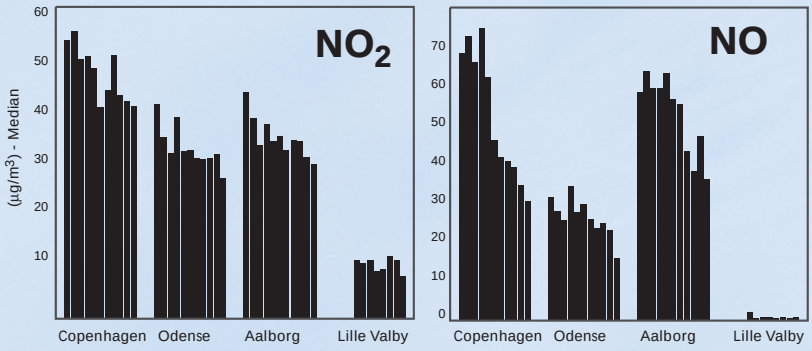
Ministry of Environment and Energy
National Environmental Research Institute

# The Danish Air Quality Monitoring Programme

Annual Report for 1998

*NERI Technical Report No. 296*



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Annual Report for 1998

***NERI Technical Report No. 296***
***1999***

*Kåre Kemp*
*Finn Palmgren*
Department of Atmospheric Environment

# Data sheet


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Abstract: The air quality in Danish cities has been monitored since 1982 within The Danish Air Quality Monitoring Programme. The purpose is to monitor the levels of toxic species, follow the trends, evaluate source contributions and support scientific programmes for a better understanding of the behaviour and dispersion of air pollution. Concentrations of Pb and $SO_2$ are reduced with an order or magnitude or more since 1982. NO and TSP (total suspended particulate matter) levels are reduced with around 30%. A slight but significant decrease is observed for $NO_2$ and $O_3$. A set of new limit values is implemented through EU Directives. The measured $NO_2$ concentrations are close to the limit values; while the particulate concentrations measured as PM10 (particles < 10 µm) probably exceed the limit values at several places.



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# Summary


*The programme*

The Danish Air Quality Monitoring Programme (LMP) was started in 1982 as the first nation-wide urban air pollution monitoring programme in Denmark. The programme has been adjusted to the pollution pattern by two revisions. The present phase (LMP III) was started in 1992. This report presents the results from 1998 and updates the trends from the start of the programme in 1982. Measurements are performed at twin sites in the cities of Copenhagen, Odense and Aalborg. One of the sites is at kerb side at a street with heavy traffic and the other is on the roof of a building a couple of hundreds meters from the street site. Two rural sites, one outside Copenhagen and one at Keldsnor in the southern part of the country are also included. NO, $NO_2$, $SO_2$, total suspended particulate matter (TSP) and elements in the aerosols are measured at the street sites. $O_3$ and the meteorological parameters, wind direction, wind speed, temperature, relative humidity and global radiation are measured at the roof sites. Additional measurements of CO at street and NO and $NO_2$ at roof sites are now performed continuously in order to improve the knowledge about the NO, $NO_2$ and $O_3$ problem complex. At the rural site outside Copenhagen the same program is conducted as at the street stations with the inclusion of $O_3$. Only NO, $NO_2$ and $O_3$ are reported from the other rural site.

*Limit values*

Air quality limit values have been implemented in Denmark for $NO_2$, $SO_2$, TSP in order to protect human health. All limit values are based on EU limit values, which also include a limit value for Pb. A set of threshold values for $O_3$ came into force in March 1994. They were laid down with consideration of the protection of both human health and plants. The EU Commission has proposed new limit values for $NO_2$, $SO_2$, $PM_{10}$ and Pb. They are implemented through the first "daughter" Directive to the Air Quality Framework Directive. The EU council adopted it in April 1999. The new limit values shall be in force within 18 month from publication and all member states must comply with the new limit values before 2005 or 2010 in accordance with the daughter directives. The new limit values were set to protect human health and ecosystems. They are based on the present knowledge about the toxicity of the species.

*Nitrogen oxides*

The measured $NO_2$ concentrations were about a factor of two lower than the limit value, while they are close to the new values proposed by the EU Commission. The trend for $NO_2$ indicates the latest years a weak but clear decrease. The introduction of three way catalytic converters (TWC) on all new petrol driven cars from October 1990 reduces mainly the NO emission. As a result of this the observed NO concentrations are significantly decreasing. $O_3$ is at present a limiting factor for the formation of $NO_2$ at street level and it remains to be seen to what extent the $NO_2$ concentrations will be reduced at highly polluted locations as result of the TWC's.

*Ozone*

Some of the threshold values for $O_3$ were frequently exceeded. The average $O_3$ concentrations are almost the same at all sites. The average levels are, especially during the winter, lowest at winds from

southeasterly directions. The highest peak concentrations were also observed at southeasterly winds. While $O_3$ is the limiting factor for formation of $NO_2$ at street level, NO is the limiting factor at roof level and in background areas. The $O_3$ concentrations seem now to be slightly decreasing.

*Sulphur dioxide and TSP*

The $SO_2$ concentrations have been continuously decreasing since 1982. They were in 1998 only about 1/10 of the limit values. They are also far below the new values proposed by the EU commission. The amount of TSP shows a slightly decreasing trend as a result of less windblown dust due to an increased number of fields with "winter crops" and better combustion control. The concentrations of TSP were approximately 1/3 of the limit value. The measured values are not directly comparable with the EU Commissions new proposed limit values, which is based on $PM_{10}$. However, the $PM_{10}$ concentration at the traffic sites exceeds probably the proposed limit values. It is estimated that the $PM_{10}$ concentrations are roughly 60% of the TSP.

*Lead*

The lead pollution has been reduced with about a factor of 50 since 1982 as a result of the removal of the lead from petrol. All petrol sold in Denmark is since 1994 in practice lead free. The development has outdated the limit value, which is more than a factor of 100 higher than the measured concentrations. Also the new EU limit value is far above the measured concentrations in Denmark.

*Carbonmonoxide and benzene*

CO and benzene are mainly emitted from petrol driven cars. The concentrations are consequently highest close to the streets. The TWC remove the main part of both CO and benzene from the exhaust. The concentrations are at present steadily decreasing, due to the increasing fraction of cars with TWC's and reduction of the benzene content in petrol. A new EU Directive, which sets limit values for CO and benzene, is in preparation. The measured CO concentrations are well below the expected limit values, while the present benzene concentrations at some places exceed the expected limit value, which should be met before 2010.

# 1 Introduction

*LMP III*

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

*Previous programme*

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

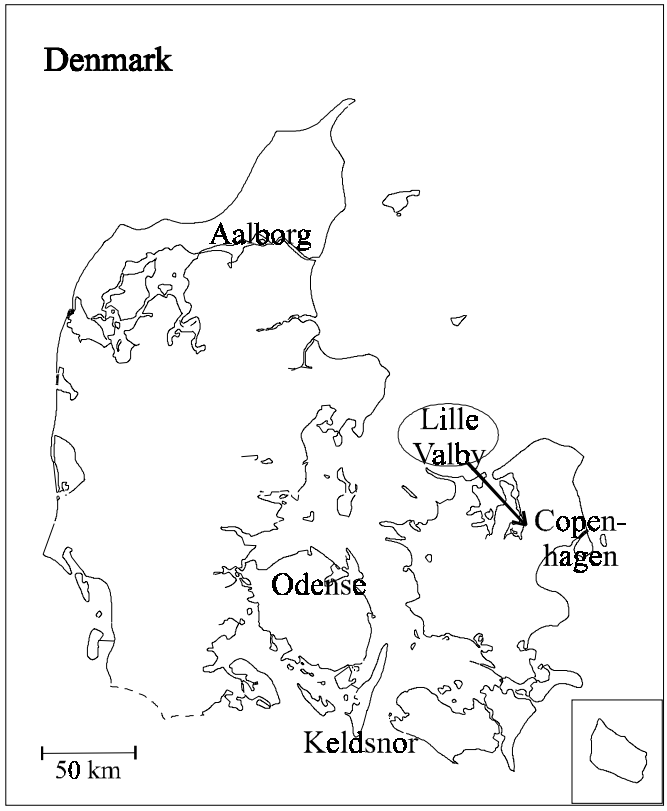


Figure 1.1 Cities and the background sites in the LMP network.

Table 1.1 LMP III stations in 1998. TSP is the total suspended particulate matter collected on a filter and determined by weighing. The station type refers to the classification given in Kemp, 1993. BTX is measurements of benzene, toluene and xylene with a monitor. The meteorological measurements comprise wind direction, wind speed, ambient temperature, relative humidity and global radiation.

| | | Measuring Programme | |
|---|---|---|---|
| | Station type | ½ hour average | 24 hour average |
| Copenhagen/1257 | Main (Traffic) | NO, $NO_2$, $SO_2$ , CO, $O_3$, BTX | $SO_2$, TSP, Elements |
| Copenhagen/1259 | Roof (Urban background) | $O_3$, meteorology,NO,$NO_2$ | - |
| Odense/9155 | Main (Traffic) | NO, $NO_2$, $SO_2$, CO | $SO_2$, TSP, Elements |
| Odense/9154 | Additional (Traffic) | - | $SO_2$, TSP, Elements |
| Odense/9159 | Roof (Urban background) | $O_3$, meteorology, NO,$NO_2$ | - |
| Aalborg/8151 | Main (Traffic) | NO, $NO_2$, $SO_2$, CO | $SO_2$, TSP, Elements |
| Aalborg/8159 | Roof (Urban background) | $O_3$, meteorology, NO,$NO_2$ | - |
| Lille Valby/2090 | Rural background | NO, $NO_2$, $SO_2$, $O_3$ | $SO_2$, TSP, Elements |
| Keldsnor/9055 | Rural background | NO, $NO_2$, ($O_3$) | - |

*Measurement programme*

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

*Campaigns*

The campaign measurements that have been performed the previous years have been extended to cover the whole year. This has been possible by contribution from the TOV programme for an intensive study of the pollution from traffic (Berkowicz et al. 1996). Beside $NO/NO_2$ and CO, $O_3$ and the VOC's benzene, toluene and xylene have been measured at Copenhagen/1257 (table 1.1).

*Annual statistics, trends, phenomenology*

The annual statistics and episodes are summarised for all groups of species. The results are compared with Danish limit and guide values and WHO guideline values. At present limit values are set for $SO_2$, suspended particulate matter, $NO_2$ and Pb in Denmark. A set of threshold values for $O_3$ was introduced in 1994 by the implementation of an EU directive (EEC 1992). The trends since the start of the first LMP programme in 1982 are illustrated using results from Aalborg/8151 and Odense/9154. These are the only stations, which have been in operation since 1982.

*New limit values implemented in the EU countries*

The present Danish limit values are almost identical with the limit values laid down in the EU directives (EEC, 1982, 1985, 1989, 1992). These limit values and the monitoring techniques and strategies are under revision. The new EU legislation consists of a framework directive (EC 1996), giving general rules for network design and limit value strategies, and a number of daughter directives giving limit values, reference methods and monitoring strategies for specific pollutants. The limit values will primarily be based on the known health effects of the species. The framework directive has already been adopted. The first daughter directive, including limit values for $NO_2$, $SO_2$, particulate matter ($PM_{10}$) and lead, was adopted in April 1999 (EC 1999) by the EU council. The EU Commission is preparing

directives covering $O_3$, benzene, CO and the heavy metals Cr, As and Cd. The new limit values in relation to the measured concentrations are discussed for the single species in the following chapters.

*Smog warning*

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

*1998 reports*

The 1998 results are found in quarterly reports (Danmarks Miljøundersøgelser 1998a, 1998b, 1999a and 1999b). The results obtained during 1998 are summarised in the present report in form of annual statistics and trends. Results for CO and benzene and toluene, which cover a whole years measurement, have been included. An overview of results from the LMP programmes together with a description of model calculations and an evaluation of the health aspects has been published in Palmgren et al., 1997. A description of the Danish air quality monitoring programmes and selected results is shown on the Internet (NERI 1999).

*Other air quality networks in Denmark*

Beside the LMP two other air quality monitoring networks are in operation in Denmark. The Greater Copenhagen Air Monitoring Unit is responsible for a network in the Greater Copenhagen area. A number of pollutants are measured at five sites. The measurements are comparable with the LMP measurements and the two programmes supplement each other in Copenhagen (Thomsen 1999). A network in rural areas (the Danish Background Monitoring Program) was established in 1978. At present gas and aerosol measurements are performed at six stations while various ions are determined in precipitation collected at 12 sites. The aim is i.a. to study acidification and eutrofication of the forests, farmland, Danish sea and freshwater areas (Frohn, Skov and Hertel 1998).

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# 2 Nitrogen oxides

*Source*

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

*Measurements*

During 1998 continuous measurements of NO and $NO_2$ were performed at all stations except Odense/9154. More than 90% of the possible results are valid for all stations except Odense/1959, where about 80% are available (see table 2.1).

## 2.1 Annual statistics

*Limit values*

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

The limit values were not exceeded in 1998, but the results from Copenhagen exceeded the WHO guide value (40 $\mu g/m^3$) and was close to the Danish guide values for the median.

*New limit values*

The EU Directive 1999/30/EC (EC, 1999) set new limit values for $NO_2$ for the protection of human health and vegetation. The limit values for protection of human health are in force 18 months after adoption, but shall be met before January 2010. The annual average for protection of health was slightly exceeded in 1998 at Copenhagen/1257 (table 2.1). It is expected that the ambient concentrations will decrease in the coming years due to already taken measures, e.g. introduction of TWC.

The annual average concentration of $NO_x$ ($NO+NO_2$) in rural area shall be below the new limit value, 30 $\mu g$(equivalent $NO_2$)$/m^3$ (= 16 ppb) from 19 July 2001 for the protection of vegetation. Keldsnor/9055 is the only station in the LMP network that fulfils the requirements for sites for measurements in relation to the limit value. The average $NO_x$ concentration at this site was 11 $\mu g/m^3$ in 1998 (cf. table 2.1).

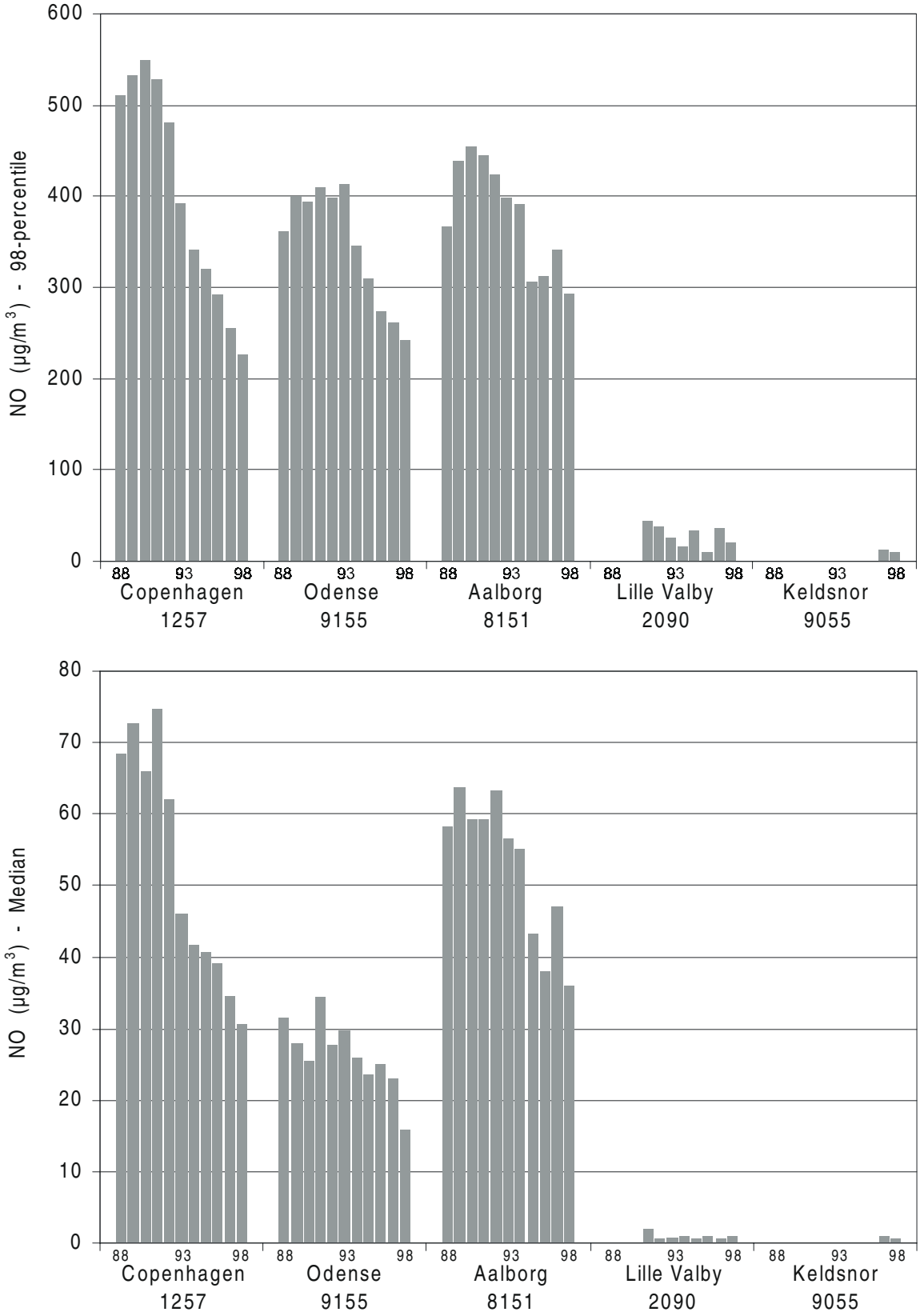


Figure 2.1 Medians and 98-percentiles for NO from 1988 to 1998.

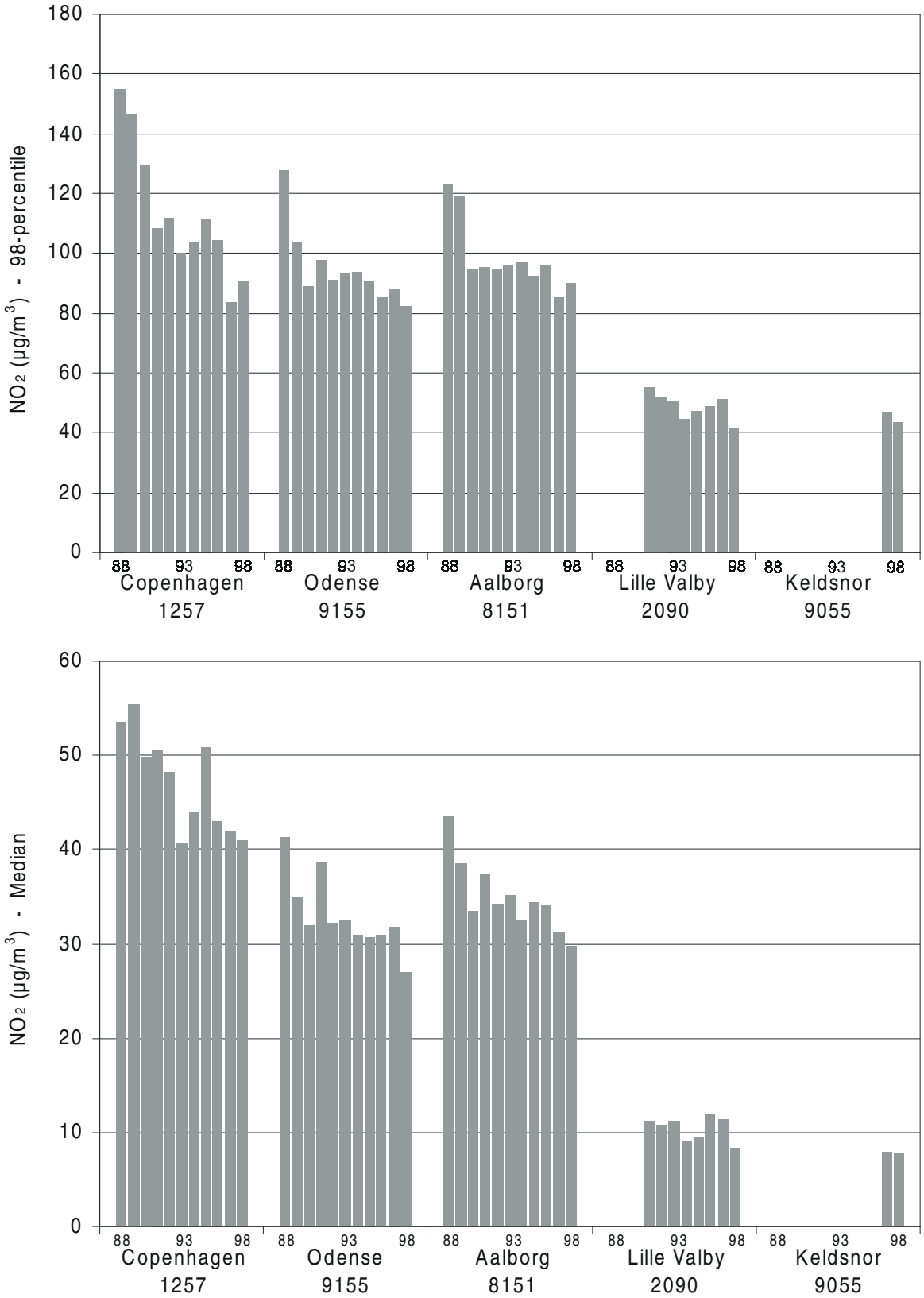


Figure 2.2 Medians and 98-percentiles for $NO_2$ from 1988 to 1998.

Table 2.1 The values are calculated for all measurements from 1998 and based on hourly average values. Values below the detection limit are included as one half of the detection limit (more than half of the NO values from Lille Valby/2090 and Keldsnor/9055 are below the detection limit). All stations did yield sufficient results for a valid comparison with the limit and guide values. The number of measurements is listed in the second column. The limit values and Danish guide values are found in Miljøministeriet, 1987, the new limit values in EC, 1999 and the WHO guide value is given in WHO (1998).

| | | NO (µg(NO)/m$^3$) | | | | $NO_2$ (µg($NO_2$)/m$^3$) | | | |
|---|---|---|---|---|---|---|---|---|---|
| Station | Num-ber | Ave-rage | Me-dian | 98-perc | 99.8-perc | Ave-rage | Me-dian | 98-perc | 99.8-perc |
| **Traffic sites:** | | | | | | | | | |
| Copenhagen/1257 | 8308 | 53 | 31 | 226 | 382 | 43 | 41 | 90 | 117 |
| Odense/9155 | 8542 | 41 | 16 | 245 | 456 | 32 | 27 | 82 | 102 |
| Aalborg/8151 | 8700 | 64 | 36 | 293 | 514 | 34 | 30 | 90 | 113 |
| **Urban background:** | | | | | | | | | |
| Copenhagen/1259 | 8392 | 5 | 2 | 42 | 107 | 24 | 20 | 60 | 86 |
| Odense/9159 | 7187 | 6 | 3 | 45 | 147 | 19 | 16 | 54 | 72 |
| Aalborg/8159 | 8559 | 7 | 3 | 52 | 230 | 17 | 13 | 54 | 81 |
| **Rural:** | | | | | | | | | |
| Lille Valby/2090 | 8672 | 2 | (1) | 21 | 77 | 11 | 8 | 42 | 54 |
| Keldsnor/9055 | 8705 | 1 | (1) | 10 | 27 | 11 | 8 | 43 | 61 |
| Limit value | >6570 | - | - | - | - | - | - | 200 | - |
| New limit value | | - | - | - | - | 40 | - | - | 200 |
| Guide value (DK) | | - | - | - | - | - | 50 | 135 | - |
| Guide value (WHO) | | - | - | - | - | 40 | - | - | - |

*Increase of NO at Aalborg/8151 in 1997*

The NO concentration was higher in 1997 than the in neighbouring years at Aalborg/8151. The reason is probably higher traffic density and queuing on the bridge over Limfjorden in connection with repair work in the highway tunnel, which ordinarily takes a major part of the traffic crossing the fjord. No effect is seen on the $NO_2$ concentrations, because $O_3$ is the limiting factor.

*NO vs. $NO_2$*

The high concentration of NO compared to $NO_2$ at traffic stations illustrates that the NO is not a limiting factor for the formation of $NO_2$ at streets. Under ordinary conditions almost all NO has been oxidised a few hundred meters away at the urban background sites.

*Low NO in Odense*

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

## 2.2 Episodes

*Smog warning*

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

Table 2.2 shows the highest values measured at the four stations. NO is included for comparison. The values are calculated according to the provisions in the warning system. The warning limit was not exceeded in 1998, but the WHO guide line value was exceeded for two consecutive hours on March 5.

The new Directive (EC, 1999) prescribes an alert threshold for $NO_2$ of 400 µg/$m^3$ measured over three consecutive hours (i.e. comparable with the 350 µg/$m^3$ in the national smog warning system).

The highest concentrations of NO are usually seen in the winter month at all stations, however local road or building construction may influence the maximum values. The peak concentrations of $NO_2$ are most frequent in spring or summer due to the higher background values of $O_3$.

*No major episodes in 1998*

Figure 2.3 illustrates a typical change during a winter episode from a situation with low to a situation with relatively high wind speed. December 2-3 only little $O_3$ was brought to the urban area of Odense. The NO emitted from the local traffic was not oxidised to $NO_2$. Concentration of NO about 50 times the average value was observed in the urban background. At December 5-7 the wind increased and "clean" air with plenty $O_3$ entered the city area resulting in NO concentrations close to zero. While $O_3$ is the limiting specie for the formation of $NO_2$ during the first days, there is a large surplus of $O_3$ the last days. This plays a role for the $NO_2$ trend as discussed in the next section.

## 2.3 Trends

*Percentiles*

The annual percentiles and average values for NO and $NO_2$ measured at Aalborg/8151 are shown in figure 2.4. The average level of NO was almost constant in the period from 1982 to 1991, but decreased during the following years synchronously with the increasing number of cars with TWC. The level seems however to be somewhat increased in 1996 and especially in 1997. It is probably a result of local changes in the traffic near the site (see section 2.1). The same pattern is not observed at the other stations (cf. figure 2.1).

The $NO_2$ median and average values have been almost constant, but slightly decreasing from the early 1990'ies. The high percentile values have been almost constant, with a weak maximum in the late 1980'ies. The change has been much less than for NO because NO only is the limiting factor for formation of $NO_2$ under conditions with high $O_3$ and low $NO_x$ concentrations (cf. fig. 2.3).

Table 2.2 Maximum concentrations of NO (not included in the smog warning system) and $NO_2$ in 1998. For comparison with the warning limit the lowest 1-hour values are identified for every consecutive three hours. (The warning criteria: that the concentration should exceed 350 µg/m$^3$ for consecutive three hour is the same as that the lowest hourly value within the three hour period exceeds 350 µg/m$^3$). The highest of these values during the whole year are listed under "max. 3 hour". The values under "max. hour" are the absolute one hour maximum values. The indication of time is the beginning of the periods.

| **NO** | Max. 3 hour (µg(NO)/m$^3$) | Day hour | Max. hour (µg(NO)/m$^3$) | Day hour |
|---|---|---|---|---|
| **Traffic sites:** | | | | |
| Copenhagen/1257 | 481 | 981209: 7 | 538 | 981209: 9 |
| Odense/9155 | 654 | 981202: 7 | 904 | 981202: 8 |
| Aalborg/8151 | 550 | 980129: 7 | 800 | 980126:10 |
| **Urban background:** | | | | |
| Copenhagen/1259 | 164 | 980122:18 | 171 | 980122:19 |
| Odense/9159 | 158 | 980123: 7 | 267 | 981201: 9 |
| Aalborg/8159 | 406 | 980129: 8 | 504 | 980126: 9 |
| **Rural:** | | | | |
| Lille Valby/2090 | 125 | 980125:21 | 163 | 980125:21 |
| Keldsnor/9055 | 35 | 980113: 8 | 39 | 980113:10 |
| Warning limit | - | - | - | - |

| **$NO_2$** | Max. 3 hour (µg($NO_2$)/m$^3$) | Day hour | Max. hour (µg($NO_2$)/m$^3$) | Day hour |
|---|---|---|---|---|
| **Traffic sites:** | | | | |
| Copenhagen/1257 | 187 | 980305:21 | 250 | 980305:22 |
| Odense/9155 | 108 | 981202: 8 | 127 | 981210: 7 |
| Aalborg/8151 | 128 | 980417:12 | 140 | 980417:13 |
| **Urban background:** | | | | |
| Copenhagen/1259 | 78 | 980518: 1 | 84 | 980518: 8 |
| Odense/9159 | 76 | 981208:15 | 80 | 981208:16 |
| Aalborg/8159 | 99 | 981208: 7 | 111 | 981208: 8 |
| **Rural:** | | | | |
| Lille Valby/2090 | 57 | 981209:15 | 60 | 981210: 8 |
| Keldsnor/9055 | 69 | 980328:19 | 73 | 980419:20 |
| Warning limit | 350 | - | - | - |
| Guide value(WHO 1998) | - | - | 200 | - |

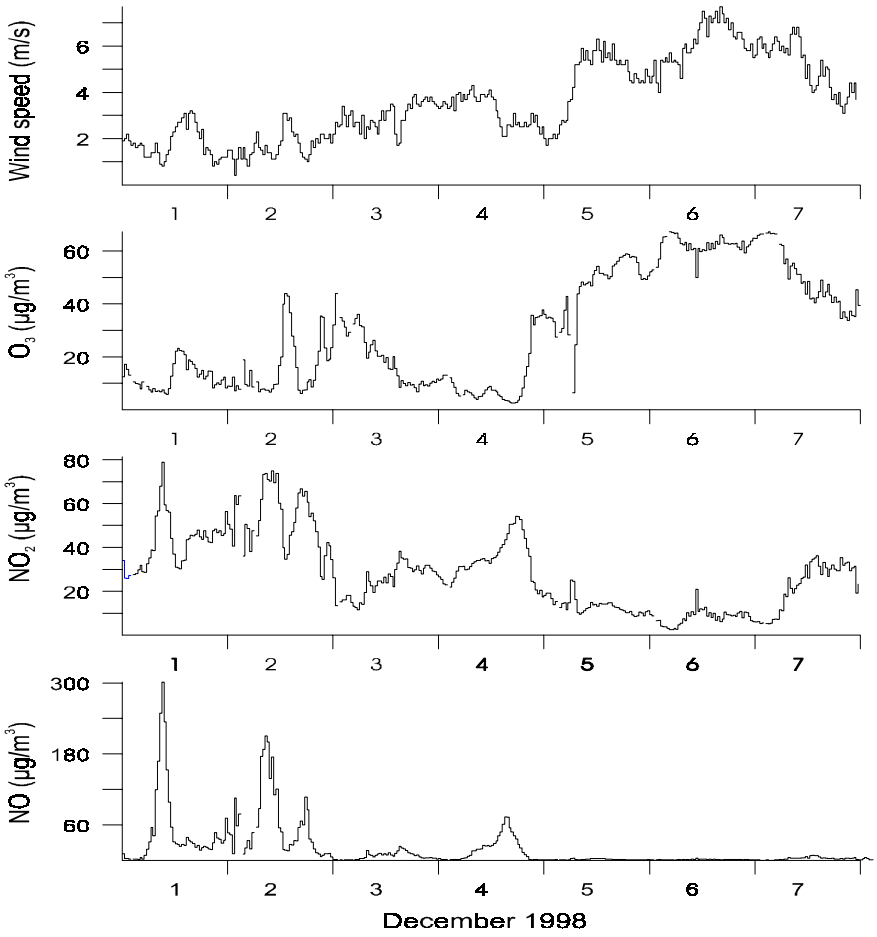


Figure 2.3 Two episodes recorded at the roof station Odense/9159. At December 1-2 high NO concentrations in urban background and December 5-7 contribution of $O_3$ from the Hemispheric background.

The new limit value, 200 µg/m$^3$ for the 99.8 percentile represent a tightening of about 30% compared to the old limit value which was also 200 µg/m$^2$, but for the 98 percentile; but it has been loosened with around 6% compared to the original proposal for the 99.9 percentile (cf. fig. 2.4).

*Averages*

The trends of the monthly average values and the annual variation are shown in figure 2.5. The variation for NO and $NO_2$ seems to be (to some extent) opposite in the sense that years with high NO concentrations correspond to years with low $NO_2$ concentrations and vice versa. There is a distinct annual variation for NO with low concentrations during the summer, when the emissions are lower and the oxidation rate is higher. The variation is much less pronounced for $NO_2$.

*Copenhagen vs. other cities*

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

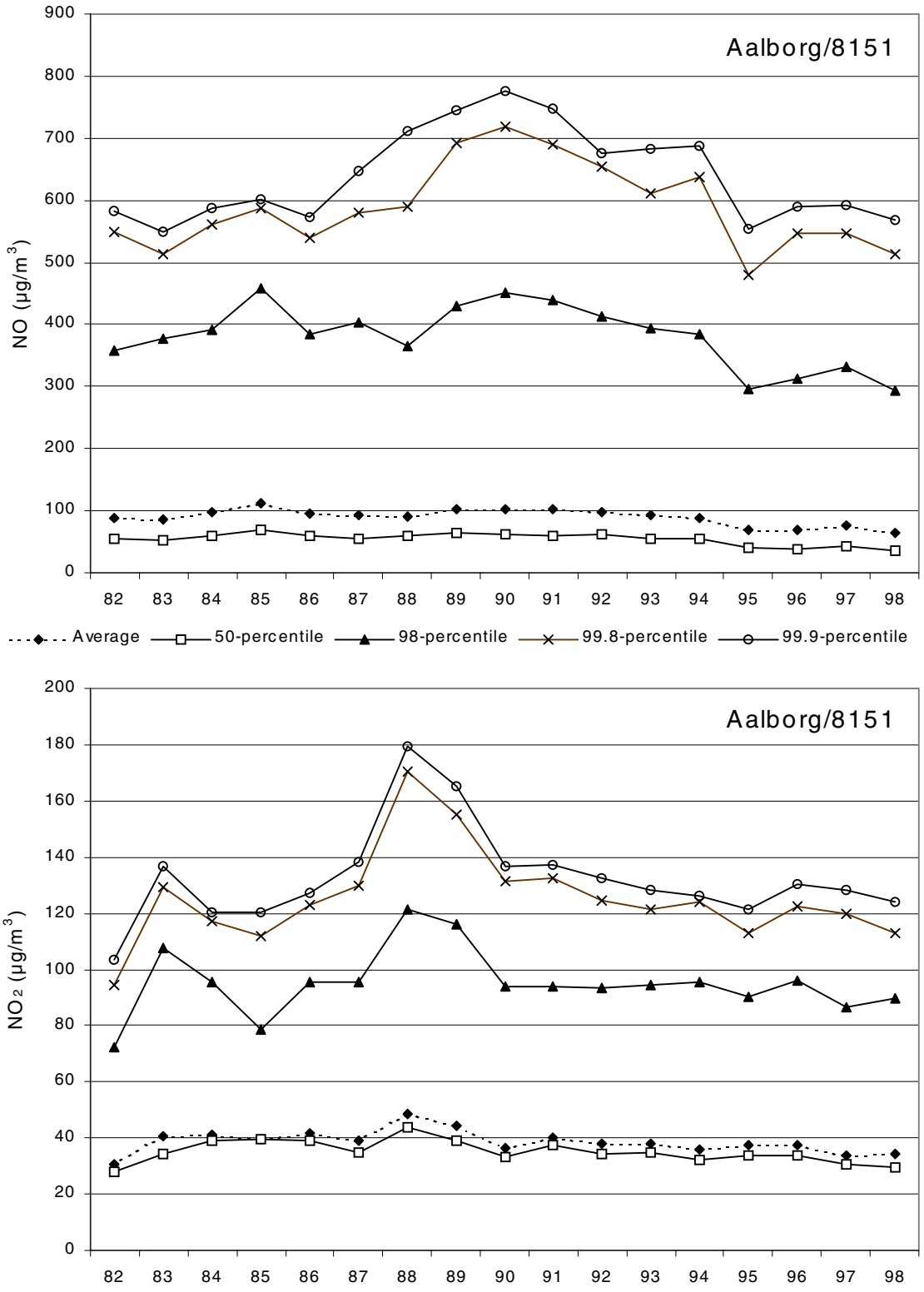


Figure 2.4 Trends for annual 99.9-, 99.8, 98-, 50-percentiles, and average value based on hourly average concentrations of $NO_2$ and NO measured at Aalborg/8151.

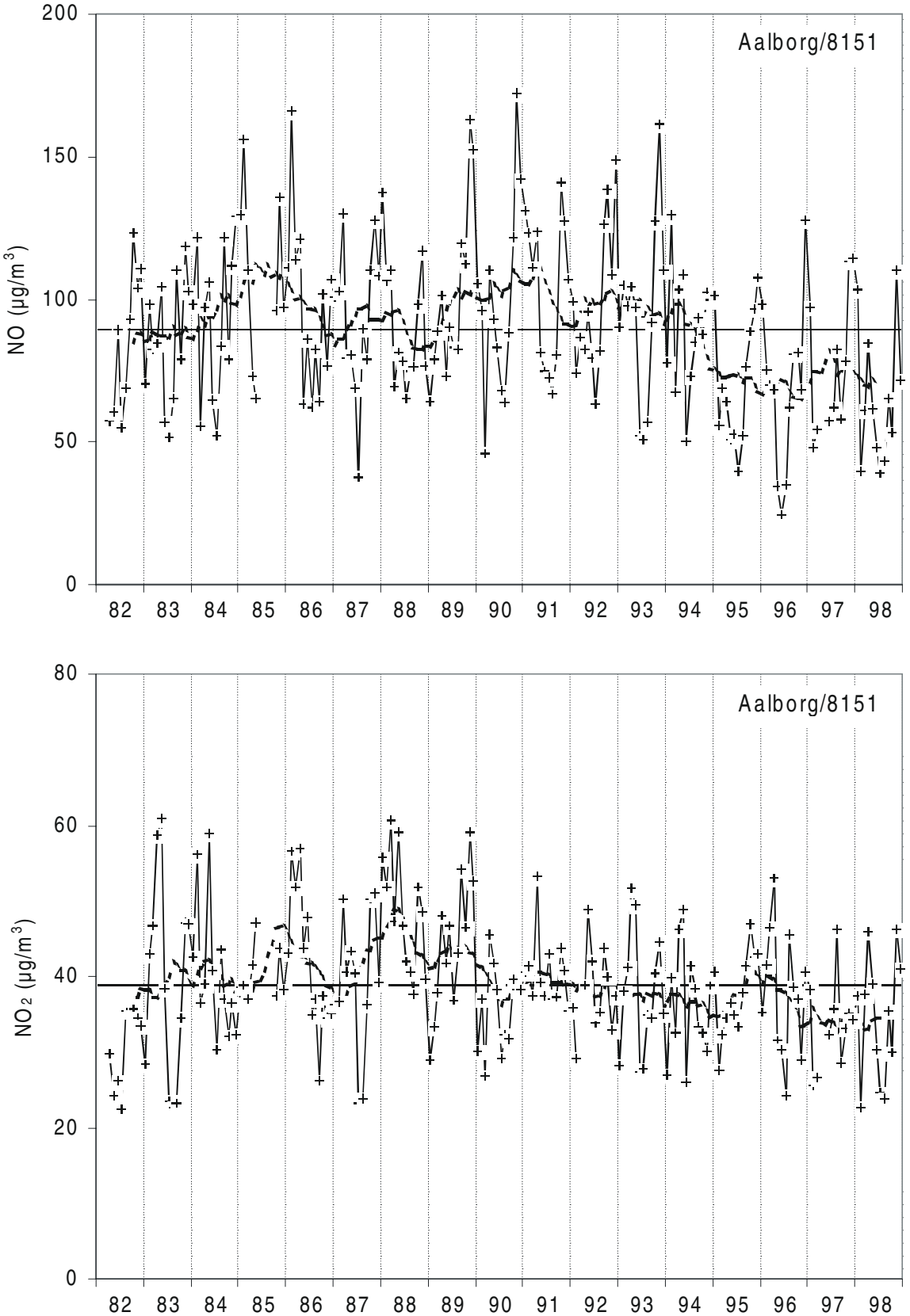


Figure 2.5 Trends for NO and $NO_2$ measured at Aalborg/8151. The points are measured monthly averages, the dotted curve is a moving average over 13 month and the straight line is the average over all years.

# 3 Ozone

*Measurements in 1998*

Measurement of $O_3$ was started mid 1991 at the rural station (Lille Valby/2090). At the end of 1992 the urban background stations (Kemp 1993) were equipped with monitors. The measurements started at Odense/9159 in August 1992 and at Aalborg/8159 in December 1992. At Copenhagen/1259 continuous measurements started in February 1993 with a DOAS instrument and a monitor was installed in April 1993. The $O_3$ measurements at Keldsnor/9055 began in January 1995 (see table 1.1). Further $O_3$ measurements were performed from April 1994 at the street station Copenhagen/1257 in connection with the TOV programme (Berkowicz et al. 1996). Almost complete series of results are available from all stations.

*Sources and formation*

The $O_3$ in the lower troposphere is formed as a secondary pollutant mainly by photochemical reactions involving i.a. volatile organic compounds (VOC) and $NO_2$. An important parameter for the reaction velocity is the ambient temperature. The VOC may either be of anthropogenic or natural origin. Oxidation of NO is the main reaction for the reduction of $O_3$ in urban areas. The climatic conditions and the emission patterns in Denmark result in a net decomposition in urban areas due to the high NO emissions from combustion processes, whereas the presence of $O_3$ in background areas, especially during the summer, exceeds the levels of reducing compounds.

## 3.1 Annual statistics

*Threshold values*

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

*Concentrations depending on site type*

The levels at the rural and the urban background stations are almost the same. The concentrations in street level are considerably lower, due to reaction with i.a. NO. This confirms that the $NO_x$ concentrations in general are lower than the $O_3$ concentrations away from the busy streets, i.e. there is not sufficient NO to remove a significant part of the $O_3$ in the urban background air.

*Exceedings*

The measured values are compared to the threshold values in table 3.1. In May the meteorological conditions were favourable for $O_3$ formation and transport. The temperature was relatively high and the air was in periods coming from Central Europe. Otherwise there were only few occasions with high concentrations. The values in 1998 were generally slightly lower than the corresponding 1997 values. The max. 24 hour and the max. 8 hour threshold values were exceeded on many occasions in 1998 at all stations. There were several exceedances as early as February and they continued up to and including August. It is always the 24 hour threshold that is exceeded in the winter. The threshold at 65 $\mu g/m^3$ is very close to the background

of the Northern Hemisphere. As shown previously (Kemp, Palmgren and Manscher, 1996a) the $O_3$ concentrations always reach this level at wind speeds above 10 m/s, especially from Northwest.

Table 3.1 Annual average values, percentiles and maximum values for $O_3$ measured in 1998 compared to threshold values. (Miljøministeriet 1994, EEC 1992). The eight-hour values are calculated in accordance with the EEC directive, as a non-overlapping moving average; they are calculated four times a day from the eight hourly values between 0 and 9, 8 and 17, 16 and 1, 12 and 21. (The results from Keldsnor/9055 are missing due to monitor problems).

| **$O_3$ (µg/m$^3$)** | Average | Median (hour) | 98-perc. (hour) | 99.9-perc. (hour) | max. 24 hours | max. 8 hours | max. 1 hour |
|---|---|---|---|---|---|---|---|
| **Urban Background:** | | | | | | | |
| Copenhagen/1259 | 48 | 49 | 97 | 125 | 102 | 123 | 145 |
| Odense/9159 | 50 | 52 | 95 | 142 | 110 | 144 | 156 |
| Aalborg/8159 | 49 | 53 | 89 | 117 | 88 | 111 | 149 |
| **Rural:** | | | | | | | |
| Lille Valby/2090 | 52 | 55 | 99 | 138 | 96 | 135 | 154 |
| Keldsnor/9055 | 58 | 61 | 104 | 137 | 108 | 134 | 156 |
| **Traffic:** | | | | | | | |
| Copenhagen/1257 | 33 | 31 | 77 | 99 | 77 | 92 | 119 |
| Threshold value | - | - | - | - | 65 | 110 | 200 |
| Average number of exceedances per station (excl. Copenhagen/1257) | - | - | - | - | 94 | 7 | 0 |

*AOT40*

UN-ECE uses the concept of critical levels to assess the effects of $O_3$ to agricultural crops and ecosystems (UN-ECE 1996). The effect parameter is calculated as the accumulated $O_3$ exposure above a threshold values of 40 ppb (≈ 80 µg/m$^3$), the so-called AOT40. The AOT40 value is calculated as the excess concentration for all hourly concentrations above 40 ppb.The guideline for crops is based on integration over all daylight hours during May-July, while the guideline for forest is based on the whole period April-September

The measured values in 1998 exceeded the UN-ECE guide value for crops (table 3.2). The reason for the high values is mainly relatively high $O_3$ levels in May (fig. 3.1) The forest related AOT40 values ended up close to the 1997 results due to low $O_3$ levels in August.

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

| Station | 1995 | 1996 | 1997 | 1998 |
|---|---|---|---|---|
| AOT40 (crops) | | | | |
| Lille Valby/2090 | 4700 | 1513 | 1409 | 3008 |
| Keldsnor/9055 | 2850 | 2540 | - | 4263 |
| Guide v. UN-ECE | | | | 3000 |
| AOT40 (forest) | | | | |
| Lille Valby/2090 | 8850 | 5510 | 5152 | 4940 |
| Keldsnor/9055 | 6800 | 8020 | - | 7040 |
| Guide v. UN-ECE | | | | 10000 |

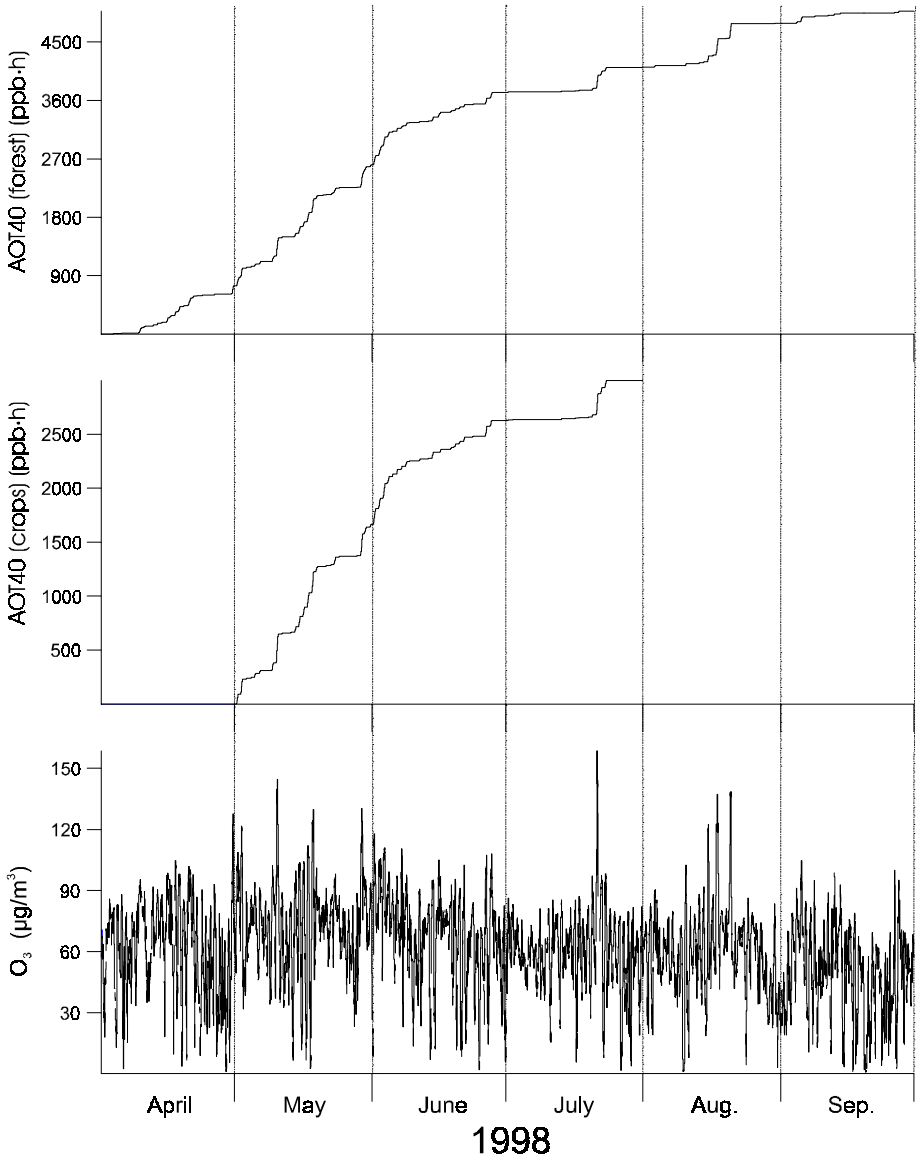


Figure 3.1 $O_3$ results from Lille Valby/2090. The lower curve is the measured ½-hour averages, while the two upper curves are the cumulated AOT40 values representing the values for crops and forest.

## 3.2 Episodes

*Threshold values*

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

- Date, hour and place of the occurrence of concentrations in excess of the above mentioned threshold values.
- Reference to the type(s) of treshold 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 highest hourly concentrations in Denmark of $O_3$ were in 1998 measured to around 150 µg/m$^3$. These values occurred at several occasions in May, July and August during short periods with warm weather during the generally rainy summer of 1998. As in 1997 no press releases were send out with reference to the information threshold at 180 µg/m$^3$.

## 3.3 Trend

*Trend for $O_3$ and $O_x$*

More than six years of data are now available from Lille Valby/2090. The development is illustrated by the annual averages and 98-percentiles in figure 3.3. The results are divided according to wind direction sectors. The sector from 40 to 160$^0$ represent the continental contribution with an addition of some regional contribution from the Copenhagen area, the sector from 180 to 240$^0$ represents the western part of Continental Europe, while the background contribution is assumed to be found in the sector from 260 to 20$^0$.

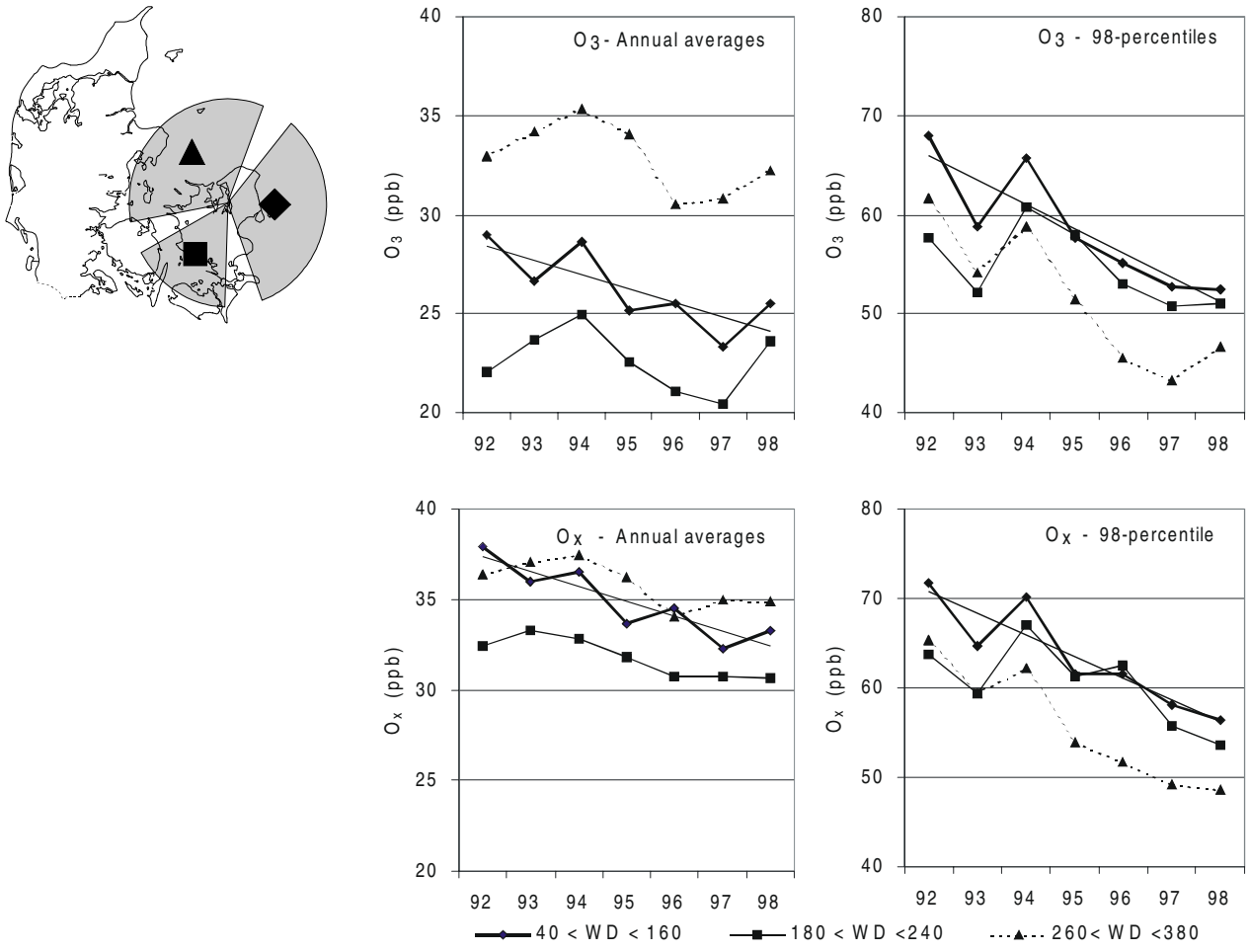


Figure 3.3 Annual averages and 98-percentiles measured at Lille Valby/2090 for $O_3$ and $O_x$ ($O_3$+$NO_2$). The wind sectors for the single curves are shown on the map. The signatures on the map correspond to the points on the curves.

The trends are in all cases statistically highly significant based on the assumption of a linear development. For the averages the decrease were 0.5-0.8 ppb/year, while it has been 1.5-3 ppb/year for the 98-percentiles. The decrease has been most evident for the 98-percentiles

and most evident for the eastern sector. This indicates that the increase of $O_3$ concentrations, which has been observed in measurements from 1876 to the end of the 1980's (Fenger, 1997) after a few years at a steady level, now have started a decrease.

The highest average concentrations of $O_3$ were observed in the background sector, while the $O_x$ concentrations were remarkably alike for all three sectors. This is in agreement with the results reported in the previous years (Kemp, Palmgren and Manscher, 1998). Further it can be noted that the difference between $O_3$ and $O_x$ is very small for the 98-percentiles.

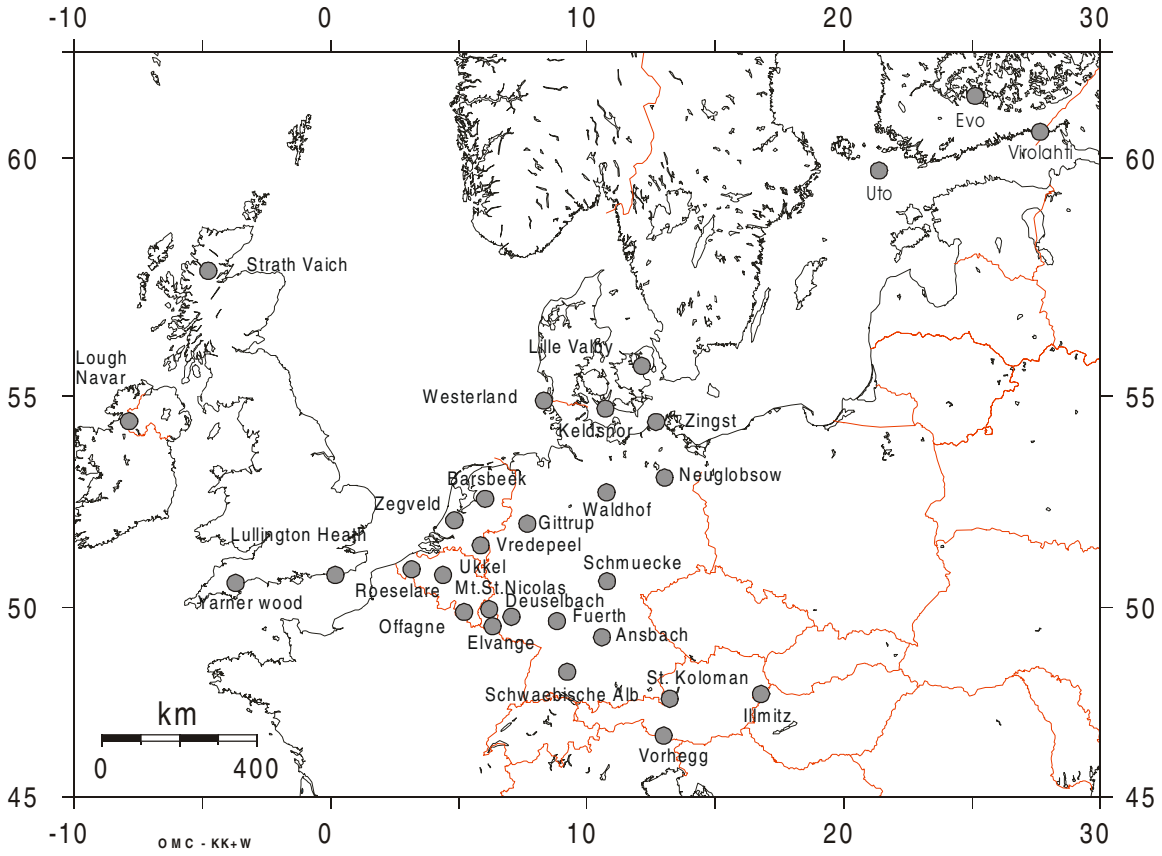


Figure 3.4 Sites participating in Smog Warners Data Exchange.

## 3.4 Smog Warners Data Exchange

A provisional system has been implemented for "on-line" exchange of $O_3$ measurement results between several north European countries. Every day before 10 am UTC the hourly maximum value for $O_3$ from the previous day and the latest available result from a number of sites in Austria, Belgium, Denmark, Finland, Germany, Holland, Luxembourg and UK are send by e-mail to AEA in UK. At 10 am UTC all collected results are returned to the participating organisations. The data exchange is established by the Technical Working Group on Data Exchange and Forecasting for Ozone episodes in Northwest Europe, which was initiated at the Ministerial Conference on Tropospheric Ozone in Northwest Europe held in London in May 1996. The purpose of the data exchange is primarily to supply data, which can be used for validation of models for forecasting of $O_3$ epi-

sodes. These episodes will usually cover a large part of the North Europe and will pass the area within a few days.

# 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 $H_2SO_4^-$ or $SO_4^{2-}$). The two main sources of the sulphate are the oxidation of $SO_2$ to $H_2SO_4$ and sulphate directly emitted from the sea. Sea spray will only contribute significantly to the sulphate at the stations in the Danish Air Quality Monitoring Programme during strong wind from west and north-west. The oxidation time for $SO_2$ in the atmosphere is of the order of one day meaning that the collected particulate sulphur to a large extent has been emitted from sources several hundred km from the stations, while the $SO_2$ may be of local origin as well as long range transported.

*Measurements*

In 1998 the concentration of $SO_2$ was determined as ½-hour average values at the three main stations (Copenhagen/1257, Odense/9155 and Aalborg/8151) and the background station (Lille Valby/2090). $SO_2$ and particulate sulphur were determined as 24-hour values at the same stations and at the additional station Odense/9154.

## 4.1 Annual statistics

*Limit values*

The measured $SO_2$ concentrations in Denmark are listed in table 4.1 together with the limit values (Miljøministeriet 1986). The set of limit values is a simplified, but more stringent, version of those laid down by EEC (EEC 1980, 1989). The medians and 98 percentiles are shown in figure 4.1. At all stations the measured values were well below the limit and guide values. The winter concentrations were somewhat higher than the values for the whole year.

Table 4.1 $SO_2$ and particulate sulphur pollution in Danish cities. The values are calculated for all valid 24 hour results from 1998. The winter is defined as the three first and three last months of the year. The number of measurements for $SO_2$ is given for the whole year/as well as for the winter.

| Station | $SO_2$ ($\mu g(SO_2)/m^3$) | | | | | | | Particulate S ($\mu g(S)/m^3$) | |
|---|---|---|---|---|---|---|---|---|---|
| | Number | Median year | Median winter | max. 3 days | 98-perc. | max. day | Average | Number | Average |
| Copenhagen/1257 | 350/179 | 3.6 | 3.9 | 16.0 | 16.0 | 23 | 4.4 | 347 | 1.37 |
| Odense/9155 | 363/182 | 1.6 | 1.7 | 9.8 | 11.1 | 13 | 2.2 | 356 | 1.29 |
| Odense/9154 | 361/179 | 1.4 | 1.6 | 11.5 | 11.4 | 16 | 2.1 | 359 | 1.31 |
| Aalborg/8151 | 348/173 | 1.6 | 1.6 | 8.0 | 14.0 | 43 | 2.7 | 346 | 1.30 |
| Lille Valby/2090 | 351/175 | 0.9 | 1.1 | 6.7 | 10.2 | 17 | 1.5 | 362 | 0.99 |
| Limit value | - | 80 | 130 | 250 | 250 | - | - | - | - |
| Guide - (EEC 1980) | - | - | - | - | | - | 40-60 | - | - |
| Guide - (WHO 1998) | - | - | - | - | - | 125 | 50 | - | - |

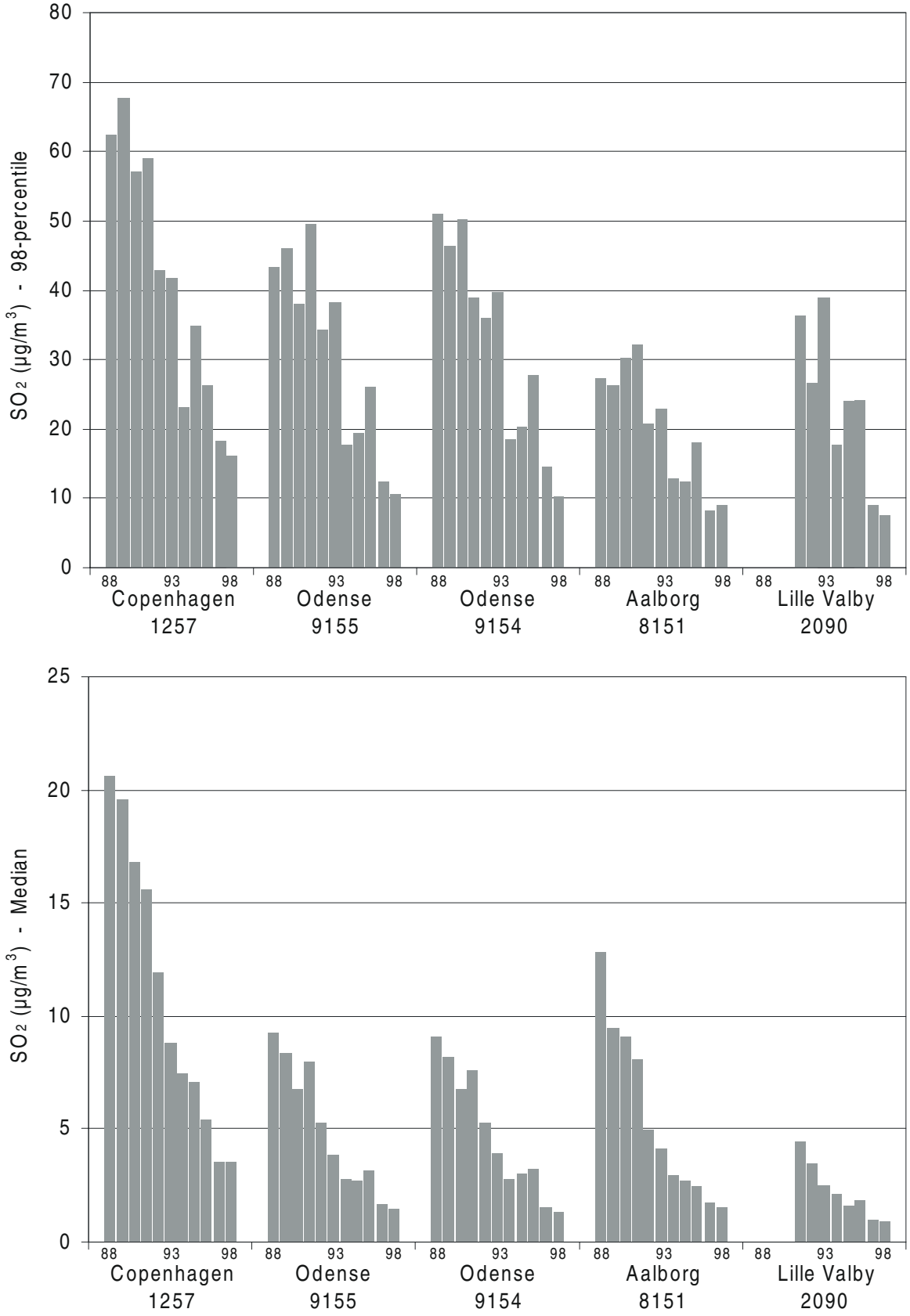


Figure 4.1 Medians and 98-percentiles for $SO_2$ from 1988 to 1998.

*New limit values*

The EU Council has adopted a new set of limit values for i.a $SO_2$ (EC, 1999) The new values are found in table 4.2 together with the measured results. The new limit values is to be met January 1, 2005. All measured values are far below the new values.

Table 4.2 Limit values in EU Directive 1999/30/EC (EC, 1999) and the corresponding measured results from 1998. The values in column 2 and 3 are for protection of human health, while the yearly and winter averages are for protection of ecosystems and shall only be met at rural sites.

| $SO_2$ µg/m$^3$ | 25$^{th}$ highest hour | Fourth highest day | Annual average | Winter average |
|---|---|---|---|---|
| Copenhagen/1257 | 36 | 17 | - | - |
| Odense/9155 | 33 | 11 | - | - |
| Odense/9154 | - | 12 | - | - |
| Aalborg/8151 | 48 | 15 | - | - |
| Lille Valby/2090 | 22 | 14 | 1.5 | 1.8 |
| New limit value | 350 | 125 | 20 | 20 |
| To be met | 2005 | 2005 | 19 July 2001 | 19 July 2001 |

*Drastic decrease in sulphur in 1997*

The measured values were considerably lower in 1997 than in 1996. The difference is mainly due to a much smaller contribution from Eastern Europe (Kemp, Palmgren and Manscher, 1998). The effect was observed for both $SO_2$ and particulate S. The pattern in 1998 was much like in 1997. This indicates that the decrease in concentration in fact correspond to a decrease in the emission in the east European countries.

*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 µg/m$^3$ for more than three consecutive hours and an immediate improvement is not expected. The new Directive (EC, 1999) includes an alert threshold at 500 µg/m$^3$ measured over three consecutive hours. Neither of these values are expected to be exceeded at any time in Denmark.

*Episode types*

The $SO_2$ episodes may occur during one of three different types of meteorological conditions:

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

*Measured maxima*

Table 4.3 shows the highest concentrations calculated according to the provisions in the warning system, at the three main stations and the background station. The $SO_2$ concentrations were far below the warning limit at 350 µg/m$^3$. The higest hour value at Aalborg/8151 was unusual high. It was connected to an incident September 23 (cf fig. 4.2)

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

| | $SO_2$ (µg($SO_2$)/m$^3$) | | | | | Particulate S (µg(S)/m$^3$) | |
|---|---|---|---|---|---|---|---|
| Station | Max. 3 hour | Day hour | Max hour | Day hour | "Hot-spot" episodes | Max. day | Day |
| Copenhagen/1257 | 47 | 981212:8 | 59 | 981212:9 | 1 | 6.0 | 980928 |
| Odense/9155 | 36 | 980122:4 | 79 | 980624:13 | 3 | 8.0 | 980927 |
| Odense/9154 | - | - | - | - | - | 7.9 | 980928 |
| Aalborg/8151 | 55 | 980515:13 | 278 | 980923:13 | 9 | 5.4 | 981125 |
| Lille Valby/2090 | 36 | 981212:7 | 43 | 981212:9 | 0 | 4.9 | 980928 |
| Warning limit | 350 | | - | | - | - | |

*Hot-spot episodes*

Hot-spot episodes are observed at irregular intervals in all three cities. We define hot-spot episodes as a more than 50 µg/m$^3$ increase and decrease of the $SO_2$ concentration within a period of less than 8 hours. The number of observed episodes are listed in table 4.3. The number of hot-spot episodes is in general decreasing. Two of the three hot-spot episodes in Odense occurred while the wind came from north, which, as in the previous years, points at the power plant north of Odense as the most likely source. In Aalborg the hot-spots occurred mainly when the wind was from north-east, indicating that the cement plant was the most likely source. No single source could be identified as the main contributor in Copenhagen.

*Episode of the year*

An unusual heavy hot-spot episode was observed in September 1998 at Aalborg/8151. In a short period from noon to midnight concentrations of $SO_2$ above 200 µg/m$^3$ were observed at several occasions (fig. 4.2). In the same period rather high concentrations of $NO_x$ were observed both at the street station Alborg/8151 and the roof station Aalborg/8159, but the course for $NO_x$ is somewhat different from that for $SO_2$. During the episode the wind was weak and the direction shifting. The high $NO_x$ values are probably caused by an accumulation of the emissions in the area due to the calm wind; while the $SO_2$ is an impact from a single nearby stack. The meteorological measurements give however not sufficient information to identify the source. Cl is the only other measured species which was found in unusual elevated concentration. The 23$^{th}$ the average concentration of Cl was measured to 5.1 µg/m$^3$, while it under similar meteorological conditions is below 1 µg/m$^3$. This episode shows that hot-spot incidents still may result in high concentrations of $SO_2$ even if the general level has been reduced by almost a factor of 10 the last 17 years.

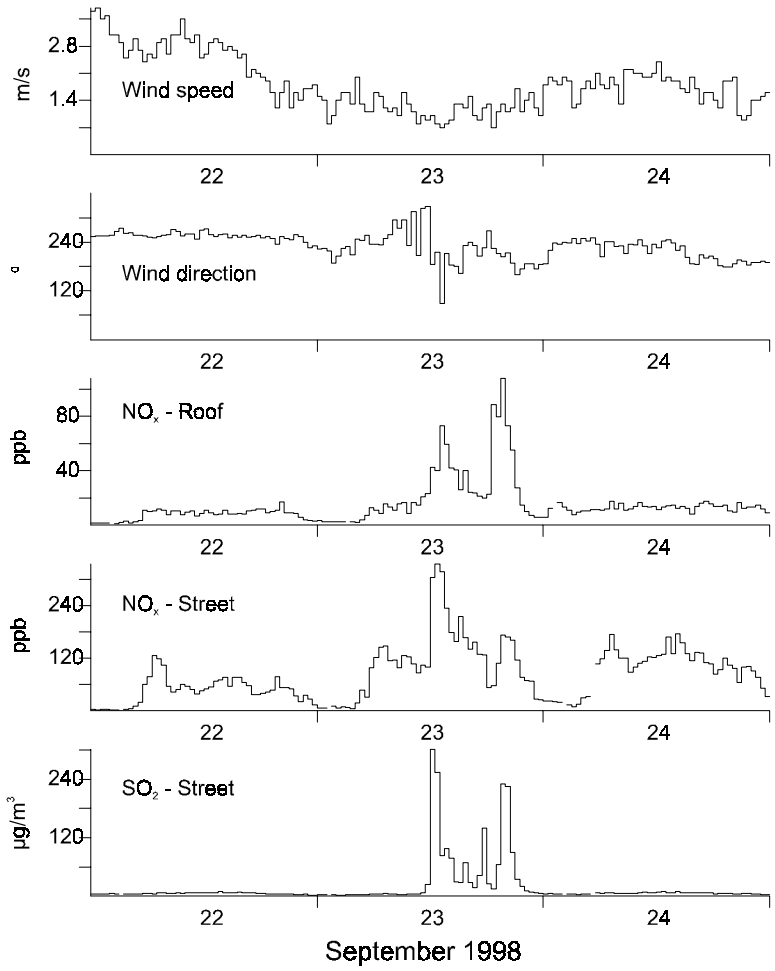


Figure 4.2 ½-hour averages from the stations Aalborg/8151 (street) and Aalborg/8159 (roof) September 22-24, 1998.

## 4.2 Trends

*Percentiles for $SO_2$*

The annual percentiles and average values based on daily average $SO_2$ concentrations measured at Aalborg/8151 are shown in figure 4.3. The level of $SO_2$ has been decreasing since 1982. The reduction is most evident for the "long term" values (median and average values), which are determined by the contributions from a number of local sources, while the long range transport episodes contribute very much to the 98-percentile and the other “short-term” values. After a couple of years with stagnation or even increase of the short term parameters the values for 1997 and 1998 were drastically reduced.

*Avarage $SO_2$ and S concentrations*

The trends for the monthly average values at Aalborg/8151 and Odense/9154 are shown in figure 4.4 and 4.5. The average $SO_2$ concentrations have been reduced with almost a factor of five, since it peaked around 1984. The steep decrease in 1985-86 was caused by a compulsory reduction of the sulphur content in fossil fuel from January 1986. Better combustion control and increased use of natural gas for domestic and district heating and introduction of lighter diesel oil are the main reasons.

Up to 1996 particulate S has, in contrast to $SO_2$, shown only a slightly downward trend. This is probably because the sulphur emission has been reduced more in Denmark than in our neighbouring countries.

The amount of particulate S may also be limited by the amount of compounds in the atmosphere that are able to oxidate $SO_2$. From 1996 to 1997 the concentrations of particulate S were reduced with more than 30 %. This is, as for $SO_2$, mainly caused by a reduction of the contribution from south-east (Kemp, Palmgren and Manscher, 1998). It will be interesting to follow the development the following years to see to what extent the decrease in concentrations is a result of reduced sulphur emissions

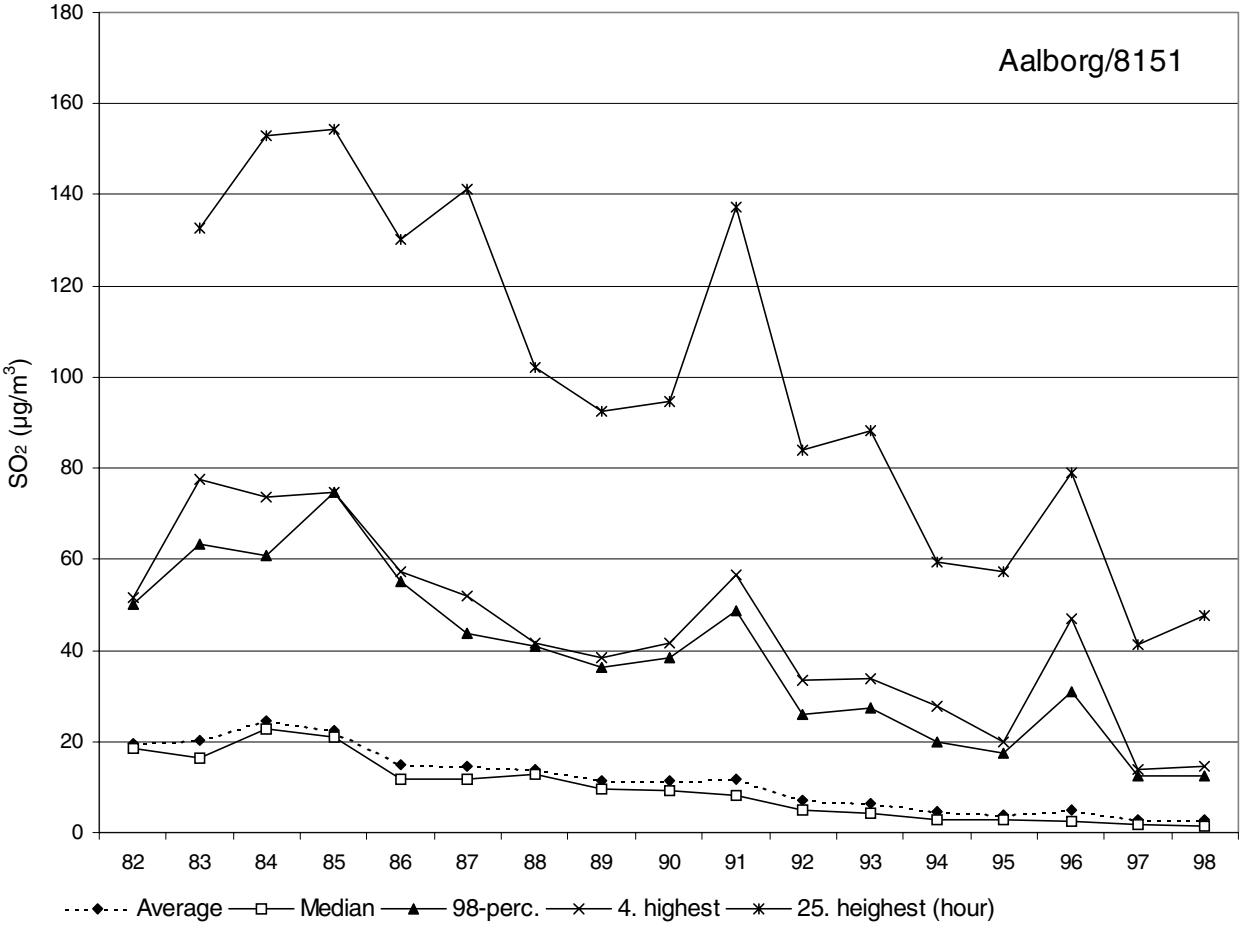


Figure 4.3 Trends for annual average value, median, 98-percentile and forth highest value based on daily results together with the 25th highest hourly average. All results are from Aalborg/8151.

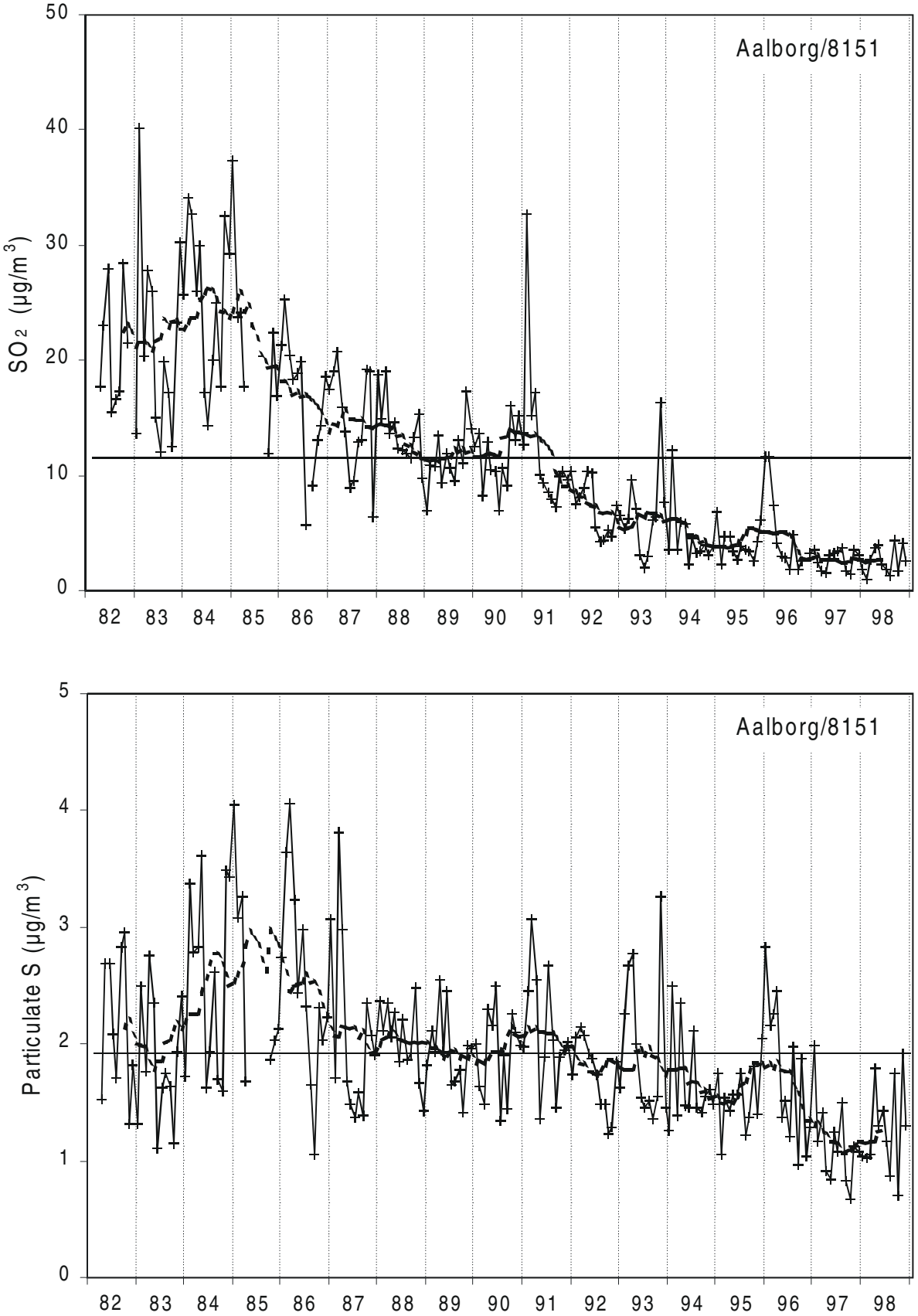


Figure 4.4 Trend for $SO_2$ and particulate S measured at Aalborg/8151. The points are measured monthly averages, the dotted curve is a moving average over 13 month and the straight line represents the average over the whole period.

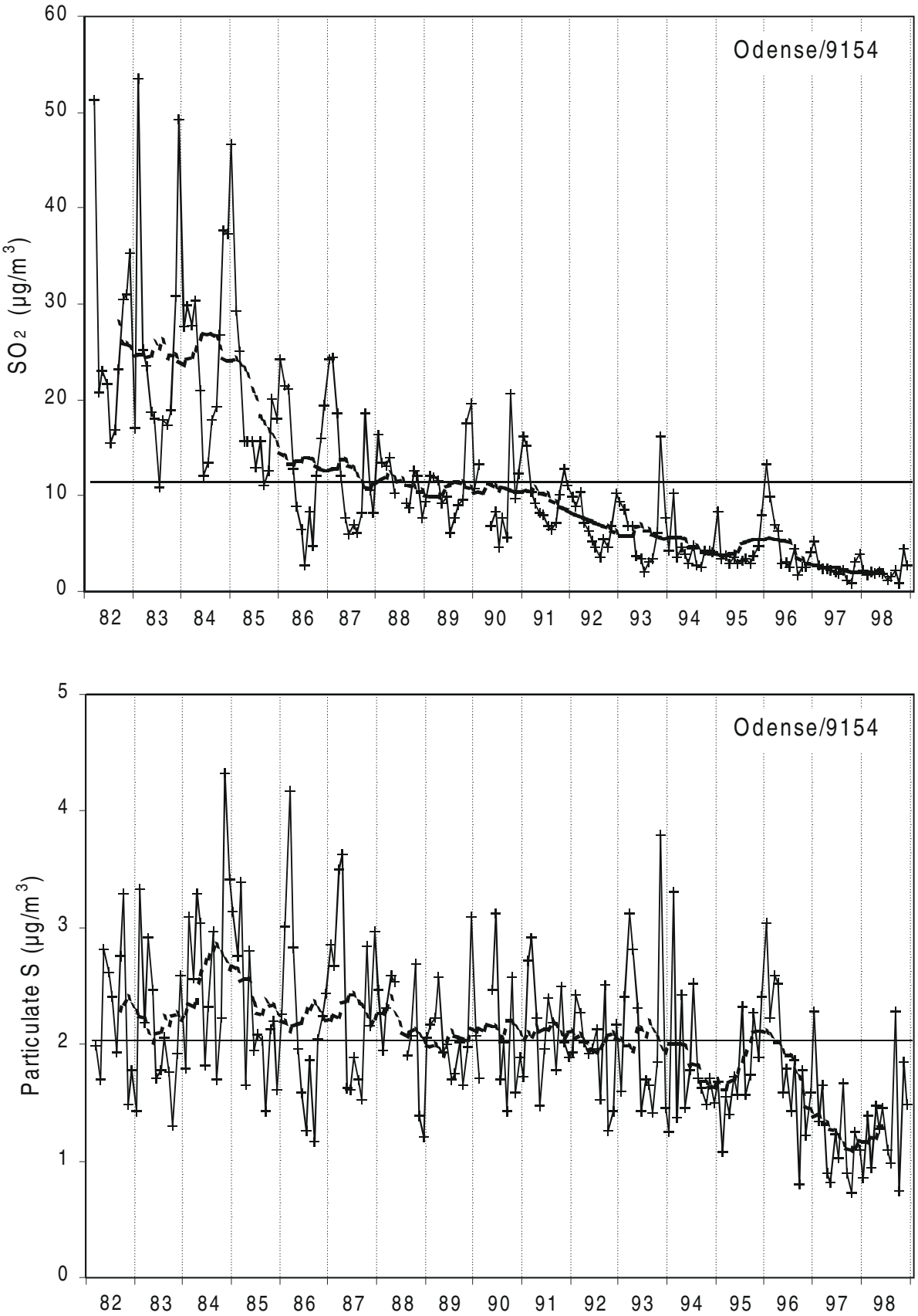


Figure 4.5 Trend for $SO_2$ and particulate S measured at Odense/9154. The points are measured monthly averages, the dotted curve is a moving average over 13 month and the straight line represents the average over the whole period.

# 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 aerodynamically diameter from about 10 to 50 µm depending on the wind speed (Kemp 1993).

*Sources*

The particles are a mixture from different source types:

- The coarse particles (> 1 µm) are windblown or resuspended soil dust of local origin, and mechanical generated particles from i.e. tires, bitumen and brakes.

- Fine particles (< 1 µm) from combustion processes as local traffic exhaust and long range transport. The "secondary aerosol" i.a. sulphate and nitrate particles, which are formed by oxidation of $SO_2$ and $NO_x$ during transport, is an important part of the long range transported aerosols.

*Sites*

TSP was in 1998 measured as 24 hour average values at Copenhagen/1257, Odense/9155, Odense/9154, Aalborg/8151 and Lille Valby/2090. The measurements at Lille Valby started in the beginning of 1995. Continuous measurement of $PM_{10}$ was started in July 1998. Sampling in 24 hour intervals is performed using an OPSIS SM200 sampler at Copenhagen/1257. The particles are collected on Membrane filters (Millipore type RA). The $PM_{10}$ is determined both on-line with the build-in β-gauge and gravimetric, using the same procedure as for TSP. The $PM_{10}$ results are described in section 5.4.

## 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 1998 are given in table 5.1. The annual 95-percentiles and average values are shown for 1988-1998 in figure 5.1, see next page.

Table 5.1 Average values, 95-percentiles and maximum values for TSP in 1998. The numbers are calculated for 24 hour average values.

| | | TSP (µg/m$^3$) | | | |
|---|---|---|---|---|---|
| Station | Number | Average - whole year | 95-perc. | Max. value | Day |
| Copenhagen/1257 | 346 | 46 | 89 | 346 | 980310 |
| Odense/9155 | 356 | 46 | 95 | 243 | 981120 |
| Odense/9154 | 359 | 39 | 76 | 125 | 981125 |
| Aalborg/8151 | 346 | 51 | 102 | 166 | 980406 |
| Lille Valby/2090 | 361 | 22 | 47 | 91 | 981124 |
| Limit value | min. 100 | 150 | 300 | - | - |

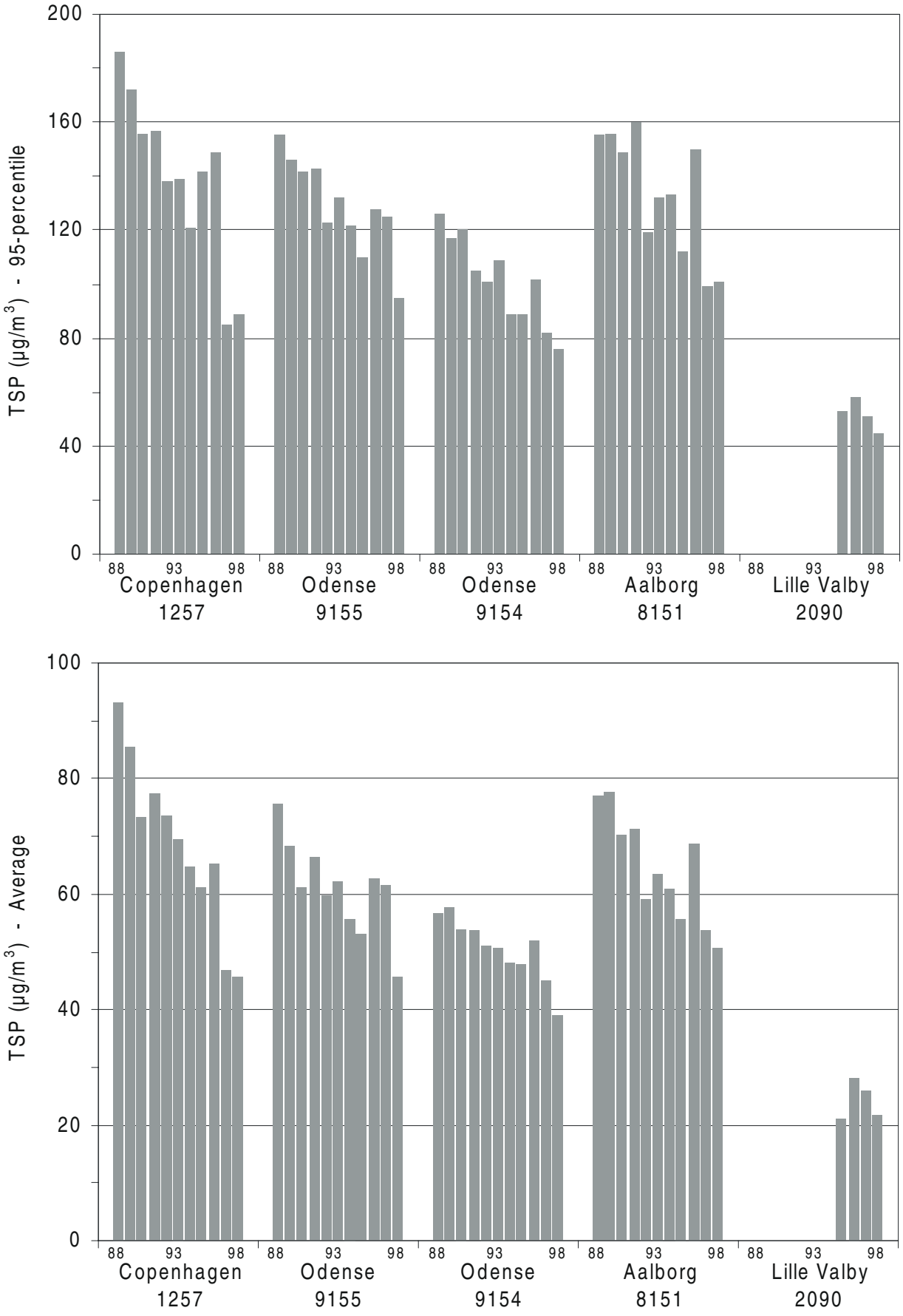


Figure 5.1 Average values and 95-percentiles for TSP from 1988 to 1998.

*Measured values*

The measured values at the urban stations were between 1/4 and 1/2 of the limit values. The 1998 results were not much different from the 1997 results. The general trend has been slightly decreasing since 1988 (figure 5.1, previous page) The concentration of particles from mechanical processes and resuspended soil particles may be expected to increase slightly in the coming years at traffic sites, if the present trend for more cars on the roads continues.

The particles from combustion processes in the fine particle fraction, is expected to decrease in the future due to reduction of the emission as a result of i.a. better cleaning of the smoke from power plants, obligatory TWC on petrol cars and restrictions on the diesel exhaust.

TSP has been measured at the rural station Lille Valby/2090 for almost 4 years. The results are between on third and one half of the results from the urban street stations.

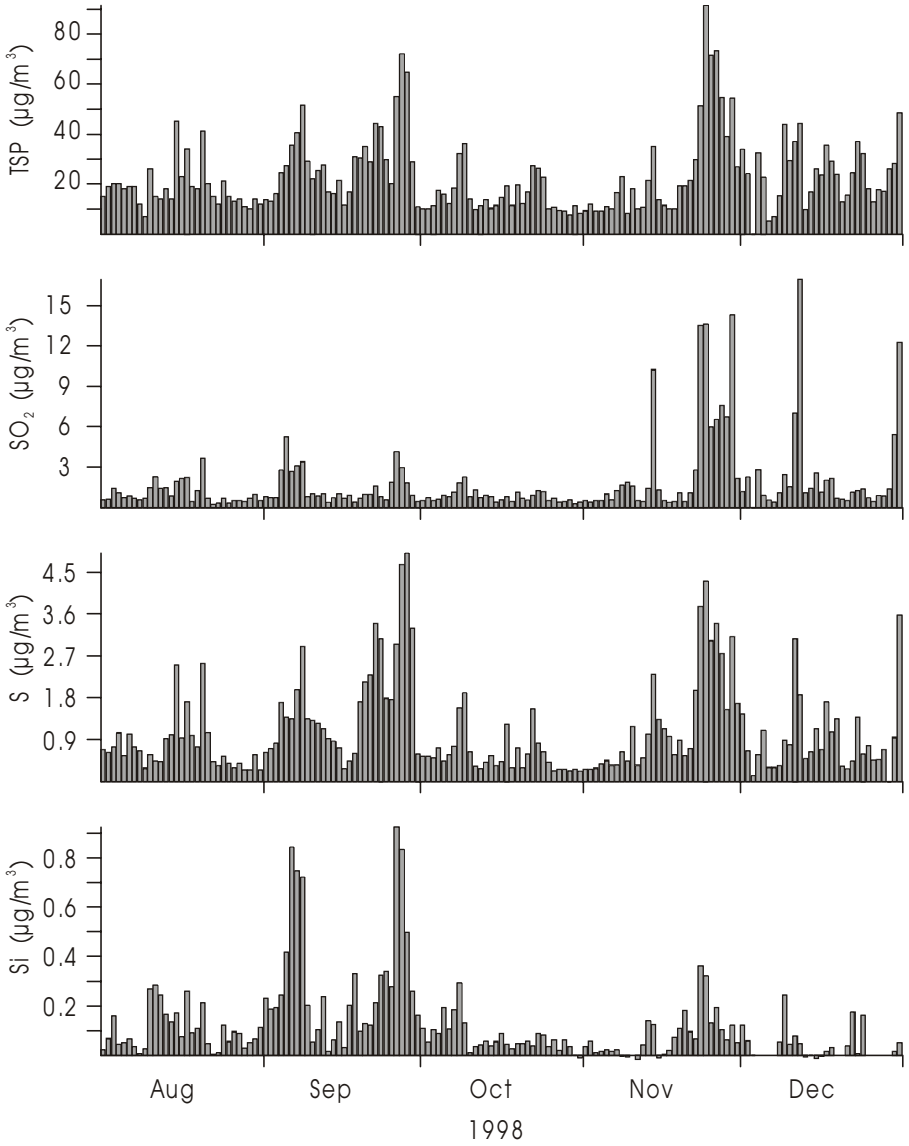


Figure 5.2 TSP episodes in September and November 1998

## 5.2 Episodes

The measured maxima of the daily average values are given in table 5.1, on page 33. There were two clear-cut episodes in 1998 (fig. 5.2). The first, in September, was a typical long range transport episode yielding relatively high concentrations of particulate S compared to $SO_2$. The wind was 4-7 m/s and stable from east. The second, November 25-29, was a local episode with relatively high values of $SO_2$ and wind speed <4 m/s during the episode.

## 5.3 Trends

*Percentiles*

The annual percentiles and average values based on daily average TSP concentrations measured at Aalborg/8151 are shown in figure 5.3. The level of TSP has been decreasing since 1986. The ratio between the "short term" values (95- and 98-percentiles) and the "long term" values (median and average) are almost constant in contrast to the case for $SO_2$ where the decrease was steeper for the long term than for the short term values.

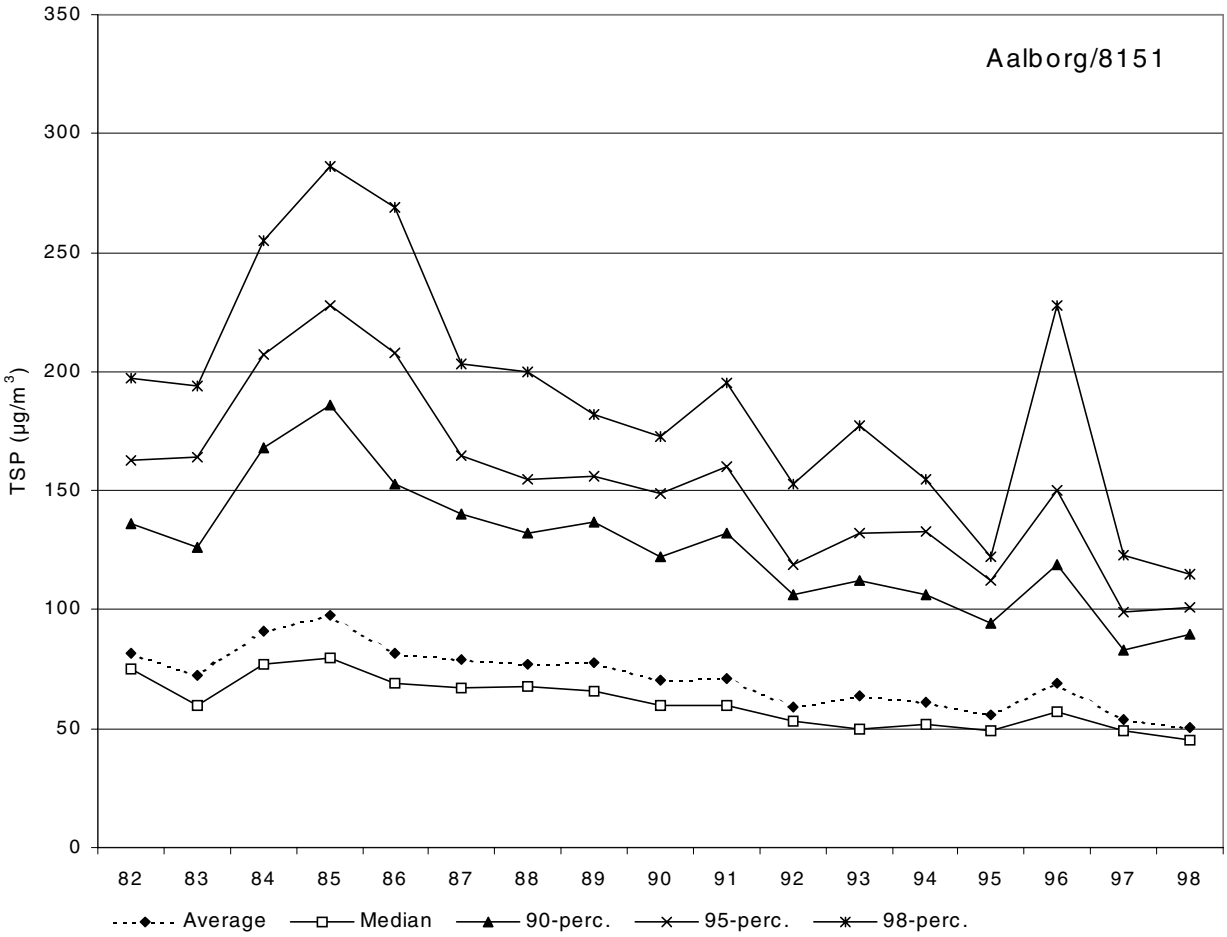


Figure 5.3 Trends for annual averages, median, 90-, 95 and 98-percentiles for TSP measured at Aalborg/8151.

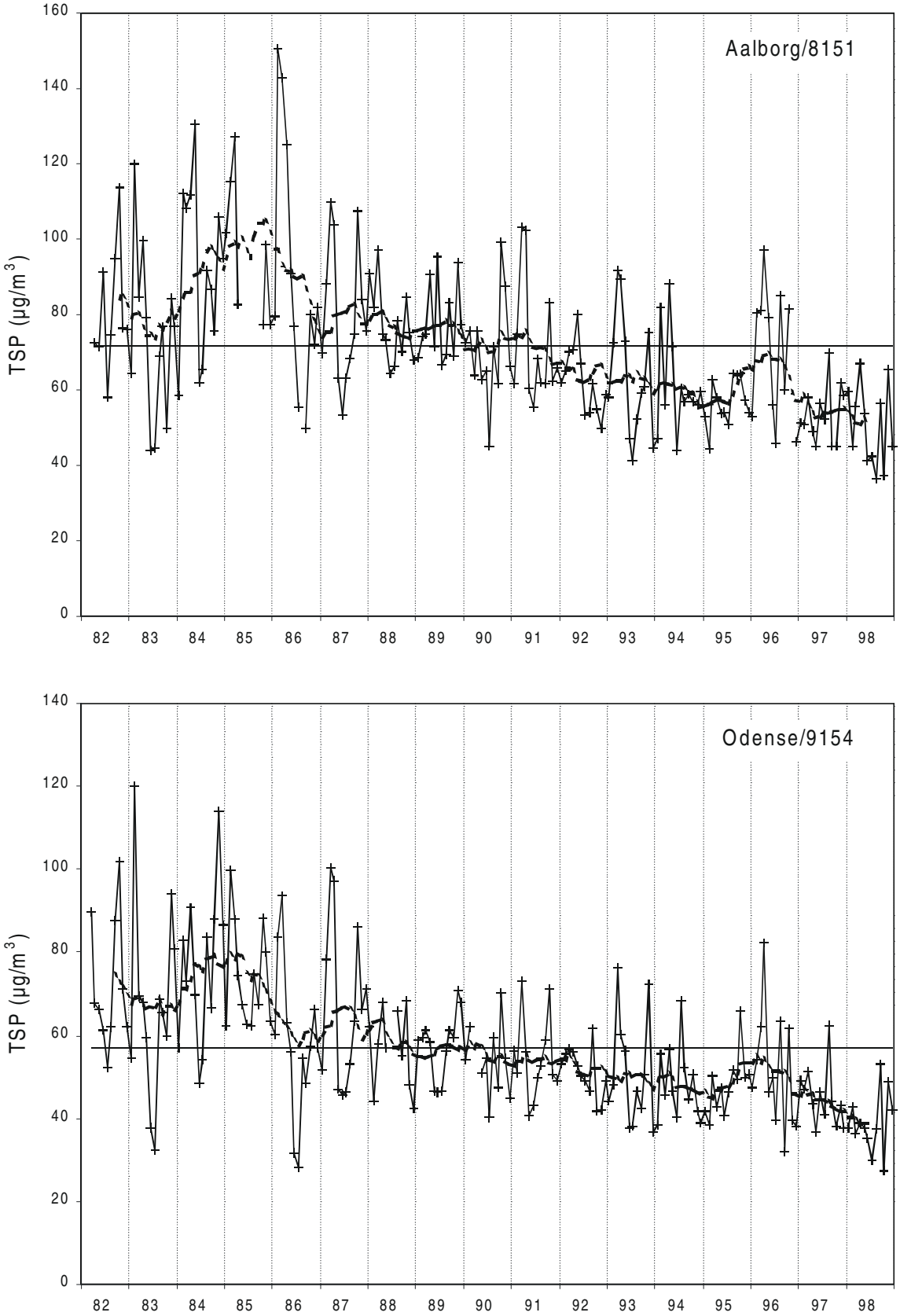


Figure 5.4 Trend for TSP measured at Aalborg/8151 and Odense/9154. . The points are measured monthly averages, the dotted curve is a moving average over 13 month and the straight line represents the average over the whole period.

*Annual average*

After relatively high concentrations from 1984-1986 there has been a continuous decrease since 1986 (figure 5.4). This is probably for mainly connected to the reduced contribution from the sources in the Central and Eastern Europe as seen for particulate sulphur (cf. chapter 4). But other factors like better emission control at power plants and other large combustion installations, the substitution of oil with natural gas for domestic heating and the obligatory demand for "winter crops" from 1987 may play an important role.

*Annual variation*

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

## 5.4 $PM_{10}$

*New limit values*

The EU Council has adopted a Directive giving new limit values based on $PM_{10}$, i.e. particles having an aerodynamical diameter <10 µm (EC, 1999). The limit values shall be met in two stages (see table 5.2). It is allowable that the limit values are exceeded if:

- It is owing to concentrations in ambient air due to natural events, which result in concentrations significantly in excess of normal background levels from natural sources. In such cases member states shall provide necessary justification to demonstrate that such exceedances are due to natural events.

- Member states have designated zones or agglomerations within which the limit values are exceeded due to resuspension of particles following winter sanding of roads. Member states shall provide the necessary justification to demonstrate that exceedances are due to resuspension and that reasonable measures have been taken to lower the concentrations.

The directive also imposes the member states to perform measurements of $PM_{2.5}$ at representative places and report the results of these measurements to the Commission.

Table 5.2 EU limit values for $PM_{10}$ (EC, 1999). All values are for protection of human health.

| | | Averaging | Limit value | Date by which limit value is to be met |
|---|---|---|---|---|
| Stage 1 | 24 hour limit value | 24 hours | 50 µg/m$^3$ not to be exceeded more than 35 times per year (90.4 percentile) | January 1, 2005 |
| | Annual Limit value | calendar year | 40 µg/m$^3$ | January 1, 2005 |
| Stage 2([1]) | 24 hour limit value | 24 hours | 50 µg/m$^3$ not to be exceeded more than 7 times per year (98 percentile) | January 1, 2010 |
| | Annual Limit value | calendar year | 20 µg/m$^3$ | January 1, 2010 |

([1]) Indicative limit values to be reviewed in the light of further information on health and environmental effects, technical feasibility and experience in the application of stage 1 limit values in the member states.

These $PM_{10}$ values are not directly comparable with the LMP results, which are based on TSP. Preliminary measurements indicate that the $PM_{10}$ values are about 75% of the measured TSP concentrations (see below). Having that in mind it seems like the concentrations at the traffic sites are somewhat higher than the new limit values.

*$PM_{10}$ and health*

The $PM_{10}$ was chosen as basis for the limit values because there exists a comprehensive collection of measurements. The only large epidemiological studies on health related effects of particles in outdoor air are based on $PM_{10}$ measurements. These studies indicate a correlation between the concentration of $PM_{10}$ in the atmosphere and the frequency of respiratory diseases. It has not been possible to derive a threshold below which no effects occur and the exposure-response curve fit probably a straight line reasonably well at concentrations below 100 $\mu g/m^3$. (WHO, 1996). The slope of this line for mortality is of the order 70 cases per one million people by a $PM_{10}$ increase of 10 $\mu g/m^3$. It is, however, not clear which effects are important for the health. The fine particles are the potential most harmful, because they penetrate deep into the lungs. The ultra fine particles (<0.1 µm) from diesel vehicles, which are emitted in a great number but carries little mass, fine particles (<0.5 µm) from traffic exhaust, and the secondary aerosols, which are formed by oxidation of e.g. $SO_2$ and $NO_{x,}$ may be the most harmful. It is expected that the knowledge in this field will be extended very much within the next few years. The $PM_{10}$ based limit values may be considered as interim limit values until we have gained the necessary knowledge (cf. footnote to table 5.2).

*$PM_{10}$ measurements*

$PM_{10}$ measurements were started in July 1998 at Copenhagen/1257 in parallel to the ongoing TSP sampling. The $PM_{10}$ particle concentration is determined both gravimetrically and with a β-gauge and the filters were analysed with PIXE, for the elemental composition of the dust, like the TSP filters. Some results of the about five months of parallel measurements are presented in the following.

The β-gauge is an indirect way of measuring the dust weight. The β absorption depends on the mass-thickness of the dust as well as on the elemental composition of the dust. Assuming that the composition does not vary very much, it is possible (with a suitable calibration) to obtain a good estimate of the thickness by measuring the difference between the absorption in the filter before and after exposure. Figure 5.5 shows a regression plot between the β-gauge and the gravimetric results. In average the results are very well correlated. A slope of 1.2 is compensated by a zero shift of around 6 $\mu g/m^3$ on the x-axis. This may be a result of the conditioning of the filters at 52% RH at room temperature prior to weighing, while the β-gauge measurement is carried out at $40^0$ C under ambient humidity.

Fig. 5.6 shows a comparison between simultaneous measurements of $PM_{10}$ and TSP. The correlation is fairly good and the average values are 36 $\mu g/m^3$ for $PM_{10}$ and 49 $\mu g/m^3$. The $PM_{10}$ results are in average around 75% of the TSP.

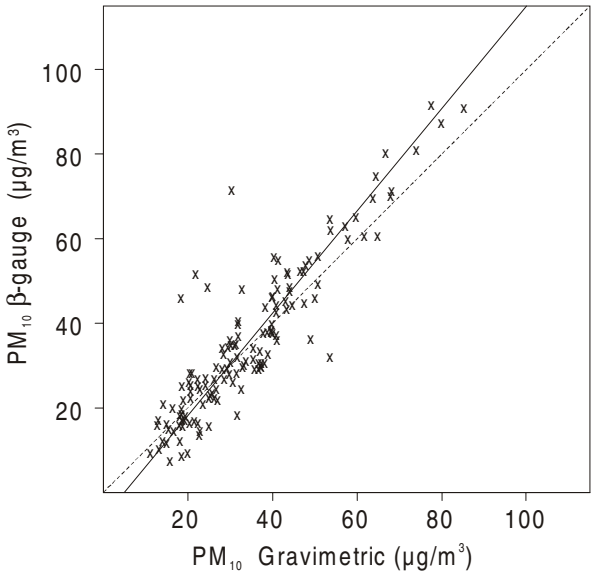


Figure 5.5 Comparison between β-gauge and gravimetric determination of the $PM_{10}$ concentration. The dotted line is 1:1 and the drawn line is the orthogonal regression line: y = 1.21 x – 5.9 µg/m$^3$ (ρ=0.93).

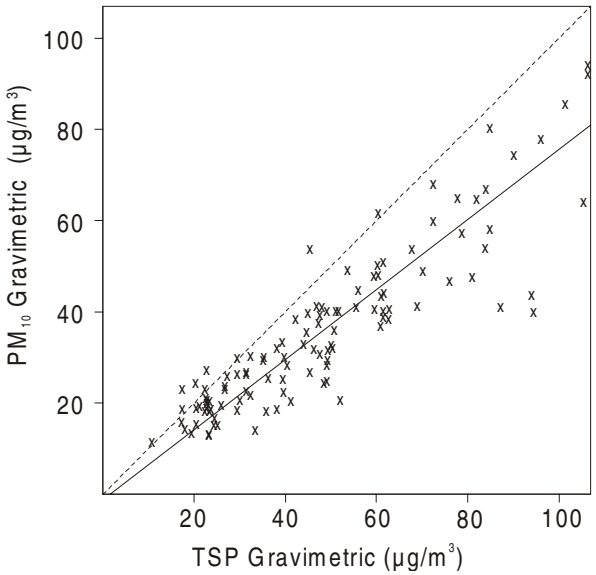


Figure 5.6 Comparison between TSP and $PM_{10}$. The dotted line is 1:1 and the drawn line is the orthogonal regression line: y = 0.77 x – 1.2 µg/m$^3$ (ρ=0.89).

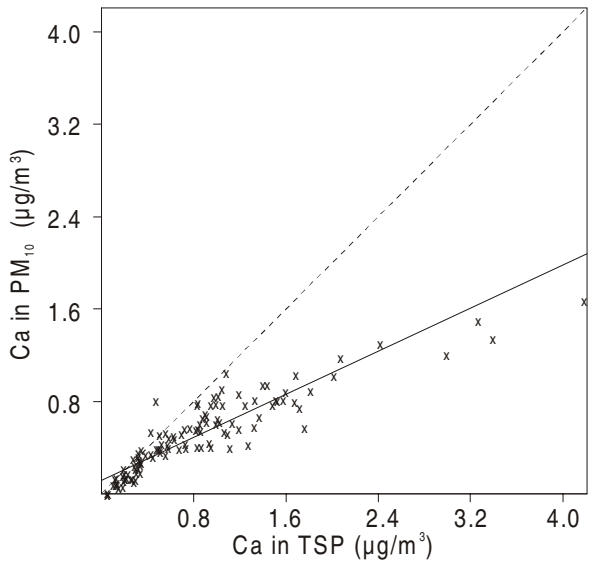


Figure 5.7 Comparison between particulate S in TSP and $PM_{10}$. The dotted line is 1:1 and the drawn line is the orthogonal regression line: y = 1.00 x – 0.1 µg/m$^3$ (ρ=0.98).

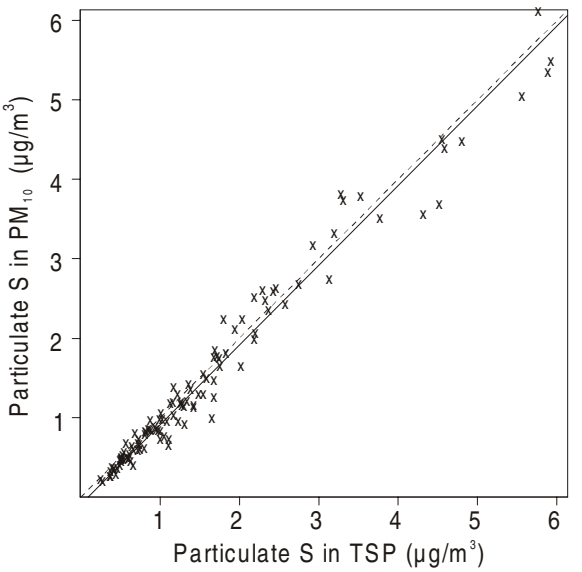


Figure 5.8 Comparison between Ca in TSP and $PM_{10}$. The dotted line is 1:1 and the drawn line is the orthogonal regression line: y = 0.47 x + 0.1 µg/m$^3$ (ρ=0.91).

The $PM_{10}$ average is almost at the level of the stage 1 limit value, but significantly higher than the stage 2 values (table 5.2). It is not possible to compare the results to the short-term values in table 5.2 because the results only cover about 1/3 of a year. A rough estimate indicates that 50 µg/m$^3$ have been exceeded around 60 times in 1998 compared to the accepted 35 times.

The difference between $PM_{10}$ and TSP is of cause the particles >10 µm. These particles are expected to be mainly windblown dust and, at the street stations, cause particles raised by the traffic. They will mainly be composed of soil minerals. Fig. 5.7 shows that there is no measurable difference between the S content in $PM_{10}$ and TSP. The S is mainly present in submicron particles as $SO_4^{--}$, which is formed in the atmosphere by oxidation of $SO_2$. Ca is a typical soil element and, as shown in fig. 5.8, about half is found in particles > 10µm.

*[Blank page]*

# 6 Elements

The aerosol samples are analysed by means of a true multi-element method (PIXE) (Kemp 1993). About 20 elements are found in concentrations above the detection limit in almost all samples, while about 5 more elements are found frequently. The elemental composition of the aerosols was in 1998 measured at all five stations in operation. In addition to monitoring purposes the measurement of the elements may be used for evaluation of the different source types that contribute to the pollution, because many of the elements mainly come from a single source type. For instance combustion of heavy oil is the main source of V and Ni, wind blown dust of Si, and particulate S is mainly caused by long range transport.

## 6.1 Annual statistics

The average values for the elements are listed in table 6.1 (next page).

*Exit lead*

Pb is at present the only element with an EU limit value. The annual average concentration must not exceed 2 $\mu g/m^3$ (EEC 1982). The limit value was laid down when the petrol was heavily leaded, app. 0.6 g/l. At present in practice all petrol sold in Denmark is unleaded. The limit value in the new daughter Directive (EC, 1999) is set to 0.5 $\mu g/m^3$ as annual average. The measured annual averages in 1998 were below 1 % of the present limit value and 2-3 % of the new limit value at the traffic sites in streets with heavy traffic (figure 6.1 and table 6.1). The main source for Pb at street level is not the local traffic any more, but long range transport (table 6.2). Pb was in 1983 closely correlated to NO, while the correlation with particulate S became dominating in 1998. At the present stage the level of Pb is comparable to other toxic heavy metals as e.g. As, Ni and Cd (cf. table 6.1). There seems to be no reason to treat Pb separately any more. In EU context the limit value for Pb is to be followed by limit values for As, Ni and Cd. A Directive is under preparation and is expected to be adopted within one to two years.

*New Years day*

New years days is an exception from the general trend for Pb due to the traditional launching of fireworks and occasional bonfires in the streets. A comparison between the annual averages and the concentrations New Years day shows that the concentration New Years day apparently have been increasing the last few years, probably as consequence of increased import of fireworks. Pb is only present in imported, i.e. mainly Chinese, fireworks as it is illegal to use Pb in fireworks produced in Denmark (Barfod, 1998). The contribution this one day may influence the annual average with some 5-10%.

Table 6.1 Average values for 1998. All concentrations are given as ng/m$^3$ (1 µg/m$^3$ = 1000 ng/m$^3$). $N_{tot}$ is the number of measurements in 1998. $N_0$ is the number of measurements above the detection limit. The arithmetic mean value are calculated for the measured concentrations, if more than 90% of the measurements were above the detection limit. If less than 90% of the measurements were above the detection limit, a fit to a log-normal distribution is calculated based on the values above the detection limit. The values in the tables represent in these cases the arithmetic mean value for the fitted distribution. The method is under normal conditions reliable if less than half of the measurements are below the detection limit and may in any case give an impression of the average values even if it is based on a few values only.

| | Copenhagen/1257 | | Odense/9155 | | Odense/9154 | | Aalborg/8151 | | Lille Valby/2090 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Element | $N_o$ | Average | $N_o$ | Average | $N_o$ | Average | $N_o$ | Average | $N_o$ | Average |
| Al | 345 | 419.0 | 342 | 473.0 | 355 | 293.0 | 343 | 428.0 | 270 | 108.0* |
| Si | 346 | 906.0 | 348 | 1090.0 | 351 | 600.0 | 341 | 929.0 | 289 | 179.0* |
| S | 347 | 1370.0 | 356 | 1290.0 | 359 | 1310.0 | 346 | 1300.0 | 360 | 999.0 |
| Cl | 347 | 1710.0 | 354 | 2190.0 | 358 | 1800.0 | 346 | 3160.0 | 347 | 545.0 |
| K | 347 | 243.0 | 356 | 272.0 | 359 | 226.0 | 346 | 250.0 | 360 | 143.0 |
| Ca | 347 | 709.0 | 356 | 845.0 | 359 | 465.0 | 346 | 763.0 | 348 | 148.0 |
| Ti | 347 | 41.3 | 355 | 47.7 | 359 | 31.3 | 346 | 40.6 | 336 | 7.0 |
| V | 345 | 6.1 | 333 | 5.0 | 341 | 4.7 | 327 | 4.4 | 339 | 3.8 |
| Cr | 342 | 5.2 | 331 | 4.4 | 342 | 4.5 | 332 | 4.0 | 126 | 0.6* |
| Mn | 347 | 15.9 | 356 | 21.1 | 359 | 17.0 | 346 | 12.0 | 354 | 3.0 |
| Fe | 347 | 983.0 | 356 | 851.0 | 359 | 549.0 | 346 | 889.0 | 360 | 84.5 |
| Ni | 347 | 3.1 | 354 | 2.5 | 358 | 2.4 | 346 | 2.6 | 355 | 1.5 |
| Cu | 347 | 49.4 | 356 | 29.2 | 359 | 19.4 | 346 | 37.5 | 337 | 2.2 |
| Zn | 347 | 50.0 | 356 | 65.4 | 359 | 41.4 | 346 | 54.7 | 354 | 16.0 |
| As | 242 | 1.2* | 226 | 1.2* | 223 | 1.0* | 187 | 1.1* | 204 | 0.8* |
| Se | 213 | 0.5* | 241 | 0.6* | 269 | 0.6* | 204 | 0.5* | 284 | 0.5* |
| Br | 346 | 4.7 | 356 | 4.9 | 359 | 4.8 | 346 | 6.2 | 359 | 3.4 |
| Sr | 346 | 3.8 | 355 | 3.7 | 356 | 2.5 | 346 | 4.1 | 305 | 1.0* |
| Zr | 331 | 3.4 | 293 | 3.0* | 311 | 1.8* | 321 | 3.0 | 38 | 0.3* |
| Mo | 262 | 2.9* | 175 | 1.9* | 163 | 1.4* | 234 | 2.2* | 12 | 0.9* |
| Cd | 32 | 1.2* | 44 | 1.1* | 29 | 1.1* | 22 | 0.9* | 30 | 1.1* |
| Sb | 300 | 13.2* | 191 | 7.6* | 171 | 4.9* | 249 | 8.9* | 8 | 2.3* |
| Ba | 265 | 25.4* | 217 | 24.7* | 204 | 15.3* | 248 | 23.0* | 3 | < 3 |
| Pb | 347 | 16.4 | 356 | 14.5 | 359 | 12.1 | 346 | 13.0 | 340 | 7.3 |
| Ntot | 347 | | 356 | | 359 | | 346 | | 361 | |

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

Table 6.2 Correlation coefficients between Pb, traffic represented by NO and long range transport represented by particulate S. The values are based on measurements at Aalborg/8151 in 1983 and1998.

| | 1983 | | 1998 | |
|---|---|---|---|---|
| | S | Pb | S | Pb |
| NO | 0.45 | 0.89 | 0.39 | 0.51 |
| S | | 0.49 | | 0.73 |

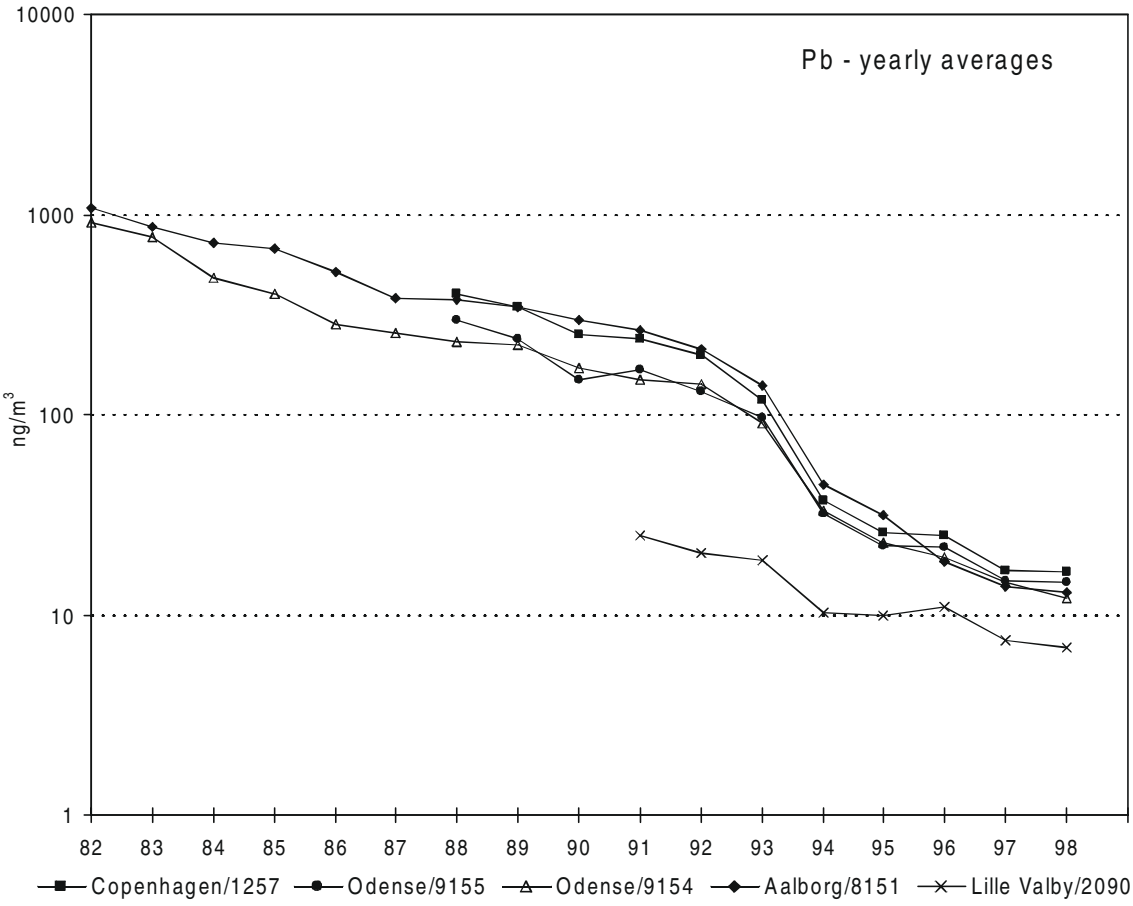


Figure 6.1 Trend for Pb measured at the LMP stations. Note that the y-axis is logarithmic.

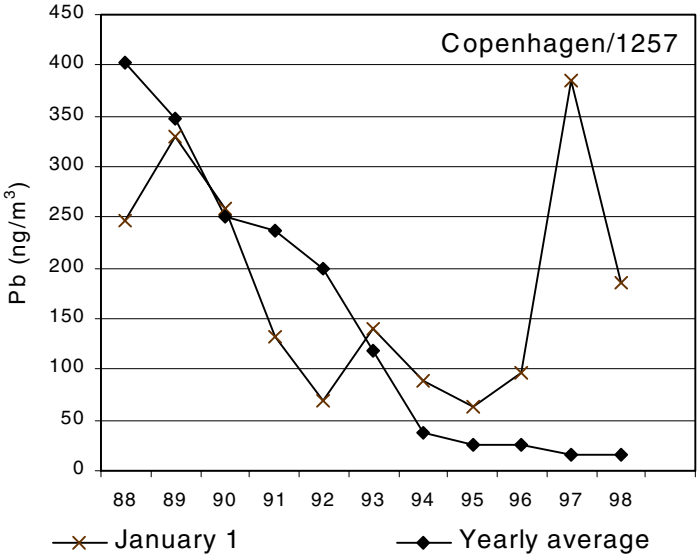


Figure 6.2 Measured concentration New Years day and annual averages at Copenhagen/1257.

## 6.2 Heavy metals in urban and rural areas

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

*Non-carcinogenic heavy metals*

Table 6.3 shows the WHO guidelines for yearly averages for the non-carcinogenic elements together with the corresponding measured values at Aalborg in 1982 and 1995 and at Copenhagen/1257, where in most cases the highest values are measured. Apart from Pb, 10 years ago, all measured values are more than a factor of 10 below the guideline values. Hg is not measured within the LMP programme, but estimates of the Hg pollution in the air in Europe indicates that the concentrations are between 0.001 and 20 ng/m$^3$ (Lahmann et al. 1986). The amount of V in urban air has decreased by a factor of 3-5 since 1982. It followed the reduction in the $SO_2$ concentrations and it is expected to decrease further in the future. Mn does only show a slightly decreasing trend.

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

| ng/m$^3$ | WHO guideline | Aalborg/8151 | Aalborg/8151 | Copenhagen/1257 |
|---|---|---|---|---|
| | | 1982 | 1998 | 1998 |
| V | 1000 | 22 | 4 | 6 |
| Mn | 150 | 20 | 12 | 16 |
| Cd | 5 | <2 | 0.9 | 1.2 |
| Hg | ~1000 | N.M. | N.M. | N.M |
| Pb | 500 | 1100 | 13 | 16 |

*Carcinogenic heavy metals*

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

Table 6.4 Estimated lifetime risks (WHO 1997) for carcinogenic heavy metals compared to measured concentrations.

| | Lifetime risk at 1 µg/m$^3$ | Aalborg/8151 1982 µg/m$^3$ | Aalborg/8151 1998 µg/m$^3$ | Copenhagen/1257 1998 µg/m$^3$ |
|---|---|---|---|---|
| Cr | [1] | 0.0029 | 0.0040 | 0.0052 |
| Ni | $3.8\times10^{-4}$ | 0.0070 | 0.0026 | 0.0031 |
| As | $1.5\times10^{-3}$ | <0.02 | 0.0011 | 0.0012 |

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

*Chromium*

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

*Nickel*

A linear extrapolation indicates that the measured Ni concentrations correspond to a life time risk above $10^{-6}$. The estimate becomes however further uncertain because the carcinogenic effect of various Ni compounds is very different and the partitioning between the different compounds in the air is not known. The WHO estimate is based on epidemiological data for workers at Ni refineries. The Ni pollution has been decreasing at all stations and it is expected to be further reduced. The major part of the Ni is emitted from oil burning and the trend is following that of $SO_2$ (see chapter 4). The difference between the concentrations at urban and background stations is decreasing, which indicates that the major part is long range transport.

*Arsenic*

The detection limit for determining As has unfortunately previously been too high to give reliable estimates of the yearly average values at the urban stations. However, data from 1994 and on are available due to the decreasing Pb concentrations (Pb interferes with the determination of As) and an improved data treatment method. The records go back to 1979 at the background stations and shows that the concentration has been reduced by a factor of 3 since 1979. The values for 1998 are almost equal at the background stations and the street stations in Odense and Aalborg, while the values in Copenhagen are somewhat higher. At present the concentrations correspond to a lifetime risk above $10^{-6}$. It can, as for Ni, be concluded that a major part of As is long range transported.

*Summary*

If the risks for the three elements are added the total lifetime risk may be estimated to more than $10^{-6}$. The variation of the concentration from station to station indicates that the occurrence of Cr is widespread over urban areas and Ni and As over the whole country.

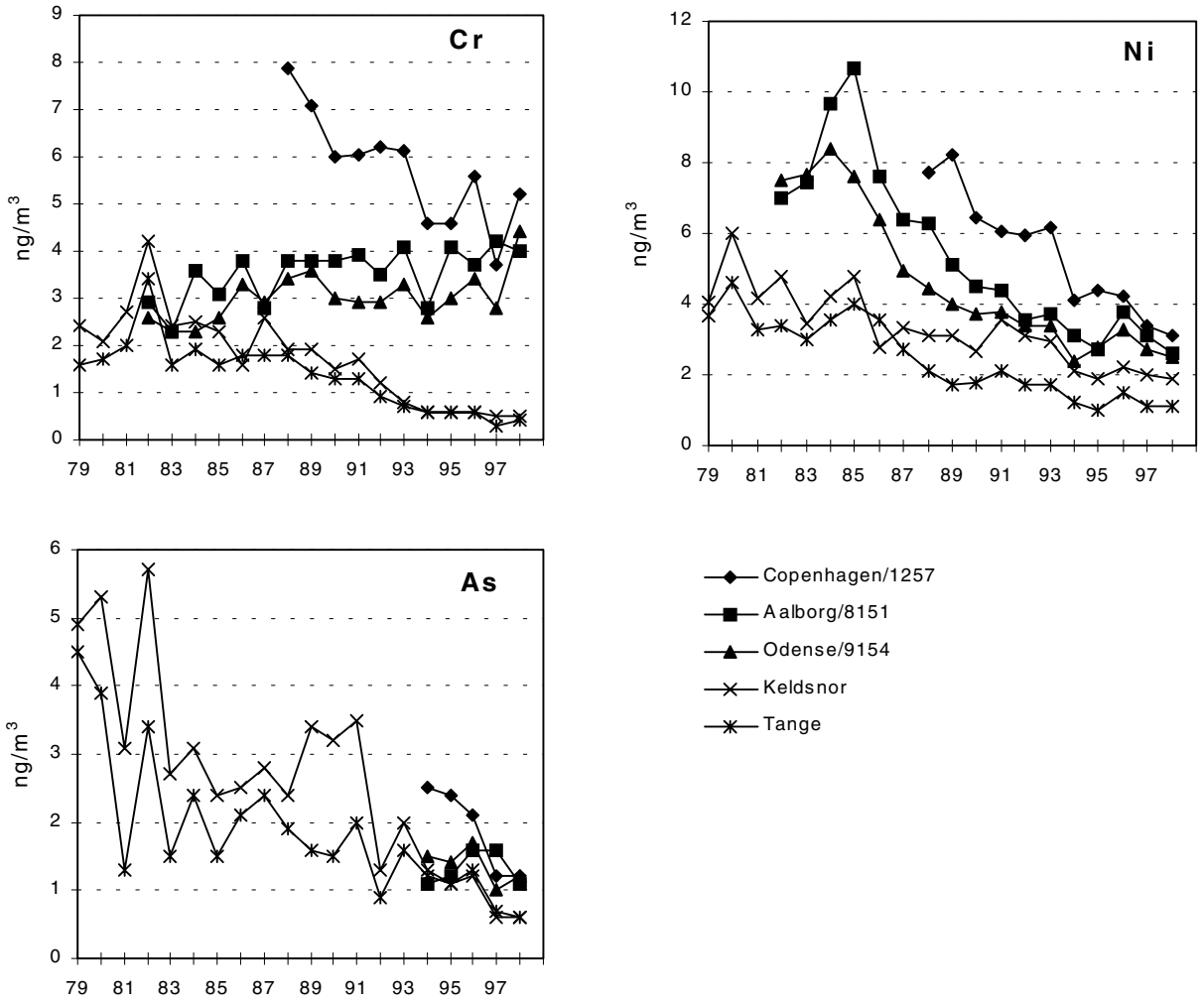


Figure 6.3 Yearly average values for the potential carcinogenic heavy metals. Results from the stations in the Danish Background Monitoring Program at Tange and Keldsnor are included for the comparison.

# 7 CO and VOC

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

*Sources*

The main source of CO, benzene and toluene is petrol vehicles. The CO is emitted due to incomplete combustion of the petrol. The TWC will remove the major part of the CO. There is practically no CO in the exhaust from diesel vehicles. It has been estimated that of the total hydrocarbon emission from motor vehicles in Denmark only about 9% came from diesel vehicles while petrol fuelled vehicles accounted for the remaining 91%; of the latter, about 59% came from the exhaust while 41% was released by evaporative emission (Danmarks Statistik 1993). The hydrocarbon content of vehicle exhausts are influenced by several factors related to driving mode and speed, ambient temperature, vehicle conditions (e.g. age and performance), fuel to air ratio and fuel type. A limit of 5% content of benzene has been introduced in 1986 in all EU-countries. The petrol in Denmark was produced with a benzene content between 3 and 5% depending on the content in the crude oil and the production processes. From 1995 petrol with approx. 2 % of benzene has been sold in the eastern part of Denmark (east of the Great Belt). The total content of aromatic compounds is 40-45 %. The emission of benzene depends on the content in petrol, but the emission is also linked to the total content of aromatic compounds in petrol, because benzene may be formed during the combustion process. The benzene content is now below 1%.

## 7.1 Annual statistics

*Statistics*

A number of statistical parameters are shown in table 7.1 and 7.2. Compared with 1997 (Kemp, Palmgren and Manscher, 1998) the CO levels were in 1998 generally slightly lower and the benzene and toluene concentrations were reduced by around 25% for the average and median and 10-20 % for the higher percentiles. For benzene the risk of cancer can be estimated to about $3 \cdot 10^{-5}$ at an life time exposure to the average value. The concentration of toluene seems not to be critical compared to the WHO guideline value. A EU Directive is in preparation for CO and benzene. A limit value for CO for the yearly maximum for a moving 8 hour average based on hourly value at 15

$mg/m^3$ is expected, while a limit value for the annual average of 5 $\mu g/m^3$ is expected for benzene. Both values are to be met in 2010. The 1998 values for CO were around half the expected new limit value (table 7.1). The measured yearly average in 1998 was close to the expected limit value; but the concentrations in 2010 will be well below the limit value if the present trend continues as expected.

Table 7.1 Statistical parameters based on hourly results for CO in 1998. All values are given in $\mu g/m^3$.

| Station | Average | Median (hour) | 98-perc. (hour) | 99.9-perc. (hour) | Max. 24 hour | Max. 8 hour *) | Max. 1 hour |
|---|---|---|---|---|---|---|---|
| Copenhagen/1257 | 1201 | 949 | 3704 | 7009 | 3741 | 5073 | 8519 |
| Odense/9155 | 866 | 570 | 3178 | 6321 | 3326 | 4970 | 11666 |
| Aalborg/8151 | 1192 | 879 | 4065 | 7250 | 3068 | 5339 | 8489 |
| Copenhagen/1259 | 352 | 303 | 949 | 2044 | 1108 | 1878 | 2465 |
| WHO guideline value | - | - | - | - | - | 10000 | 30000 |

*) The 8 hours values are calculated as a moving average based on hourly results.

Table 7.2 Statistical parameters based on hourly results for benzene and Toluene in 1998 measured at Copenhagen/1257 and Odense/9155. All values are given in $\mu g/m^3$. The values from Odense 9155 are based on only 8 months results. The lifetime risk and guideline value are from WHO, 1997. The 7 days maximum is calculated as a moving average based on 24 hour averages.

| Specie | Station | Average | Median (hour) | 98-perc. (hour) | 99.9-perc. (hour) | Max. 7 days | Lifetime risk at 1 $\mu g/m^3$ | Guideline for 7 days average |
|---|---|---|---|---|---|---|---|---|
| Benzene | Copenhagen/1257 | 7.0 | 5.3 | 21 | 41 | - | $4.4\text{-}7.5 \cdot 10^{-6}$ | - |
| | Odense/9155 | 4.8 | 2.8 | 20 | 43 | | | |
| Toluene | Copenhagen/1257 | 23 | 17 | 80 | 158 | 47 | - | 260 |
| | Odense/9155 | 16 | 9.3 | 75 | 150 | 34 | | |

## 7.2 Trends

The aromatic compounds show very high correlation with CO (Kemp, Palmgren and Manscher, 1998), which confirms that they were emitted from petrol powered vehicles. This was expected since the contribution of CO from diesel vehicles was relatively low at Jagtvej (~2%) and the emission of aromatic VOCs from diesel powered vehicles were expected to be unimportant. The main emission of aromatic compounds from diesel vehicles is expected to be heavier hydrocarbons and PAHs. The correlations between CO, benzene, toluene, ethylbenzene, n-, o- and p-xylene were generally high indicating that they have been emitted from the same type of sources.

*Emission*

The emissions and the meteorological conditions influence the trends of the air pollution concentrations. A technique to determine the emission from road traffic has been developed at NERI (Palmgren et al. 1999) based on inverse model calculations by the OSPM model (Berkowicz et al., 1997). The technique has been applied on CO, benzene and $NO_x$ data from Jagtvej in Copenhagen. In figure 7.1 are shown the measured concentrations of $NO_x$, benzene and CO from 1994 to 1998. In addition, the calculated daily emissions are shown

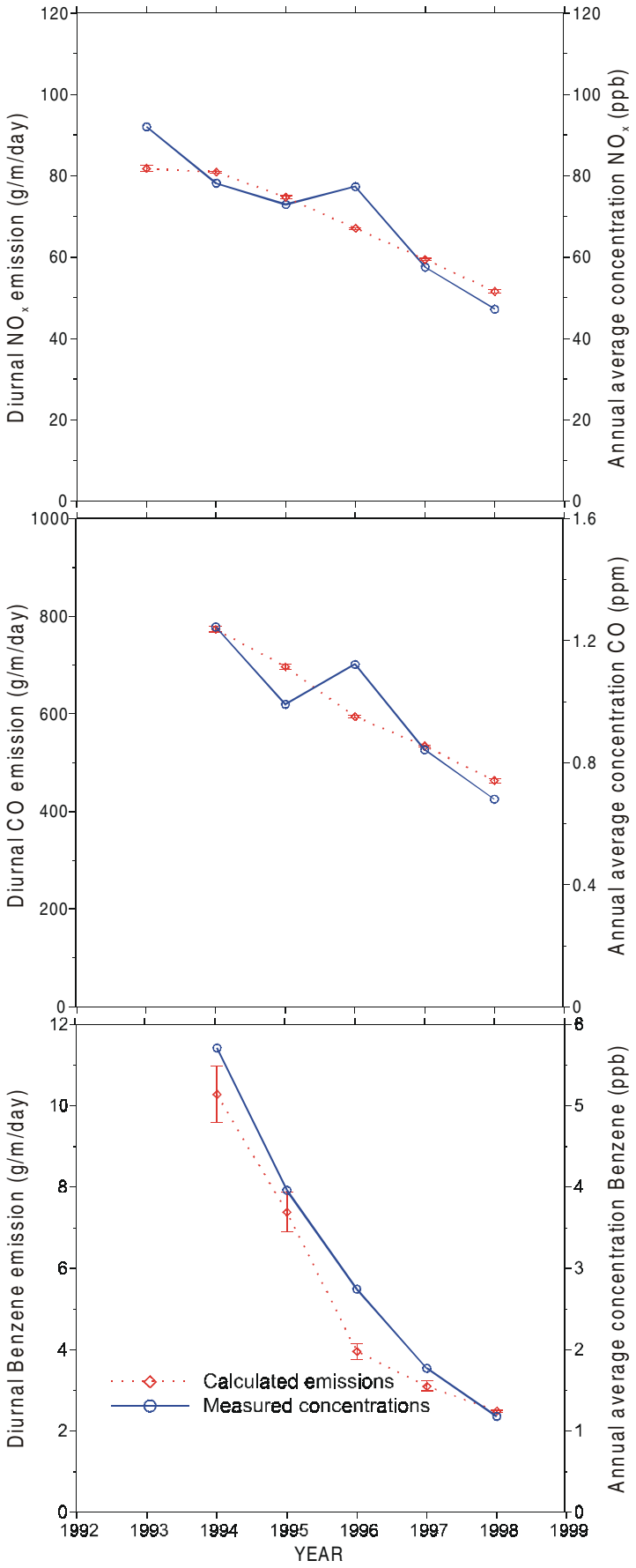


Figure 7.1 Trends of annual averages of $NO_x$, CO and benzene concentrations and calculated traffic emissions in Copenhagen (street canyon, Copenhagen/1257 (Jagtvej)). The concentrations are calculated as the contribution from the street by subtracting an estimated urban background from the measured values.

based on the inverse model calculation. Fluctuations in the concentrations of $NO_x$ and CO were observed due to the meteorological conditions, e. g. the concentrations were higher in 1996 than in 1995. However, the emissions decreased continuously from 1994 to 1998 due to the increasing number of TWC cars and nearly constant traffic flow at Jagtvej. For benzene more steep negative trends were observed for the concentration as well as for the emission. This is due to the reduced content of benzene in petrol from 1995 from approx. 3.5% to approx. 1% in 1998.

*Benzene/CO ratio*

The ratio between benzene (ppb) and CO (ppm) in 1994 -95 was 4.3. In the period 1998 the ratio was 1.6. The reduction in this ratio corresponds to the relative reduction in the benzene content of approx. 60%.

# 8 Conclusion

*Nitrogen dioxide*

The measured 98-percentiles for $NO_2$ were about half the limit value (200 µg/m$^3$), whereas medians were approximately close to the guide value (50 µg/m$^3$). The measured values were in 1998 slightly lower than in the previous years. A trend analysis covering the last 16 years showed that the $NO_2$ level has now started to decrease, while a more substantial decrease is observed for NO since 1993 as a result of the increasing number of cars with three way catalytic converters. The measured concentrations are close to the new EU limit.

*Ozone*

A set of threshold values for $O_3$ has been implemented in Denmark in 1994. The values are based on an EEC directive for protection of human health and vegetation. During 1998 some of the threshold values were exceeded frequently. The reduction of $O_3$ concentrations can only be obtained in an international co-operation, because the precursors to a large extent are emitted in other countries and because $O_3$ in the lower troposphere is a secondary pollutant. The precursors are $NO_x$ and organic gases which may be of either natural or anthropogenic origin. The present time series seems to indicate a downward going trend at a rate of around 0.5 ppb per year for the yearly averages..

*Sulphur dioxide*

The actual measured values at all stations were more than a factor of 10 lower than the limit values for $SO_2$. The measured values were more than a factor of 5 below the EEC guide values and the new EU limit values. There is a marked decrease of the $SO_2$ levels since 1982. The most pronounced reduction was observed in 1986 as a result of the decrease of the sulphur content in the fossil fuel products used in Denmark. But even in the recent years the concentrations have been decreasing due to better emission control on larger installations and the introduction of natural gas for i.e. domestic heating. The negotiation of international protocols for a further reduction of the $SO_2$ emission in the European countries will probably lead to a continuation of the downward going trend. The 1997 and 1998 results were considerably lower than the previous years. The decrease is mainly due to lower concentrations under winds from south-east. The results reflect probably lower emissions in eastern Europe.

*Particles (TSP and $PM_{10}$)*

The collected TSP is a mixture of "natural" wind blown dust (including the particles generated by the traffic) in form of coarse particles and anthropogenic derived fine particles. The measured concentrations were lower than half the limit values. A slightly decreasing trend has been observed for the last 10 years. The reduced contribution from long range transport is probably the main reason for this, but other factors as the "winter crops" during the winter and better control with the combustion processes do contribute. The decrease can thus be expected to continue in the future, i.a. due to the introduction of catalysts on all new gasoline driven cars, and as limitations on the particle emission from diesel vehicles become more stringent. The TSP values were slightly lower in 1998 than in the previous years. $PM_{10}$ measurements were started at the street station Copenhagen/1257. The available results, which cover the last five

months of 1998, show good correlation with TSP at a ratio of 3:4 between $PM_{10}$ and TSP. The average value is slightly below the new 2005 EU limit value, while the 50 $\mu g/m^3$ limit, which is not to be exceeded more then 35 times a calendar year, was exceeded 21 out of 118 days.

*Elements*

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

*CO and benzene*

CO was found in concentrations below the WHO guideline values, while the average concentration of benzene was approx. 4 $\mu g/m^3$, which is below the proposed new EU limit value for annual average. Petrol cars are the dominating source for both compounds at street level. The concentration of benzene decreased significantly from 1995 to 1998 due to less benzene in petrol.

*Smog warning*

A smog warning system was implemented from April 1994. It is for $SO_2$ and $NO_2$ a continuation of the provisional system, which was started in 1987. The population is warned through the public broadcast stations, if the concentration of either $SO_2$ or $NO_2$ exceeds 350 $\mu g/m^3$ in more than three consecutive hours and an immediate improvement is not expected. No warnings have been issued since the start in 1987 and, taking the measured concentrations and the expected development into account, it can with almost certainty be excluded that the warning limits will be exceeded in Denmark. $O_3$ has been included in the new system: The population is informed immediately if the hourly average concentration exceeds 180 $\mu g/m^3$ and if the hourly concentration exceeds 360 $\mu g/m^3$ a warning is issued to the population. The information threshold was not exceeded in 1998. The information threshold will statistically be exceeded once every second year. It is not realistic to assume that the warning threshold will be exceeded.

*Ultra short summary*

The results from the Danish Air Quality Program in 1998 showed that the concentrations found in the Danish cities were below the existing limit values, but the new EU limit values for $NO_2$ and $PM_{10}$ may be exceeded. The $O_3$ threshold values, which were implemented in 1994, are however frequently exceeded. The $NO_2$ concentrations were around half the limit value and a clear downward going trend was observed. The level of $O_3$ seems also to be slightly decreasing. The measurements in LMP III program aims i.a. at a description of the $O_3$-$NO_x$ interaction in order to reveal the effect of actions already taken to reduce the $NO_x$ emissions (obligatory three way catalysts on new gasoline driven cars and reduction of the emission from power plants) and the effect of future reductions, which hopefully will be realised through international protocols within the ECE-LRTAP convention and the coming EU acidification strategy for the emission of the $O_3$ precursors.

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# Danish Summary - Dansk resumé

**Det Landsdækkende Luftkvalitets Måleprogram**
**Årsrapport for 1998**

**Faglig rapport fra DMU nr. xxx**

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*LMP*

Luftkvaliteten i de danske byer overvåges gennem Det Landsdækkende Luftkvalitets Måleprogram (LMP). LMP startede i 1982 og er ændret med henblik på belysning af de aktuelle forureningsproblemer ved revisioner i 1987 og 1992. I det nuværende program (LMP III) foretages målinger i København, Odense og Aalborg i et samarbejde mellem Danmarks Miljøundersøgelser (DMU), Miljøstyrelsen, Hovedstadsregionens Luftovervågningsenhed (HLU), Fyns Amt og Ålborg kommune. Det praktiske arbejde udføres af DMU sammen med Miljøkontrollen i København, 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). Kampagnemålingerne er fra 1997 blevet udvidet så de foregår kontinuert gennem hele året. På basisstationen foretages således kontinuert måling af NO, $NO_2$, $SO_2$, CO, svævestøv samt grundstofindholdet i svævestøvet. På tagstationerne måles NO, $NO_2$ og $O_3$ koncentrationen i "taghøjde" samt følgende meteorologiske parametre: vindretning, vindhastighed, relativ fugtighed, temperatur og global stråling. I København måles desuden CO på tagstationen og $O_3$ i gadeniveau. Benzen og toluen måles i gadeniveau i København og Odense. Baggrundsforureningen måles på en station ved Lille Valby ca. 25 km vest for København og på Keldsnor på sydspidsen af Langeland. Ud over den generelle overvågning af luftkvaliteten er et væsentlig formål med LMP III programmet at give mulighed for at beskrive vekselvirkningen mellem, og dannelsen af $NO_x$ og $O_3$.

*Nye grænseværdier*

EU er igang med at indføre luftkvalitetsnormer, som skal gælde i alle medlemslandende. Det sker i form at et "rammedirektiv", som fastlægger de generelle retningslinierfastlæggelse af grænseværdier og strategier for vurdering af luftkvaliteten på grundlag af målinger på udvalgte steder kombineret med vurderinger af luftkvaliteten i større områder, bl.a. ved brug af modelberegninger. Rammedirektivet suppleres med en række "datterdirektiver", som fastlægger grænseværdier for enkelte stoffer. Rammedirektivet blev vedtaget i 1996 og det første datterdirektiv, som omfatter $SO_2$, $NO_2$, $NO_x$ ($NO+NO_2$), partik-

ler og Pb, er vedtaget i 1999. Der er desuden direktiver under udarbejdelse for CO, benzen og tungmetallerne Cr, As og Ni.

*Specialprogrammer*

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

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

*Nitrogenoxider*

For $NO_2$ (kapitel 2) er de målte koncentrationer i alle tilfælde under den gældende grænseværdi på 200 µg/m$^3$ for 98-percentilen og de vejledende værdier på 135 µg/m$^3$ for 98-percentilen og 50 µg/m$^3$ for medianen. Afstanden til de vejledende værdier er ikke ret stor. WHO's vejledende værdi på 40 µg/m$^3$ for årgennemsnittet og på 200 µg/m$^3$ for timegennemsnittet er overskredet i København. Emissionen af $NO_x$ fra benzindrevne bliver reduceret efterhånden som der kommer katalysatorer på flere og flere biler. Det er nu tydeligt at niveauet for NO er blevet reduceret siden begyndelsen af 1990'erne. Der kan nu også konstateres en svagt faldende tendens for $NO_2$; men reduktionen er ikke så stor som for NO fordi dannelsen af $NO_2$ i gaderum i væsentlig grad er begrænset af manglen på $O_3$. Emissionen fra de øvrige hovedkilder, dieselbiler og kraftværker, vil ikke blive ændret ret meget de første par år. Der er vedtaget et nyt EU Direktiv som bl.a. giver nye, væsentlig strengere, grænseværdier for $NO_2$ og $NO_x$ ($NO+NO_2$). De nye værdier er fastlagt udfra en vurdering af den skadelige effekt af kvælstofoxider. Grænseværdierne for $NO_2$ er fastlagt på grundlag af en helbredsmæssig vurdering. Grænseværdierne, 50 µg/m$^3$ for årsgennemsnittet og 200 µg/m$^3$ som 99,8 percentilen, er gældende fra 1. januar 2010. Den kommende grænseværdien for årsgennemsnittet var i 1998 overskredet i København. Til beskyttelse af plantevækst skal årsgennemsnittet for $NO_x$ i landområder være under 30 µg(ækvivalent $NO_2$)/m$^3$ fra 19. juli 2001. De målte koncentrationer er under halvdelen af denne værdi.

*Ozon*

De målte $O_3$ værdier (kapitel 3) var som tidligere næsten ens over hele landet. 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 1998. $O_3$ 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 µg/$m^3$. Hvis timemiddelværdien overskrider denne værdi, skal befolkningen underrettes. Det skete ikke i 1998. Målingerne på Lille Valby/2090, som startede i 1991, viser at der er en svagt faldende tendens for $O_3$ niveauerne.

*Svovldioxid*

Forureningen med $SO_2$ (kapitel 4) er klart faldende i Danmark. De målte koncentrationer var mere end en faktor 10 under grænseværdierne og mere end en faktor 5 under den i EU gældende vejledende værdi. De målte koncentrationer ligger også langt under de nye grænseværdier, som findes i det nye EU datterdirektiv. 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. Der der et markant fald i 98 percentilen for $SO_2$ og gennemsnitskoncentratioen af partikulært svovl i 1997 og 1998. Begge dele kan bruges som indikatorer for forurening transporteret over lange afstande. Det er ikke klart i hvor høj grad nedgangen skyldes mindre emissioner i Østeuropa, idet forskellige meteorologiske faktorer også kan have været afgørende.

*Svævestøv*

Den totale partikelkoncentration i luften, TSP (=Total Suspended Particulate matter) (kapitel 5) findes i byerne i koncentrationer på mellem 1/2 og 1/4 af grænseværdierne. TSP består af en blanding af bidrag fra flere kilder, hvoraf ophvirvlet og vindblæst støv, trafik og langtransporteret forurening er de væsentligste. Der er generelt en svagt nedadgående tendens for TSP. Den kan til dels forklares ved bedre kontrol med partikeludslippet ved forbrændingsprocesser (især kraftværker og trafik); men også de "grønne marker" om vinteren, som er blevet mere og mere udbredt, synes at have haft en virkning. De nye grænseværdier, som er vedtaget af EU, er baseret på $PM_{10}$ (dvs partikler med en aerodynamisk diameter mindre end 10 µm) i stedet for TSP. De målte TSP værdier er derfor ikke umiddelbart sammenlignelige med de nye grænseværdier. I sidste halvdel af 1998 er der gennemført $PM_{10}$ målinger på Jagtvej i København. På grundlag af disse målinger kan det skønnes, at årsgennemsnittet er tæt på grænseværdien på 40 µg/$m^3$, som er gældende fra 2005; mens døgnmiddelværdier på over 50 µg/$m^3$ forekommer 2 til 3 gange så hyppigt som de tilladte 35 gange pr. år. Det ventes, at grænseværdierne vil blive revideret i løbet af nogle år, da $PM_{10}$ næppe er den mest relevante partikelfraktion til vurdering af partiklernes sundhedsskadelige virkning. Det er med den nuværende viden ikke klart, hvilken fraktion der vil være den bedste. Men efter alt at dømme er helt små partikler (0.01 – 1 µm) de mest skadelige.

*Tungmetaller*

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 1998 var mere end en faktor 50 lavere end ved LMP-programmernes start i

1982. Der er i praksis ikke mere bly i benzin. Blyforurening er nu på niveau med flere andre tungmetaller. De målte koncentrationer i 1998 var en til to størrelsesordner under den gældende grænseværdi for årsgennemsnittet på 2 µg/$m^3$ og den nye på 0.5 µg/$m^3$. De øvrige tungmetaller findes gennemgående i lave koncentrationer. Cr, Ni og As kan findes i forbindelser, som er carcinogene. På grundlag af WHO's vurderinger kan det skønnes, at de målte koncentrationer udgør en livstidsrisiko på omkring 1:$10^6$ for udvikling af kræft.

*Kulmonoxid, benzen og toluen*

Der er gennemført målinger af CO på alle gadestationer samt på tagstationen i København. Der er målt flere organiske forbindelser, bl.a. benzen og toluen på gadestationerne i København og Odense (kapitel 7). CO-koncentrationerne var i 1998 under WHO's vejledende værdier. Benzenkoncentrationerne er faldet klart siden 1994 som følge af katalysatorerne og en nedsættelse af benzenindholdet i benzin. Målingerne bekræfter, at såvel CO som benzen hovedsageligt stammer fra benzinbiler.

*Resumé*

LMP resultaterne fra 1998 viser, at den forurening, der findes i de danske byer, var under de gældende grænseværdier, men tærskelværdierne for $O_3$ blev overskredet jævnligt. Selv om $NO_2$ koncentrationerne var under grænseværdien, var de dog ret tæt på. LMP III programmet har bl.a. til hensigt at give grundlag for en beskrivelse af $O_3$-$NO_x$ vekselvirkningen i byatmosfæren, så virkningen af emissionsbegrænsende foranstaltninger (katalysatorer på nye biler og reduktion af udslippet fra kraftværker) kan dokumenters. På længere sigt vil konsekvenserne af internationale protokoller for reduktion af udslippet af udgangsstofferne for $O_3$ forhåbentlig også slå igennem.

# National Environmental Research Institute

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