The Danish Air Quality Monitoring Programme

Annual Report for 1994

NERI Technical Report No. 150

Kåre Kemp
Finn Palmgren
Ole H. Manscher
Department of Atmospheric Environment

Ministry of Environment and Energy
National Environmental Research Institute
January 1996

Data Sheet

Title:	The Danish Air Quality Monitoring Programme
Subtitle:	Annual Report for 1994
Authors:	Kåre Kemp, Finn Palmgren & Ole H. Manscher
Department:	Department of Atmospheric Environment
Serial title and no.:	NERI Technical Report No. 150
Publisher:	Ministry of Environment and Energy National Environmental Research Institute ©
Year of publication:	January 1996
Fieldwork:	Tom Rasmussen Technicians of the municipalities
Technical assistance:	Axel Egeløv, Lone Grundahl
Laboratory assistance:	Axel Egeløv, Lone Grundahl, Bjarne Jensen, Christina F. Jensen, Jens Tscherning Møller, Birgit Thomsen, Kenneth Vinther
Typist:	Bodil Chemnitz
Please quote:	Kemp, K., Palmgren, F. & Manscher, O.H. (1996): Danish Air Quality Monitoring Programme. Annual Report for 1994. National Environmental Research Institute, Roskilde Denmark. 66 pp. - NERI Technical Report No. 150.
ISBN:	87-7772-239-6
ISSN:	0905-815X
Paper quality:	Cyclus Kopi
Printed by:	Grønager's Bogtryk & Offset
Impression:	300
Number of pages:	66
Price	DKr. 80 (incl. 25% VAT, excl. freight)

For sale at:

National Environmental Research Institute
Department of Atmospheric Environment
Postbox 358
Frederiksborgvej 399
DK-4000 Roskilde
Denmark
Tel: +45 46 30 12 00
Fax: +45 46 30 12 14

Miljøbutikken
Information & books
Læderstræde 1
DK-1201 Copenhagen K
Denmark
Tel: +45 33 37 92 92

Content

Summary

The Danish Air Quality Monitoring Programme (LMP) was started in 1982 as the first nationwide 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 1994 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 the pavement 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. A "city-near" background site outside Copenhagen is also included. NO, NO_2, SO_2, 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. 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. The same program as at the street stations, with exclusion of TSP, is conducted at the background site.

Air quality limit values have been implemented in Denmark for NO_2, SO_2, total suspended particulate matter (TSP) in order to protect human health. All limit values are based on corresponding EU 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.

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. 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 as result of the TWC's.

The SO_2 concentrations have been continuously decreasing since 1982. They were in 1994 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 around 1/3 of the limit value.

The lead pollution has been reduced with about a factor of 10 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.

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 levels are, especially during the winter, lowest at winds from southeasterly directions. 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 cooperation between the Danish Environmental Protection Agency, the National Environmental Research Institute (NERI), 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.

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. All instruments were operating as planned during 1994 (*Kemp, 1993*).

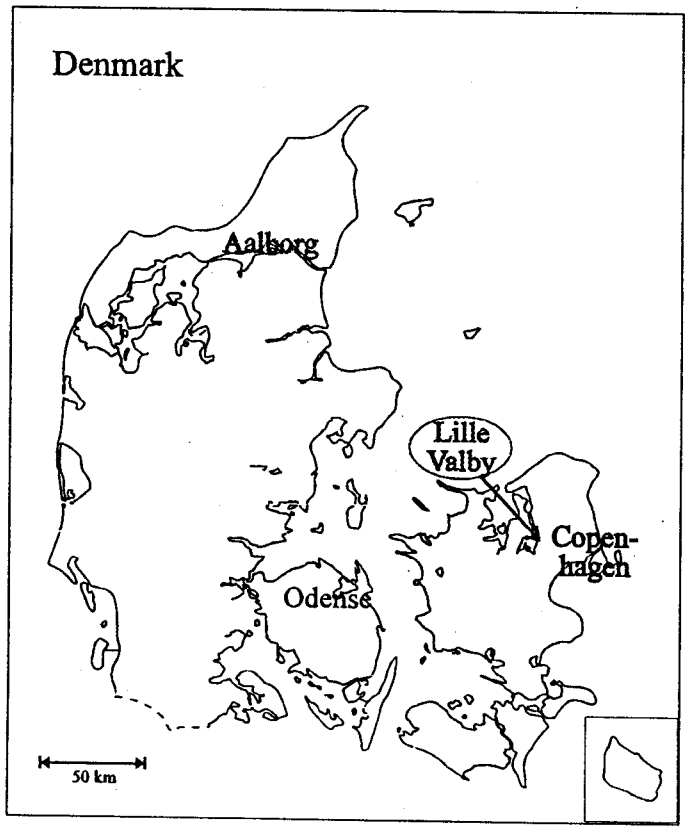

Figure 1.1. Cities and the background site in the LMP network.

Measuring programme

The measuring programmes at stations in operation during the major part of 1994 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*.

Table 1.1. LMPIII stations in 1993. 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. Meteorological measurements were started at Aalborg/8159 by the end of 1993.

		x Measuring Programme	
	Station type	½ hour average	24 hour average
Copenhagen/1257	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, Elements

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 ia. carried out in order to retail information about 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 summarized 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 unchanged 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 mean concentration exceeds 180 $\mu g/m^3$, while an alarm is sent to the population, if the hourly mean concentration exceeds 360 $\mu g/m^3$.

1994 reports

The 1994 results are found in quarterly reports *(Danmarks Miljøundersøgelser, 1994a, 1994b, 1995a 1995b)*. The results obtained during 1994 are summarized in the present report in form of annual statistics and trends. The phenomenology of O_3 is again in 1994 treated as a special topic since O_3 is a key specie in the present studies of the atmospheric chemistry of ia. transformation of nitrogen oxides and VOC compounds. Further the programme for campaigns with intensive measurements was continued in 1994. The results of a campaign in Aalborg and Odense are reported separately (*Kemp, 1995*). The campaign measurements in Copenhagen are still an integrated part of an intensive programme for studying the pollution from traffic (*Berkowicz et al., 1995*). Results from the campaigns are summarized in the present report. A summary of a VOC campaign (*Palmgren et al., 1995)* is also given in this report.

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 (around 95%). 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 of course very much on the actual concentrations and the temperature.

Measurements

During 1994 continuous measurements of NO and NO_2 were performed at four stations: Copenhagen/1257, Odense/9155, Aalborg/8151 and Lille Valby/2090. More than 85% of the possible results for the whole year are available at all stations. The three first stations are located in urban areas at kerbside on streets with heavy traffic, whereas the last one is located approximately 25 km outside Copenhagen, without any nearby sources of importance.

2.1 Annual statistics

Limit values

The limit value for Denmark is 200 $\mu g/m^3$ for the 98-percentile of hourly mean values of NO_2 measured over one year. The guide values are 130 $\mu g/m^3$ for the 98-percentile and 50 $\mu g/m^3$ 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 1994, but the guide values were approached in Copenhagen. The very low values for NO at Lille Valby/2090 illustrate the fast conversion of NO to NO_2.

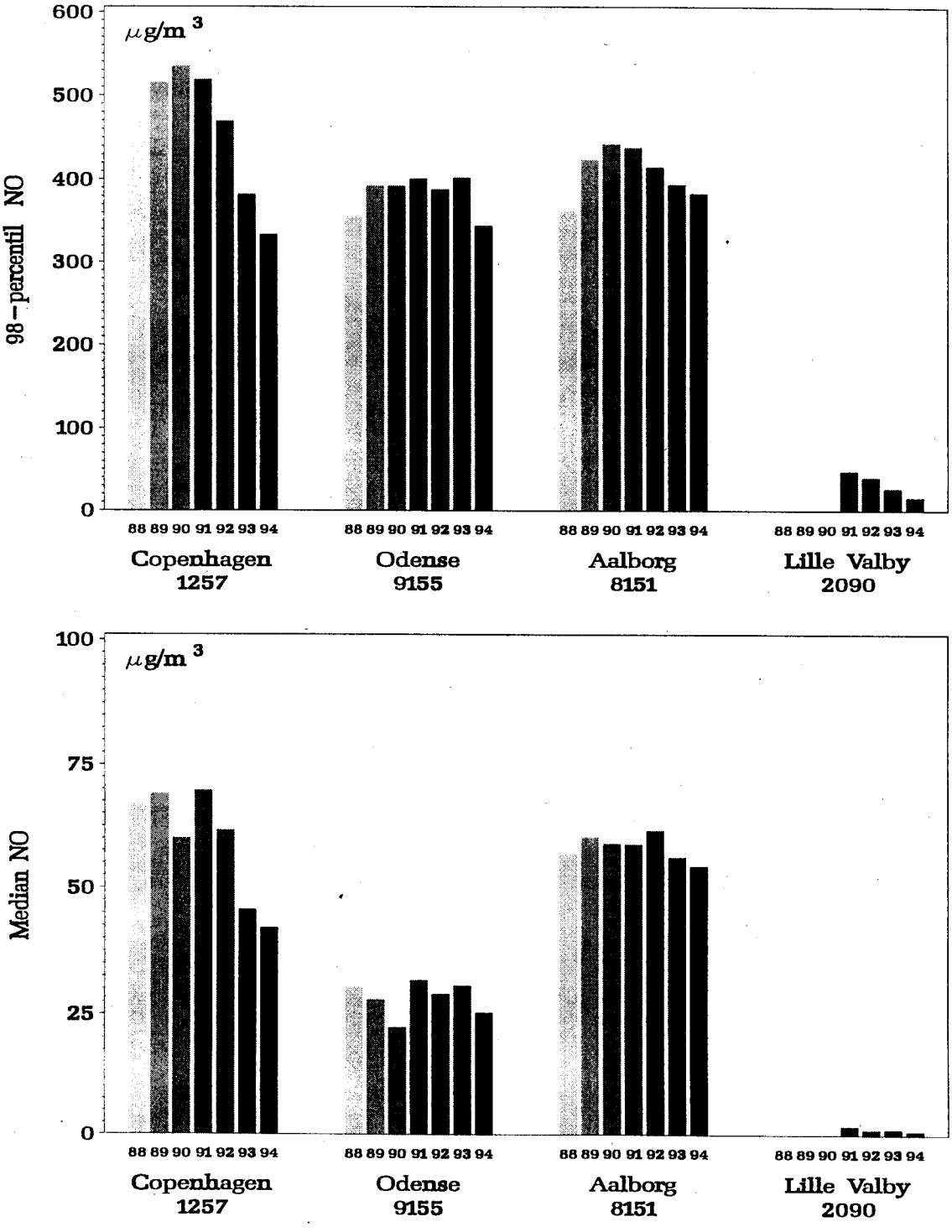

Figure 2.1. Medians and 98-percentiles for NO from 1988 to 1994.

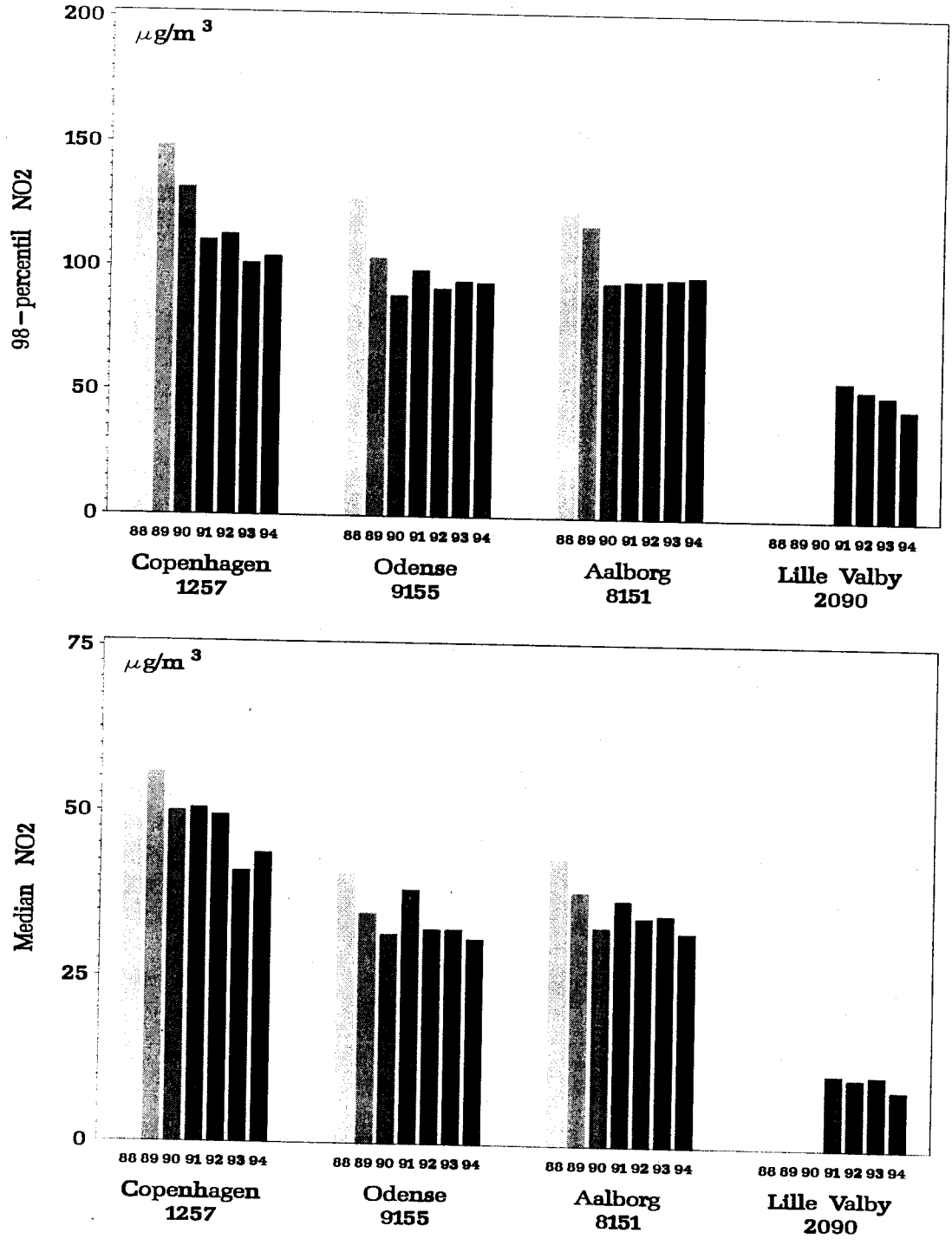

Figure 2.2. Medians and 98-percentiles for NO_2 from 1988 to 1994.

Table 2.1. The values are calculated for all measurements from 1994 and based on hourly mean 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 are below the detection limit).

	NO (µg(NO)/m³)					NO_2 (µg(NO_2)/m³)			
Station	Number *	Mean Value	Median	98-perc	99.9-perc	Mean Value	Median	98-perc	99.9-perc
Copenhagen/1257	8081	78	45	335	584	47	44	102	131
Odense/9155	8235	62	27	346	578	36	31	93	122
Aalborg/8151	8244	91	58	384	673	37	33	96	126
Lille Valby/2090	7503	(2)	(0)	15	108	12	9	44	59
Limit val.	>6570	-	-	-	-	-	-	200	-
Guide -		-	-	-	-	-	50	135	-

* Number of measurements

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 site.

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)/m³ 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.

Table 2.2. Maximum concentrations of NO (not included in the smog warning sytem) and NO_2. For comparison with the the warning limit the lowest 1 hour values are identified for every consecutive three hours. The highest of these 1 hour values are listed under "max. 3 hour". The values under "max. hour" are the absolute one hour max 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	607	941130:21	755	941130:19
Odense/9155	513	940218:08	744	940823:06
Aalborg/8151	598	941130:09	916	941130:08
Lille Valby/2090	101	941201:06	144	941201:08
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	150	940728:09	157	940728:07
Odense/9155	114	940321:09	208	941108:08
Aalborg/8151	116	940510:09	176	941222:13
Lille Valby/2090	57	940217:22	64	940722:07
Warning limit	350	-		

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 for O_3 in summer.

Winter episode

The difference between the winter and summer conditions, which favors respectively high NO and NO_2 concentrations, is illustrated by the episodes around November 30 and July 28 at Copenhagen/1257. *Figure 2.3* shows the NO and NO_2 concentrations at Copenhagen/1257 and Lille Valby/2090. In the evening on November 30 there was almost no air movement at 1257 and the NO pollution was accumulated in the air. At the same time the NO_2 level was determined by the background O_3 level corresponding to around 40 $\mu g/m^3$ and the direct emission, which is around 10% of NO (calculated as $\mu g/m^3$). The air moved slowly towards west and the NO_x concentration was increasing at 2090. In the beginning the major part was present as NO_2, but as the background O_3 was used up the NO increased abruptly. Quite a large amount of NO loafed around in the air for several hours without possibilities for being oxidized.

Summer episode

The O_3 concentrations peaked at the end of July (see chapter 3), which meant that NO in the atmosphere could be rapidly converted to NO_2. *Figure 2.4* shows that only short peaks occurred in the NO concentrations at Copenhagen/1257 during the morning rush-hours, while the NO_2 was dominating the remaining time. Nearly no NO was measured at Lille Valby/2090.

2.3 Trends

Percentiles

The annual percentiles and mean values for NO and NO_2 measured at Aalborg/8151 are shown on *figure 2.5*. The level of NO may have a slightly increasing trend over the whole period, reflecting the trend in the traffic intensity. It has, however, been decreasing for the last three 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 only are 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 concentration.

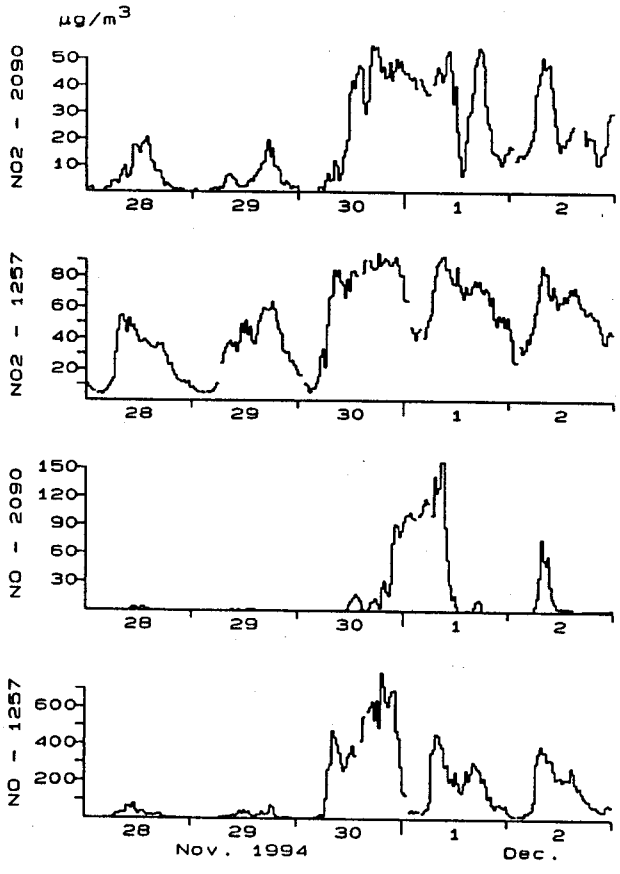

Figure 2.3. The course of the NO_2 winter episode in November/December 1994.

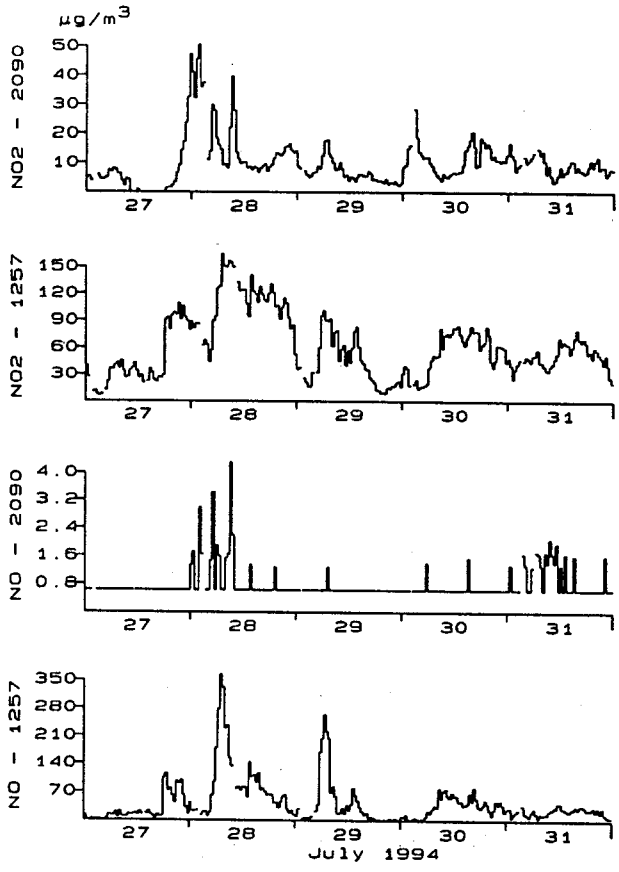

Figure 2.4. The course of the NO_2 summer episode in July 1994. The horizontal parts of the NO curve represent half of the detection limit for the monitor (0.6 µg/m³).

Explanation to the trend figures: 2.5, 4.4, and 5.2

The bars represent annual percentiles measured at Aalborg/8151. The bar sections are from the top defined by the 98-, 95-, 75-, 25- and 5- percentiles. The horizontal line in the middle section is the median and the bottom represents the minimum value. The interconnected points are the mean 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 the skew frequency distributions.

Means

The trend of the monthly mean values and the annual variation are shown at *figure* 2.6. 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.

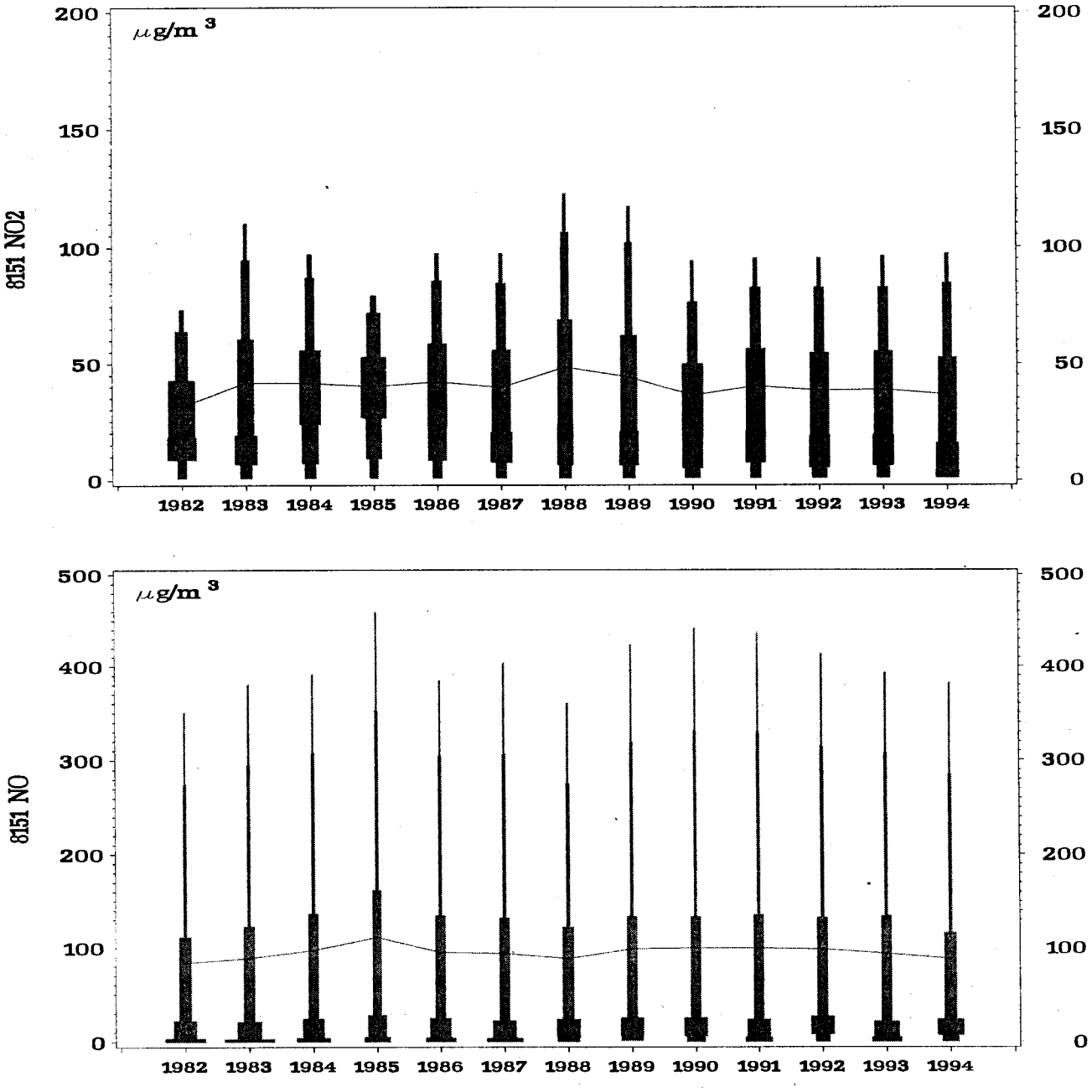

Figure 2.5. Trends for annual 98-, 95-, 75-, 50-, 25- and 5-percentiles, mean and minimum value based on hourly mean concentrations of NO_2 and NO measured at Aalborg/8151. (See explanation on p. 15).

Explanation to the trend figures: 2.6, 4.5-6, 5.3 and 6.3

The figures are intended to illustrate these properties:

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

Copenhagen vs other cities

Figure 2.1 and *2.2* indicate that the NO and NO_2 concentrations in Copenhagen have been decreasing for the last few year, while no changes can be shown in the two smaller cities Odense and Aalborg. The reason for this is not obvious, but it may be caused by a reduction of the urban background levels, which are higher in Copenhagen than in the two other cities.

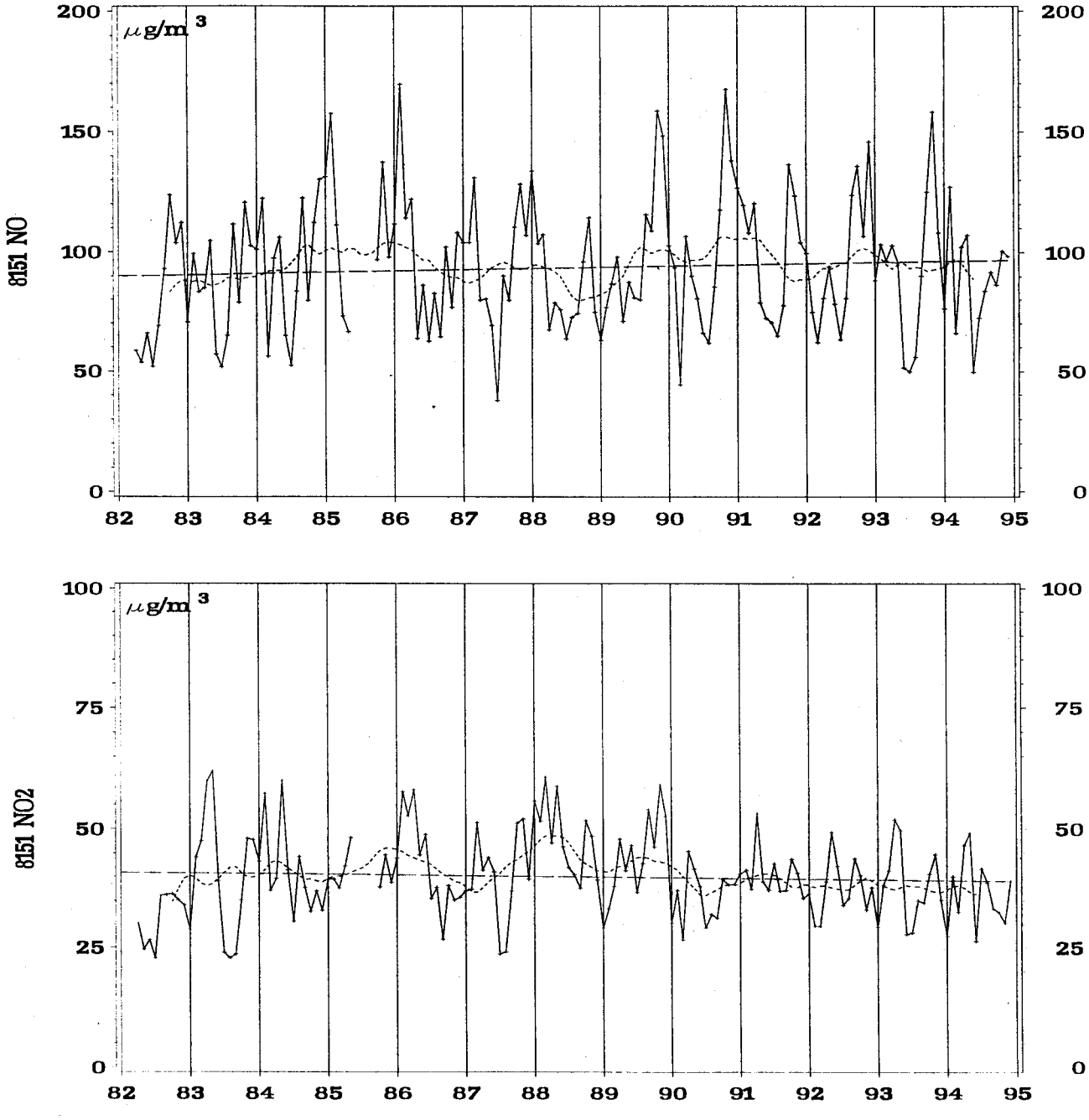

Figure 2.6. Trend for NO and NO_2 measured at Aalborg/8151. The points are measured monthly averages, the dotted curve is a moving annual average and the straight line is a linear regression line. (see explanation p. 16).

2.4 Representativity of NO_2 measurements

It is essential for the assessment of the measured concentrations of a compound in relation to the limit values that the measuring site is typical for the area it should represent. In street level at busy streets the concentrations of NO and NO_2 depend very much of the wind direction relative to the street. In open streets the concentrations may be a factor of ten higher for NO and a factor of three for NO_2, when the wind is blowing from the street compared to off street directions. The opposite is the case for "street canyons" (*Kemp, Palmgren, Manscher, 1994*). It will be expected that quite different percentiles and mean values would be measured, if the measuring stations were moved to the opposite side of the street. We have employed a simple empirical model for NO_2 based on the measurements alone in order to assess this problem.

Model

The model is mainly based on average wind direction and wind speed variations of the NO_2 concentrations and the weekly variations of NO_2 and wind velocity (*Kemp, Palmgren, Manscher, 1994*). The model represents the measuring site, if the measured average wind direction distribution $W_1(wd)$ is used. If it is assumed that the variation of $W_1(wd)$ is caused only by the street traffic, i.e. that the background contribution is isotropic, the model for the opposite side of the street is obtained by mirroring $W_1(wd)$ along an axis parallel to the street.

Two sides of the street

The model is applied for the stations Copenhagen/1257, Odense/9155 and Aalborg/8151, where meteorological measurements are available from the nearby stations Copenhagen/1259, Odense/9159 and Aalborg/8159. Data from 1994 are used for the calculation of the average variation functions except for the annual variation. This is determined based on monthly values for the long time series from Aalborg/8151. The correlation between the measurements and the results of the models for the same side of the street as the stations are good while the relative poor correlation to the models for the opposite side of the street indicates the actual concentrations of the two sides of the street may be quite different. The yearly statistical values are however rather similar. The model results for 1994 indicate that somewhat lower values would have been obtained in Copenhagen and Aalborg and somewhat higher values in Odense if the measuring stations had been placed on the opposite site of the street. But the differences are generally less than 20%. The values from Copenhagen and Odense confirm the 1993 results (*Kemp, Palmgren, Manscher, 1994*).

Table 2.3. Comparison between mean values and percentiles for ½-hourly NO_2 concentrations. All concentrations are in $\mu g/m^3$. ρ is the linear correlation coefficient to the measurements.

	Copenhagen/1257				Odense/9155				Aalborg/8151			
	Mean value	Medi-an	98-perc.	ρ	Mean value	Medi-an	98-perc.	ρ	Mean value	Medi-an	98-perc.	ρ
Measured	47	44	103	1	36	31	94	1	36	30	96	1
Model same side	47	43	104	0.80	36	29	105	0.82	38	34	92	0.80
Model opposite side	42	40	86	0.41	40	40	109	0.27	32	32	97	0.29

3 Ozone

Measurements in 1994

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. Results are thus available for all 1994 from all the stations, where it was planned to measure O_3, i.e. Copenhagen/1259, Odense/9159, Aalborg/8159 and Lille Valby/2090. 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., 1995).*

Sources and formation

The O_3 in the lower troposphere is formed as a secondary pollutant mainly by photochemical reactions involving i.a. 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 in July and August 1994 favorable 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. Both the max. 24 hour and the max 8 hour threshold values were exceeded in many occasions in 1994 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 month January and February.

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

O_3 (µg/m³)	Mean value	Median (hour)	98-perc. (hour)	99.9-perc (hour)	max. 24 hours	max. 8 hours[1)]	max. 1 hour
Copenhagen/1259	51	50	119	169	124	166	178
Odense/9159	50	50	118	172	126	169	189
Aalborg/8159	52	53	108	144	106	134	162
Lille Valby/2090	57	58	124	184	129	184	197
Threshold value	-	-	-		65	110	200
Average number of exceedings per station	-	-	-		101	23	0

[1)] The eight hour values are calculated in accordance with the EEC directive, as a non-overlapping moving average without; 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 mean concentration of the O_3 exceeds 180 µg/m³ and to issue a warning, if the hourly mean 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

The concentrations exceeded threshold for information of the population at two days in 1994. Press releases were transmitted by the nation wide radio at July 26 and 28 in the news broadcasts. In the last part of July and the beginning of August an almost stable high pressure over the eastern part of Scandinavia gave frequent air transport from Central Europe to Denmark. The concentrations were at several occasions above 150 µg/m³. Fig. 3.1 shows the results from Lille Valby in the eastern part and Aalborg/8159 in the western part of Denmark.

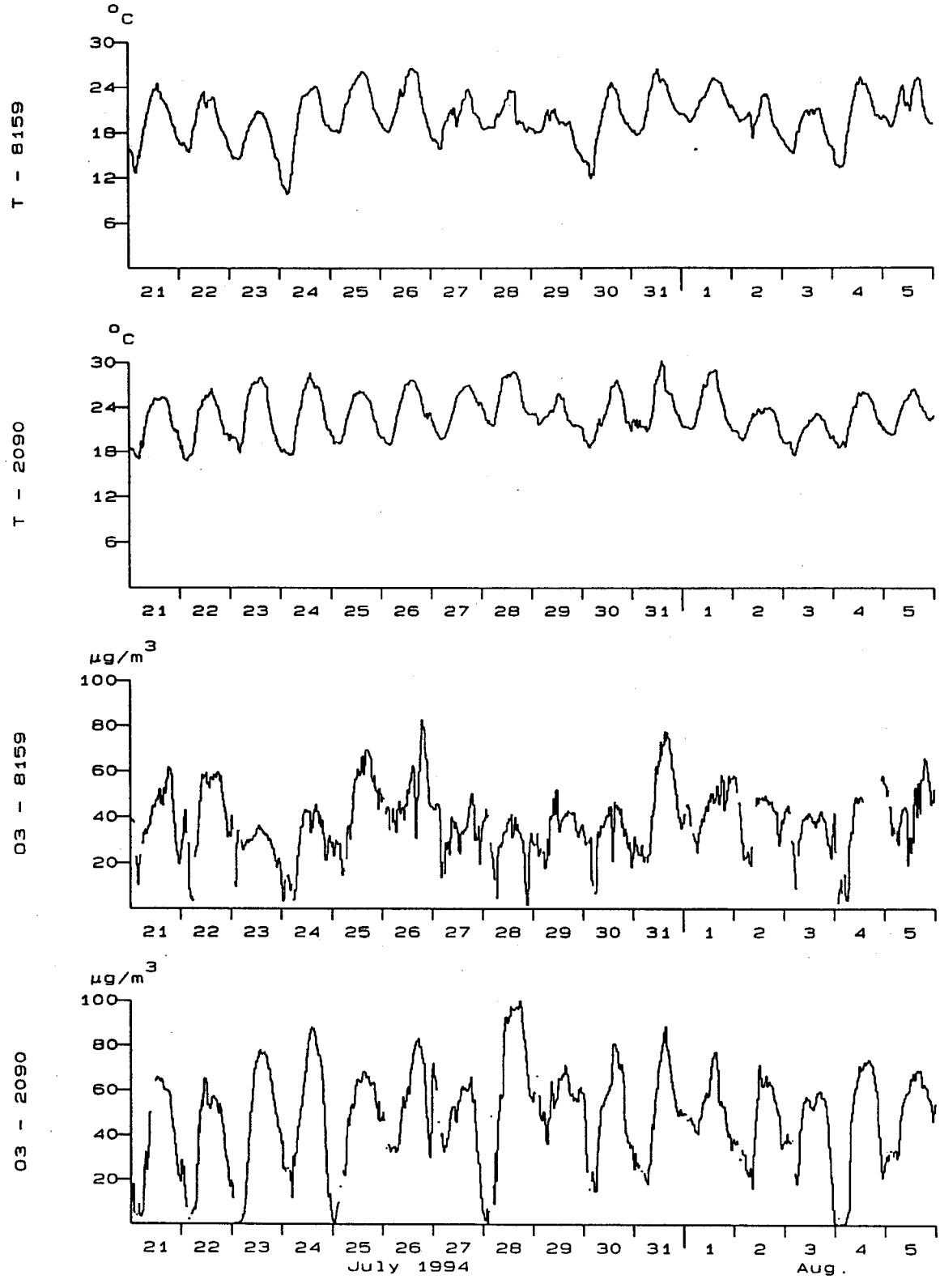

Figure 3.1. O_3 measured at Lille Valby/2090 and Aalborg/8151 during the high pressure situation in July and August 1994.

3.3 Phenomenology

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.

Wind direction are dependency

The average concentrations corresponding to different wind directions 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 1994 are divided on summer (May-August) and winter (November-February) periods. Concentrations around 80 $\mu g/m^3$ in average are found for winds from NW both summer and winter. This represent probably the hemispheric background concentrations. At winds form south and south east the concentration exceeds the background level in the summer period, while it is much 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.

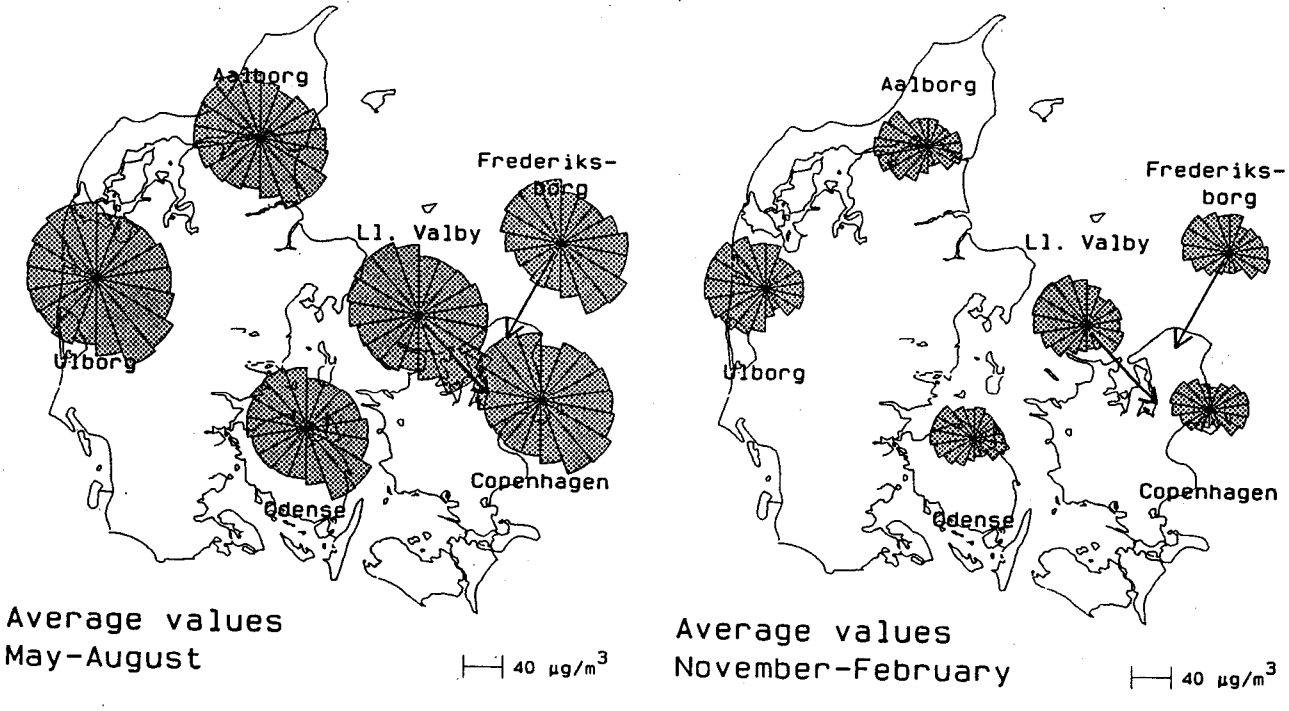

Figure 3.2. Wind direction distribution for O_3 for results from 1993 and 1994. The radii of the circle sections are proportional to the mean concentrations for winds coming from the direction the section points towards.

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 20^0 wind sector. Nearly all concentrations above the 98-percentile are found at winds from ESE.

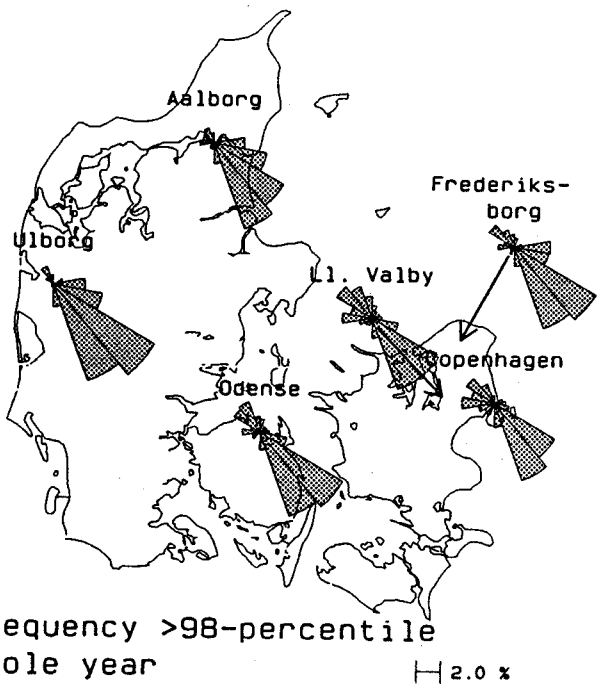

Figure 3.3. Frequency of O_3 concentrations above the 98-percentile as function of the wind direction. Results from 1993 and 1994 are included. The frequencies should be compared to 2%, which is the frequency of values above the 98% percentile. The radii of the circle sections are proportional to the relative frequency for winds coming from the direction the section points towards.

Other meteorological parameters

Correlation between O_3 and global radiation and ambient temperature was shown for 1993 data in the previous annual data report (*Kemp, Palmgren and Manscher, 1994*). The results from 1994 showed a similar pattern. This year we present the correlation between O_3 and wind velocity and atmospheric pressure.

Figure 3.4 shows the correlation between O_3 and wind velocity. It is characterized by an almost constant value of around 70 $\mu g/m^3$ at velocities above 10 m/s. The high wind velocity favors mixing between the planetary boundary layer and the free troposphere where the O_3 concentration is almost constant. Further the high O concentrations did not occur at low wind speeds, when the NO_x emissions are less mixed and the transport of new O_3 is limited.

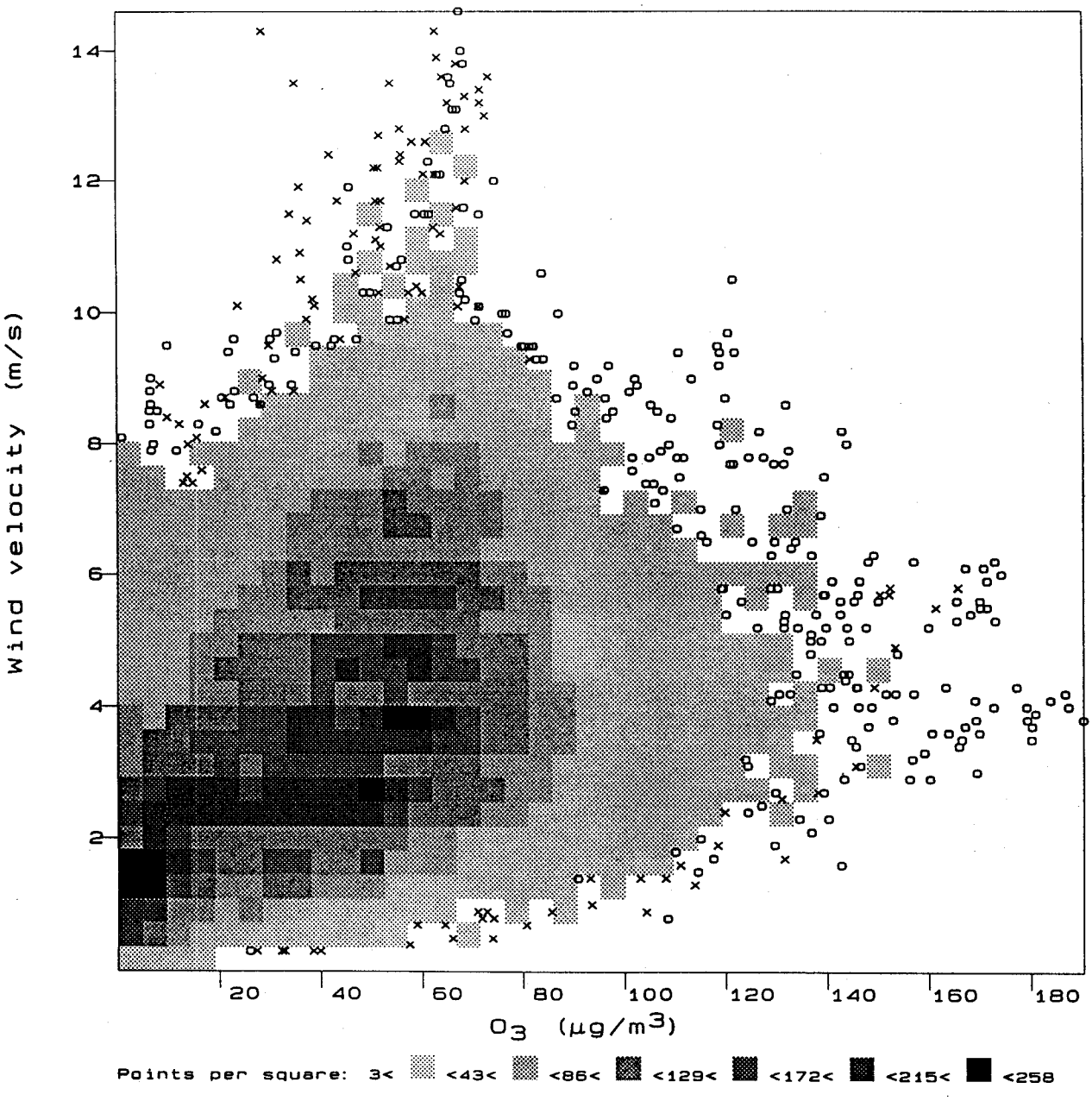

Figure 3.4 Regression plot for O_3 vs. wind velocity measured at Odense/9159 in 1993 and 1994. (see explanation p. 27).

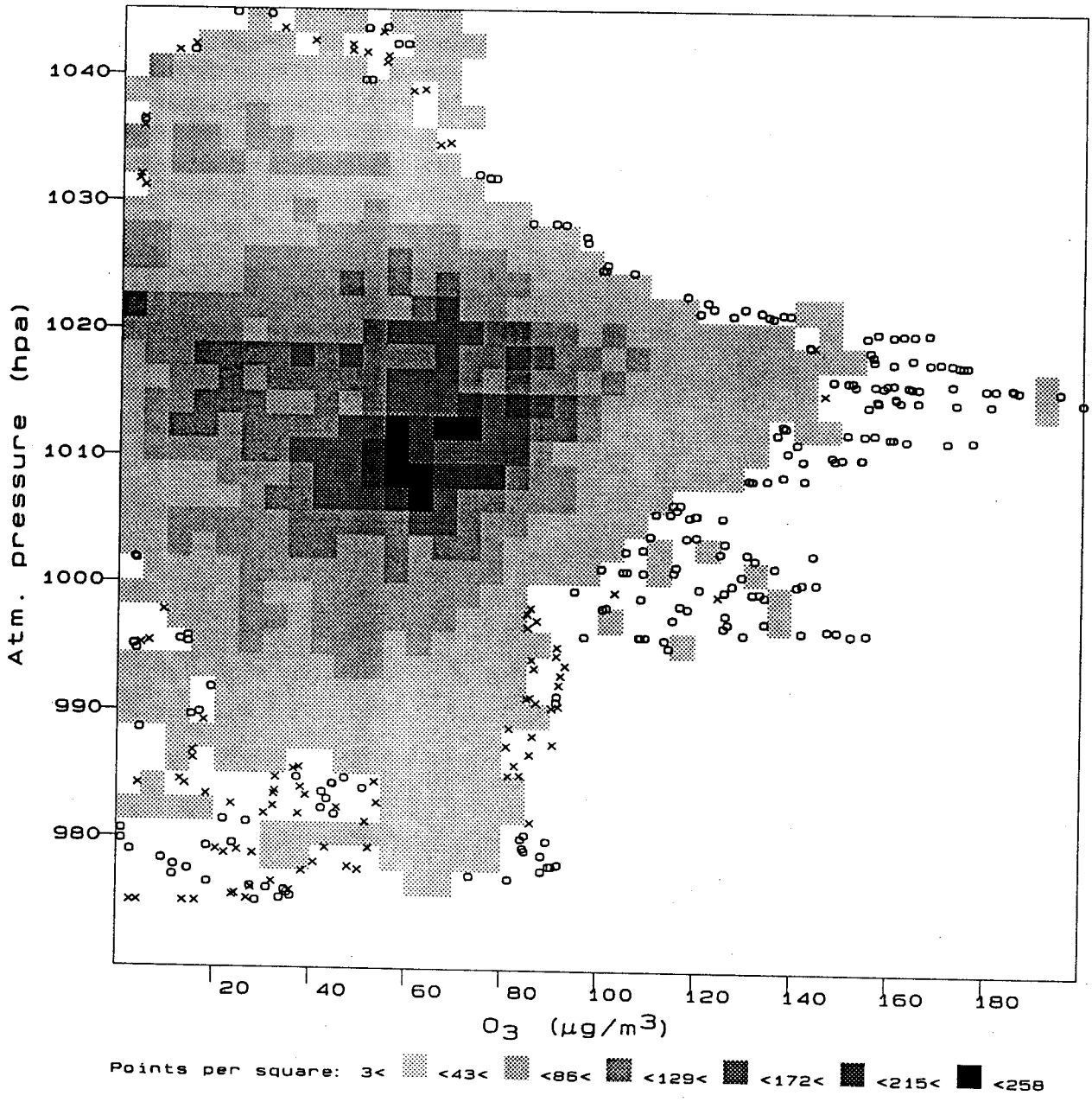

Figure 3.5 Regression plot for O_3 vs. atmospheric pressure for data from 1993 and 1994. The O_3 is measured at Lille Valby and the pressure at the test station for wind mills at research center Risø. (see explanation p. 27).

Explanation to figure 3.4-6

The figures represent regression plots between the ½-hourly mean values measured during 1993 and 1994. Each data set consists of around 30,000 points. The plot area is divided in 40×40 squares. Squares including more than three points are shaded, according to the scale below the figure, in order to improve the clarity.

The individual points are drawn as an o for day measurement (i.e. between sunrise and sunset) and as an x for night measurements.

The orthogonal regression lines are drawn on some of the figures.

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 1993 (*Kemp, Palmgren, Manscher, 1994*) 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 (α) are in all cases close to one. There are small differences for the cut-off values (β), which may be related to the NO_x concentrations at the stations. *Figure 3.6* shows the correlation between Lille Valby and the other stations.

Table 3.2. Correlation between O_3 concentrations for measurements from 1994. The parameters for the orthogonal regression line $y = \alpha \cdot x + \beta$ and the correlation coefficient, ρ, are given for all combination of stations.

x \ y	Odense/9159			Aalborg/8159			Lille Valby/2090		
	α	β ($\mu g/m^3$)	ρ	α	β ($\mu g/m^3$)	ρ	α	β ($\mu g/m^3$)	ρ
1259	0.97	0.4	0.80	0.90	4.9	0.72	1.01	6.4	0.87
9159				0.93	4.6	0.74	1.04	6.0	0.81
8159							1.13	0.5	0.73

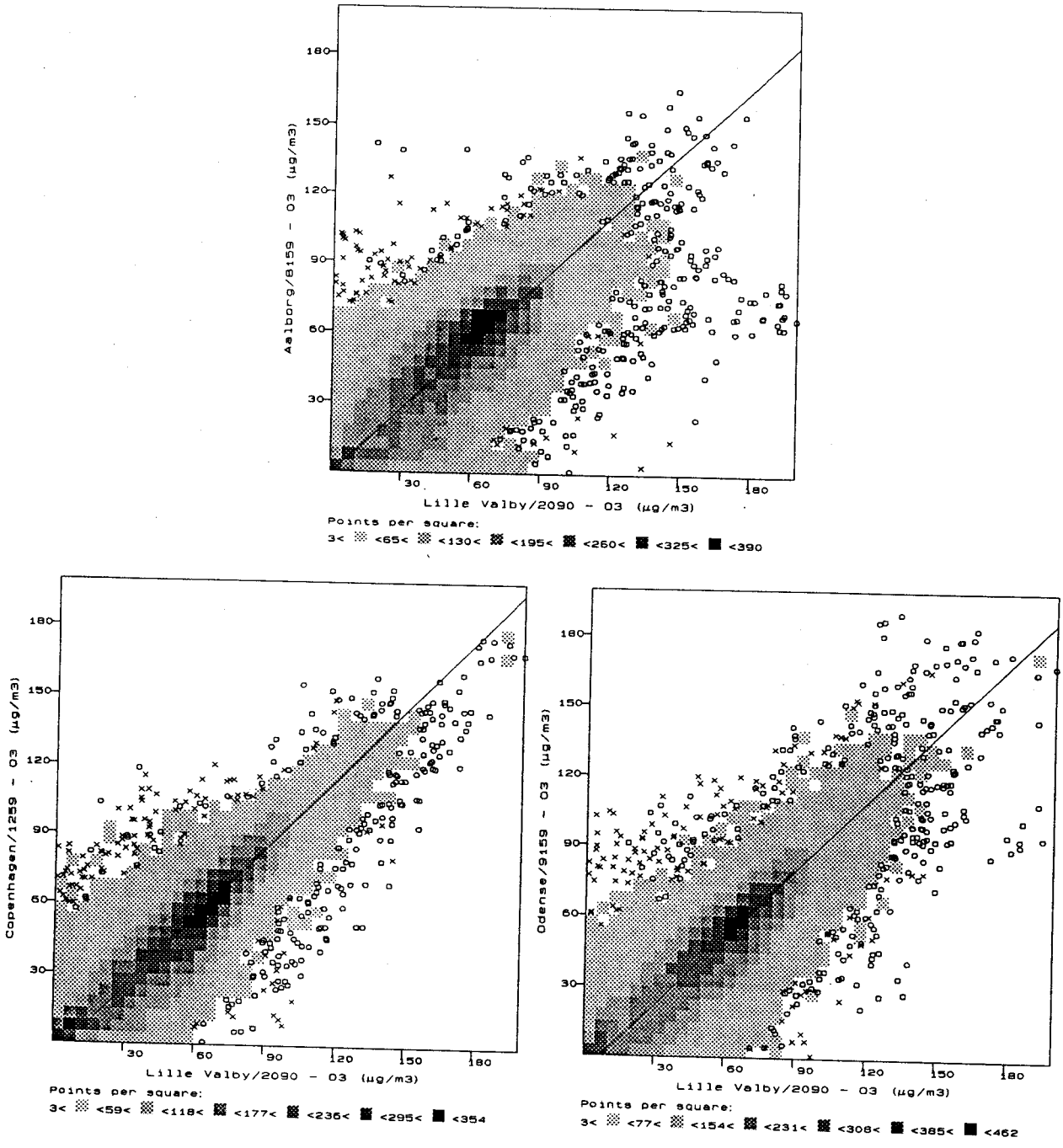

Figure 3.6. Regression plots for simultaneous measurements of O_3 at Lille Valby/2090 and other stations (see explanation p. 27).

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-} 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 extend 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 1994 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 mean 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. Sulphur pollution in Danish cities. The values are calculated for all valid 24 hour results from 1994. The winter is defined as the three first and 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 ($\mu g(SO_2)/m^3$)						Part. S ($\mu g(S)/m^3$)	
Station	Number	Median year	Median winter	max. 3 days	98-perc.	Mean value	Number	Mean value
Copenhagen/1257	360/181	7.5	9.6	16	23	8.7	360	1.89
Odense/9155	361/182	2.8	2.8	17	18	4.3	361	1.79
Odense/9154	362/182	2.8	2.9	13	19	4.3	362	1.81
Aalborg/8151	358/177	3.0	2.9	13	20	4.6	358	1.66
Lille Valby/2090	348/180	2.1	2.8	19	18	3.3	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.

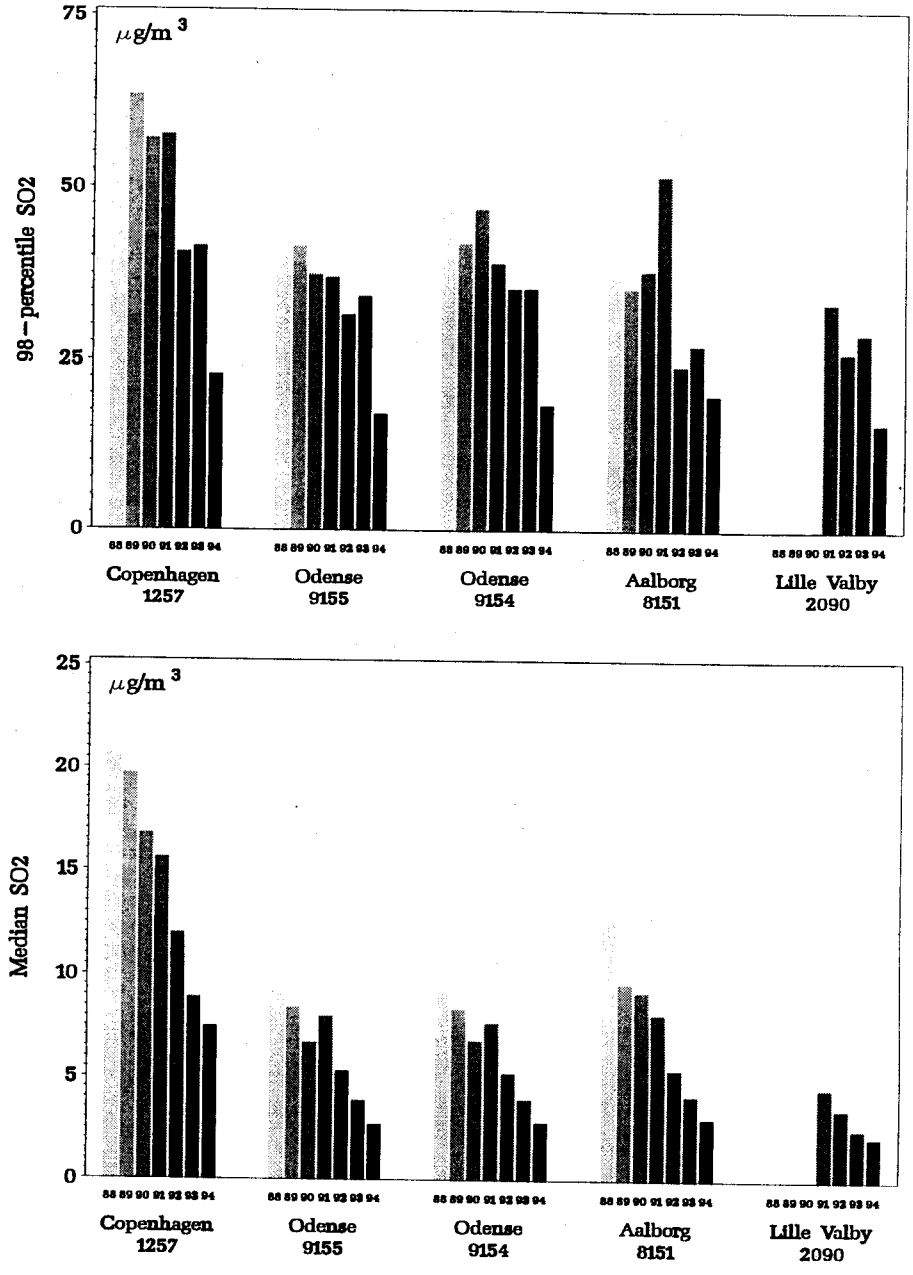

Figure 4.1. Medians and 98-percentiles for SO_2 from 1988 to 1994.

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:

1) Long range transport: A stable transport from directions between east and south may be established. Often in connection with a warm front passage.

2) Inversion: An inversion layer may prevent the dispersion of the local emitted pollution.

3) 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 the warning limit the lowest 1 hour values are identified for every consecutive three hours. The highest of these 1 hour values are listed under "max. 3 hour". The values under "max. hour" are the absolute one hour max values. The indication of 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	172	941202:14	324	941130:12	13	8.1	940101
Odense/9155	63	940708:15	118	940708:12	6	8.7	940221
Odense/9154	-		-		-	9.5	940221
Aalborg/8151	62	940228:20	188	940228:03	10	4.8	940423
Lille Valby/2090	66	941202:14	104	941202:13	1	6.3	940222

Episodes in 1994

There were no severe long range or inversion episodes in 1994. Two long range transport episodes are shown on *figure 4.2 and 4.3.* The easterly wind during the episode in the end of February opened for transport of polluted air presumably from East Europe. In average a comparable amount of the sulphur was present an gas phase and particulate form, showing that the emission must have taken place more than one day prior to the sampling, probably several hundred kilometers away. Both prior to and after the episode relatively clean air was coming from North. The local contribution from the city is seen at Copenhagen/1257, while the concentrations at the background station Lille Valby/2090 were very low. The episode at December 2 and 3 occurred in connection with a warm front passage. The course of the episode was typical. Prior to front passage a stable air transport from south was established. The concentration of SO_2 at both the

urban and the background station was high until the front had passed indicated by the steep increase in temperature late on December the 3rd. The concentration of particulate S was however low during this episode. The pollution had to be relatively fresh and the sources were probably located in the northern part of Germany.

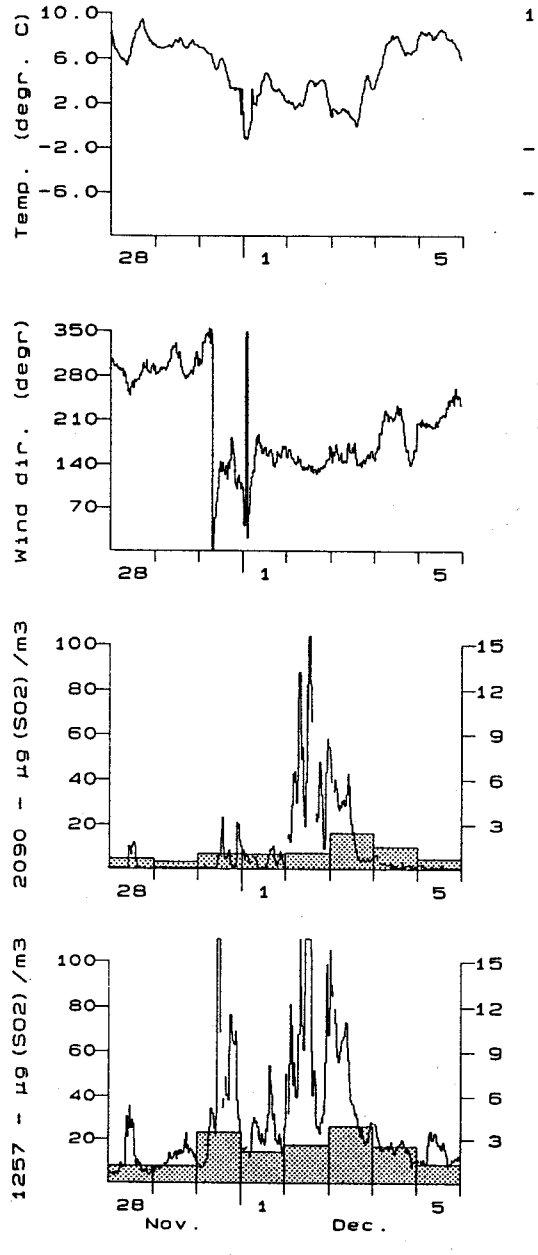

Figure 4.2. Course of the sulphur episode in February.

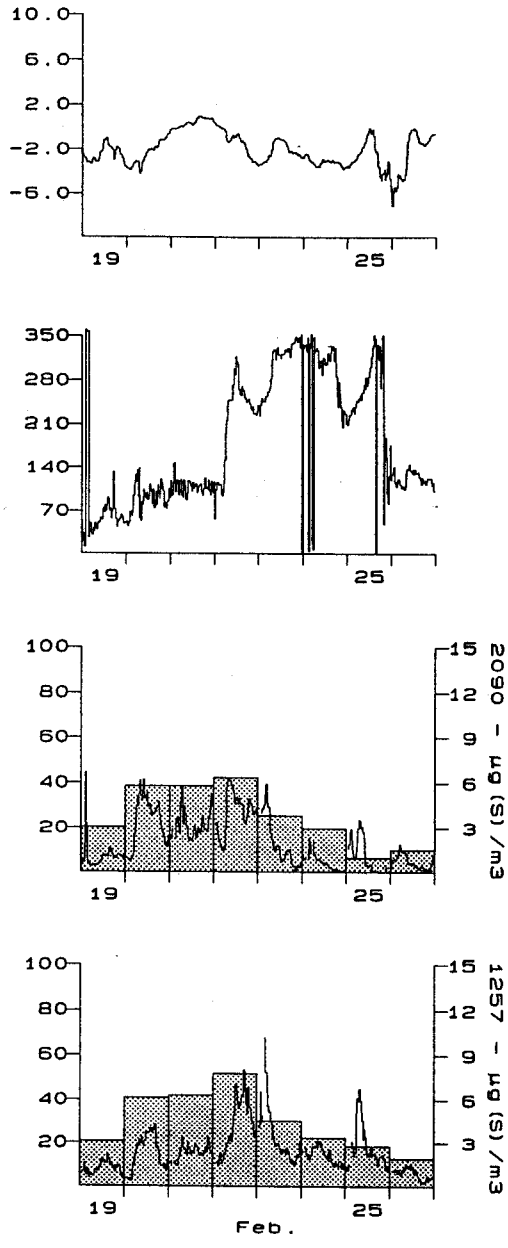

Figure 4.3. Course of the sulphur episode in December.

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 episode

November 30 at Copenhagen/1257 gave the highest hourly concentration measured since the start of the LMP III program in 1991. But the number of hot-spot episodes in 1994 are much lower in 1994 compared to the previous years. In Aalborg the number is reduced from 39 in 1993 to 10 in 1994. This drastic decrease is probably caused by the closing down of an old coal fired boiler installation at the cement works in January 1994. It was replaced by a new installation using low-sulphur oil.

4.3 Trends

Percentiles for SO_2

The annual percentiles and mean values based on daily mean SO_2 concentrations measured at Aalborg/8151 are shown on *figure 4.4*. The level of SO_2 has been decreasing since 1982. The reduction is most evident for the "long term" values (median and mean 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. The results from 1994 are however considerable lower for both short and long term parameters.

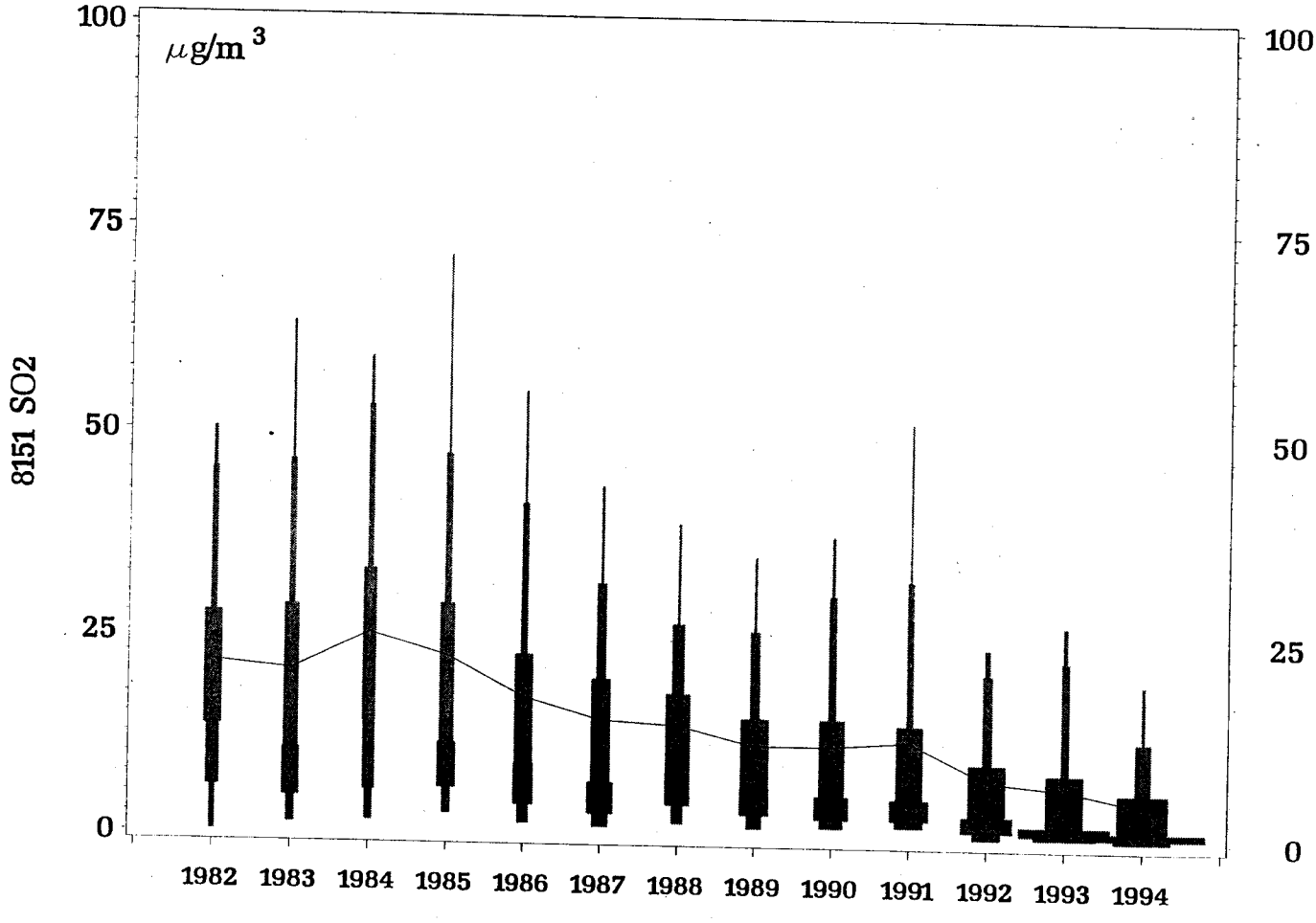

Figure 4.4. Trends for annual 98-, 95-, 75-, 50-, 25- and 5-percentiles, mean and minimum value based on hourly mean concentrations of SO_2 measured at Aalborg/8151. (See explanation on p. 15).

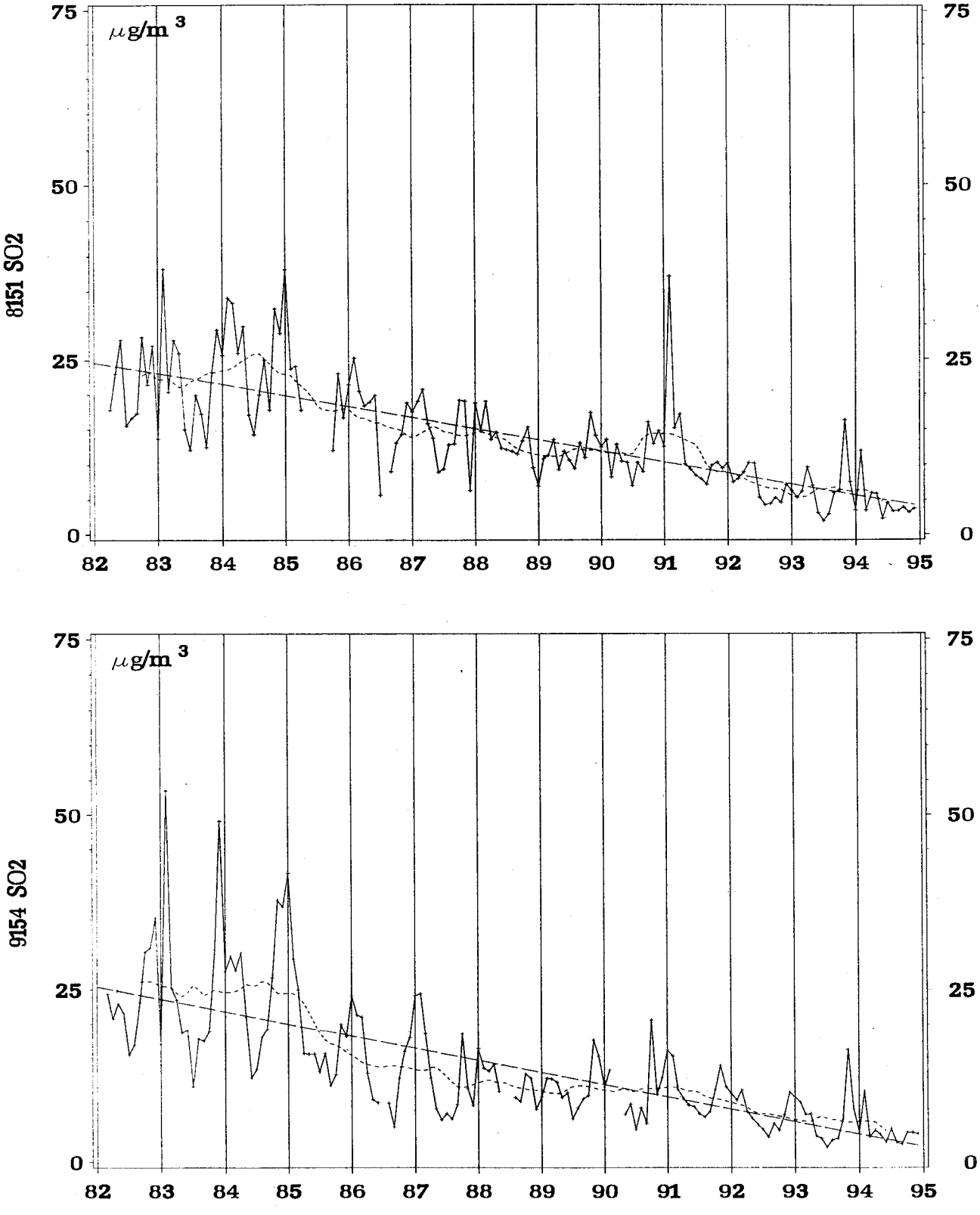

Figure 4.5. Trend for SO_2 measured at Aalborg/8151 and Odense/9154. The points are measured monthly averages, the dotted curve is a moving annual average and the straight line is a linear regression line (see explanation on p. 16).

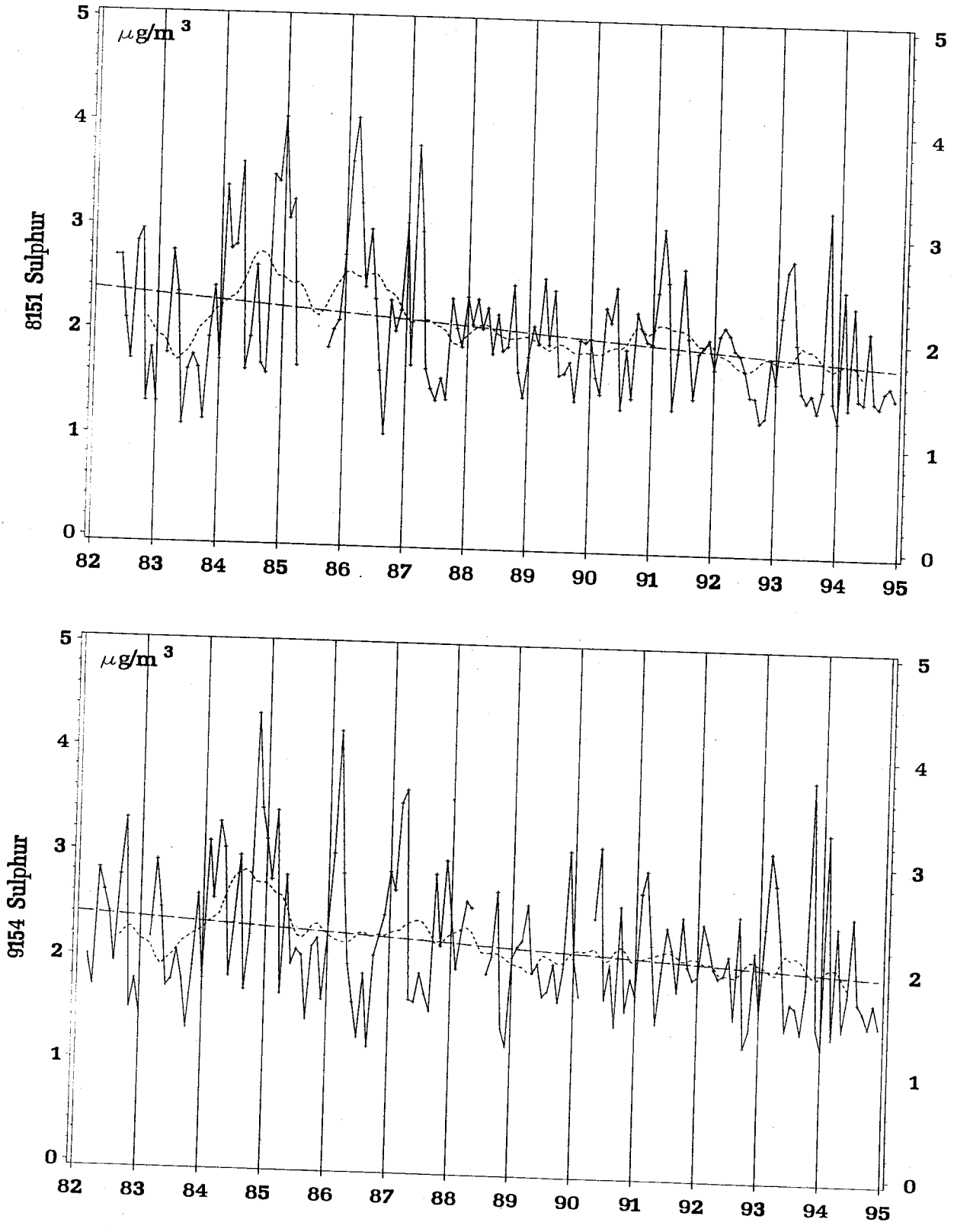

Figure 4.6. Trend for particulate S measured at Aalborg/8151 and Odense/9154. The points are measured monthly averages, the dotted curve is a moving annual average and the straight line is a linear regression line (see explanation on p. 16).

Average SO_2 and S

The trends for the monthly mean values at Aalborg/8151 and Odense/9154 are shown on *figure 4.5* for SO_2 and on *figure 4.6* 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. The cut-off vary 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 1994 measured as 24 hour mean values at Copenhagen/1257, Odense/9155, Odense/9154 and Aalborg/8151.

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 1994 are given in *table 5.1*. The annual 95-percentiles and mean values are shown for 1988-1994 on *figure 5.1*.

Table 5.1. Mean values, 95-percentiles and maximum values for TSP in 1994. The numbers are calculated for 24 hour mean values.

		TSP (µg/m³)			
Station	Number	Mean value whole year	95-perc.	Max.value	Day
Copenhagen/1257	359	49	109	199	940422
Odense/9155	359	42	111	341	941111
Odense/9154	360	37	85	183	940707
Aalborg/8151	358	46	122	178	940407
Limit value	min. 100	150	300	-	-

Measured values

The measured values were between 1/4 and 1/3 of the limit values. The level has been almost constant (*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 may be expected to decrease in the future due to reduction of the emissions as the result of i.a. obligatory three way catalysts on gasoline cars and restrictions on the diesel exhaust. The fact that the 1994 values, especially the

mean values, were much lower than the previous year is, however, probably more a result of favorable meteorological conditions than reduced emissions.

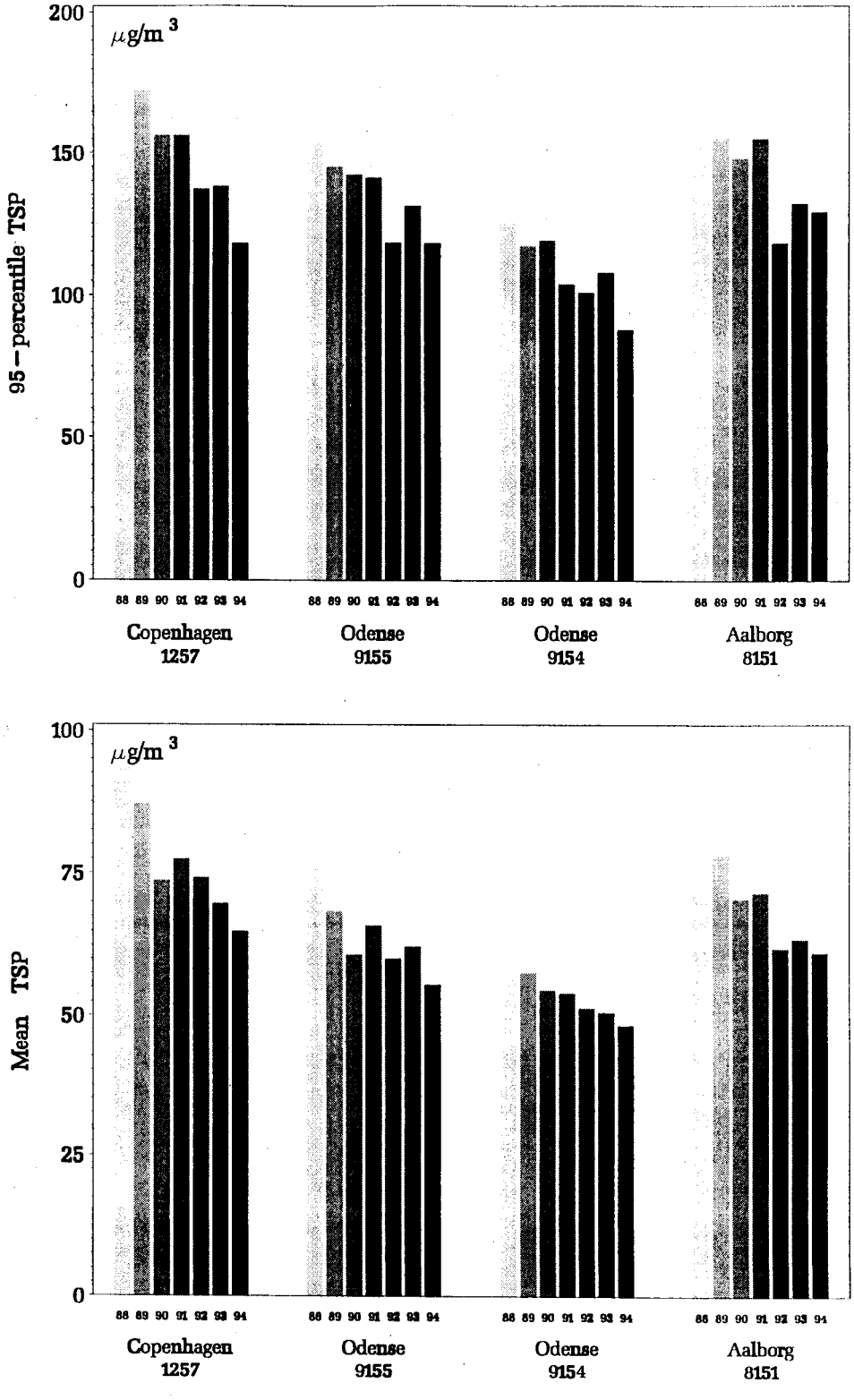

Figure 5.1. Mean values and 95-percentiles for TSP from 1988 to 1994.

5.2 Episodes

The measured maxima of the daily mean values are given in *table 5.1.* There was no outstanding episodes in 1994. 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 mean values based on daily mean 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 mean) 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.

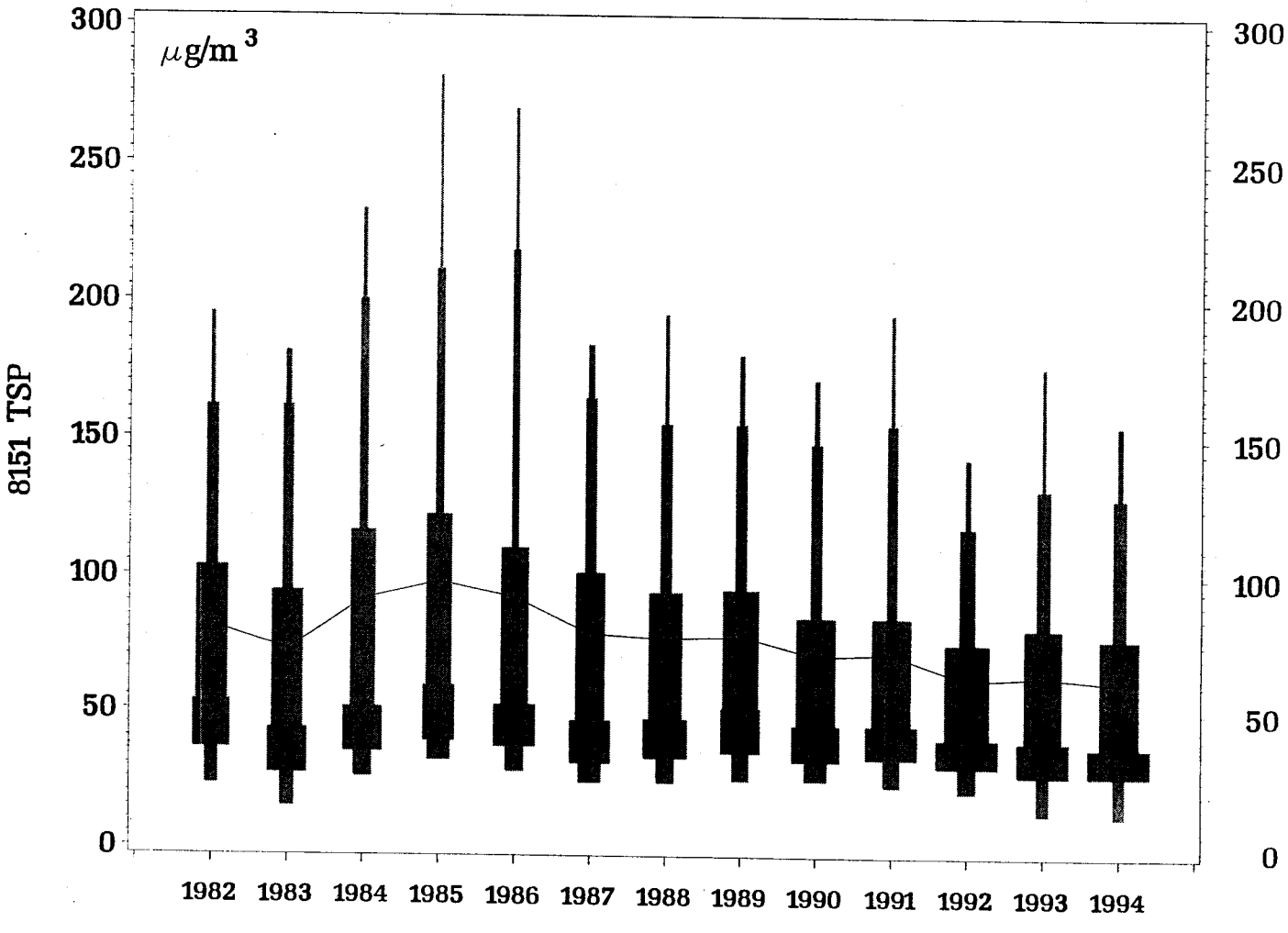

Figure 5.2. Trends for annual 98-, 95-, 75-, 50-, 25- and 5-percentiles, mean and minimum value based on daily average concentrations of TSP measured at Aalborg/8151. (See explanation on p. 15).

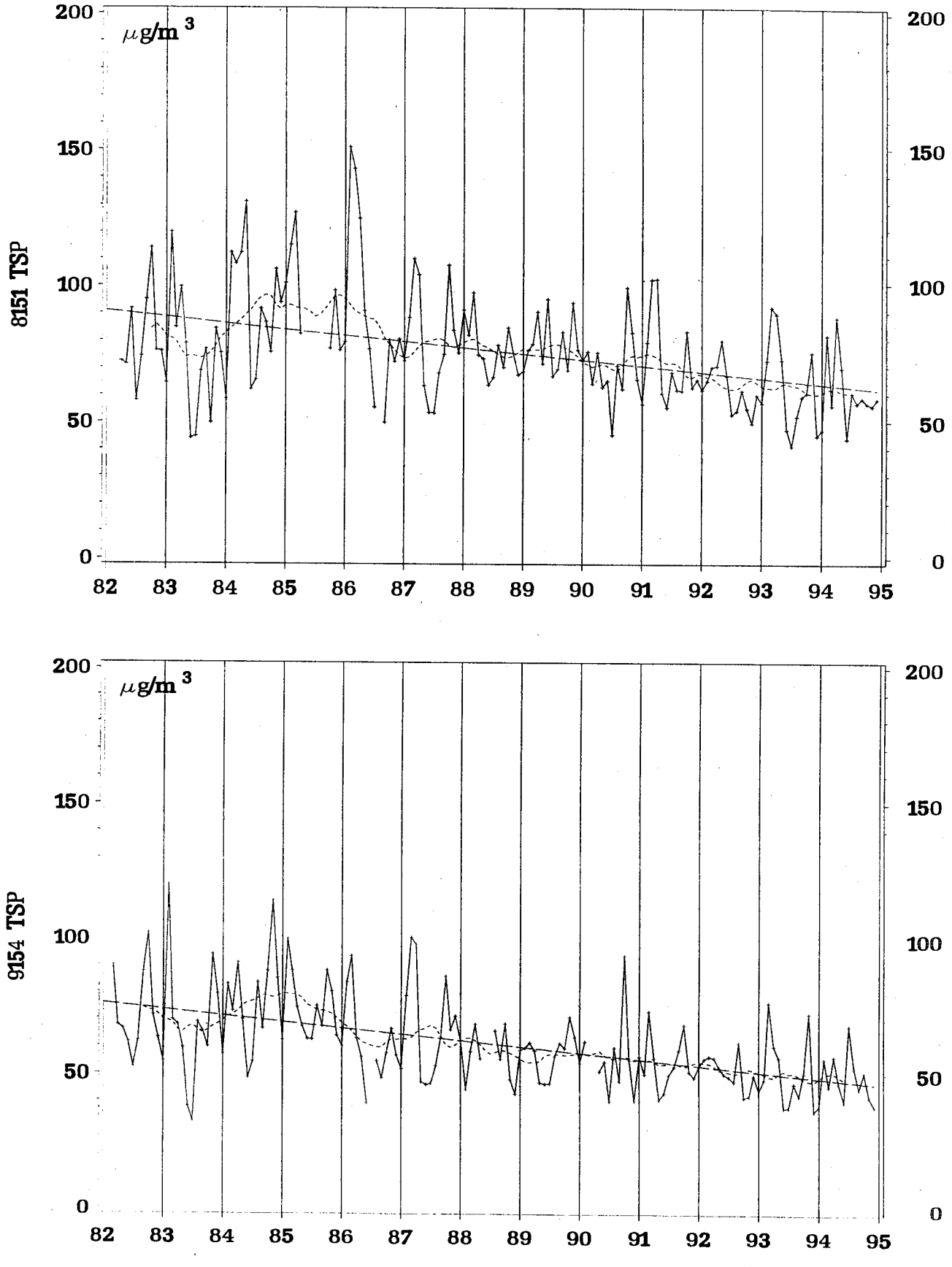

Figure 5.3. Trend for TSP measured at Aalborg/8151 and Odense/9154. The points are measured monthly averages, the dotted curve is a moving annual average and the straight line is a linear regression line (see explanation on p. 16)

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 previous annual report (*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 mean values for the elements are found in *table 6.1*.

Limit value

Pb is the only element for which, there is limit value within EU. The annual mean 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 1994 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

Trend for Pb

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, As are carcinogenic in certain compounds and only life time cancer risks are estimated.

Table 6.1. Mean values for 1994. All concentrations are given as ng/m^3 (1 µg/m^3 = 1000 ng/m^3). N_{tot} is the number of measurements in 1993. 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 mean values even if it is based on a few values only.

	Copenhagen /1257		Odense /9155		Odense /9154		Aalborg /8151		Lille Valby /2090	
Ele-ment	N_0	Mean	N_0	Mean	N_0	Mean	N_0	Mean	N_0	Mean
Al	317	701.0*	281	658.0*	279	352.0*	283	553.0*	112	92.9*
Si	360	1850.0	359	1670.0	362	1020.0	358	1540.0	331	301.0
S	360	1890.0	361	1790.0	362	1810.0	358	1660.0	351	1380.0
Cl	360	2340.0	361	2300.0	362	1850.0	358	3760.0	342	686.0
K	360	327.0	361	281.0	362	228.0	358	265.0	351	132.0
Ca	360	1500.0	361	1130.0	362	597.0	358	1150.0	351	177.0
Ti	360	79.8	354	84.1	356	49.6	355	54.4	258	9.3*
V	352	9.9	297	6.7*	307	5.8*	293	6.4*	286	4.3*
Cr	358	4.4	344	3.7	351	2.6	343	2.8	260	0.7*
Mn	360	25.4	361	28.6	362	19.0	358	16.3	350	4.3
Fe	360	1330.0	361	972.0	362	635.0	358	958.0	351	112.0
Ni	360	4.1	353	2.6	354	2.4	347	2.9	337	1.6
Cu	360	48.1	361	27.7	362	18.7	358	29.7	301	2.0*
Zn	360	82.8	358	71.7	362	46.1	358	64.6	318	19.2
As	290	2.5*	260	1.8*	237	1.5*	178	1.1*	273	1.1*
Se	251	0.6*	298	0.7*	342	0.8	268	0.5*	335	0.7
Br	360	7.5	361	6.5	362	7.1	358	9.9	351	4.0
Sr	360	7.1	359	4.8	362	3.4	358	6.0	343	1.4
Zr	345	5.2	327	4.2	325	2.6*	322	3.2*	167	0.3*
Mo	278	2.8*	241	1.9*	252	1.2*	254	1.7*	86	0.3*
Cd	59	0.6*	76	0.7*	67	0.6*	47	0.5*	77	0.5*
Sb	294	11.0*	261	6.6*	258	4.6*	263	6.9*	129	1.2*
Ba	318	46.4*	280	32.9*	288	21.1*	290	28.5*	100	2.6*
Pb	360	37.1	360	32.0	362	33.0	358	44.7	343	10.4
Ntot	360		361		362		358		351	

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

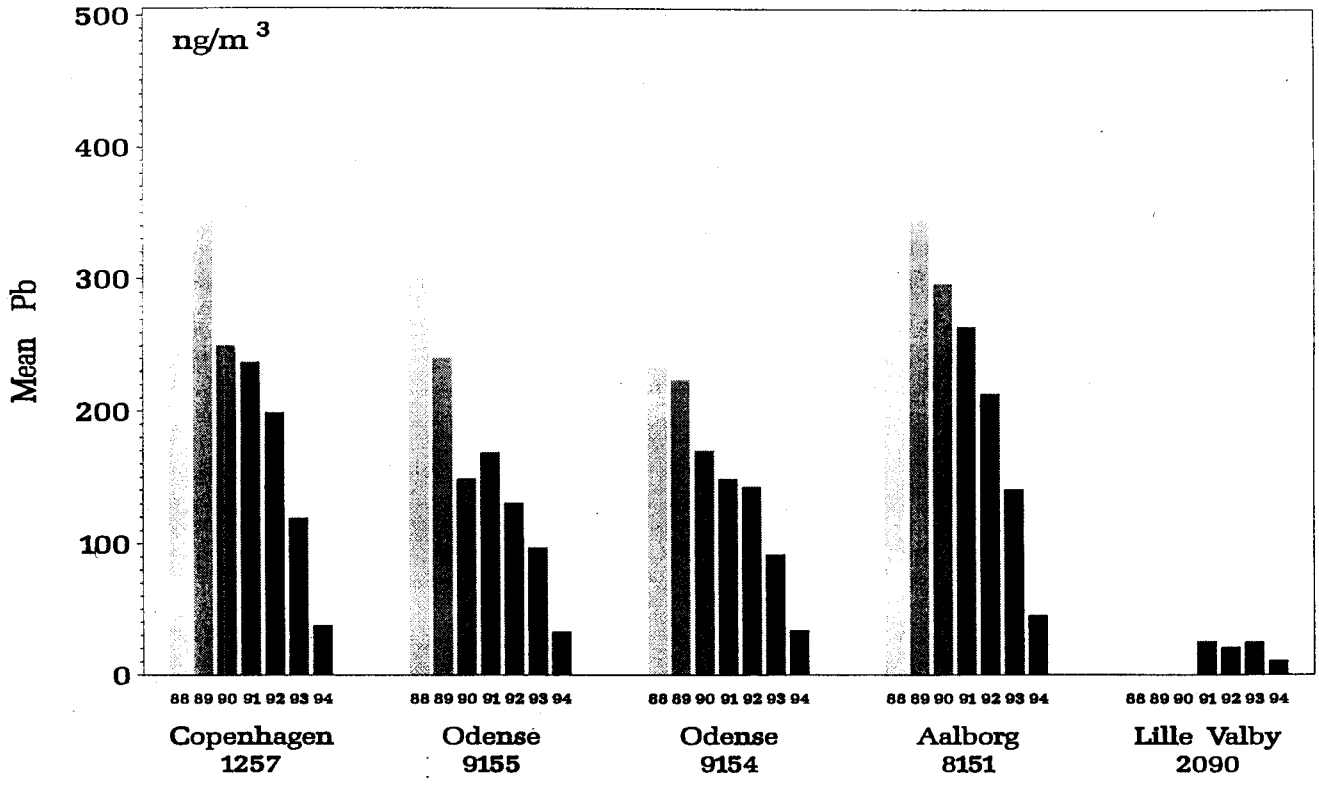

Figure 6.1. Annual mean values for Pb from 1988 to 1994.

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 1994 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 concentrations at street level. N.D. = not determined.

ng/m^3	WHO guideline	Aalborg/8151 1982	Aalborg/8151 1994	Copenhagen/1257 1994
V	1000	22	6	10
Mn	1000	20	16	25
Cd	10-20	<2	0.5	0.6
Hg	~1000	N.D.	N.D.	N.D.
Pb	500-1000	1100	45	37

Carcinogenic

The estimated lifetime risks are estimated for air concentrations of 1 $\mu g/m^3$. These values and the corresponding urban concentrations are shownin 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. 6.2* 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 1994 $\mu g/m^3$	Copenhagen/1257 1994 $\mu g/m^3$
Cr	*)	0.0029	0.0028	0.0044
Ni	$4 \cdot 10^{-4}$	0.0070	0.0029	0.0041
As	$3 \cdot 10^{-3}$	D.L.	0.0011	0.0021

*) the WHO estimated life time risk for Cr(VI) is $4 \cdot 10^{-2}$, 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 source 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.

As

The detection limit for determining As has unfortunately previously been to high to give reliable estimates of the yearly mean values at the urban stations. However data from 1994 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 1994 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 transport.

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 the occurrence of Cr is wide spread over urban areas and Ni and As over the whole country.

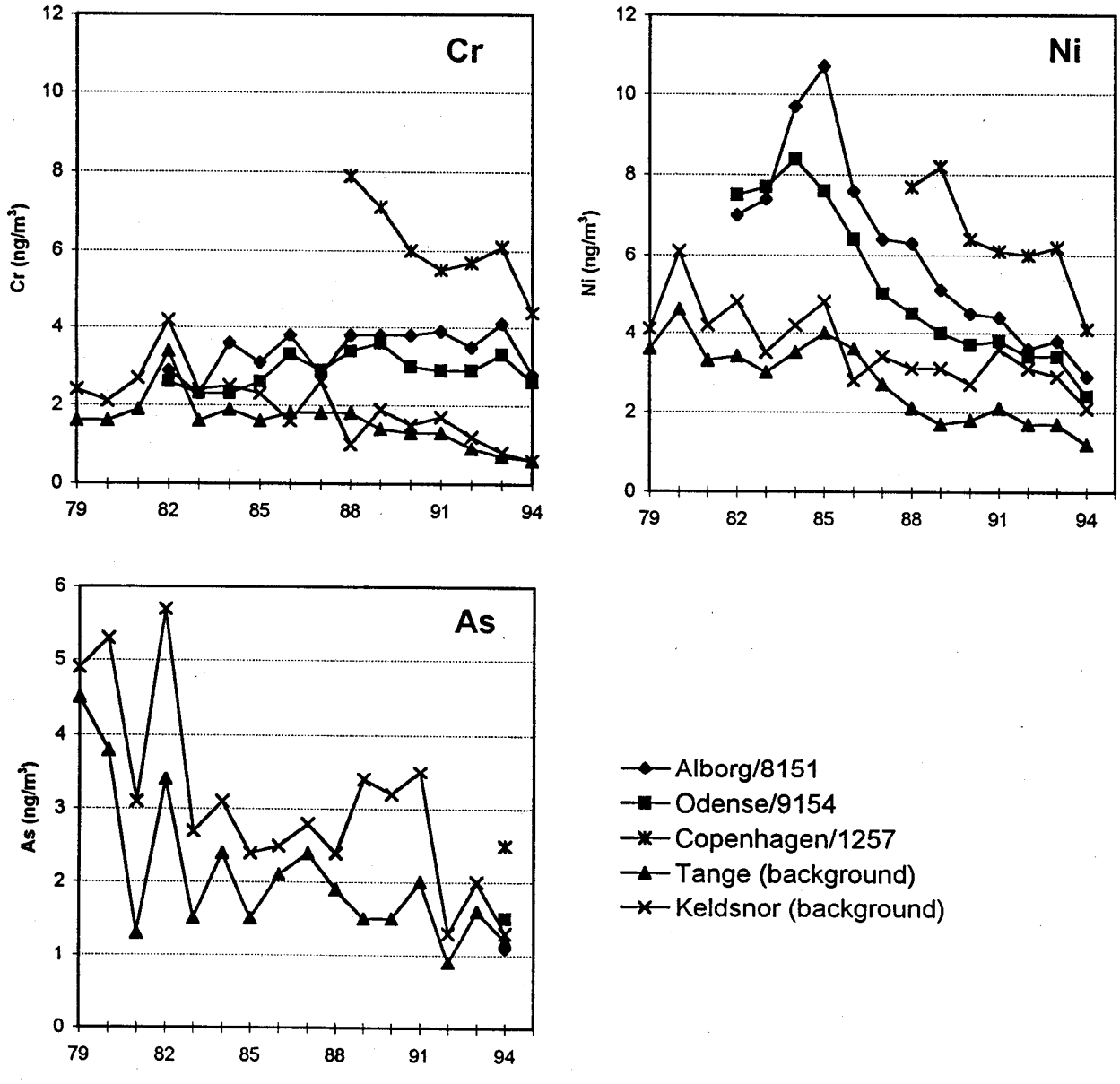

Figure 6.2. Yearly mean values for the potential carcinogenic heavy metals. Results from the stations in the Danish Background Monitoring Program at Tange and Keldsnor are included for the comparison.

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.

Related measurements

Measurements of PAH as monthly averages have been carried out in the period of February 1992 to February 1994 in Copenhagen, Odense and Aalborg at LMP III sites and at rural sites (*Poulsen, Grundahl, Palmgren, 1995).* The research project Air Pollution from traffic (*Berkowicz et al., 1995*) includes i.a. VOC measurements several campaigns have been carried out in 1994 (*Palmgren et al., 1995*), and continuous measurements of CO and O_3 at Copenhagen/1257 and NO_x and CO at Copenhagen/1259. Some of the results are summarized in the following.

7.1 NO_x and CO, Copenhagen, Odense and Aalborg

The measurements at Aalborg/8151 was supplemented with measurements of CO, and at Aalborg/8159 with NO_x from May 3 to September 4. From October 3 1994 to March 10 these measurements were carried out at Odense/9155 and Odense/9159 (*Kemp, 1995*). 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 summarized in the following.

Statistics

Some statistical parameters are summarized in table 7.1. The different values for NO and NO_2 at the street stations and roof stations are remarkable. The ratios between the mean 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 greater 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.

Table 7.1. Statistical parameters for campaign periods. The Aalborg results are from the summer 1994, while the Odense results are from the winter 1994/95 and the Copenhagen measurements are from all 1994.

Compound	City	Street station				Roof station			
($\mu g/m^3$)		mean	medi-an	98-perc.	99.9-perc.	mean	medi-an	98-perc.	99.9-perc.
NO	Copenhagen	78	45	335	755	6	3	41	147
	Odense	48	18	321	502	9	3	64	230
	Aalborg	82	53	337	641	4	2	29	116
NO_2	Copenhagen	47	44	102	131	26	23	66	97
	Odense	31	28	77	182	23	21	56	71
	Aalborg	39	34	102	128	16	12	56	100
CO	Copenhagen	1690	1270	5480	9000	320	280	910	1800
	Odense	820	550	3730	12010	-	-	-	-
	Aalborg	1190	870	4270	7000	-	-	-	-

CO and NO_x

Motor vehicles are the main source for both CO and NO in urban areas, but there is considerable differences in the emission factors depending i.a. of the type of vehicles (*Miljøstyrelsen, 1991*). The average workday concentrations (*figure 7.1*) shows that the ratio between CO and NO_x is lowest during the day time from 6-15 and highest from the after-noon rush hours till the early morning. The pattern is very much alike at Odense/9155, Aalborg/8151 and Copenhagen/1259, where the ratio vary from 12-15 at evenings and nights, when the road traffic consists mainly of light vehicles, down to around 10 at noon, when the heavy traffic is at a maximum. This values fits well with ratios between the emission factors around 12 for light vehicles and around 1 for heavy diesel vehicles. The ratios are somewhat higher at Copenhagen/1257. The reason for this is not clear, but it may be connected to the driving pattern for the traffic passing the station.

7.2 Ozone in street and urban background, Copenhagen

O_3 in urban air

O_3 is a very reactive component. One of most important reactions in urban air is the oxidation of NO to NO_2.

$$NO + O_3 \Rightarrow NO_2 + O_2$$

The reaction is very fast and is important for formation of NO_2 in street canyons, where the residence time is less than a minute. It means that O_3 is the limiting component for formation of NO_2 in streets with high traffic intensity and consequently large emission of NO, when the emission of NO is highest. At some distance from the sources, i.e. urban background, NO is often the limiting component.

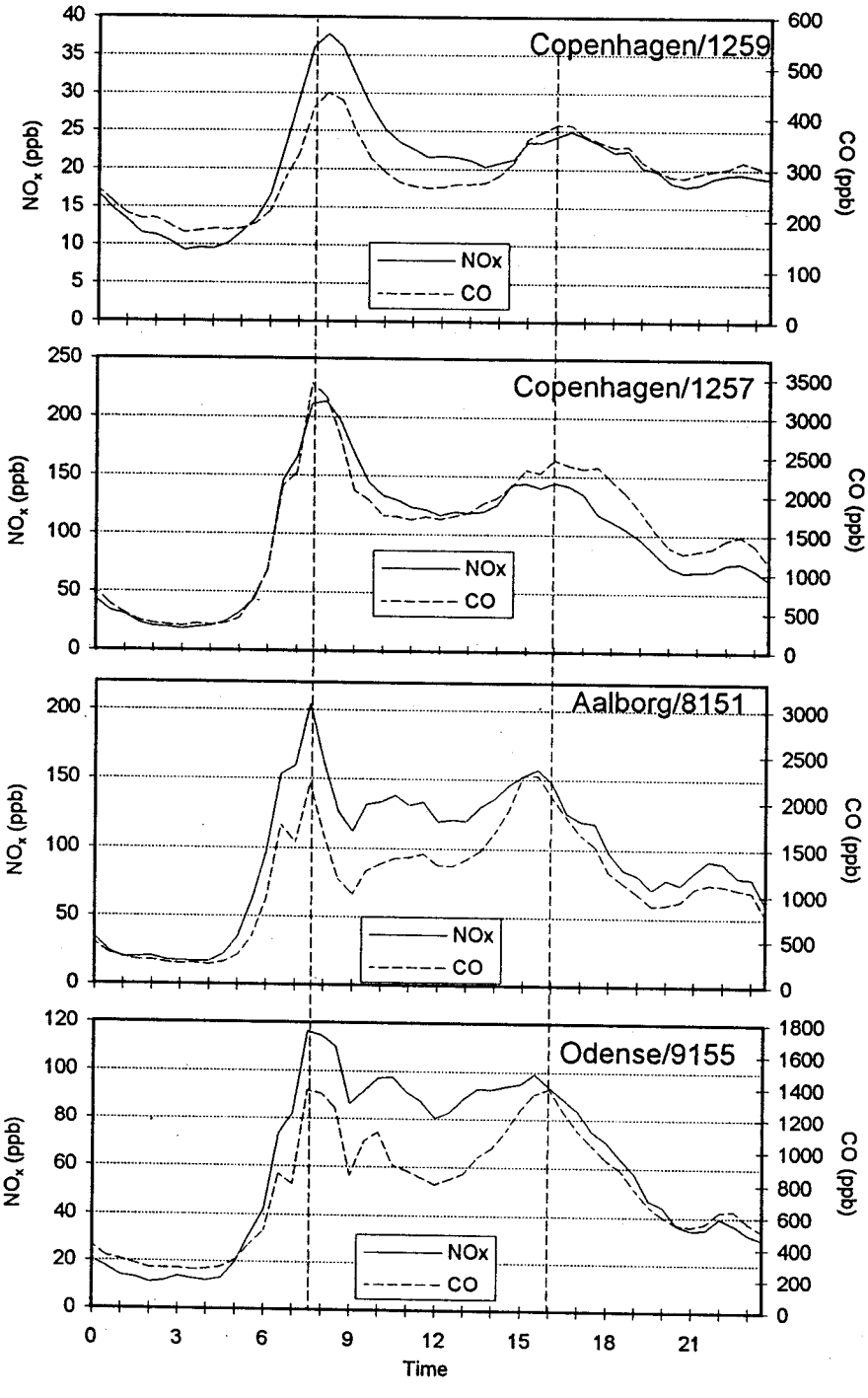

Figure 7.1. Average ½-hourly concentrations at workdays (monday-friday). The time is the local time (summertime in the summer). The ratio between the CO and the NO_x scales are 15 in all cases in order to ease comparison.

Weekly variation

Figure 7.2 shows the weekly variation of O_3 at Copenhagen/1257 (street), Copenhagen/1259 (urban background) and Lille Valby/2090 (regional background). The O_3 concentration at the urban background shows nearly the same pattern as the rural background with highest levels early in the afternoon and lowest levels early morning before sunrise. The minimum at the urban background is lowest due to some influence from the morning rush hours. They are more similar at the weekends, when the traffic density is small.

The O_3 concentration at the street site during day time on weekdays is lower and more constant, because O_3 is consumed by oxidation of NO emitted from the traffic in the street. The O_3 level during rush hours is very small at the street due to consumption by reaction with NO. During weekends it is more similar to the urban background, but lower.

Wind direction dependency wind *for* O_3

Figure 7.3 shows the relations between the O_3 concentrations and the direction at the street and urban background (upper right). The concentration of O_3 is much lower at the street site and it depends more on the wind direction than at the urban background site. This corresponds to the opposite wind direction dependence of NO (upper left). It is also seen that the urban background of NO is very small indicating that NO here is the limiting component for formation of NO_2. The wind direction dependence of NO at the street site is smaller than for NO, because the urban background contribution of NO_2 is significant.

$O_x = O_3 + NO_2$

If no other processes are important and if the direct emission of NO_2 is relatively small, the sum of O_3 and NO_2 ($O_x = O_3 + NO_2$) will be the same at street sites and at urban background sites. *Figure 7.3 (buttom)* shows the wind direction diagrams for O_x at the two sites. They are, as expected, nearly isotropic and the concentration levels for every wind sector are very close to be the same at the two sites. The results also indicate that no other processes are significant in general and that the direct emission is NO_2 small, i.e. less than a few percent.

OH-radicals

In addition, O_3 is the most significant source of tropospheric OH-radicals, which is considered as a trigger for the complex reaction chain leading to formation of oxidizing species. OH radicals, which are very reactive species, are able to oxidize NO into NO_2, carrying a perturbation in the photochemical cycle. In this case, O_3 is no longer able to react with NO and O_3 starts to build up. In the same way, the concentration of other pollutants including PAN and formaldehyde also starts to build up. NO_2 is removed by photolysis, oxidation by OH-radicals and heterogeneous reactions with water to generate nitrite and nitrates.

$NO_2 + h\upsilon \Rightarrow NO + O$ and then $O + O_2 \Rightarrow O_3$
$NO_2 + OH \Rightarrow HNO_3$
$2NO_2 + H_2O \Rightarrow HNO_3 + HNO_2$

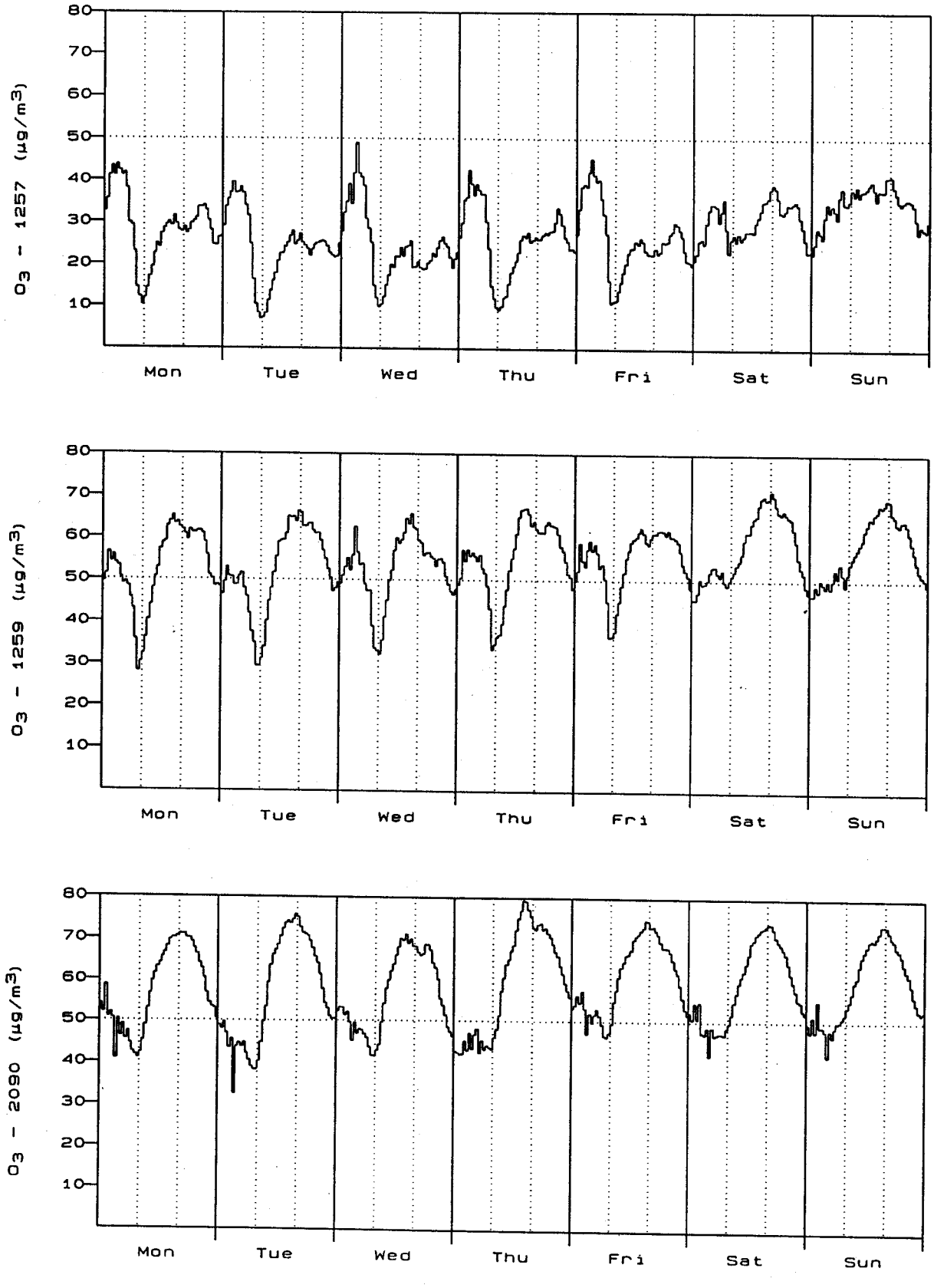

Figure 7.2. Weekly variation for O_3 measured at Copenhagen/1257, Copenhagen/1259 and Lille Valby/2090 from April to December 1994.

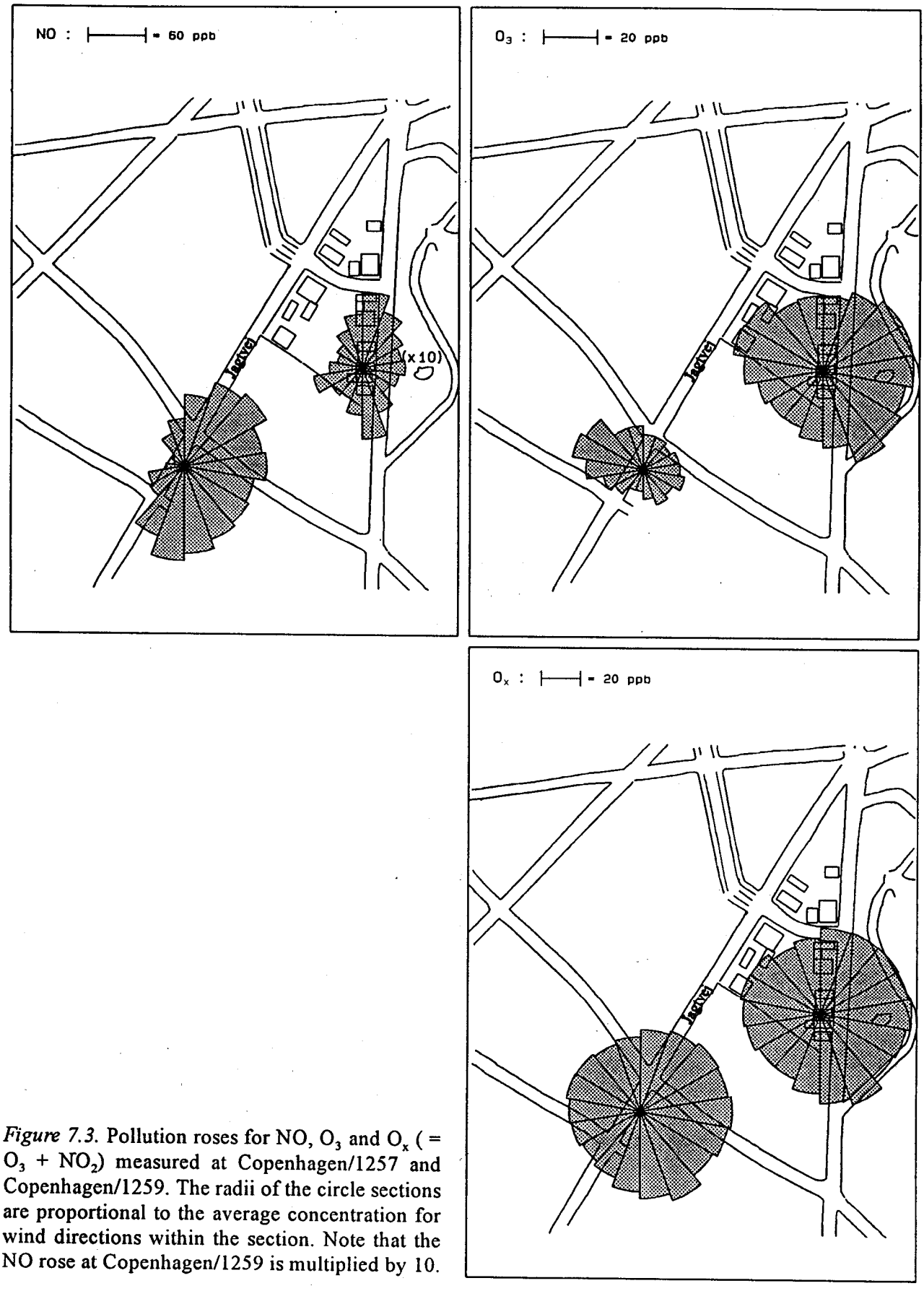

Figure 7.3. Pollution roses for NO, O_3 and O_x (= O_3 + NO_2) measured at Copenhagen/1257 and Copenhagen/1259. The radii of the circle sections are proportional to the average concentration for wind directions within the section. Note that the NO rose at Copenhagen/1259 is multiplied by 10.

Such processes are more important in Southern European urban areas, but may also be important in Denmark in a regional scale and during photochemical summer high pressure episodes with warm weather and low wind speeds also in Danish urban areas.

7.3 Volatile organic air pollutants from road traffic

This section is a summary of the background for and the results of a series of measurements of volatile organic compounds (VOCs) performed at the LMP stations in Copenhagen. A more detailed description including references is given by *Palmgren et al., 1995.* VOCs play an important role in formation of photochemical oxidants in urban and rural areas and there is an increasing concern about the role of VOCs in air pollution and their adverse health effects in urban air. The VOCs are recognized as important contributors to oxidant formation (smog) and the photochemical formation of O_3, formaldehyde (HCHO) and PAN (peroxyacetyl nitrate). Several VOCs and oxidation products such as 1,3-butadiene, benzene and formaldehyde have been identified as hazardous air pollutants (i.e. toxic, mutagenic or carcinogenic), and the potential health impacts of exposure to tropospheric VOCs have given rise to increased concern.

Sources

In rural areas VOCs of biogenic origin may dominate, whereas in urban areas VOCs are mainly of anthropogenic origin with contributions from e.g. traffic, natural gas leakage, fossil fuel combustion, petroleum refining and industry (solvents, manufacturing). However, the VOC emissions from motor vehicles probably have the most serious effect on urban air quality. The emission of VOCs related to motor vehicles occurs either by evaporative emission of fuel (e.g. spillage, hot soaks, running, tank leakage) or from the exhaust.

Emission from vehicles

Of the total hydrocarbon emission from motor vehicles in Denmark only about 9% come from diesel vehicles, and petrol fuelled vehicles accounted for the remaining 91%; of the latter, about 59% came from the exhaust, and 41% was released by evaporative emission *(Danmarks Statistik 1993).* The hydrocarbon content of vehicle exhausts are influenced by several factors related to driving mode and speed, ambient temperature, vehicle conditions (e.g. age and performance), fuel to air ratio and fuel type.

A limit of 5% content of benzene has been introduced in 1986 in all EU countries. The petrol in Denmark is produced with a benzene content between 3 and 5% depending on the content in the crude oil and the production processes. If further increase of the octane number is necessary, it is at Danish refineries obtained by adding MTBE (Methyl Tert-Butyl Ether). The emission of benzene depends on the content in petrol, but the emission is also linked to the total content of aromatic compounds in petrol, because it is formed during the combustion process. No general limits have been set for other

aromatic VOC, but in some countries, e.g. in Sweden, lower prices have been set for petrol with lower content of total aromatic compounds.

Measurements and analyses

The VOCs measurements were carried out at two sites in central Copenhagen. One is located at kerb side about 3 m above street level at Copenhagen/1257. The other site is at the roof of a university building (Copenhagen/1259). Five detailed VOC measuring campaigns (winter-summer) of two to three weeks each have been carried out in 1994-95. Continuous monitoring has been carried out by a BTX-monitor at the street station August-December 1994.

The method for detailed VOC measurements included 1-3 hour sampling of polluted air into glass syringes (250 mL) equipped with timer-controlled motor-driven pistons followed by the transfer of 100-200 mL of the sampled air to a gas chromatograph for analysis (*Hansen, Palmgren, 1995*).

The continuous monitoring of benzene, toluene, ethylbenzene, m-, o- and p-xylene was performed as 20 minutes sampling and analysis by an automatic gas chromatograph (BTX-monitor, Chrompack) every half hour. Reported concentrations are in ppbv with a sensitivity at the sub-ppbv level.

Results and assessment of origin

The campaign measurements were mainly used for assessment of the relative concentrations of the different VOCs. The data from the relatively short campaigns could not give representative results for a whole year or the seasons, mainly due to meteorological variations. Longer time series for a few aromatic VOCs have been obtained by the continuous monitoring by the BTX-monitor at the street site. These results were also used for investigations of the correlation with other pollutants from the traffic, e.g. CO and for estimates of the emission factors.

Table 7.2 lists the average VOC concentrations based on the three one-hour and one three-hour time-integrated samples measured on weekdays, mainly during rush hours, at kerb side at Copenhagen/1257 in the five campaigns from February 1994 to March 1995 and the mean values of all five campaigns. The average concentration of saturated compounds (alkanes) vary between 2 to 7 ppbv, highest for *iso*-pentane and n-butane and lowest for propane, whereas levels of unsaturated (alkenes and alkynes) and aromatic compounds vary between 2 and 16 ppbv, highest for toluene and ethyne and lowest for the butenes. The concentration of benzene was between 4 and 10 ppb.

For comparison mean values for central London from mid 1991 to mid 1992 are also listed in Table 7.2. The VOC concentration profiles measured in Copenhagen are comparable to those from London, whereas the mean concentrations are similar (ethene, ethyne and pentanes) or lower by a factor of two (ethane, C3- and C4-components). Surprisingly, benzene and toluene seem to be a little higher in Copenhagen. It could be due to differences in fuel composition and the extension of TWC.

Table 7.2. Average concentrations of NMHC VOCs at street level at Copenhagen/1257 during campaigns in 1994 and 1995.

Period Compound	Feb. 94 (ppbv)	May 94 (ppbv)	Aug. 94 (ppbv)	Dec. 94 (ppbv)	Mar. 95 (ppbv)	Mean (ppbv)	London91-92[a] (ppbv)
Ethane	4.2	3.5	2.9	2.8	4,3	3.6	7.4
Ethene	16.5	9.1	9.1	9.4	8.0	10.4	10.8
Propane	2.1	0.8	0.8	1.9	2.5	1.6	3.5
Propene	4.1	2.3	2.1	2.5	2.2	2.6	5.8
Ethyne	26.9	14,1	11.4	14.0	13.0	15.9	19.3
iso-Butane	4.1	3.1	3.5	2.7	2.5	3.2	6.4
n-Butane	9.0	5.9	7.2	5.9	4.6	6.5	12.2
Butenes	n.m.	n.m.	n.m.	n.m	1.5	1.5[b]	3.6
iso-Pentane	8.9	7.7	8.0	5.8	4.4	7,0	7.5
n-Pentane	3.5	2.3	2.8	2.1	1.6	2.4	2.6
Me-Pentanes	n.m.	n.m.	n.m.	n.m	2.2	2.2[b]	1.7
n-Hexane	n.m.	n.m.	n.m.	n.m.	0.8	0.8[b]	0.6
Benzene	9.7	8.2	5.0	4.4	3.8	6,2	4.6
Toluene	22.3	16.8	11.2	8.7	8.3	13.5	7.5
Et-Benzene	n. m.	n.m.	n.m.	n.m.	1.3	1.3[b]	1.2
m+p-Xylenes	n. m.	n.m.	n.m.	n.m.	3,5	3.5[b]	3.8
o-Xylene	n.m.	n.m.	n.m.	n.m.	1.1	1.1[b]	1.5

[a]Data from *(Derwent et al. 1995).* [b]Data from Mar. 95 only. n m. = not measured.

Correlation between compounds

The strong correlation between benzene and CO (*figure 7.4*) confirms that the traffic is the main source for benzene at street level. The correlation between the total VOC (i.e. the sum of the 11 compounds measured in all campaign periods) and CO is high. The correlation between benzene, toluene, ethylbenzene, m-, o-, and p-xylene were strong. They are all constituents of petrol.

Assessment of health risks

Benzene is presumed to have carcinogenic properties.Long term mean values (e.g. annual averages) are necessary for the estimation of the health risks. The available measurements, which only cover a few months in 1994, are not sufficient for the calculation of a reliable annual average. An estimation is, however, obtained by using the OSPM dispersion model. The calculated monthly average values are shown on *figure 7.5* together with the measured values. No limit values are implemented in Denmark, but e.g. in The Netherlands an annual average of 10 $\mu g/m^3$ (approx. 3 ppb) is used. *Figure 7.5* shows that the concentrations at Copenhagen/1257 are higher than that for all months of the year.

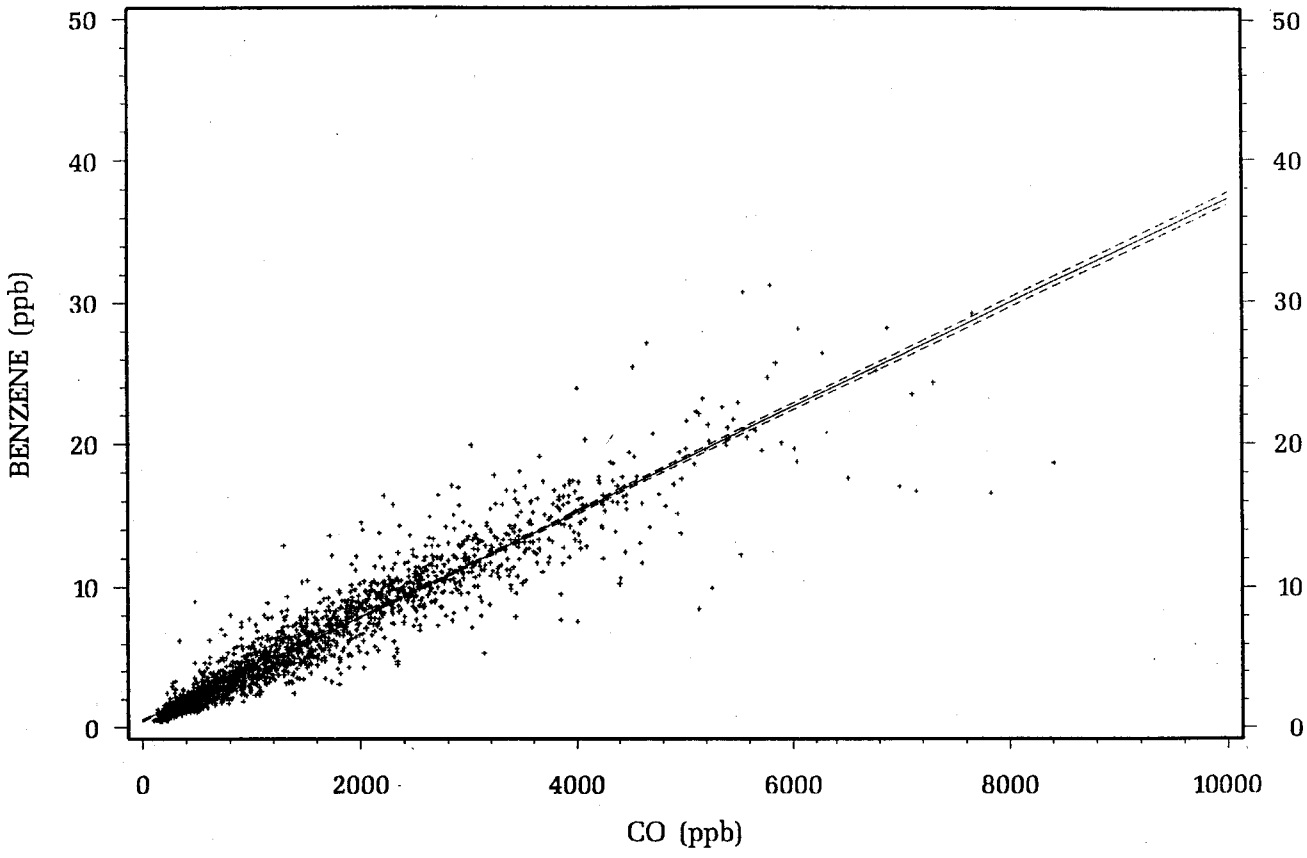

Figure 7.4. Concentrations of CO and benzene measured as hourly averages at Copenhagen/1257 August-December 1994.

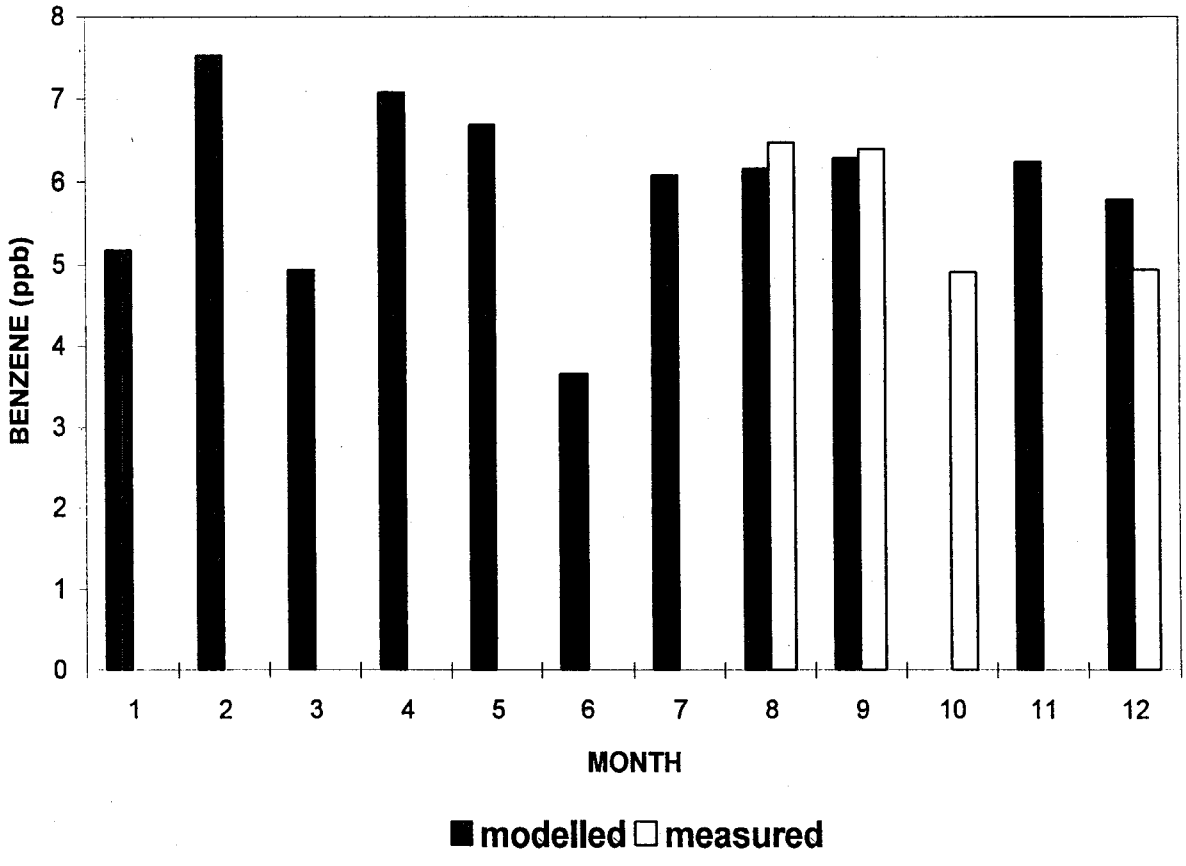

Figure 7.5. Monthly averages of benzene at Copenhagen/1257 in 1994.

8 Conclusion

NO_2

The measured 98-percentiles for NO_2 were about half the limit value (200 µg/m^3), whereas medians were approximately equal to the guide value (50 µg/m^3). The measured values were in 1994 slightly lower than the previous years. A trend analysis covering the last 13 years showed that the NO_2 level have been almost constant. A simple empirical model, which was applied to the results from Copenhagen/1257 and Odense/9155, showed that the exact location in a street is of less importance for the 98-percentile and the median and hence the limit value, while the simultaneous ½-hour concentrations can be quite different.

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 1994 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. The sum of O_3 and NO_2 in a "city-near" background area behaves like one specie. The results showed that the difference between the urban "roof level" and the background concentrations is remarkable small.

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 9 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 at 2 µg/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 new 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 mean concentration exceeds 180 $\mu g/m^3$ and if the hourly mean concentration exceeds 360 $\mu g/m^3$ a warning is issued to the population. The threshold for information of the population was exceeded two times in 1994. The summer was unusual warm and sunny. It can be expected that the information threshold will be exceeded with a few years interval. 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 1994 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 rather close to 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 already taken actions to reduce the NO_x emission (obligatory three way catalysts on new gasoline driven cars and reduction of the emission from power plants) and to see the effect of the reduction, which hopefully will be realized through international protocols, of the emission of the O_3 precursors.

9 References

Berkowicz, R., Palmgren, F., Hertel, O., Vignati, E. (1995). Using measurements in streets for evaluation of urban air quality - meteorological analysis and model calculations. Presented at the Fifth International Highway and Urban Pollution Symposium, 22-24 May 1995, Copenhagen, Denmark. To be published in The Science of the Total Environment.

Danmarks Miljøundersøgelser (1994a). Data report for LMPIII, 1. quarter 1994. Report LMP-3/94. National Environmental Research Institute. Roskilde, Denmark. (In Danish)

Danmarks Miljøundersøgelser (1994b). Data report for LMPIII, 2. quarter 1994. Report LMP-4/94. National Environmental Research Institute. Roskilde, Denmark. (In Danish)

Danmarks Miljøundersøgelser (1995a). Data report for LMPIII, 3. quarter 1994. Report LMP-1/95. National Environmental Research Institute. Roskilde, Denmark. (In Danish)

Danmarks Miljøundersøgelser (1994b). Data report for LMPIII, 4. quarter 1994. Report LMP-2/95. National Environmental Research Institute. Roskilde, Denmark. (In Danish).

Danmarks Statistik (1993). Emissions from motor vehicles 1990. Statistiske efterretninger, Miljø (1993), 1-6 (in Danish).

Derwent, R.G., Middleton, D.R., Field, R.A., Goldstone, M.E., Lester, J.N., Perry, R. (1995). Analysis and interpretation of air quality data from an urban roadside location in central London over the period from July 1991 to July 1992. Atm. Environ. , 29, 923-946 Doskey, P.V., Porter, J.A. and Scheff, P.A. (1992). Source fingerprints for volatile nonmethane hydrocarbons. J. Air Waste Manage. Assoc., 42, 1437-1445.

EEC (1980). Directive 80/779/EEC of July 15 on Air Quality Limit Values for Sulphur Dioxide and Suspended Particles. J. Europ. Commun. L229/30.

EEC (1982). Directive 82/884/EEC of December 3 on Air Quality Limit Values for Lead. J. Europ. Commun. L378/15.

EEC (1985). Directive 85/203/EEC of March 7 on Air Quality Standards for Nitrogen Dioxide. J. Europ. Commun. L87/1.

EEC (1989). Directive 89/427/EEC of June 21 on Revision of Directive 80/779/EEC on Air Quality Limit Values for Sulphur Dioxide and Suspended Particles. J. Europ. Commun. L201/53.

EEC (1992). Directive 92/72/EEC of September 21 on Ozone Air Pollution. J. Europ. Commun. L297/1.

Hansen, A.B., Palmgren, F. (1995). VOC Air Pollution in Copenhagen. Paper presented at the Fifth International Highway and Urban Pollution Symposium, 22-24 May 1995, Copenhagen, Denmark. To be published in The Science of the Total Environment.

Hovmand, M.F., Andersen, H.V., Bille-Hansen, J., Ro-Poulsen, H. (1994): Atmospheric deposition to Danish forest ecosystems.
NERI Technical report no. 98. National Environmental Research Institute, Roskilde, Denmark. (In Danish).

Kemp, K. (ed.) (1993). Danish Air Quality Monitoring Network. Technical Description (1993). Report LMP-4/93. National Environmental Research Institute. Roskilde, Denmark.

Kemp, K., Manscher, O.H. (1993). Danish Air Quality Monitoring Network. Annual Data Report (1992). Report LMP-5/93. National Environmental Research Institute. Roskilde, Denmark.

Kemp, K., Palmgren, F., Manscher, O.H. (1994): Danish Air Quality Monitoring Program. Annual Data Report 1993. National Environmental Research Institute, Denmark, 79 pp. - NERI Technical Report No. 113.

Miljøministeriet (1986). Regulation on limit values for sulphur dioxide and suspended particulate matter in air. Regulation no. 836 of December 10. Ministry of Environment, Copenhagen, Denmark. (In Danish)

Miljøministeriet (1987). Regulation on limit values for nitrogen dioxide in air. Regulation no. 119 of March 12. Ministry of Environment, Copenhagen, Denmark. (In Danish)

Miljøministeriet (1994). Regulations on supervision of the ozone content in the Air. Regulation no. 184 of March 11. Ministry of Environment, Copenhagen, Denmark. (In Danish)

Palmgren, F., Kemp, K., Manscher, O.H. (1992). The Danish Air Quality Programme (LMP II). Annual Data Report 1991. NERI Technical Report No. 60. National Environmental Research Institute. Roskilde, Denmark

Palmgren, F., Hansen, A. B., Berkowicz, R. and Egeløv, A. H. (1995). Volatile organic air pollutants from road traffic. In proceedings from Trafikdage på AUC, Aalborg, Denmark.

Poulsen, M., Grundahl, L., Palmgren, F. (1995): Atmospheric PAH in Denmark. NERI Technical Report No. 124. National Environmental Research Institute. Roskilde, Denmark.

WHO (1987). Air Quality guidelines for Europe, WHO regional publications, European series No. 23, Copenhagen.

Danish Summary - Dansk resumé

Det Landsdækkende Luftkvalitets Måleprogram Årsrapport for 1994

Faglig rapport fra DMU nr. 150

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, 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. 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 kræftframkaldende 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 og der har ikke været nogen væsentlig ændring i niveauet siden 1982. Emissionen af NO_x fra benzindrevne bliver reduceret efterhånden som der kommer katalysatorer på flere og flere biler. Emissionen fra de øvrige hovedkilder, dieselbiler og kraftværker, vil ikke blive ændret ret meget de første par år. En simpel empirisk model viser, at de målte koncentrationer af NO_2, er meget afhængig af den nøjagtige placering af målestationen i gaderummet. For årsværdierne for medianen og 98-percentilen er dog næsten uafhængig af placeringen.

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 1994. 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 $\mu g/m^3$. Hvis timemiddelværdien overskrider denne værdi skal befolkningen undererrettes. Det skete to gange i 1994.

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 koncentrationer på mellem 1/3 og 1/5 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 1993 var næsten en faktor 10 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. Sammenlignes NO_2 og O_3 på gadestation og tagstation er der en overvægt af NO_2 i gadeniveau og af O_3 i tag niveau, mens O_x (=NO_2+O_3) forekommer i praktisk taget samme koncentrationer begge steder. Der er gennemført en række målinger af flygtige organiske forbindelse (VOC=volatile organic compounds) på de to Københavnske stationer. VOC i gadeniveau stammer især fra motorkøretøjer. Benzindrevne biler bidrager med ca. 90%. VOC'erne kan være tilsat benzinen eller dannes ved forbrændingen. Resten kommer fra dieseldrevne køretøjer. En række VOC'er findes på samme eller lidt lavere niveau i København i forhold til London. Det er dog bemærkelsesværdigt at benzene og toluene findes i større koncentrationer i København. Der ikke grænseværdier for VOC i Danmark; men koncentrationen af benzene på gadestationen i København var 2-3 gange større end den hollandske grænseværdi.

Resumé

LMP resultaterne fra 1994 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 $_2$NO 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.

National Environmental Research Institute

The National Environmental Research Institute - NERI - is a research institute of the Ministry of Environment and Energy. NERI's tasks are primarily to do research, collect data and give advice on problems related to the environment and Nature.

Addresses:

National Environmental Research Institute
Frederiksborgvej 399
P.O.Box 358
DK-4000 Roskilde
Tel: +45 46 30 12 00
Fax: +45 46 30 11 14

Management
Personnel and Economy Secretariat
Research and Development Secretariat
Department of Atmospheric Environment
Department Environmental Chemistry
Department Policy Analysis
Department of Marine Ecology and Microbiology

National Environmental Research Institute
Vejlsøvej 25
P.O.Box 413
DK-8600 Silkeborg
Tel: +45 89 20 14 00
Fax: +45 89 20 14 14

Department of Freshwater Ecology
Department af Terrestrial Ecology

National Environmental Research Institute
Grenåvej 12, Kalø
DK-8410 Rønde
Tel: +45 89 20 14 00
Fax: +45 89 20 15 14

Department of Wildlife Ecology

National Environmental Research Institute
Tagensvej 135, 4
DK-2200 København N
Tel: +45 35 82 14 15
Fax: +45 35 82 14 20

Department of Arctic Environment

Publications:

NERI publishes professional reports, technical instructions, reprints of scientific and professional articles, a magazine of game biology and the Annual Report.

Included in the annual report is a review of the publications from the year in question. The annual reports and an up-to-date review of the years' publications are available on application to NERI.