m^3$. But the concentration did not exceeded 180 $\mu g/m^3$ during this period.

Single episode

Figure 3.1 shows the results from Lille Valby in the eastern part and Aalborg/8159 in the western part of Denmark in the period around the May episode.

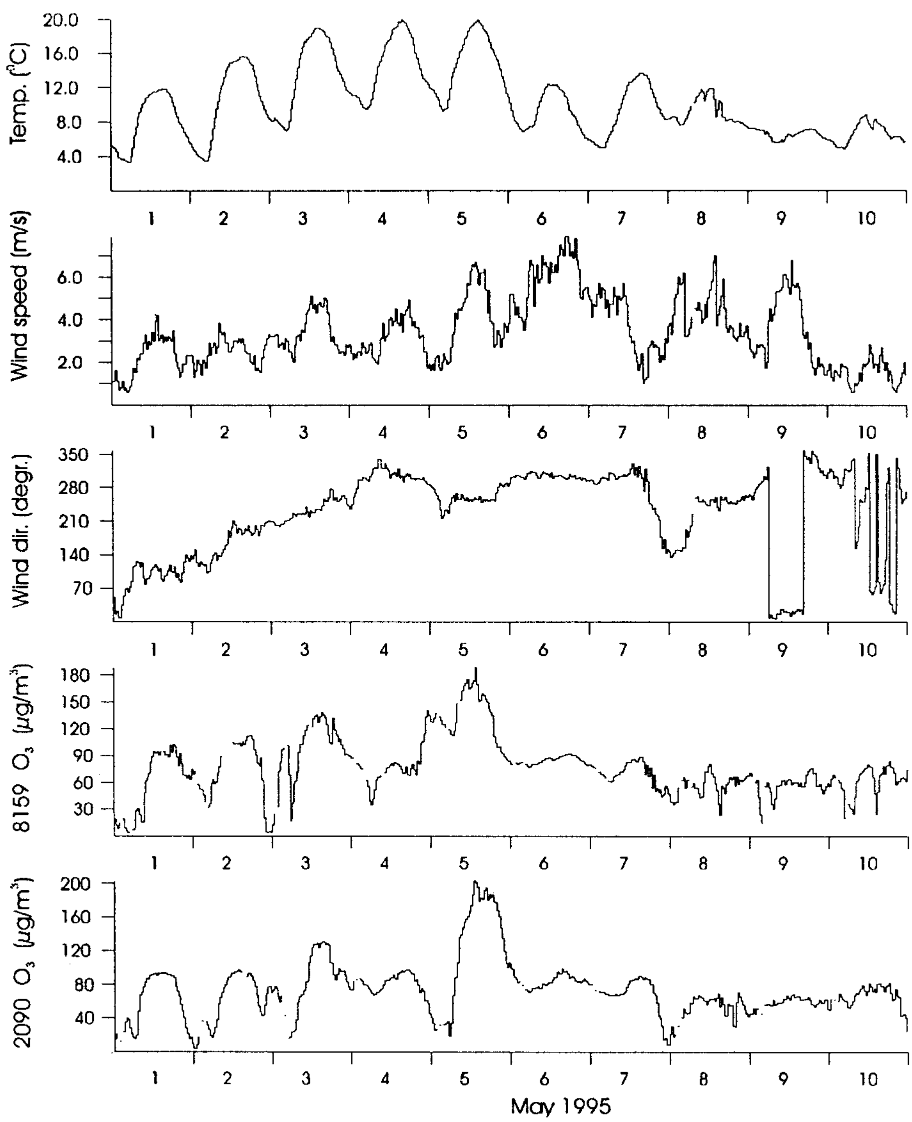


Figure 3.1 O_3 measured at Lille Valby/2090 and Aalborg/8159 during the "unusual" episode in May 1995. The meteorological results are from Aalborg/8159.

The wind was coming from west and the temperature around 20 ^{0}C when the O_3 level reached the maximum during the afternoon. It is very unusual to observe that high concentrations already in May. Further the temperature will normally be above 25 ^{0}C and the wind from east or south-east during episodes (cf. figure 3.3). A back-trajectory calculation showed that the air mass were transported from central Europe out over the North Sea before it turned back towards east.

3.3 Phenomenology

Wind direction dependency

The reaction mechanisms for formation and decomposition, 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 on fig 3.2. Results from the rural stations at Frederiksborg and Ulborg (*Hovmand et al., 1994)* are included for comparison. The results from 1993 and 1995 are divided on summer (May-August) and winter (November-February) periods. Concentrations around 80 μg/m^3 in average are found for winds from NW both summer and winter. This represent probably the hemispheric background concentrations. At winds from south and south east the concentration exceeds the background level in the summer period, while it is 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 is very similar but the levels are slightly reduced at the urban stations (Copenhagen/1259, Odense/9159 and Aalborg/8159) as a result of the presence of i.a. NO.

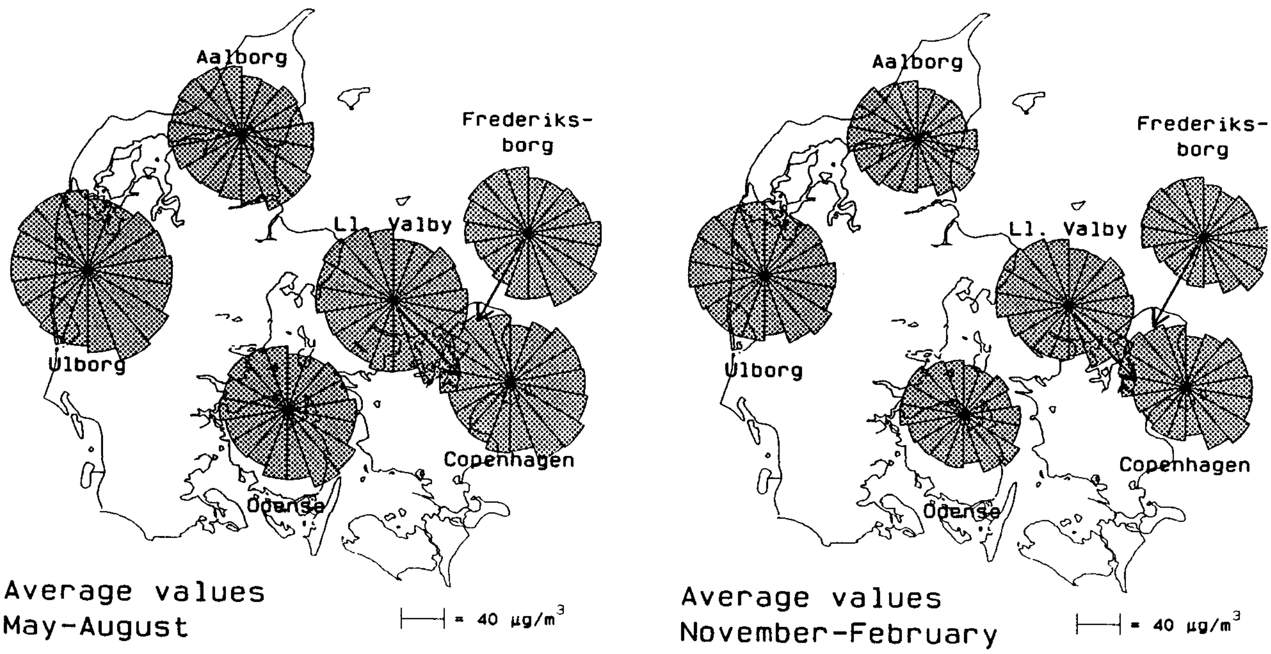


Figure 3.2 Wind direction distribution for O_3 for results from 1993-1995. The radii of the circle sections are proportional to the average concentrations for winds coming from the direction the section points towards.

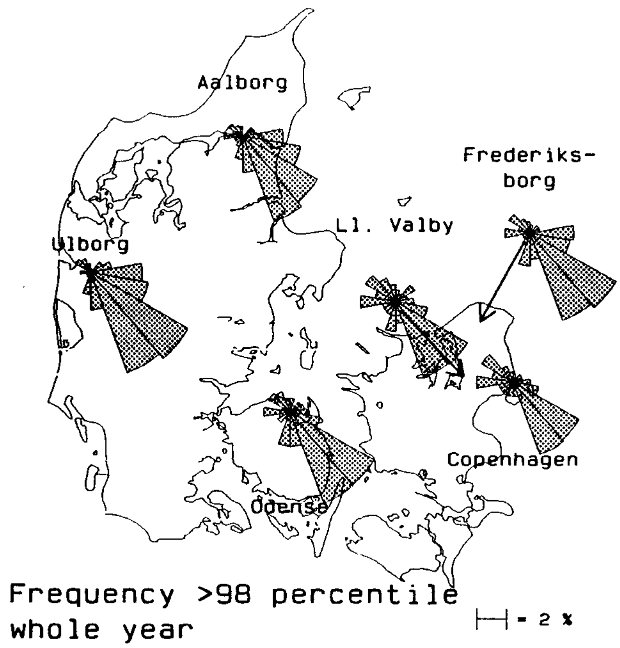


Figure 3.3 Distribution with wind direction of the upper 2 % of the O_3 concentrations (above the 98-percentile) drawn as frequency in the wind sectors compared to the number of measurements in the same sectors. Results from 1993 to 1995 are included. The radii of the circle sections are proportional to the relative frequency 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 20^0 wind sector. Nearly all concentrations above the 98-percentile are found at winds from ESE.

Trend for O_3 and O_x

More than four years of data are now available from Lille Valby/2090. The development is illustrated by means of the monthly average values on *figure 3.4.* The results are divided according to the wind directions sectors. The sector from 40 to 160^0 represent the continental contribution with an addition of some regional contribution from the Copenhagen area, the sector from 180 to 240^0 represents the western part of Continental Europe, while the background contribution is assumed to be found in the sector from 260 to 20^0. No significant trend is observed in the period, but the seasonal variation is a factor of 1.5 to 3. The relatively low variation in the background sector illustrates the lower O_3 production in the dark winter periods. This variation is enhanced in the sectors with anthropogenic pollution by a lower conversion rate of the anthropogenic precursors to O_3, i.e. nitrogen oxides and VOC's. O_x (= O_3 + NO_2) is, as shown by other examples in the previous annual reports (*Kemp, Palmgren and Manscher, 1993, 1994 and 1996*), remarkably alike for all three sectors. Both the absolute concentrations and the seasonal variation for the sectors with anthropogenic contribution are close to the O_3 background.

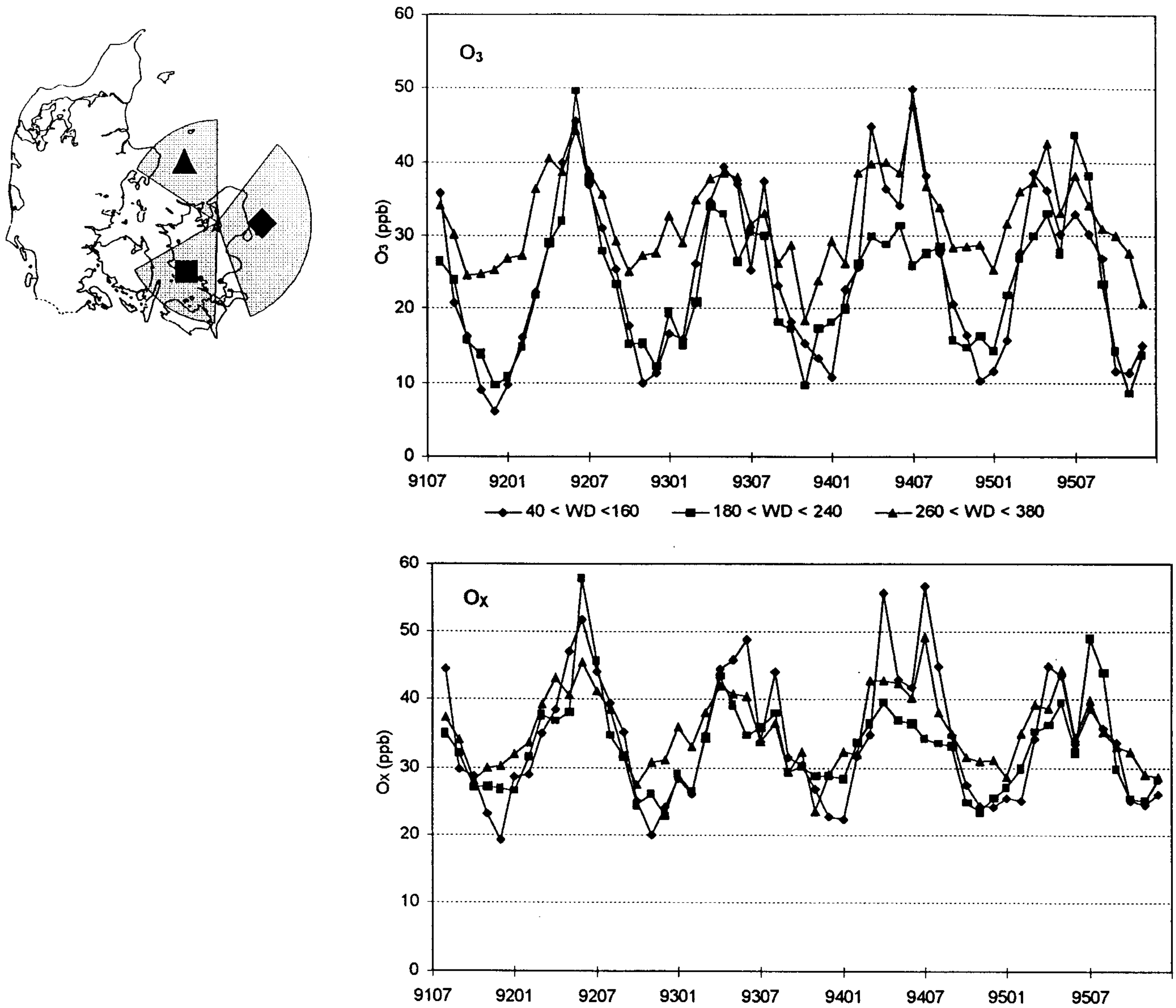


Figure 3.4 Monthly average values measured at Lille Valby/2090 for O_3 and O_x (O_3+NO_2). The wind sectors for the single curves are shown on the map. The signatures on the map correspond to the points on the curves.

Correlation between stations

Correlation between simultaneous measurements is highly significant 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 1996*). 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 1995. 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 µg/m³	ρ	a	b µg/m³	ρ	a	b µg/m³	ρ	a	b µg/m³	ρ
1259	0.80	20	0.70	1.00	6.4	0.88	0.93	6.8	0.69	0.96	4.0	0.80
9159	0.85	17	0.75	1.05	1.8	0.82	0.99	2.8	0.76			
8159	0.87	14	0.56	1.06	-0.6	0.72						
2090	0.81	16	0.71									

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 oxidation of SO_2 and SO_4^{2-} 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 is 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 1995 the concentration of SO_2 and particulate sulphur were measured as 24 hour averages at all stations within the network, while SO_2 concentrations were 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).

4.1 Annual statistics

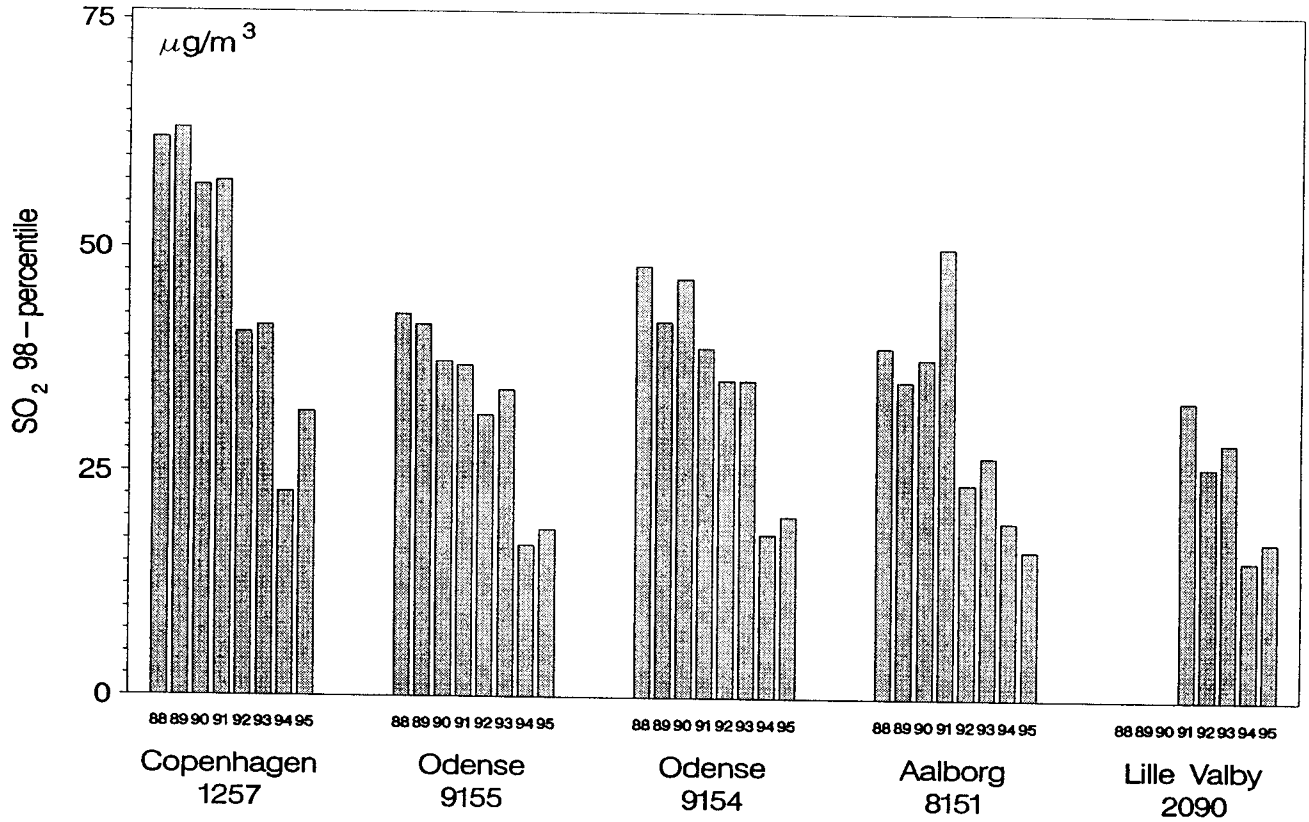
Limit values

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 on *figure 4.1*. At all stations the measured values are well below the limit and guide values. The winter concentrations are 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 1995. 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.

	SO_2 (µg(SO_2)/m³)						Part. S (µg(S)/m³)	
Station	Number	Median year	Median winter	max. 3 days	98-perc.	Average	Number	Average
Copenhagen/1257	256/181	7.0	8.2	38	32	9.0	257	1.92
Odense/9155	322/153	2.7	2.8	25	19	3.8	321	1.78
Odense/9154	332/155	3.0	3.6	25	20	4.2	327	1.79
Aalborg/8151	319/158	2.7	2.8	15	17	4.0	319	1.57
Lille Valby/2090	354/175	1.6	2.3	36	18	3.1	351	1.38
Limit value	-	80	130	250	250	-	-	-
Guide v.[1)]	-	-	-	-	-	40-60	-	-

[1)] The guide value is given in EEC directive (*EEC, 1980*), but not implemented in Denmark.



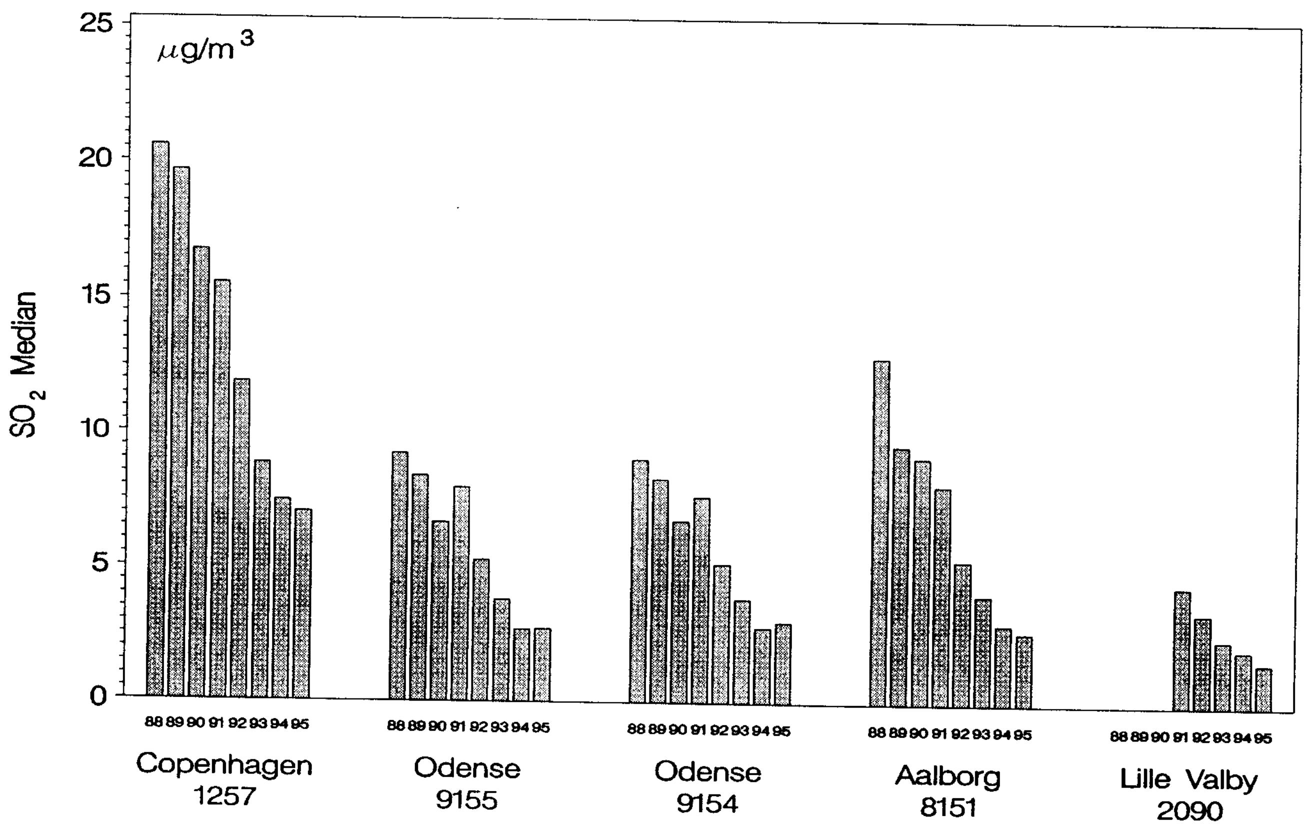


Figure 4.1 Medians and 98-percentiles for SO_2 from 1988 to 1995.

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 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. 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 1 hour 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 are given in the sixth column.

	SO_2 ($\mu g(SO_2)/m^3$)					S (part.) ($\mu g(S)/m^3$)	
Station	Max. 3 hour	Day:hour	Max hour	Day:hour	"Hot-spot" episodes	Max. day	Day
Copenhagen/1257	67	950108:07	143	950412:14	5	6.9	951015
Odense/9155	79	950106:04	92	950106:03	4	6.5	951015
Odense/9154	-		-	-	-	4.3	950714
Aalborg/8151	65	950430:11	586	950510:15	16	5.4	950107
Lille Valby/2090	59	950119:21	64	950119:21	2	5.2	950119

Long range episode

The most pronounced SO_2 episode in 1995 occurred in January in the eastern part of the country. From January 16 to January 21 the wind direction was very stable from south. The SO_2 levels were elevated to approximately 50 $\mu g/m^3$ at Copenhagen/1257 and Lille Valby/2090 (see fig. 4.2), while the levels were less than 25 $\mu g/m^3$ at all other stations. In the same period the concentration of particulate S was about 5 µg/m^3. The correlation between the Copenhagen/1257 and Lille Valby/2090 and the wind direction indicates that the source is south of Denmark. But probably not too far away, since the plume did not cover e.g. Odense and the concentration of particulate S was relatively low. The Berlin area seems to be a reasonable guess.

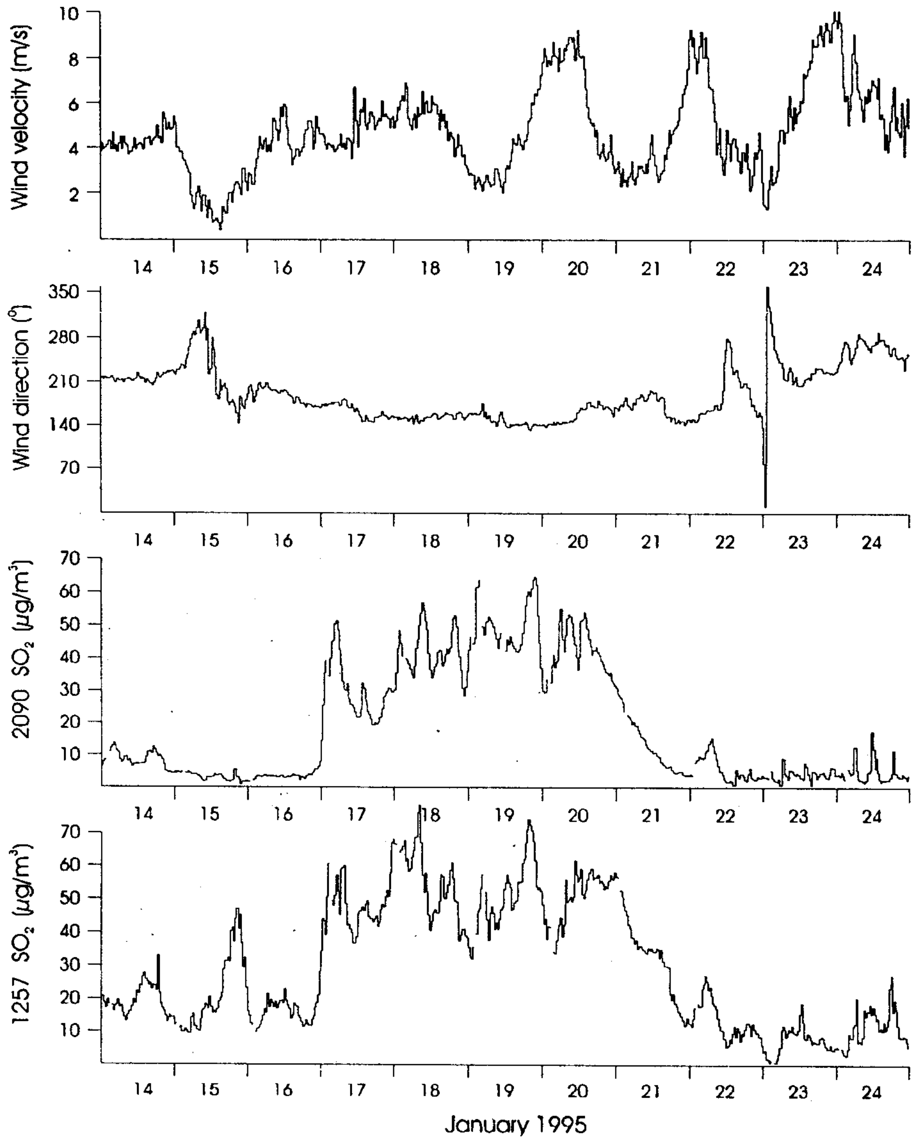


Figure 4.2 Course of the SO_2 episode in January 1995 at Copenhagen/1257 and Lille Valby/2090.

Hot-spot

Hot-spot episodes are observed at irregular intervals in all three cities. In order to be able to present an overview of the occurrence of the hot-spot episodes, we have, rather arbitrarily, defined a hot-spot episodes as an incident, where the SO_2 concentration increases and again decreases more than 50 µg/m^3 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 have not changed much from 1994 to 1995. They are far most abundant in Aalborg, where they in almost all cases are observed at NE winds. One of these, on May 10, gave the highest hourly concentration measured since the start of the LMP III program in 1991.

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 on *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 is 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. Except for Aalborg/8151 the results from 1995 show an increase of especially the short term parameters compared to 1994 (cf *figure 4.1*).

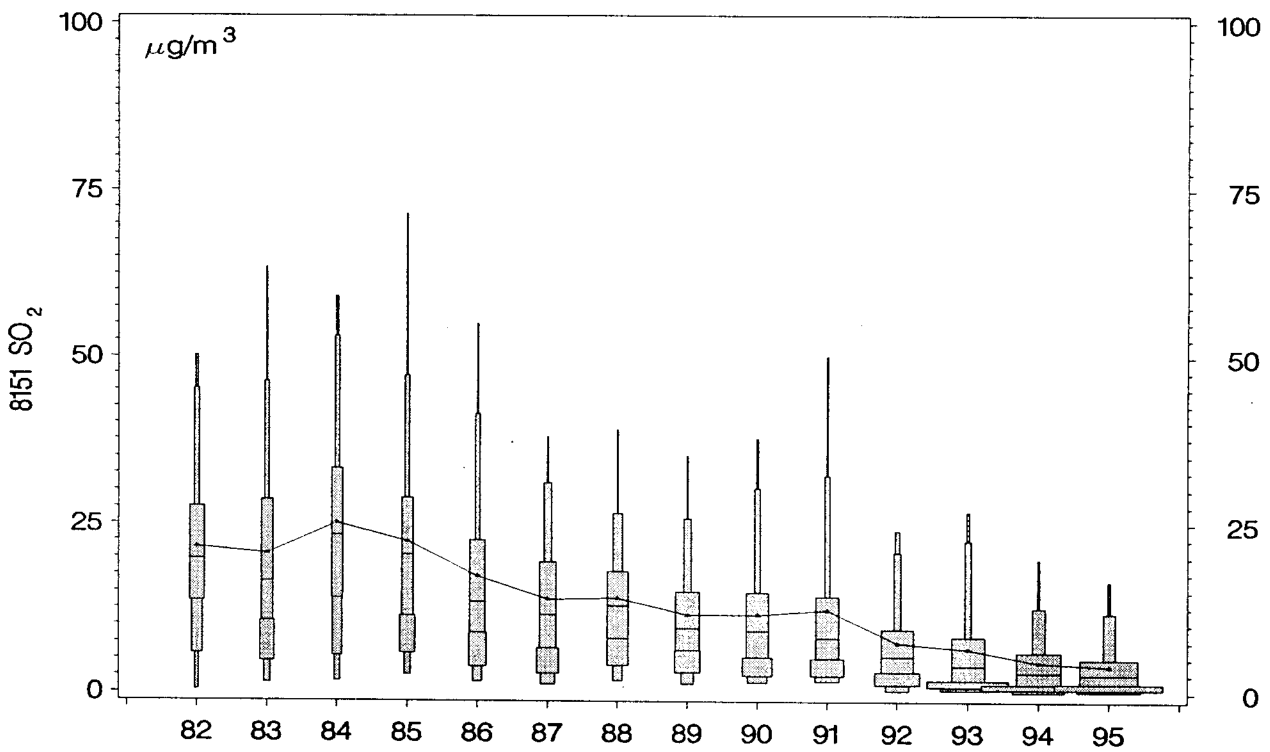


Figure 4.3 Trends for annual 98-, 95-, 75-, 50-, 25- and 5-percentiles, average and minimum value based on hourly average concentrations of SO_2 measured at Aalborg/8151. (See explanation on p. 15).

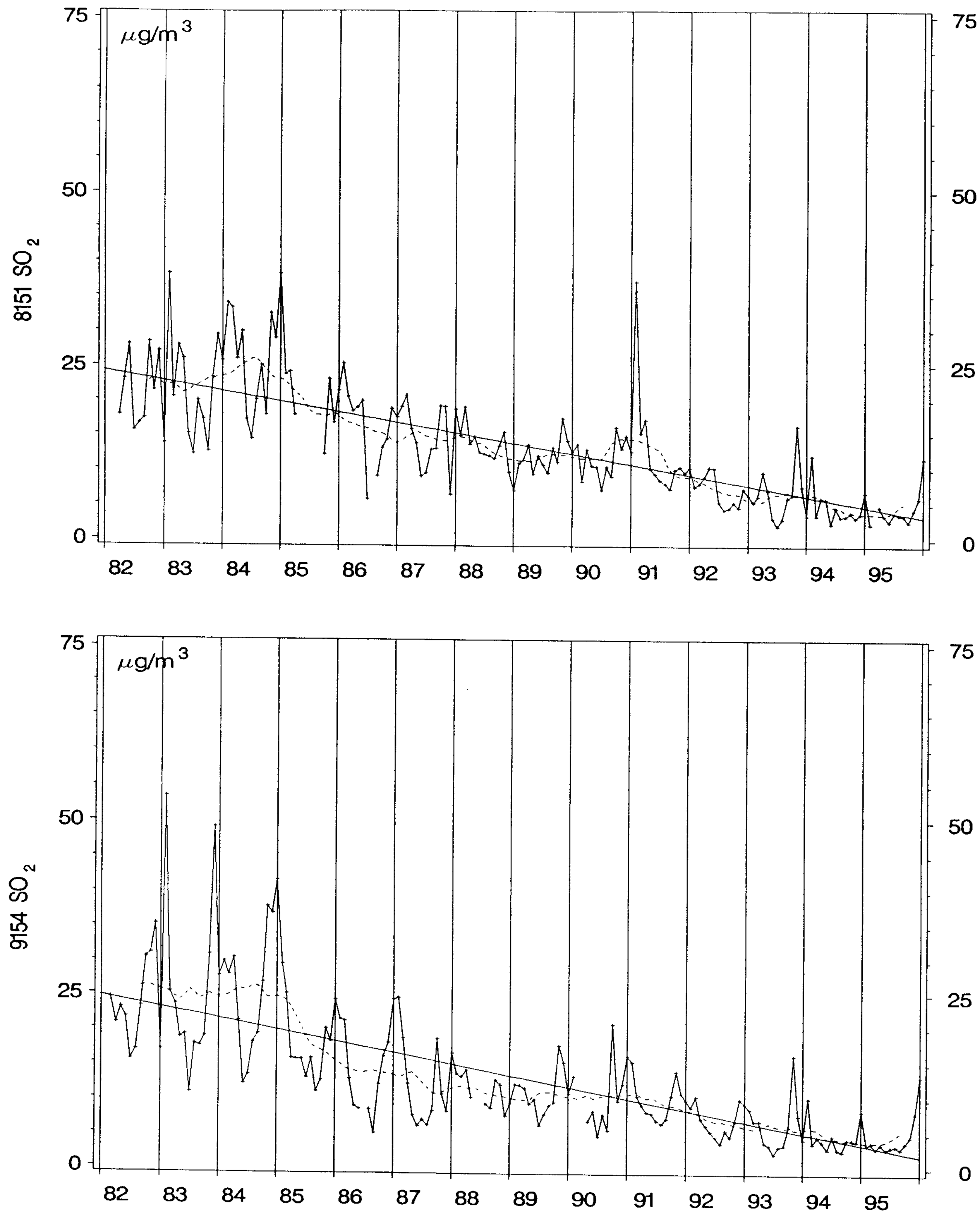


Figure 4.4 Trend for SO_2 measured at Aalborg/8151 and Odense/9154. The points are measured monthly averages, the dotted curve is a moving average over 12 month and the straight line is a linear regression line (see explanation on p. 15).

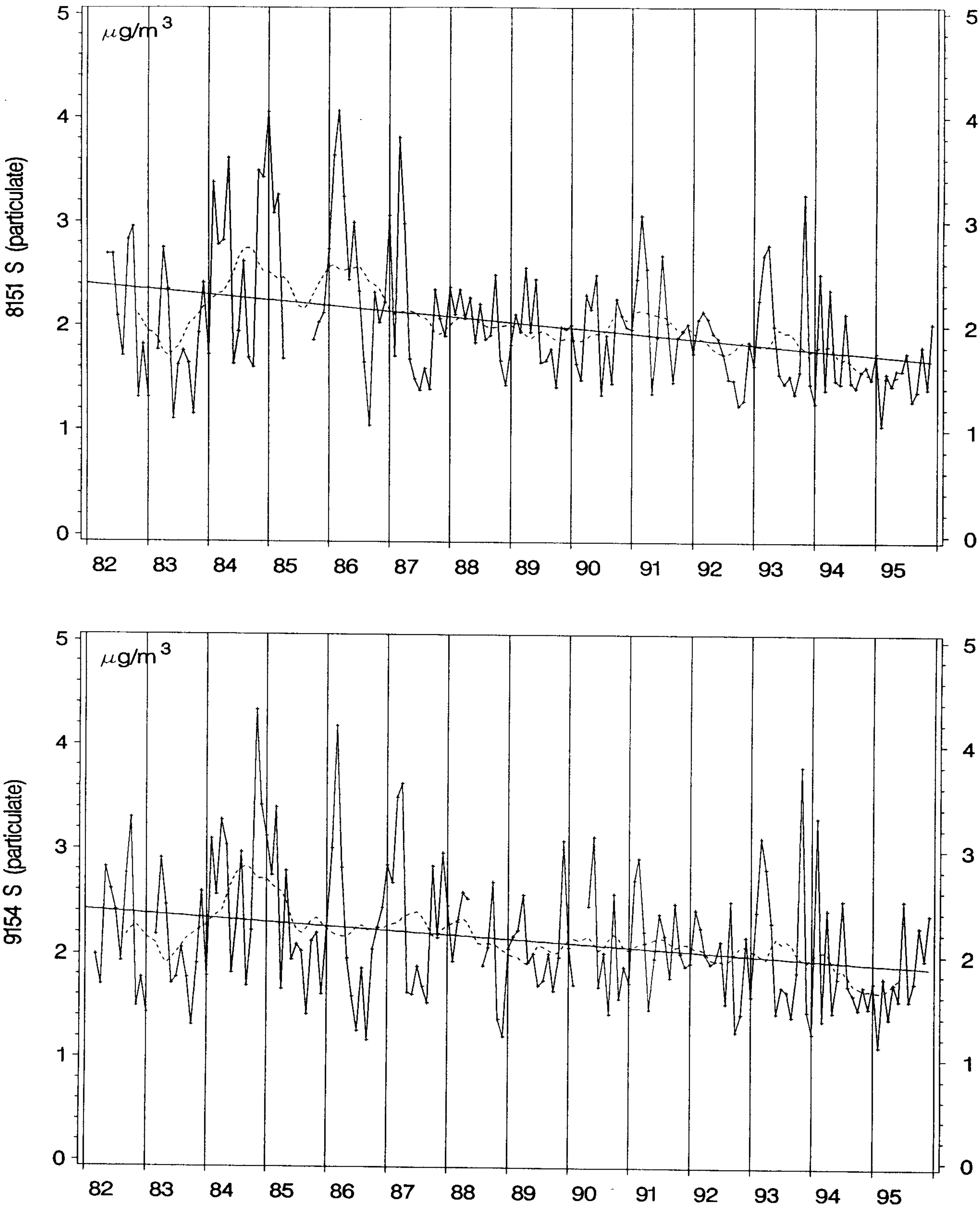


Figure 4.5 Trend for particulate S measured at Aalborg/8151 and Odense/9154. The points are measured monthly averages, the dotted curve is a moving average over 12 month and the straight line is a linear regression line (see explanation on p. 15).

Average SO_2 and S concentrations

The trends for the monthly average values at Aalborg/8151 and Odense/9154 are shown on *figure 4.4* for SO_2 and on *figure 4.5* for particulate sulphur. The average SO_2 concentrations are 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 heating and introduction of lighter diesel oil are the main reasons, together with a number of mild and windy winters, for the continuous decrease in the later years. Particulate S shows, in contrast to SO_2, only a slightly downward going trend. This shows probably that the sulphur emission has been reduced more in Denmark than in our neighbouring countries, but the conversion rate may to some extent have been limited by the amount of oxidants in the atmosphere.

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 1995 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 on March 18.

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 1995 are given in *table 5.1*. The annual 95-percentiles and average values are shown for 1988-1995 on *figure 5.1*.

Table 5.1 Average values, 95-percentiles and maximum values for TSP in 1995. The numbers are calculated for 24 hour average values.

		TSP (μg/m^3)			
Station	Number	Average - whole year	95-perc.	Max.value	Day
Copenhagen/1257	256	61	142	202	950310
Odense/9155	320	53	110	166	950425
Odense/9154	327	48	89	160	950330
Aalborg/8151	317	56	112	180	950901
Lille Valby/2090	279	21	53	96	950423
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 level has been slightly decreasing (*figure 5.1*) and there is no reason to believe that it will change much within the coming years. As mentioned 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 road traffic. The particles from combustion processes are in the fine particle fraction, and it expected to decrease in the future due to reduction of the emissions as may be the result of i.a. obligatory three way catalysts on gasoline cars and restrictions on the diesel exhaust.

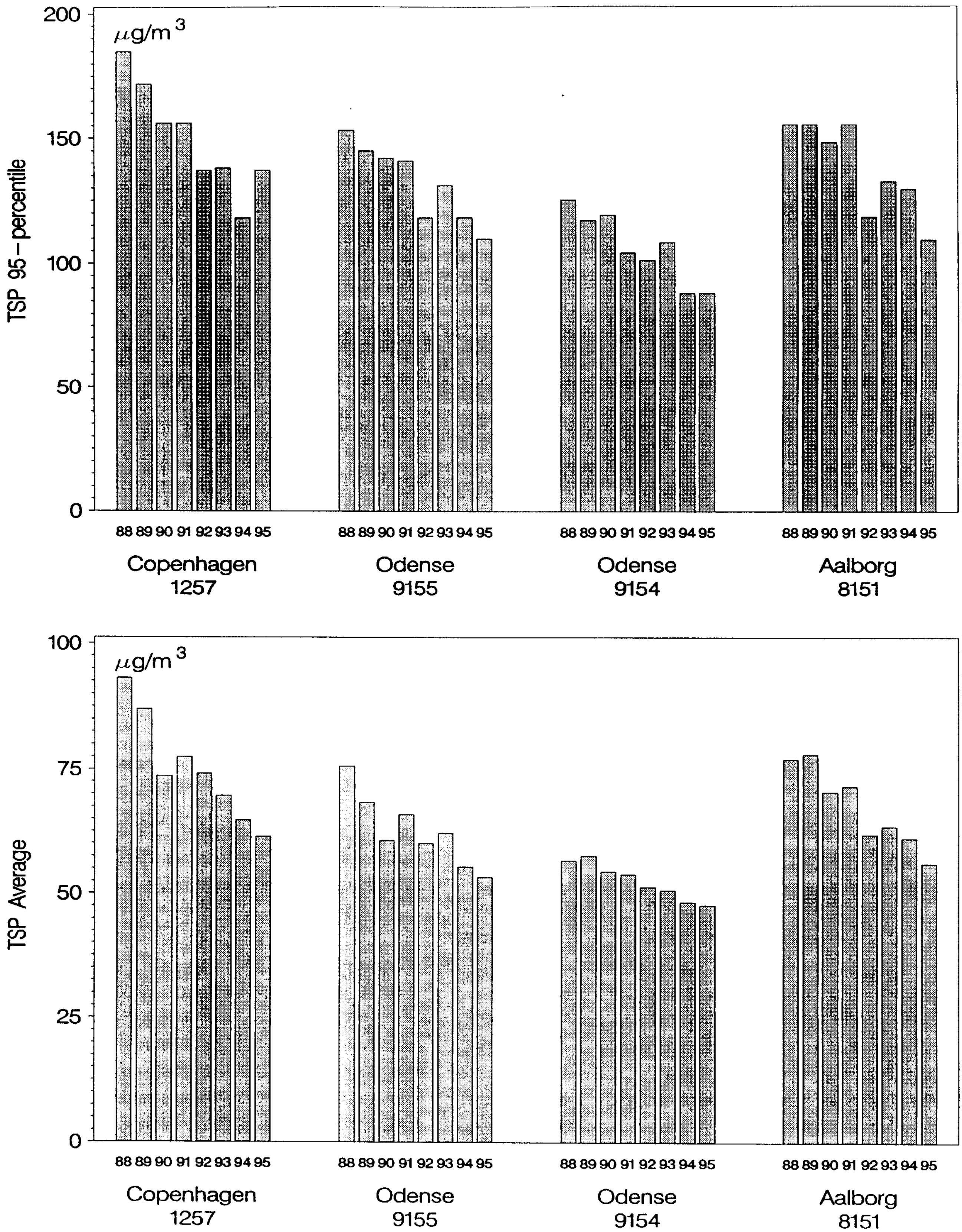


Figure 5.1 Average values and 95-percentiles for TSP from 1988 to 1995.

1995 was the first year TSP was measured at the rural station Lille Valby/2090. The results were about half of the results from the urban street stations.

5.2 Episodes

The measured maxima of the daily average values are given in *table 5.1*. There was no outstanding episodes in 1995. The maximum values occurred at different days at the single stations without any apparent connection. They were most probable caused by local road works.

5.3 Trends

Percentiles

The annual percentiles and average values based on daily average TSP concentrations measured at Aalborg/8151 are shown on *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.

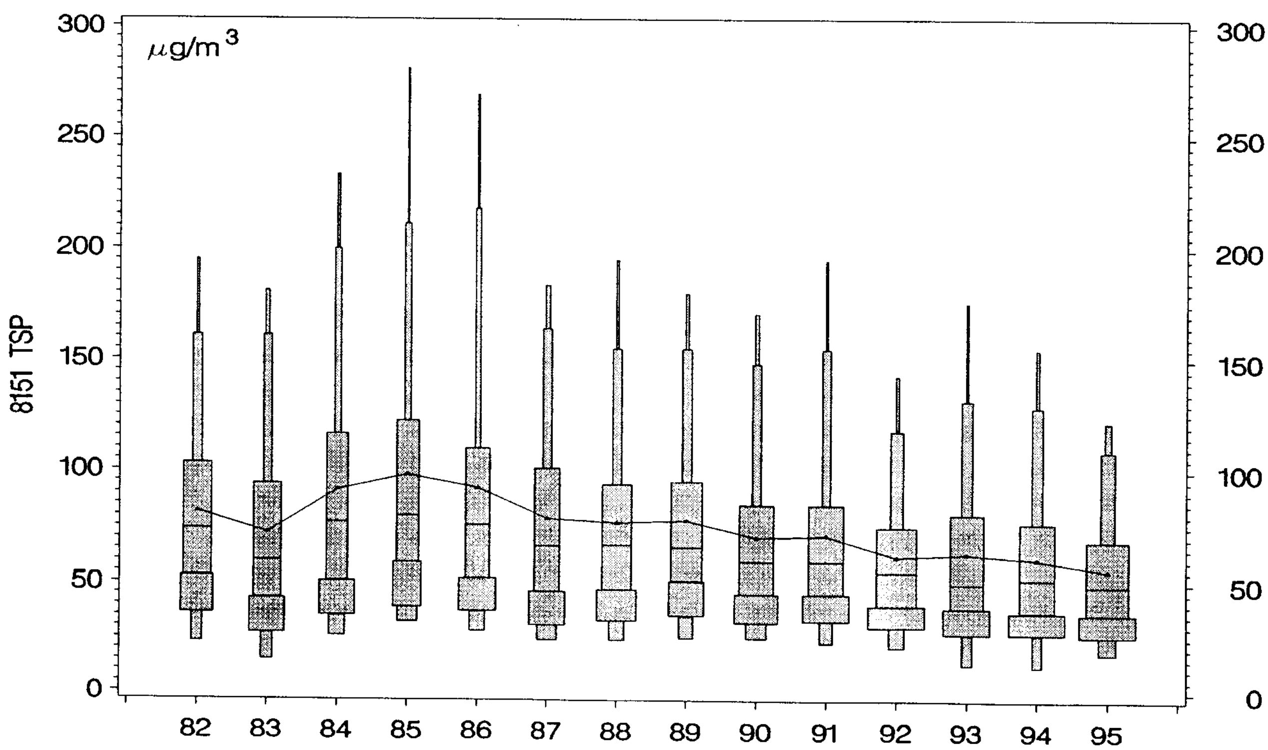


Figure 5.2 Trends for annual 98-, 95-, 75-, 50-, 25- and 5-percentiles, average and minimum value based on daily average concentrations of TSP measured at Aalborg/8151. (See explanation on p. 15).

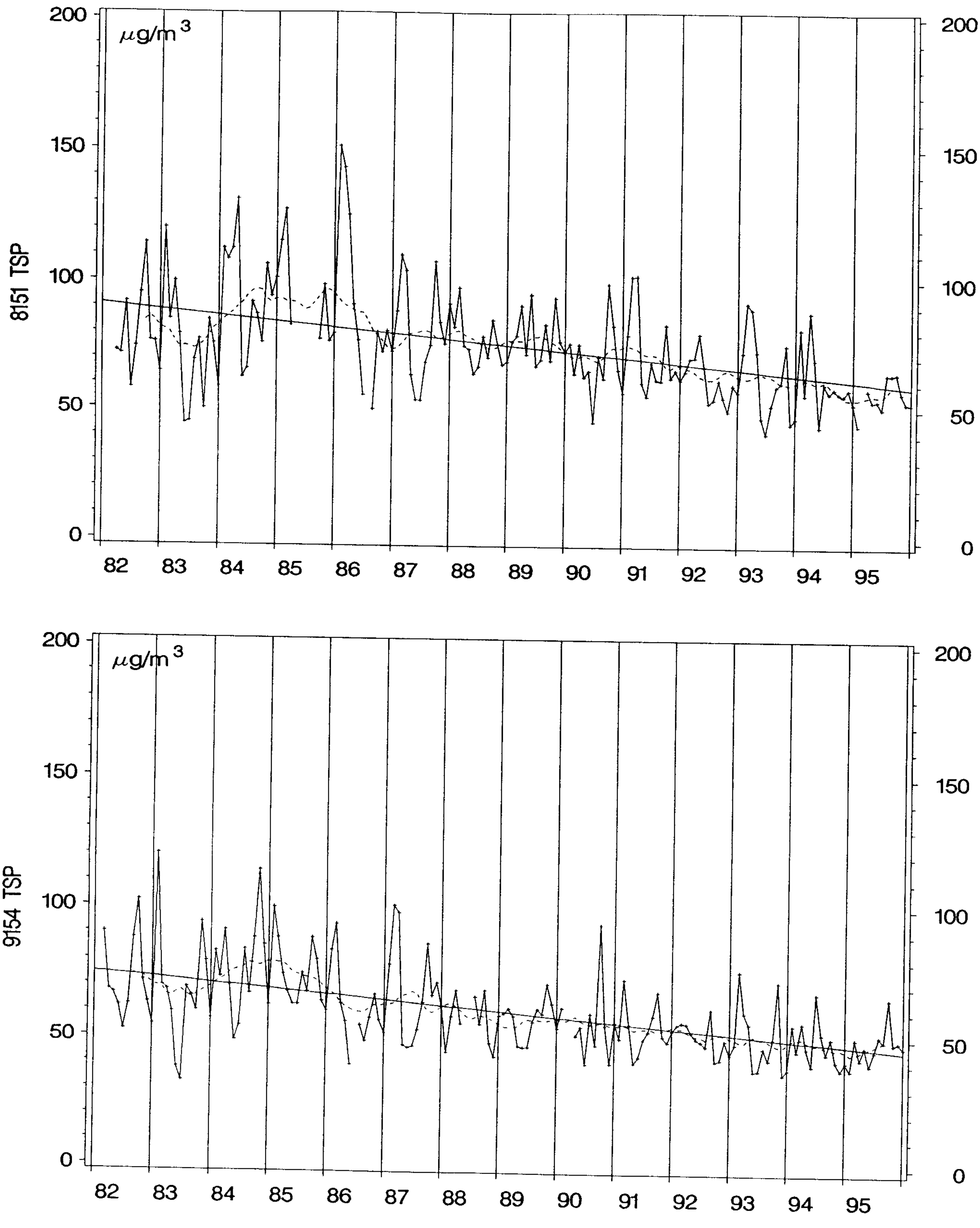


Figure 5.3 Trend for TSP measured at Aalborg/8151 and Odense/9154. The points are measured monthly averages, the dotted curve is a moving average over 12 month and the straight line is a linear regression line (see explanation on p. 15)

Annual average

After relatively high concentrations from 1984-1986 it appears that 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 natural gas for oil for domestic heating, but other factors like the obligatory demand for "winter crops" from 1987 may, as discussed in the annual report for 1993 (*Kemp, Palmgren and Manscher, 1994*) also play an important role.

Annual variation

The highest concentrations are found in the early spring and in the autumn. The low summer concentrations are 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 keep the dust grounded in the winter month.

6 Elements

The aerosol samples are analyzed 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. The measurement of the elements may, beside for monitoring purposes, 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 burning of heavy oil the main source for V and Ni, traffic for Pb and wind blown dust for Si.

6.1 Annual statistics

The average values for the elements are found in *table 6.1*.

Pb is the only element for which, there is limit value within EU. The annual average concentration must not exceed 2 $\mu g/m^3$ (*EEC, 1982)*. The limit value was laid down when the automobile petrol was heavily leaded. At present almost all petrol sold in Denmark is unleaded and the lead content in the remaining few per cent is less than 0.1 g/l. It was around 0.6 g/l, when the limit value originally was proposed by the EEC. The measured annual averages in 1995 were less than 1/50 of the limit value at the main stations, which are placed on streets with heavy traffic (*figure 6.1* and *table 6.1*). It is expected that leaded petrol will be withdrawn completely from the market within the next few years.

6.2 Trends

Of the elements, 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 ten (see *figure 6.2*) and a further decrease is expected (cf. chapter 6.1).

6.3 Heavy metals in urban and rural areas

Among the elements that are determined are several toxic heavy metals. WHO has assessed the toxic effects of some heavy metals (*WHO, 1987*). These are Cr, V, Mn, Ni, As, Cd, Hg and Pb. Guidelines are suggested for V, Mn, Cd, Hg and Pb, while the remaining i.e. Cr, Ni, and As are carcinogenic in certain compounds and only life time cancer risks are estimated.

Table 6.1 Average values for 1995. All concentrations are given as ng/m³ (1 µg/m³ = 1000 ng/m³). N_{tot} is the number of measurements in 1995. 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_o	Average	N_o	Average	N_o	Average	N_o	Average	N_o	Average
Al	222	645.0*	282	609.0*	278	376.0*	277	507.0*	116	106.0*
Si	257	1520.0	321	1550.0	327	1010.0	319	1560.0	336	297.0
S	257	1920.0	321	1680.0	327	1790.0	319	1570.0	351	1380.0
Cl	257	4520.0	321	2780.0	327	2360.0	319	3320.0	351	657.0
K	257	306.0	321	285.0	327	261.0	319	283.0	351	183.0
Ca	257	1240.0	321	1010.0	327	595.0	319	1120.0	351	189.0
Ti	257	58.4	321	71.9	327	46.1	319	53.3	301	10.1*
V	253	7.2	284	5.1*	286	5.0*	285	4.9*	305	4.2*
Cr	254	4.2	310	4.4	309	3.0	313	4.1	264	0.8*
Mn	257	22.2	321	28.3	327	19.2	319	15.4	351	4.6
Fe	257	1120.0	321	1060.0	327	668.0	319	973.0	351	132.0
Ni	257	4.4	320	2.8	326	2.8	318	2.7	347	2.7
Cu	257	41.8	321	31.0	327	19.6	319	29.4	317	3.3
Zn	257	68.9	319	78.1	326	50.1	319	94.1	318	20.4
As	237	2.5	241	1.5*	267	1.4*	224	1.2*	305	1.4*
Se	211	0.7*	282	0.8*	319	0.8	270	0.6*	344	0.7
Br	257	6.4	321	6.0	327	6.5	319	6.8	351	4.1
Sr	257	6.1	321	4.7	327	3.5	319	5.9	348	1.3
Zr	253	3.9	319	4.1	319	2.6	315	3.1	220	0.4*
Mo	225	2.5*	269	2.0*	256	1.3*	267	1.6*	107	0.3*
Cd	61	0.7*	68	0.7*	85	0.7*	85	0.8*	112	0.6*
Sb	241	10.3	293	8.4	291	5.5*	297	7.3	169	1.5*
Ba	245	36.9	299	35.3	299	21.6	309	29.7	115	3.2*
Pb	257	26.0	321	22.3	327	23.0	319	31.4	351	9.9
N_{tot}	257		321		327		319		351	

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

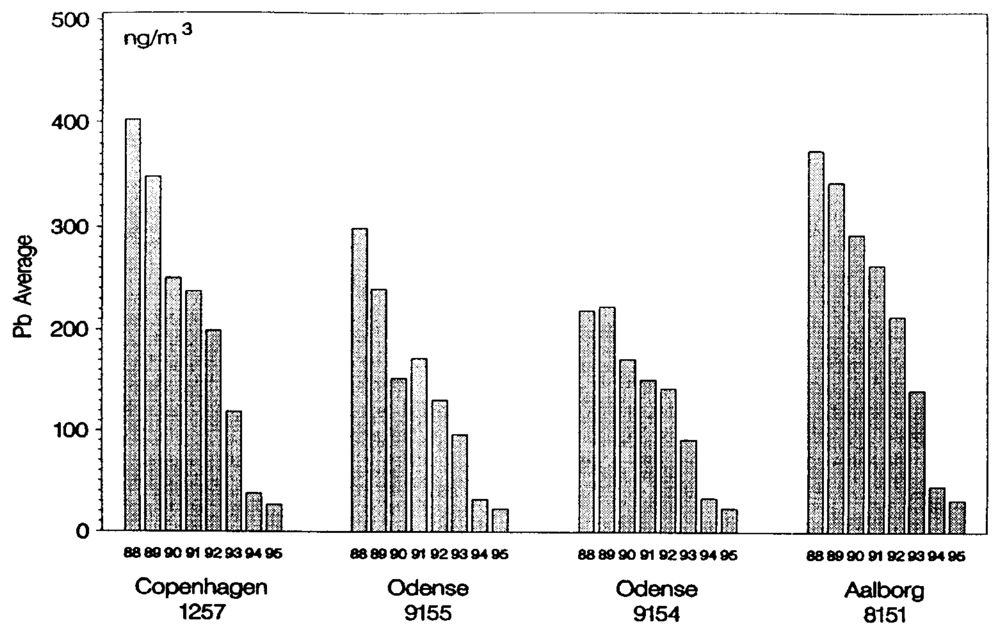


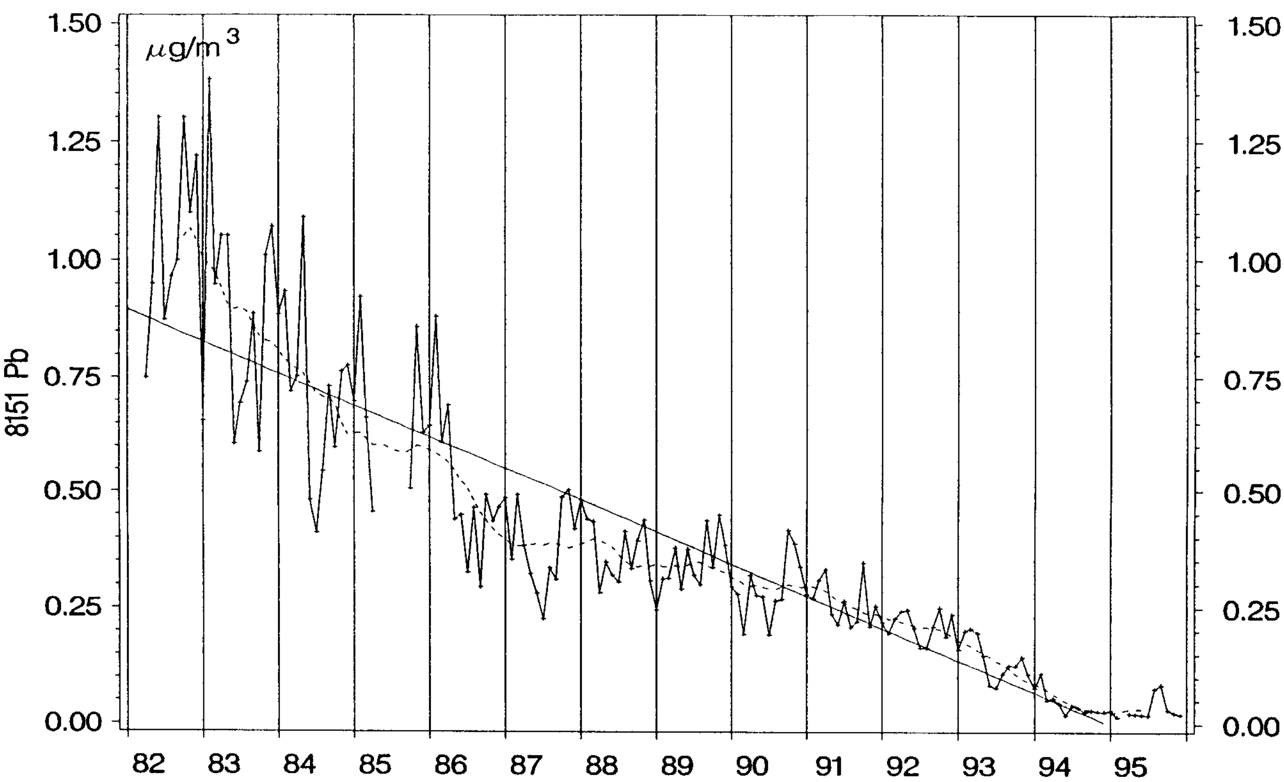
Figure 6.1 Annual average values for Pb from 1988 to 1995.

Non-carcinogenic

Table 6.2 shows the WHO guidelines, which all are based on 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 has followed the reduction in the SO_2 concentrations and it expected to decrease further in the future. Mn do only show a slightly decreasing trend.

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

ng/m^3	WHO guideline	Aalborg/8151 1982	Aalborg/8151 1995	Copenhagen/1257 1995
V	1000	22	5	7
Mn	1000	20	15	22
Cd	10-20	<2	0.8	0.7
Hg	~1000	N.D.	N.D.	N.D.
Pb	500-1000	1100	31	26



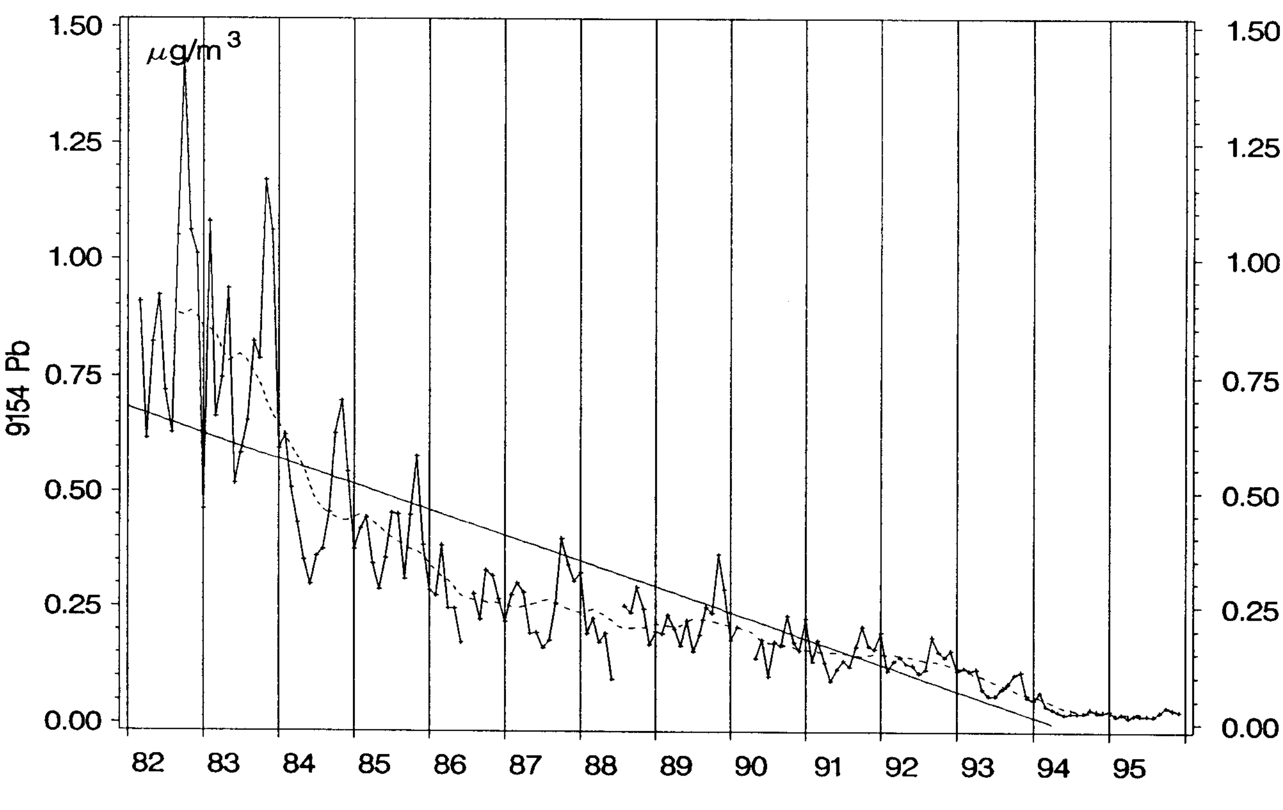


Figure 6.2 Trend for Pb measured at Aalborg/8151 and Odense/9154. The points are measured monthly averages, the dotted curve is a moving average over 12 month and the straight line is a linear regression line (see explanation on p. 15).

Carcinogenic

The estimated lifetime risks are estimated for air concentrations of 1 mg/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. *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, 1987*) 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 1995 $\mu g/m^3$	Copenhagen/1257 1995 $\mu g/m^3$
Cr	1)	0.0029	0.0041	0.0042
Ni	4×10^{-4}	0.0070	0.0027	0.0044
As	3×10^{-3}	D.L.	0.0012	0.0025

[1]) the WHO estimated life time risk for Cr(VI) is 4×10^{-2}, while the measurements are total Cr (see text).

Cr

Only hexavalent Chromium (Cr(VI)) is carcinogenic, while the most abundant trivalent Chromium (Cr(III)) is relatively harmless. Little is known about the amount 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 a corresponding almost constant level at the urban stations indicates that the Cr gradually is becoming an urban problem. 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).

Ni

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.

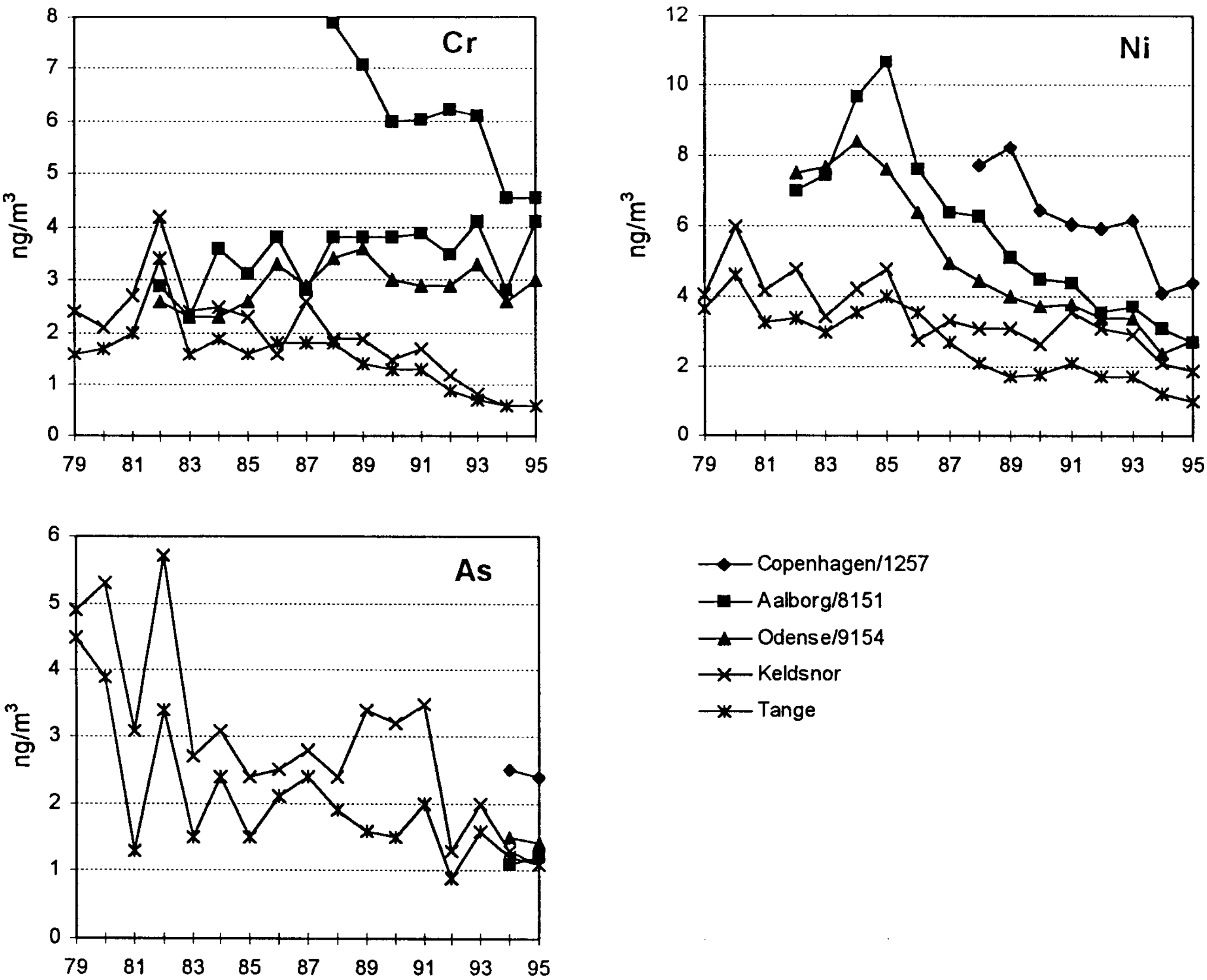


Figure 6.3 Yearly average values for the potential carcinogenic heavy metals. Results from the stations in the Danish Background Monitoring Program at Tange and Keldsnor are included for the comparison.

As

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 an on are available due 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 1995 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 is long range transported.

Summary

If the estimated risks for the three elements are added they correspond to a lifetime risk at more than 10^{-6}. The variation of the concentration from station to station indicates that the occurrence of Cr is wide spread 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. Motor vehicles are the main source for both CO and NO_x in urban areas, but there is considerable differences in the emission factors depending i.a. of the type of vehicles (*Miljøstyrelsen, 1991*).

7.1 NO_x and CO, Copenhagen, Odense and Aalborg

The measurements at Aalborg/8151 was in 1995 supplemented with measurements of CO, and at Aalborg/8159 with NO_x from June 1 to August 30. From January 1 to March 9 and from October 3 to December 31 these measurements were carried out at Odense/9155 and Odense/9159). In Copenhagen measurements of CO and O_3 were performed at Copenhagen/1257 and of NO_x and CO at Copenhagen/1259 the whole year. The results are briefly summarised in the following.

Statistics

Some statistical parameters are shown in table 7.1 The ratios between the average values at the street and 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 $NO \rightarrow NO_2$ is almost complete after the transport, which normally takes a few minutes, to the roof level. The NO distributions at the roof stations are extremely skew. The ratios between the 99.9 and 98 percentiles are around a factor 4. The highest NO concentrations are greater than the corresponding NO_2 concentrations. The conversion of NO is at these occasions limited by the amount of O_3. The ratio for CO at street and roof level is 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.

NO, NO_2 at street vs. roof

The difference between street and roof concentrations are illustrated for NO on *figure 7.1*. The wind direction distribution for the street stations is strongly influenced by the street direction. The street goes along the flat side of the distribution at all three stations, which are placed in "street canyons". The concentrations are lowest when the wind above roof level is coming from the direction from the street, due to the turbulence created in the canyon (*Kemp, Palmgren and Manscher, 1996*). Almost all NO have been converted to NO_2 at roof level because the O_3 supply under normal conditions is sufficient to a complete conversion.

Table 7.1 Statistical parameters for campaign periods. The Aalborg results are from the summer 1995, while the Odense results are from the first and last three month of 1995 and the Copenhagen measurements are from all 1995.

Compound ($\mu g/m^3$)	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	76	43	320	640	7.1	2.2	58	220
	Odense	61	26	370	550	12	3.6	82	270
	Aalborg	48	30	202	380	4.5	2	30	176
NO_2	Copenhagen	52	51	102	170	29	26	69	91
	Odense	34	32	83	118	25	23	58	71
	Aalborg	35	31	94	133	15	12	55	92
CO	Copenhagen	1650	1270	5170	9300	400	310	1150	3010
	Odense	890	580	3950	6670	-	-	-	-
	Aalborg	670	470	2690	5780	-	-	-	-

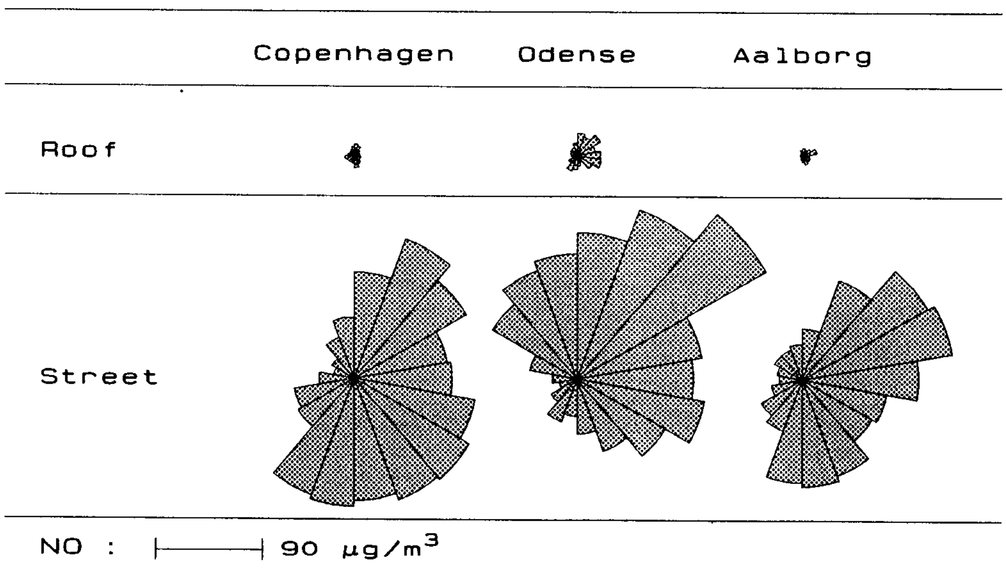


Figure 7.1 Wind roses for campaign results. The radii of the circle sections are proportional to the average concentrations for wind coming from the direction the section points towards.

The corresponding distributions for NO_2 (*figure 7.2*) show, in agreement with the NO results, that the roof concentrations are closer to the street levels than the NO values.

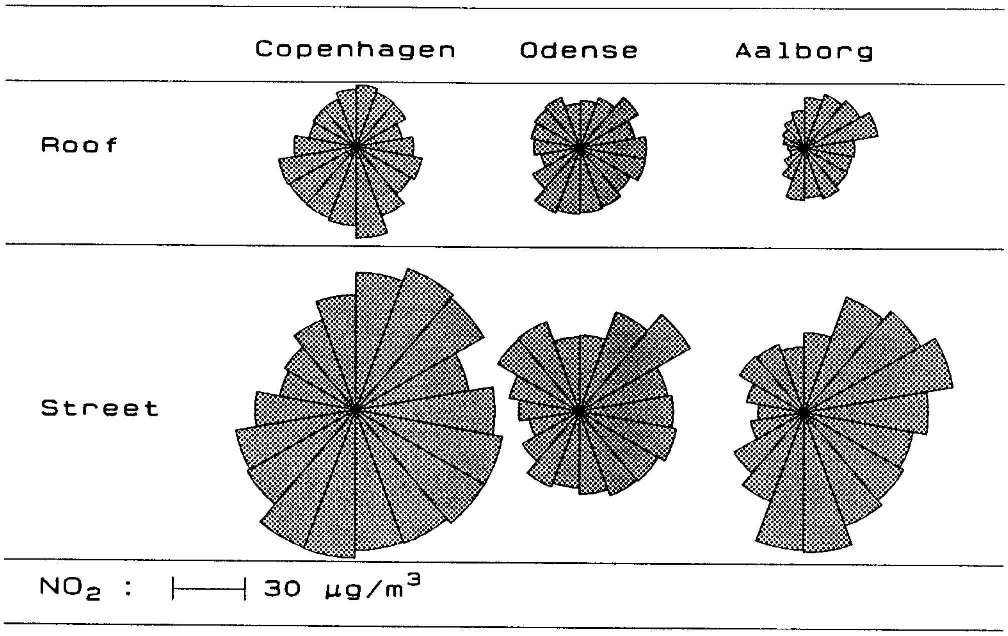


Figure 7.2 Wind roses for campaign results. The radii of the circle sections are proportional to the average concentrations for wind coming from the direction the section points towards.

8 Conclusion

NO_2

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 1995 almost the same or slightly higher than the previous years. A trend analysis covering the last 14 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.

O_3

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 1995 some of the threshold values were exceeded frequently. However, it is not a simple task to reduce the O_3 concentrations 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.

SO_2

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.a. 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.

TSP

The collected TSP is a mixture of "natural" wind blown dust 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 about 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 expected limitations on the particle emission from diesel vehicles become more stringent.

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. Almost 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.

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 by the radio 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. The threshold for information of the population was exceeded once in 1995. The information threshold will statistically be exceeded about one time per 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 1995 show that the concentrations found in the Danish cities are below the existing limit values, but that some of the new O_3 threshold values, which are implemented in 1994, will be exceeded frequently. The NO_2 concentrations were around half the limit value and no clear decreasing trend was observed. The measurements in LMP III program take i.a. aim at giving 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 to see 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 1995

Faglig rapport fra DMU nr. 180

Kåre Kemp, Finn Palmgren, Ole H. Manscher

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, Hovedstads-regionens 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. 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 i én by i perioder på ca. 4 måneder.

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 $\mu g/m^3$ for 98-percentilen og de vejledende værdier på 135 $\mu g/m^3$ for 98-percentilen og 50 $\mu g/m^3$ for medianen. Afstanden til de vejledende værdier er ikke ret stor. Emissionen af NO_x fra benzindrevne bliver reduceret efterhånden som der kommer katalysatorer på flere og flere biler. Med resultaterne fra 1995 er det nu tydeligt at niveauet for NO er blevet reduceret; mens der ikke kan påvises nogen ændring for NO2. 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 forbløffende 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 1995. 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 undererrettes. Det skete én gang i 1995.

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 gammel forurening, der er 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 væsentligste. Der er 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 1995 var omkring en faktor 30 lavere end ved LMP programmerne start i 1982. Efterhånden som blyet forsvinder helt fra benzinen vil blyforurening komme ned på niveau med andre tungmetaller som fx krom og kadmium.

Kampagner

Der blev gennemført kampagnemålinger i alle LMP byerne i 1994 (kapitel 7). Formålet med kampagnerne er at give et konkret grundlag til beskrivelse af forekomsten af NO_x'er i danske byer og deres omdannelse med særlig henblik på den rolle baggrunds O_3 spiller for de kemiske reaktioner. I København var kampagnemålingerne også en del af projektet "Luftforurening fra trafikken", som er et projekt under det strategiske miljøforskningsprogram. Kampagnemålinger af NO og NO_2 på tagstationerne viste at praktisk taget al NO under normale omstændigheder er omdannet til NO_2 før luften fra gaderne når tagstationerne. Ved meget høje NO koncentrationer er der imidlertid en stor del, der ikke omdannes fordi der ikke er tilstrækkelig O_3.

Resumé

LMP resultaterne fra 1995 viser at den forurening, der findes i de danske byer var under de gældende grænseværdier, men at de nye tærskelværdier 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 dokumenteres. 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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