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TNO-report

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In search for trends of ozone and precursors
– First Progress Report TROTREP
Workpackage 3, partner 4 –

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Foreword

TROTREP (TROpospheric ozone: TREnds, budgets and Policy) is an EU Fifth Framework project to study trends of ozone and precursors in Europe over the last 10-20 years. TROTREP started in February 2000 and runs until February 2003. Workpackage 3 of TROTREP is concerned with data quality, statistical modelling and trends in the observations. This progress report describes a study carried out by TNO (partner 4) towards trends in a polluted area of Europe. The area consists of The Netherlands, Flanders and Northrhine-Westphalia, with additional information from one site in Wallonia, and two sites in neighbouring German provinces.

This study in workpackage 3 is about halfway. Chapter 5 outlines activities and ideas for the next 12 months. The intention is to finish this study with a second progress report, followed by one or more articles in a scientific journal.

This study reviews the suitability of a few of the regular networks in Europe for trend detection. The author realises that the regular monitoring networks in Europe were designed in the first place to provide information on air quality. Initially the focus was on air quality and air quality exceedences in polluted places, later interest grew to monitor also the less polluted (non-urban) areas. Criticism on the data collection and processing in the network must be seen in the context of reviewing a network in its ability to provide information (trends) for which it was not intended. A similar consideration holds for the Moerdijk VOC data. There, the measurement strategy was directed to monitor VOC concentrations near a large refinery. In this study the data is examined whether the refinery influence can be filtered out in order to link the remaining data to larger scale developments.

Summary

The European Commission has proposed the Ozone Daughter Directive in order to avoid, or to reduce as much as possible, exposure of the population and the ecosystem to harmful levels of ozone and acidifying and euthrophying species. Tropospheric ozone, acidification and euthrophication are interrelated themes with partially overlapping pollutants and sources, and with chemical interaction in the atmosphere. The proposal is based on an integrated approach to reach the environmental targets in a cost effective manner. In order to achieve the protection targets substantial emission reductions of NO_x, VOC, SO_2 and NH_3 are required, which are described in the accompanying Emission Ceiling Directives. In most of the EU-15 countries the NO_x and VOC emissions in 2010 are capped at a value that is 50-60% lower than their 1990 levels.

It is clear that in the case of ozone substantial emission reductions of the precursors are required to reduce ozone levels. However, the precise amount of reductions is difficult to estimate, and therefore models are indispensable tools to quantify emission reductions and to indicate regional differences. A weak aspect is that chemical dispersion models have never been adequately tested and validated in their predictive power of trends. Although the model's ability to describe a wide range of concentration levels produces confidence in a proper response of ozone to emission changes it is obvious that the models are not able to determine emission reductions with accuracy better than 30%. In other words: a 50% reduction is a reduction in the 40-60% range. The obvious questions then are: are the proposed reductions sufficient, or are they insufficient or perhaps overdone?

An indication of the effectiveness of emission reductions might come from looking in retrospect. In various countries ozone related measures were taken over the last 10-15 years. The emission changes can be considered as a large-scale experiment which allows testing our knowledge of the atmosphere's response. If the processes in the atmosphere behave according to the modelled processes, the time series of ozone should bear the corresponding signal.

In the EU Fifth Framework project TROTREP, long time series of observations are examined with the purpose to detect changes in the ozone concentrations that could be linked to emission changes. If so, it would provide information about the effectivity of measures in the past, which could be instrumental in assessing the potential of future measures.

An area in North-western Europe was selected to develop and apply methods to improve the reliability of trend estimates of the observed ozone and precursor concentrations. The Netherlands, Flanders and Northrhine-Westphalia are three relatively small but highly polluted areas with a high density of monitoring stations.

The conclusion is that trend detection of ozone and precursors requires a thorough and extended analysis of the observational data. Data quality aspects are extremely

important to trends, and especially to small trends, such as those of ozone. The intercomparison of data provided by different institutes appeared essential in detecting data quality problems. In at least one case a jump in the data was seen that could be ascribed to instrumental matters. Other problems that were observed related to shifts in the lower detection limit, or in the processing of near zero concentrations (especially NO and NO_2).

The current NO_x monitors are not sensitive enough to accurately follow changes in the lowest segments of the distribution. A better account of NO_x changes in the atmosphere comes from the changes under more polluted conditions (winter; higher percentiles). Under these conditions coherent trends of NO_x in The Netherlands and Northrhine-Westphalia were found. Over the last 10 years the average NO_x concentrations have dropped by about 30%. There are indications that in Northrhine-Westphalia the onset of reductions started a few years earlier. These findings are in good agreement with the trends of the national NO_x emissions in The Netherlands and Germany. The officially reported Belgian emissions show a much smaller trend but this is not reflected by less downward trends at the Netherlands sites close the border with Belgium. More Belgian NO_x data from observations is needed to corroborate this.

The only time series of VOCs with a length of more than 10 years is at Moerdijk in The Netherlands, near a large VOC emitting refinery. Although the Moerdijk station is set up and designed to monitor the concentration levels near the refinery, the data contain useful information in the other wind sectors. A discontinuity in sampling time (hourly versus daily averages) and a discontinuity in the wind data complicate the filtering of data from the influence of the refinery. Application of a provisional filter resulted nevertheless in an excellent agreement between the trends of the filtered concentrations of ethene and acetylene, and the Netherlands traffic emission trends of these components.
For propene however the trends did not match. It is not clear whether the discrepancy is due to the filtering method, or to a discrepancy between reported and actual emissions. For ethene and acetylene a reduction of 50-60% was found over the 1981-1999 period. The reduction seems to have started after 1985.

Due to various instrumental limitations the time series of ozone and oxidant selected for further analysis was rather short (1993-1998). A statistical regression model, incorporating various meteorological terms and two trend terms, appeared able to explain about 80% of the daily maximum ozone summer variance. Coherent trends for ozone and oxidant at two neighbouring stations at both sides of the German-Dutch border were found only for the 1993-1998 period. Including earlier years produced significant discrepancies in trends.
Downward trends of ozone and oxidant are observed for the higher percentiles of the distributions. Upward trends are seen for the lower percentiles of the distributions. There is clearly a contribution to the upward ozone trends from the reduced titration by NO. Whether the upward trend of the lower oxidant concentrations

(when titration does not play a role) is a result of changes in the chemistry of the atmosphere (OH, UV,..), or a result of an increase of the northern hemispheric background concentrations is not clear yet. Extending the analysis with more stations and also including the winter period could shed more light on this.
A preliminary comparison with model calculations indicated that the sign of the ozone and oxidant changes were correct, but that the magnitude of the observed changes was larger than in the model results. The first impression is that the ozone (and oxidant) peaks are more efficiently scavenged than expected, whereas the lower part of the ozone (and oxidant) distribution increases faster than according to the models.

In the next phase of this study the implications of this finding (if confirmed by trends at the other stations) on policy relevant parameters like the AOT40 and AOT60, and the number of exceedances of 60 ppb, will be investigated.

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1. Introduction

TROTREP which stands for: TROpospheric ozone: TREnds, budgets and Policy, is an EU Fifth Framework project that aims to evaluate, validate and predict the effectiveness of past and future EU air quality legislation with respect to ozone and its precursors. The incentive to formulate such a project has been the notion that the ever growing time series of observations could be used to retrieve information concerning the realisation of measures taken to comply with past and current ozone policy. The work is organised along two different but complementary lines: 1) the collection and detailed analysis of observational data, and 2) the analysis of model data.
The work is divided in ten work packages. In work package 3, long time series of ozone and precursor data are analysed. A polluted area is selected as well as a few less polluted areas in Europe.

This progress report describes a trend analysis of ozone and precursor data in a polluted area in Europe. The area covers: The Netherlands, Flanders in Belgium and Northrhine-Westphalia in Germany (Figure B1). Data providers in this area are respectively RIVM (Rijksinstituut voor Volksgezondheid and Milieu), VMM (Vlaamse Milieumaatschappij) and Landesumweltamt Nordrhein-Westfalen (LUA-NRW). Added to this is one site in Wallonia, the French speaking part of Belgium (data from Institut Scientifique de Service Public (ISSEP)), and three German sites operated by Umweltbundesamt (UBA). The Belgian data are obtained through the Belgian Interregional Cell for the Environment (IRCELINE).

There are various reasons to select this area:

- The three main sub-areas (Netherlands, Flanders and Northrhine-Westphalia) have similar characteristics in terms of population density (Table 1), and consequently, in emission density of nitrogen oxides (NO_x) and Volatile Organic Compounds (VOC);
- The data comes from 35 non-urban sites operated by 5 different institutes and covering an area less than 100.000 km^2. Additional measurement data (NO, NO_2, meteorology, CO, SO_2) is available. VOC data is sparsely available.
- The three sub-areas have undergone a transition from relatively little change in emissions in the 1980s to a rapid decrease in the 1990s. Although the rate of decrease has not been the same, in all three sub-areas there has been a substantial drop of emissions.
- The data providers are nearby and air quality data are quickly provided.
- According to chemical dispersion models (EMEP, LOTOS, ..) this area is the NO_x-heart of Europe: NO_x emission reduction (up to –50%) will result in ozone increases (for most of the ozone distribution).

Table 1 *Characteristics of the three sub-areas*

	Size (km^2)	Population (inhabitants)	Population density (inh/km^2)
Northrhine-Westphalia	34.000	17.700.000	520
Netherlands	33.000	15.500.000	470
Flanders	14.000	6.000.000	428

The objective of the study (the data analysis) is to investigate whether there are trends in ozone and precursors and if they can be quantitatively related to emission changes. Trends in ozone are, if any, usually small, in the order of 1 %/yr or less. It will be obvious that linking such small trends to changes in anthropogenic emissions requires the utmost to the quality of the data over a long period of time, and the identification of all processes that might have affected the ozone concentrations in the course of time. Briefly, the followings aspects are distinguished as potentially relevant to short-term and long-term changes in the ozone concentrations:

1. monitoring aspects;
2. local effects;
3. changes in the meteorological conditions;
4. changes in the chemical composition of the atmosphere (changes in OH, variation in biogenic emissions, changes in UV);
5. changes in the anthropogenic emissions.
6. hemispheric background

Based on experiences of the past the following steps are envisaged, applicable not only to ozone, but also to NO and NO_2, and to the combined species oxidant (O_x) and nitrogen oxides (NO_x):

- An analysis to the data quality, based on the data themselves, and later compared to the instrumental history, local changes (inlet height, local surroundings, local emissions).
- Quantification of the meteorological variability, for instance by means of a statistical model to connect meteorological data to air quality data.
- The development of a historical data base to account for regional differences in trends of emission factors, activity rates and abatement measures.
- An analysis of model calculations that connect emissions over the last 10-20 years to concentrations. This not only concerns the anthropogenic emissions, but also the biogenic emissions (as far as they depend on surface temperature). It also includes changes in the background ozone (outside the European lower troposphere, data provided by a global model), UV intensity and, again, meteorological variability (the model is driven by analysed meteorological fields).

In workpackage 3 of TROTREP the attention is on data quality and trend analysis of observational data. Emissions and modelling are the topics of workpackages 5 and 7 respectively.

Data quality aspects are addressed in Chapter 2 for ozone and chapter 4.1 and 4.3 for NO_x and a few selected VOCs. The effect of meteorological variability on ozone is examined by means of a statistical model (Chapter 3). A start has been made to quantify the effect of meteorological variability on NO_x concentrations by means of a dispersion model (Chapter 4.2). Discussion of the results and conclusions are given in chapter 5 and 6 respectively.

2. Data and data quality of ozone

The data quality aspect has been addressed in two steps: a careful examination of the data, followed by interviewing the data providers about the quality assurance and quality control procedures in their laboratories, and confronting them with “remarkable features” in the data. The emphasis of the analysis is on the 1987-1998 period. At the end of this chapter a short excursion will be made to data from the earlier years.

2.1 Data

The set of ozone stations consists of 18 RIVM sites, 6 VMM sites, 1 ISSEP site, 7 LUA-NRW sites and 3 UBA sites (Fig. B.1). The location of the stations, and the length of the ozone records is given in Table B.1. The information about monitoring – and calibration equipment, sampling strategy, local surroundings, and historical developments is not complete. In this section a condensed description of monitoring procedures and local surroundings will be given.

2.1.1 RIVM

A description of the Dutch monitoring network after the reconstruction of the network in 1986 is given by RIVM (1989). It gives the specifications of the monitors at that time, the dimensions of the cabins, the inlet height (3.5 m) and the data handling procedures. For all monitoring sites the characteristics of the vicinity are given, such as characteristics of the landscape, direction and distance to highways and main roads (plus traffic density), and emissions of surface and point sources of NO_x and SO_x within about 10 km of the station (reference year emissions: 1980 or a few years earlier). A detailed map of the vicinity within about 5 km of the station is included.

An updated description of the network is given in Elzakker and Buijsman (1999).

Panorama photographs of the sites are present in the RIVM archives, but not available in an official document.

Ozone is measured in units of ppb, but stored in the data base in units of $\mu g.m^{-3}$. The conversion factor has always been 2.00 (Stolk, 2000). Data are stored as hourly averages of the hour preceding the marker hour. So, a value at 15.00h is the hourly average of 14.00h to 15.00h. All data is expressed in Central European Time (winter time).

The ozone monitor in operation in the network until the beginning of the 1990s was a Philips PW 9771 based on the chemiluminescent reaction of ozone and rhodamine B. This monitor type was replaced in a period between November 1990 and June 1992 by a Thermo Environmental Instrument (TEI) model 49W based on UV absorption at 254 nm. A more detailed description of both instruments can be found in Uiterwijk et al., 1990. It also reports the comparison between the old monitor and four candidate new monitors (including the TEI49W) according to a field campaign of two weeks conducted in the summer of 1989. The comparison showed a near 1-to-1 relation between the two instruments in the range from 0 to 60 $\mu g.m^{-3}$. At higher concentrations the new instrument tended to overpredict the ozone concentrations compared to the old instrument. After the replacement no parallel measurements were conducted at none of the stations. However, in 1992/1993 the operational accuracy and precision of the ozone monitoring in the National Monitoring Network was investigated by comparing monitoring station results with measurements by a comparison instrument, transported along a selection of 17 monitoring sites (Swaan, 1994). The conclusion was that the precision of the instruments is in agreement with the specification of the manufacturer, but that the status of calibration is highly variable, which lead to a large scatter in the measured concentrations (with respect to a reference monitor, and also with respect to the ambient air).
Participation in a European wide inter-comparison programme in October 1999 (Borowiak et al., 2000) showed that the Netherlands National Monitoring Network instrument configuration produced results for ozone which were consistently low by 5%, as compared to the assigned values of the supplied concentrations. (Note that all NO concentrations and the NO_2 concentrations of 100 ppb and more were also systematically high by 5%.*)*
The history of ozone monitoring is however more complicated than just a replacement of monitoring instruments. It involves also a change in on site calibration instruments, calibration method and practice, leading to the introduction of a 'correction' factor of 0.91 for the monitoring result to comply with the laboratory reference. This correction factor was built into the station processors software. The information on the calibration methods, reference and transfer standards in the section below is based on interviews with two elderly RIVM technicians, running the calibration laboratory from the early days of ozone monitoring.

From the beginning of ozone monitoring in the National Monitoring Network in about 1975 calibration was carried out during periodic (or as required additional) maintenance by and in the laboratory of the maintenance contractor. For this purpose a portable ozone source and a chemiluminescent (based on gas phase reaction with ethylene) ozone monitor were available.
On a monthly basis, the maintenance laboratory ozone source output was compared with the output of a similar source residing at the RIVM laboratory. The latter was calibrated against the RIVM gas phase titration (GFT) primary laboratory standard, using the excess nitric oxide method.

Proper functioning of the monitoring instruments during field operation was checked by daily zero and span measurements, ozone being produced by an internal ozone source. When results were outside established tolerance limits recalibration was carried out at the maintenance laboratory.
At about 1985 the transfer standards were replaced by TEI model PS49 UV-photometric analysers with built in ozone source. The TEI PS 49 UV-photometric system compared well (within 3%) with the existing GFT laboratory standard. Since than the photometric system was in fact used as the primary laboratory standard, but occasionally checked against the GFT system.

After replacement of the solid state chemiluminescent analysers by UV photometric type ozone analysers (about 1990), automatic calibration was not available until also the PW 9762 NO_x analysers were replaced by TEI model 42W NO_x analysers with Environics 101 (GPT) calibration units.
This occurred in 91-92. The current NO_x-O_3 stations consist of a NO_x and a O_3 analyser and a NO_x-O_3 calibration unit (GPT). Each day the zero-point is determined . The span of the NO and NO_x channel is determined by offering a known concentration of NO from a certified standard gasmixture. From an ozone source O_3 is then added to the (excess) NO and from the reduction of its concentration the ozone concentration is determined (GPT). This amount of ozone is finally offered to the ozone analyser, to check its span.

During tests of the new station GPT calibrators (Environics 101) it appeared that the ozone produced by its internal ozone source according to the GPT system differed by 10% from the ozone output according to independent UV photometric measurements (the former transfer and primary laboratory standard). In order to avoid discontinuities in the ambient ozone measurement, the GPT values where corrected downwards by a factor 0.91, which was built into the station processors software. This correction is anno 2001 still applied.
During 1996-97 the NO_x-O_3 calibration units were technically modified, however not resulting in a change of the concentration correction.
In Participating in a European wide intercomparison exercise in October 1999 it was discovered that RIVM results (including the correction factor 0.91) were low by 5% with respect to other participants and the organizer assigned ozone concentrations. This led to a new laboratory investigation into the course of the discrepancy of the field calibrators and the UV-photometric and GFT primary laboratory standards. This investigation confirmed that the early correction factor still in use led to an underestimation of ozone concentrations, the correct value of the correction factor in fact being 0.96. This may well relate to the modifications of the calibrators carried out in 1996-97.
As numerical changing a long record of ozone monitoring is an important decision, which should be supported by thorough understanding of the course of the discrepancies, definite corrective action is yet to be undertaken, pending further investigation into the problem.

Summarising it can be concluded that since the early 1990s the Monitoring Network in The Netherlands has been subject to various changes. From the individual RIVM employees much and detailed information emerged, but at the same time it is clear that an overarching and entirely fitting description of the instrumental history is not available. There is nobody who has the complete and final story. Furthermore, it must be concluded that the documentation of changes is rather poor. The fact that a multiplication factor of 0.91 is incorporated in the processing software of the field monitor is known to only a few. Moreover, the study on which this factor is based upon could not be retrieved (at least not within the time span of this study).

2.1.2 Belgium

Information about the Belgian air quality monitoring networks (Flanders, Wallonia, Brussels) is given in the annual reports of the Belgian Interregional Cell for the Environment (i.e.: IRCELINE, 1997). It describes the location of the stations, the measurement techniques as well as the calibration techniques for the components.

For the six Flemish stations the following monitoring types have been in operation (Table 2).

Table 2 Overview of ozone monitoring types in Flanders.

Station	Period	Monitor
N012	08-09-1986 -> 31-03-1996 01-04-1996 -> ...	Meloy CSI Environnement O3 41M
N016	01-01-1995 -> ...	Monitor Labs 9812
N035	01-01-1995 -> ...	Monitor Labs 9812
N046	01-01-1995 -> ...	Monitor Labs 9812
N050	09-09-1986 -> ...	Meloy CSI 3100
R740	02-09-1983 -> 30-06-1990 01-07-1990 -> ...	Meloy OA Environnement O3 41M

Photographs of the sites are available at the website (http://www.irceline.be/).

Ozone is measured in units of ppb, but stored in the data base in units of $\mu g.m^{-3}$. The conversion factor has always been 2.00 (Dumollin, 2000).
Data are stored as half hourly values in Belgium. Hourly values were constructed under the condition that both half hourly values were present. Data are stored as hourly averages of the hour preceding the marker hour. So, a value at 15.00h is the hourly average of 14.00h to 15.00h. All data is expressed in Greenwhich Mean Time.

2.1.3 Landesumweltamt Northrhine-Westphalia

Ozone is measured in units of ppb, but stored in the data base in units of $\mu g.m^{-3}$. The conversion factor has always been based on 20 °C. Data are stored as half-hourly averages of the half-hour preceding the marker hour. So, a value at 15.00h is the half-hourly average of 14.30h to 15.00h. In this study the half-hourly values were converted (by TNO) into hourly values by requiring at least one half-hourly value present. All data are expressed in Central European Time.

2.1.4 Umweltbundesamt

Information concerning the instrumental aspects has not been asked for in detail as yet. From an exchange of letters the following relevant information comes out (Wallasch, 2000). Due to inconsistent calibration the ozone values from before 1995 are not very reliable, especially in connection to trend detection. Since 1996 the UBA ozone monitors are calibrated twice a year by transfer standards (Thermo Environmental TE49PS). These transfers are regularly compared with the German primary ozone standard (UV-absorption) kept at UBA.

Ozone is measured in units of ppb, but stored in the data base in units of $\mu g.m^{-3}$. The conversion factor is 2.0 but it is not clear whether the conversion factor has always been the same all the time. Data are stored as hourly averages of the hour preceding the marker hour. So, a value at 15.00h is the hourly average of 14.00h to 15.00h. All data is expressed in Central European Time (winter time).

2.2 Data quality

The examination of data consisted of:

1. reproducibility of parameters (averages, percentiles,..) reported by the institutes in their annual reports.
2. visual inspection (outliers, offsets, ...) of the data
3. comparing the differences of ozone and oxidant by pairing nearby sites.

2.2.1 Reproduction of parameters

Data transfer from one institute to another includes a few processing steps which might introduce errors. Experience from the past has learned that extraction of large data sets can lead to errors if the processing software is not fully equipped for this. A check on the received data by comparing with reported parameters is essential.

The reported ozone parameters by RIVM and IRCELINE (RIVM, 1990; RIVM, 1996; IRCELINE, 1997) could be entirely reproduced. The calculated ozone parameters of UBA sites agreed with the reported values in EMEP-CCC ozone reports (Hjellbrekke, 1999). The NRW reports are yet to come. This demonstrates that the data transfer from the institutes to TNO has been dealt with properly, and that the software calculating the reported values is correct.

2.2.2 Visual inspection

Visual inspection was done by plotting all data for one year of one station as a time series in a figure. The data were screened for apparent features such as offsets ("a white line near the zero line"), outliers, values above 40 ppb in the winter, sudden jumps in the data for a period of time. The visual inspection revealed for a few stations occasional suspect data such as offsets, strange dips and outliers (Table B2). A more thorough analysis was done on the offsets (Table B3). Offset is perhaps not the best description, it relates to the lower detection limit and the resolution of intervals used in the lowest segment of the distribution.

The RIVM ozone data is stored in units $\mu g.m^{-3}$ as integer numbers. The lowest value regarded as non-missing is 0, and then 1, 2, etc. It is remarkable that the number of zeros in Kollumerwaard (Table B3) is relatively high in the late 1980s up to 1990 with 300 values and more stored as zero. This pattern is also seen in the period 1978-1986 with never less than 300 values in the "zero"-class. From 1991 onwards the population of the "zero"-class drops to values often less than 100. This pattern of an abrupt change in population distribution in the lowest segments in 1991 is also observed at the other RIVM stations. As a consequence the subsequent classes of 1, 2 and 3 $\mu g.m^{-3}$ are more densely populated in 1991 and later years. Very low ozone values usually occur at night and during the winter under stagnant conditions with little air-exchange with layers aloft. Deposition and titration by NO are then dominating processes in the ozone destruction. It is not impossible that the reduction of NO_x emissions (see also Chapter 4) which has started in the early 1990s has been of influence to this phenomenon. However, it remains curious that the transition is so abrupt while the emission change is of a gradual nature. Another explanation should be sought in instrumental matters, such as the ozone monitor shift in the Dutch network in 1990/91, or a different practice of rounding off and/or storage.

Evidence of an instrumental problem in the Dutch network comes from the comparison with the Flemish sites (Sint-Kruiswinkel). The VMM ozone data is also stored in units $\mu g.m^{-3}$ as integers. A jump in the population density of the lowest classes is absent, even more, there seems to be an upward tendency, with more zero ozone values in the last years. For reasons yet unknown the ozone storage or monitoring practice at Sint-Kruiswinkel has been different in 1998, with a lowest threshold of 5.0 $\mu g.m^{-3}$. This feature is not seen at the other Flemish sites.
The situation at the Walloon site of Eupen is a bit different. The monitoring and storage practice seems to have been the same as in Flanders, but the years 1997 and

1998 are obviously different with threshold values of 2.0 and 4.0 respectively (Table B3).

All the Northrhine-Westphalia ozone sites in the period up to 1994 have 1.9 $\mu g.m^{-3}$ as minimum non-missing value with the next value being 2.8 $\mu g.m^{-3}$. From 1996-1998 this has shifted to 2.2 and 3.3 $\mu g.m^{-3}$ respectively. The year 1995 is a transition year. It should be noted that the data were provided as 30-minutes values which were averaged under the condition that also one value would count as hourly value as the partner value would be missing. So, a number of the values are genuine values and not averaged ones. Above 3.0 $\mu g.m^{-3}$ the resolution is at sub-$\mu g.m^{-3}$ level.

For the UBA sites there is again a different practice. Here the minimum value is 1.0 $\mu g.m^{-3}$ with a resolution of tenths of $\mu g.m^{-3}$ above this value. In 1996 and later years this practice has changed a bit by introducing integer intervals. Whether this is due to a change of monitoring or storage at UBA, or a change of storage in the EMEP data base is not known yet.

The conclusion is that five different data-providers produce five different procedures. The distribution of ozone in the lowest classes is particularly relevant when for instance winter trends are involved. (This could be of interest to compare with the summer trends and to test the hypothesis that summer and winter time atmospheres have evolved differently over the last 10 years.) The study has identified changes in data practice in all networks, changes that cannot be neglected when trends in the lowest segment of the ozone distribution are under investigation.

2.2.3 Pairing of sites

For various combinations of stations the difference of ozone concentrations was calculated. This was done for *daytime (12-20h) averaged ozone,* and plotting the difference as a running weekly or monthly average. Daytime hours were selected to favour the best possible dispersion conditions. Night-time ozone is generally much more affected by local features than daytime ozone.
Daytime averaged ozone concentrations were calculated only when 75% or more of the possible 8 hours were available. The difference of daytime values of two sites was calculated if they both had a non-missing value. Running averages on a monthly basis of the differences were accepted only if 50% or more of the daily values were present.

Various sets of ozone combinations were calculated for the 1987-1998 period, the following sets will be discussed:
set 1: Eibergen (RIVM), Wesel (NRW) and Borken (NRW), also for oxidant. (Figure B2a and B2b);

set 2: Wijnandsrade (RIVM), Nettetal (NRW), Vredepeel (RIVM). (Figure B2c);
set 3: Wijnandsrade (RIVM), Eupen (ISSEP) and Eifel (NRW). (Figure B2d);
set 4: Braakman (RIVM), Moerkerke (VMM), St-Kruis-Winkel (VMM). (Figure B2e);
set 5: Bielefeld (NRW), Meinerzhagen (UBA) and Bassum (UBA). (Figure B2f).
set 6: Wijnandsrade (RIVM), Rodenkirchen (NRW), Meinerzhagen (UBA). (Figure B2g).

A few sensitivity analyses were carried out to see if the fraction of acceptable data did have an effect on the outcomes of the comparison. Under very stringent conditions especially the Flemish-Dutch comparison suffered then of lack of data. Features in the German-Dutch pairs remained virtually unaffected.

Fluctuations in the differences seem to have, for most of the cases, a seasonal pattern. Moreover, there are fluctuations seen on much shorter time scales, which are perhaps related to synoptical time scales. Finally, there are jumps and drifts visible, which might be due to monitoring effects, or sudden local changes.
Since the area under investigation is abundant in NO_x it could be argued that part of the differences, and perhaps changes therein, could be due to differences in local NO_x concentrations. In the RIVM-NRW comparison the differences for oxidant revealed that certain ozone differences should be attributed to local NO titration (Fig.B2a and B2b). The summer minimum of the Eibergen-Wesel pair is to a certain extent explainable by local NO_x conditions. However, the most outstanding characteristics remain untouched if oxidant is used instead of ozone. The RIVM-NRW pairs show relatively more ozone for the Dutch sites in the summer than in the winter for the 1987-1990 interval, when the differences are small or even negative. After 1990, this feature is absent or even reversed with more ozone in the summer for the German sites.

In all comparisons involving RIVM data it is clearly seen that the character of the difference is completely different in 1991 and later, as compared to pre-1991 years. It is seen in the RIVM-NRW pairs, in the RIVM-UBA pairs, in the RIVM-ISSEP pairs, and, although less convincingly, in the RIVM-VMM pairs. Also the RIVM-RIVM pairs show a change in structure after 1990. The noise of the differences is reduced in its amplitude.

Many (but not all) of the RIVM-VMM pairs indicate a change in difference after 1990, and another one halfway 1995. Since the latter is not seen in the combinations with other providers it must be attributed to a change in the Flemish data. Another feature that emerges is the rather high degree of variability in the VMM-VMM pairs, in general much more than in the other national pairs. It is not impossible that the larger number of missing data in most of the Flemish records has been of influence to the larger degree of variability.

An almost similar large degree of variability is also seen in the internal pairing of UBA sites; smaller irregularities are seen for instance in the combinations with Bielefeld (NRW).

From the various combinations it can be inferred that the Walloon site Eupen suffers from a drift, most notably due to an increase of concentration since the summer of 1997. It should be sorted out if there is a connection with a change in monitoring/storage practise in the last two years (Table B3).

Summarising this comparison of paired sites yields the following:

It has been demonstrated that the RIVM data has undergone a transition at the end of 1990 and the beginning of 1991. This transition is most likely the cause of the remarkable winter ozone trends in The Netherlands (Roemer and Bosschert, 1996; Roemer and Bosschert, 1997; Roemer, 2001). In contrast to the trends in the surrounding countries the winter trends of ozone in The Netherlands are downward, and of the same magnitude as the summer trends. This is rather peculiar given the burden of NO_x in the Netherlands boundary layer and the decrease of NO_x emissions. Consistent downward trends were found almost irregardless which subsection of the data was taken (high-percentiles versus low-percentiles; marine air versus continental air). It seems inevitable to conclude that the change of ozone monitors in the Dutch network which occurred in the same period has been the cause of this transition. It is hoped that the RIVM archives contain more information to corroborate this finding (see also 2.1.1 and 2.4).

There is strong evidence that various Flemish sites have undergone a transition halfway 1995. Also the large degree of variability in the internal VMM pairs is reason to concern. It is hoped that the VMM archives contain information to corroborate this finding.

Irregular long-term changes are seen in various other sites, such as Eupen (WAL), the UBA sites and a few of the NRW sites.

2.2.4 Eibergen-Wesel

After the comparison of a large number of pairs, one combination (Eibergen-Wesel) was selected to study in more detail the differences. For each of the years three panels of comparison were plotted: 1) the annual variation of the difference of the daily average ozone concentration between 12.00h and 20.00h; 2) a histogram of the differences per year, and 3) a scatter plot of the differences (Fig. B3). Three years were selected for discussion.

In 1987 the ozone in Eibergen is nearly always higher than in Wesel, with on average a difference of about 10 ppb, and mounting up to more than 20 ppb in the summer. The comparison for oxidant showed that to a large extent the differences are also present when oxidant is considered. The scatter diagram shows a systematic difference of about 10 ppb over the whole range of concentrations.
Four years later, in 1991, the two sites behave almost identically with Eibergen slightly higher except for mid-summer. For oxidant Eibergen prevails slightly in the summer, whereas in the winter it is Wesel with a few ppb more oxidant. The distribution of ozone differences is almost Gaussian distributed around zero. The scatter diagram does not show any sign of systematic differences in certain concentration intervals. In 1995 the two sites show an annual variation of which the amplitude is certainly influenced by NO titration. Up to about 50 ppb the sites behave identically, at higher concentrations it is Wesel to prevail.

The development of ozone concentrations in different segments of the distribution is given for Eibergen and Wesel individually in the figures B4a and B4b respectively. For each month percentiles and averages were calculated from a subset consisting of all hourly values between 12.00h and 20.00h. The figures B4 show the time evolution of the averages, the 10th-percentile, the 50th-percentile and the 99th-percentile (A data coverage of at least 75%). For oxidant concentrations the same parameters were calculated (Fig. B5a/b).

The two figures reveal a few interesting characteristics. The 10th-percentile in Wesel is dominated in the winter months by the offset value of 1.9 $\mu g.m^{-3}$, in Eibergen zeros are observed in the first years (winter). The low values of ozone in the winter and at the lower percentiles are a result of titration by NO as is seen in the comparison with oxidant.
The structure of the variations from one month to another are often seen at both sites, reflecting that both are influenced simultaneously by the same weather system.

The first four years in Wesel show eminent summertime increases over the entire distribution. The monthly summer averages of ozone in Wesel increase from 30 ppb in 1987 and 1988 to 40 ppb or more in the following years. This jump of concentrations is throughout the entire distribution. The 99th-percentiles in Wesel for the summer months are below 80 ppb for 1987 and 1988, but in the following years there is always a summer month with at least 100 ppb of ozone. Also oxidant concentrations in 1987 and 1988 are low compared to other years, although the differences are less pronounced.
This pattern is not seen in Eibergen. There, the first four years are not lower in ozone and oxidant concentrations than the other years for the higher percentiles, whereas for the lower percentiles they rank amongst the highest for the entire time series.

2.3 1978-1999 The Netherlands

For three sites with a history back to the late 1970s the analysis of pairing was extended to the entire length of the records. Kollumerwaard and Balk are in the north, Hellendoorn is in the northeast. Daylight averages (12.00-20.00h) were calculated under the condition that not more than 1 out of the 8 eight hourly values was allowed missing. Differences between the sites were calculated and for each year-pair combination the population of a theoretical maximum of 365 (366) values was examined with respect to average, median, and standard deviation. Also the correlation coefficient (R^2) of daily values at two sites was calculated for each year-pair combination. The temporal development of the annual average and the standard deviation of the daily difference between two sites as well as the temporal development of the correlation coefficient of the daily averages between two sites might yield information regarding the quality of the data. It is obvious that other factors are important as well. For instance, the local NO_x concentration and possible trends therein would certainly affect these parameters, especially if the trends diverge for the sites making the pair. If the composition of air becomes more homogeneous and less disturbed by local events it will decrease the daily differences between the sites and increase the correlation.

The two most rural sites are Kollumerwaard and Balk, which are 66 km apart in a less densely populated area. The annual average of the daily differences is close to zero over the last years of the time series. From 1988 onwards the annual averages of the daily differences are rather constant and close to 0 for ozone and about 2 ppb for oxidant (Fig. B6a). The oxidant follows the ozone closely, so the titration effect by NO is not very relevant in this case. The standard deviation of the annual distribution of daily differences is 4-5 ppb at the end of the time series, and gradually increasing going back in time to 6-7 ppb in 1991 (Fig. B6a). It seems that before 1991 the pattern is different, with larger changes from year to year in the standard deviation. The pattern of the averages of daily difference remains stable until 1988 and is subject to larger interannual changes from 1987 backwards.
The correlation coefficient of the daily averages of the two sites shows a similar pattern (Fig. B6b). At the end of the time series the correlation is very high (0.9). Going back in time the correlation gradually decreases to 0.85 in 1988. Before 1988 much lower correlation coefficients are observed.

It is obvious that the first ten years (1978-1987/1988) show a rather unstable behaviour in terms of intercomparibility. This is also seen when the combinations with Hellendoorn are made (Fig. B6c). Hellendoorn is respectively 105 and 80 km apart from Kollumerwaard and Balk.
Since oxidant shows nearly the same pattern as ozone, trends in the local NO_x burden are not likely to have contributed much to the stabilisation of the paired differences. It is interesting to inspect the time series of the individual data. Figure B7a/b show the hourly time series from 1978-1983 for Kollumerwaard and Balk respectively.

A rather suspicious feature are the high (more than 40 ppb) winter time ozone values at Kollumerwaard. The background monthly average ozone concentration in Europe (Mace Head, Atlantic unpolluted air) is about 35 ppb in the winter (Simmonds et .al, 1996). In the winter the European continent acts as a sink to ozone due to the dominance of dry deposition and NO-titration (Roemer et al., 1996). The measurements at Mace Head show that in the winter polluted air from the European continent is much lower in ozone than the unpolluted background air. It is hard to imagine how elevated ozone concentrations can be established for several weeks. Stratospheric intrusion might offer an explanation for short-lasting events, but are unlikely for long-lasting periods which, remarkably, are not observed at a nearby site. Figure B7a/b shows that Kollumerwaard suffers from several such events in 1978, 1981 and 1982, events which are absent in Balk.
Another noteworthy feature is the fact that in 1982 from March to September Balk has much higher ozone concentrations than Kollumerwaard. This consistent "overprediction" is not observed in any of the other years. Compared to 1982 the ozone in 1983 in Balk is rather low despite the fact that the summer of 1983 was as conducive to ozone formation as the previous summer.
These findings strongly suggest that the data from before 1983 are unsuitable for trend studies. The usefulness of the data in the 1983-1988/90 period for trend detection is questionable.

2.4 Visits to laboratories

The results from the data analyses as described in 2.2 were sent to the data providers. A few months later three institutes (RIVM, VMM/IRCEL and LUA-NRW) were visited to discuss the results and to inquire for information in the archives that could be linked to the data analyses. This information is incorporated in 2.1. From the laboratory visits the following general impressions emerged.

The technicians responsible for the networks are dedicated to their work, and eager to maintain a high level of accuracy and precision.

The monitoring departments seem understaffed. It looks like that all energy and efforts are required to fulfill obligations in the ordinary tasks such as maintenance, data bases and annual reports. The appreciation for measurement activities has decreased over the last decade.
Much and relevant information about the history of the network (calibration, monitors, housing, ..) is not available in documents but stored in the minds of a few elderly technicians (human data discs) who were engaged in the network since the start of measurements. It is obvious that this sort of information should be documented soon in order to be able to trace back the monitoring history of the network when key personnel has left.

There seems to be a gap between the community of researchers working with the observational data, and the community of technicians producing the data. The researchers are seldom aware of the peculiarities of the measurements, they are often inclined to use the data in confidence that the data are fully correct. Practice has learned that still a small amount of erroneous data (technically wrong data) slips through and is stored in the database. However, even data that is technically valid could be rejected for interpretational reasons. This applies on a very small amount of data. Interpretational validation should come from the scientists who are usually not in a position to do this type of work. A major problem however is that interpretation could change in time due to scientific developments. It is therefore probably better to flag these data as questionable on grounds of interpretation, but to keep the data in the database.

A change of monitors based on different principles might have an effect on the concentrations, but a change of monitors from different manufactures is perhaps as much important. The experience shows that it takes time before the technical staff is accustomed to the new equipment. Certain types of monitors pose more and other problems than other types. It has occurred that replacements of monitors have lead to less reliable ozone measurements, and that it took several months or more before the confidence in the data came close to the level from before the replacement.

As yet it is unclear whether a full documentation of the history of ozone measurements at one of the stations can be retrieved. Such a documentation should include all aspects that have a potential effect on the measurements. It is more likely that such a documentation does not exist.

In order to trace back the history of the ozone measurements it is recommended to start with an inspection of the data as described in 2.2. This requires the presence of at least one other nearby stations, and preferably a station serviced by another institute. Other statistical techniques could be added as well for inspection. Then the data provider should be confronted with the findings of the data inspection followed by a search in archives and interviewing involved personnel. This looks a more promising route than the reverse route starting from the archives and then looking in the data. It is expected that more information will come from the data itself than from the archives.

The transition in the Dutch ozone that occurred in 1990/91 can be matched with a change in the network. At the moment information from the other data providers is not yet available to link discontinuities and drifts that were found to changes in their networks.

In general the networks in this study have reached a high level of quality which has increased in the course of time. However, it seems that this quality is not sufficient for ozone trend detection when the entire length of the records is considered. Special care is required to make a station or a network suitable for trend detection. Interest in ozone trends and the awareness of its requirements are just gradually developing.

3. Statistical modelling of ozone

The literature gives many studies that address the problem of quantifying the effect of meteorological variability on ozone concentrations (Annex A). The statistical model presented here is derived from a study by Bloomfield et al., (1996). Bloomfield et al. who worked with local meteorological parameters report a large fraction of explained variance of the ozone time series.

3.1 The model

A multiple linear regression model was developed and applied for the ozone season. The ozone season is defined here as the five months from May to September. The model is given by the following relation:

$$\begin{aligned} O_{3,max} \;=\; & A0 + A1{*}T_{max} + A2{*}RH + A3{*}T_{max}^{\;2} + A4{*}trend(T{>}25C) \\ & + A5{*}trend(T{<}25C) + A6{*}C1 + A7{*}S1 + A8{*}C2 + A9{*}S2 + \\ & A10{*}(1./(1{+}WS(T{>}25C)) + A11{*}IVOC \end{aligned}$$

and:

$O_{3,max}$: daily maximum ozone (ppb) between 12.00h and 20.00h (MET);

A0 : the baseline;

T_{max} : daily maximum temperature (C) between 12.00h and 20.00h (MET);

RH : average relative humidity (%) between 12.00h and 20.00h (MET);

Trend(T>25C) : trend (ppb/yr) only for T_{max} greater than or equal to 25 C;

Trend(T<25C) : trend (ppb/yr) only for T_{max} less than 25 C;

C1 : cosine function with period of 1 year;

S1 : sine function with period of 1 year;

C2 : cosine function with period of 0.5 year;

S2 : sine function with period of 0.5 year;

WS(T>25C) : average wind speed (m/s) when daily maximum temperature is greater than or equal to 25 C;

IVOC : integrated VOC emissions (expressed in ppb) at 12.00h MET.

The meteorological information (wind speed, wind direction, temperature, global radiation and relative humidity) comes from the German sites Wesel, Rodenkirchen and Eifel. The integrated VOC emissions are available for three sites: Kollumerwaard, Vredepeel and Meinerzhagen over the 1988-1996 period, and accessible at the NILU-ftp site (Solberg 2001).

This model has been applied on two ozone sites: Wesel in Germany, and Eibergen in The Netherlands (Table 3). The distance between the sites is about 50 km. The model explains nearly 80% of the variance in the daily maximum summer ozone concentrations, and the relative model error is close to 20%, which can be considered as a very good result. The core of the model are the first four terms: the baseline, the relative humidity and the two temperature terms. These four terms explain about 65-70 % of the variance. The four sine and cosine functions, representing the seasonal variation, explain additionally about 5% of the variance. For Eibergen the trends terms contribute 5%, in Wesel it is less than 1%. The wind speed factor (applied only under conditions when daily maximum temperature exceeds 25 C) and the integrated VOC emissions are good for about 1% additional explained variance each.

Table 3 *Coefficients of statistical model fitting daily maximum ozone (May-September) for Wesel and Eibergen for the period 1988-1996; meteo from Wesel, IVOC from Meinerzhagen. Standard error at 1σ-level, no correction for autocorrelation.*

	Eibergen (NL)		**Wesel (NRW)**	
	coefficient	**Standard error**	**coefficient**	**Standard error**
Baseline	75.74	7.41	67.25	7.12
Temperature max.	-4.35	0.45	-4.26	0.43
Rel. humidity	-0.35	0.02	-0.38	0.02
Temperature max. ^2	0.16	0.01	0.15	0.01
Trend (T>25C)	*-3.49*	*0.25*	*+0.02*	*0.23*
Trend (T<25C)	*-1.82*	*0.12*	*+0.35*	*0.12*
C1	-27.79	8.35	-25.54	8.08
S1	0.96	2.63	0.37	2.53
C2	-12.10	2.79	-7.71	2.71
S2	-6.75	1.89	-3.60	1.83
F(Windspeed)	41.71	5.56	19.44	5.40
Integrated VOC	0.13	0.03	0.24	0.03
Avg.$O_{3,max}$(T>25C) (ppb)	72.67		73.24	
Avg.$O_{3,max}$(T<25C) (ppb)	39.55		37.94	
Explained variance (%)	78.19		78.84	
rel. standard error of model (%)	21.02		21.13	

The seasonal term is, averaged over the May-September period, zero. Constructing a curve on the fitted seasonal terms gives positive values for May, near zero values for June and July, and negative values for August and September. The difference between May and September is about 10 ppb for these sites. In other words: identical meteorological situations in May produce on average 10 ppb more ozone than in September. This finding reflects the seasonal variation of ozone in this part of Europe.

Two trend terms were included to allow for opposite trends in different segments of the ozone distribution. Many sites in Europe report a downward trend for the peak values in the summer, and an upward trend for the averages.
The ozone dependence on wind speed is complicated. At low temperatures an increase of wind speed means more ozone as more ozone-rich air is mixed in. At high temperatures (implying episodic conditions) the vertical ozone profile near the ground is reversed, and an increase of wind speed means less ozone. For most of the conditions occurring in the May-August period there is no clear relationship between wind speed and ozone. Only at high temperatures a clear relationship can be distinguished.

The integrated VOC emissions are (in this case) based on the receptor point Meinerzhagen, approximately 100 km southeast of Wesel. The integrated VOC emissions (12.00h) are the accumulated emissions over a 96h trajectory arriving at Meinerzhagen, and adjusted for mixing layer height and dilution factors (Simpson, 1993; Simpson, 1995; Solberg et al., 1997). This information contributes to a slightly better statistical model with a significant coefficient. Integrated VOC emissions for 06.00h did slightly worse.
Similarly, the integrated NO_x emissions were incorporated in the model (apart and in conjuction with integrated VOC) but, in this case, without improvement of the model. The fitted coefficient associated with integrated NO_x emissions was negative (but not signicant at the 95% confidence level). The small contribution of the integrated emissions to the model is likely due to overlap with the temperature and humidity parameters. In the next phase the performance of the integrated emissions will be tested in a model with less or no meteorological parameters.

Addition of global radiation and wind direction did not improve the model. A few variations of this model were examined by including lagged parameters (previous day) but none of them resulted in a better performance. Although improvement (in terms of explained variance) is possible, the performance of the model with the current parameters is considered as good enough for further analysis.

Figures B8a/b show the time evolution of the observed (squares-solid line) and modelled ozone concentrations for Eibergen and Wesel respectively, combined with the Wesel meteorological information and the trajectory information for Meinerzhagen. The stippled line is the statistical model without trend terms, the dashed line also includes the two trend terms. The figure shows that the full statistical model (including the trend terms) performs well for a large portion of the concentration distribution, but that for the highest concentrations (95-percentile and higher) the agreement between observations and model becomes less. Disagreement at the higher percentiles is apparent in the beginning of the time series: 1989 and 1990 in Eibergen where the model underestimates the observations, and 1988 and 1990 in Wesel with respectively overestimation and underestimation of the observations. This finding cannot be seen without pointing at the likelihood of data quality problems during the late 1980s and 1990. It seems that the peak values in

1990 are hard to cover by such a model. The meteorological conditions conducive to very high ozone concentrations in 1994 were at least as good as in 1990, but the observations show especially at Eibergen (Fig. B9a/b) less and lower peak values in 1994 than in 1990.

This might be due to data quality aspects, but could also point towards deficiencies in the model. This needs to be sorted out in future work.

3.2 Sensitivity runs

With a slightly different model (omitting the integrated VOC emissions, and changing the threshold temperature value from 25° C to 22° C) a few sensitivity runs were performed. The model (meteo+season+trends) is:

$$O_{3,max} = A0 + A1*T_{max} + A2*RH + A3*T_{max}^{2} + A4*trend(T>22C) + A5*trend(T<22C) + A6*C1 + A7*S1 + A8*C2 + A9*S2 + A10*(1./(1+WS(T>22C))$$

Three variations were investigated.

A model with meteorology, seasonal variation and one trend term:

$$O_{3,max} = A0 + A1*T_{max} + A2*RH + A3*T_{max}^{2} + A4*trend(all\ T) + A5*C1 + A6*S1 + A7*C2 + A8*S2 + A9*(1./(1+WS(T>22C))$$

A model with only the seasonal variation and one trend term:

$$O_{3,max} = A0 + A1*trend(all\ T) + A2*C1 + A3*S1 + A4*C2 + A5*S2$$

And a model with only a trend term:

$$O_{3,max} = A0 + A1*trend(all\ T).$$

Table 4a *Ozone trends (ppb/yr) and standard error (1 σ; no correction for auto-correlation) for different models and time intervals.*

Meteo + season + 2 trends	Eibergen Trend (T<22 C)	 Trend (T>22 C)	Wesel Trend (T<22 C)	 Trend (T>22 C)
87-98	-1.12 ± 0.08	-2.41 ± 0.11	+0.60 ± 0.08	-0.01 ± 0.11
88-98	-1.13 ± 0.09	-2.63 ± 0.12	+0.40 ± 0.09	-0.28 ± 0.12
89-98	-1.10 ± 0.11	-2.81 ± 0.13	+0.22 ± 0.10	-0.60 ± 0.12
90-98	-0.72 ± 0.12	-2.55 ± 0.15	+0.33 ± 0.11	-0.67 ± 0.14
91-98	-0.12 ± 0.13	-1.86 ± 0.16	+0.49 ± 0.13	-0.43 ± 0.16
92-98	+0.22 ± 0.16	-1.81 ± 0.19	+0.61 ± 0.16	-0.41 ± 0.20
93-98	+0.59 ± 0.19	-1.60 ± 0.24	+0.44 ± 0.19	-1.26 ± 0.24
Meteo + season + 1 trend	**Trend (all T)**		**Trend (all T)**	
87-98	-1.52 ± 0.09		+0.40 ± 0.07	
91-98	-0.75 ± 0.11		+0.16 ± 0.11	
93-98	-0.19 ± 0.16		-0.18 ± 0.16	
Season + 1 trend	**Trend (all T)**		**Trend (all T)**	
87-98	-1.06 ± 0.13		+0.72 ± 0.13	
91-98	-0.92 ± 0.23		-0.05 ± 0.23	
93-98	-0.19 ± 0.35		-0.20 ± 0.36	
1 trend	**Trend (all T)**		**Trend (all T)**	
87-98	-1.10 ± 0.14		+0.67 ± 0.14	

Table 4b *Oxidant trends (ppb/yr) and standard error (1 σ; no correction for auto-correlation) for different time intervals.*

Meteo + season + 2 trends	Eibergen Trend (T<22 C)	 Trend (T>22 C)	Wesel Trend (T<22 C)	 Trend (T>22 C)
87-98	-1.12 ± 0.08	-2.37 ± 0.12	+0.54 ± 0.08	-0.21 ± 0.11
91-98	-0.23 ± 0.14	-1.76 ± 0.18	+0.52 ± 0.14	-0.32 ± 0.18
93-98	+0.44 ± 0.20	-1.54 ± 0.27	+0.10 ± 0.20	-1.31 ± 0.26

It is apparent that only for the last 5 years (1993-1998) common trends are observed at both stations (Table 4a). This is due to the transition of ozone data that occurred at the end of 1990. In Eibergen the trend for the higher temperatures (and ozone values) remains constant as long as at least one pre-transition year is included. After the transition the trend for the higher temperatures drops to a less downward trend and remains stable. For the lower temperatures the trend shows a gradual change in Eibergen from negative to positive. In Wesel the situation is different. For the lower temperatures the trend remains stable and positive. Here the higher temperature trend behaves variable, changing from zero to slightly downward and finally over the 93-98 period it is considerably downward.

The explained variance in the model with meteorology, season and 2 trends ranges from 78% for the entire 1987-1998 period to 84% for the 1993-1998 period. Wesel has always 1-2 % more explained variance than Eibergen, which could be due to the use of local Wesel meteorology. The relative standard error of the model was less than 20%. It can be concluded that the model is able to describe a large part of the ozone variability.

Ozone trends at the higher temperatures are hardly affected by reduced titration through NO, ozone and oxidant trends are almost identical. At lower temperatures there is a small difference between ozone and oxidant trends. The oxidant trends are 0.2-0.3 ppb/yr less upward than the ozone trends indicating the effect of reduced titration by NO. The question arises what causes the low temperature ozone and oxidant concentrations to increase. It is noted that at the moment only two stations are examined. The rest of the stations can be done when meteorological data for these stations have arrived. Assuming that the other stations yield the same picture of trends two obvious contributors need to be examined. There might be a contribution from an increase of background ozone concentrations. A study of winter trends of ozone might shed more light on this matter. In the winter the advection of background ozone is (with respect to chemistry) of more importance to the ozone budget over Europe than during the summer (Roemer et al., 1996).
The second candidate is a change in the chemical production of ozone. Above a certain threshold value of NO_x concentrations (~ 2 ppb in models) an increase of NO_x results in less OH, and consequently in less ozone and oxidant. Vice-versa, a decrease of NO_x emissions (as observed in this area) will lead to more oxidant and ozone. Calculations with the LOTOS model indicate that moderate reductions of NO_x emissions in western Europe not only result in an increase of ozone but also of oxidant (Roemer, 1996). However, the observed trends are also influenced by downward trends of VOC emissions. The models calculate a downward trend of ozone and oxidant in response to VOC emission reductions. At the moment the contributions of chemistry and background remains speculation.

When the statistical model involves only one trend term it reflects the developments in time of the average situation. However, it masks the fact that in different segments of the ozone distribution opposite trends occur.
When the meteorological terms are omitted the explained variance drops to about 13% (season + trend) and to about 1-2% for the model with only a trend term. The inclusion of meteorological terms in the statistical model greatly improves the performance of the model (block2 versus block 3 and 4 in Table 4a) which is reflected in smaller uncertainty margins. It can also have an effect on the trends themselves. For instance, the ozone trends over the 1987-1998 period are much more downward when meteorology is accounted for. This period has seen an increase in the number (or strength) of situations conducive to ozone formation. Including the meteorological terms forces (correctly) the trends to become more downward than without meteorological terms.

4. Precursor trends

A similar procedure as conducted for ozone can be followed for the precursors in order to detect possible data quality problems. Also a statistical model (albeit with other variables) is an indispensable tool to account for meteorological influences in the observations. The data quality procedure is started to investigate characteristics in the NO and NO_2 of about 25 sites (not all 35 sites measure NO or NO_2). At the same time preliminary trend studies are conducted. Such exploratory studies are often useful in identifying peculiar features in the data.
For VOC one site is selected and research to data quality and local influences has started but awaits completion.

The statistical models for precursors require partly other components than the ozone statistical model. Earlier studies on PM10 and methane have shown that a useful parameter in a statistical model for precursors (which are not too reactive) is the APA index (Visser, 1999). APA stands for Air Pollution Accumulation, and is indicative for the accumulating potential of the mixing layer. Several formulations are in use but they all involve mixing layer height and wind speed (inversely proportional) and the strength of the entrainment zone as expressed by the temperature gradient in this zone. In order to calculate mixing layer height and the inversion strength, cloud cover information is required besides other variables. Development of the statistical model is postponed until the requested meteorological data has been received.

4.1 Data quality of NO and NO_2

As for ozone, the NO and NO_2 data were examined on the developments in the lowest segments of the distribution. For the period 1987-1998 the number of observations in certain intervals was determined for all sites. The results for a selection of sites are given in Tables B4 and B5 for NO_2 and NO respectively. After the findings for ozone it is not surprising that also for NO and NO_2 the data providers have different procedures in handling the low values. In The Netherlands and Belgium the data are hourly values and they are stored as integer numbers in $\mu g.m^{-3}$. In Northrhine-Westphalia the data are stored as half-hourly values and they are stored in $\mu g.m^{-3}$ with one decimal.

The measurement principle used in The Netherlands allows small negative numbers to occur. Values down to –5 $\mu g.m^{-3}$ are accepted, more negative values are rejected (Stolk, 2001). Occasionally however, values below –5 are seen in the data base. The programs processing the data at TNO reject lower than –5 values and treat them as missing values. The distribution of negative values varies substantially from one year to another. For instance, in Balk the number of negative NO_2 values is 590 in 1990 and only 67 one year later. In Kollumerwaard no negative values for NO_2 occur in 1988 and 1989 and more than 750 negative values in 1991. Similar features are seen in the NO distribution. Years with no or hardly any negative NO or NO_2 values occur at most of the sites, but they vary from one site to another and from component to component. The practice is to swap instruments from one site to another (after inspection at RIVM) once a year (Stolk, 2001). When malfunctioning of an instrument is detected the instrument is brought to RIVM and replaced by another monitor. As a consequence, the time series is based upon sampling by a series of instruments. Although instruments are based on the same principles and come from the same manufacturer their performance may not exactly be the same. Before being installed at the site, the instruments are calibrated and adjusted at RIVM, but differences in performances can not be excluded, also because in a large ensemble of instruments a few are known to be less stable than the rest.

In Belgium the lowest accepted value is 0 $\mu g.m^{-3}$. The number of values in the lowest classes varies substantially from one year to another. In Moerkerke there is a tendency of reducing the number in the 0 and 1 $\mu g.m^{-3}$ class in 1997 and 1998. In Eupen no numbers are seen below 6 $\mu g.m^{-3}$ in 1997 and 1998. This ought to be related to change in data handling, or a change of instrument or detection limit.

In Northrhine-Westphalia the practice is different. The lowest class is 3.5-4.0 $\mu g.m^{-3}$ for NO and 5.0-5.5 $\mu g.m^{-3}$ for NO_2. The second lowest class for both components is a few $\mu g.m^{-3}$ higher, while the rest of the distribution is at a much finer resolution. A possible explanation (which needs to be confirmed by the data provider) is that values below the detection limit are set at a value of 0.5 or 0.667 times the detection limit. In the case of NO a change in practice has occurred in the years 1992-1994 with a wider gap between the lowest and second lowest populated class (Table B5). It is also remarkable that in heavily polluted places such as Rodenkirchen (annual average NO_x concentration in 1980s: 70 ppb) 20-30 per cent of the data falls in the lowest concentration class.

Information on instruments, changes of instruments, calibration, data storage has not been asked for yet. Pairing of sites has been carried out for a limited number of pairs. It was found that NO_2 concentrations in the summer of 1996 at Vredepeel differed substantially from other nearby sites in relation to other years.

4.2 Trends of NO_x and NO_2

The temporal developments of the concentrations at 25 NO_x stations in The Netherlands and Germany have many features in common (Fig. B10a-e). Rather strong interannual fluctuations are seen in the annual averages of NO_x in the period 1985-1992. Upward and downward changes fluctuate from year to year. The magnitude of the changes seems to depend on the local NO_x burden: moderate fluctuations at the least polluted stations (Kollumerwaard, Balk, Wieringerwerf, Hellendoorn, Witteveen, Biddinghuizen) to substantial at the most polluted sites (Zegveld, Cabauw, Houtakker, Huijbergen). The fluctuations from year to year in this period are predominantly caused by interannual fluctuations in the four winter months. The winter months contribute about a factor of three more to the annual average than the summer months. The observed pattern in the time series of the annual averages is also seen in the time series for only the winter months. The summer months display another pattern.

The OPS-model (van Jaarsveld, 1996) is a statistical trajectory model for distances ranging from the local to continental scale, driven by analysed meteorological fields. Preliminary calculations for the 1981-1999 period with constant emissions (for 1995), showed that the model was able to simulate quite accurately the observed annual averages. It also indicated that to a large extent the interannual fluctuations in the 1985-1992 period can be explained by interannual variability in the meteorological fields. How much of this variability relates to changes in the circulation (advected material), or to changes in the accumulative potential (in particular: mixing layer height) or to changes in deposition rate will be investigated in the near future.

The situation in the 1992-1998/99 period is different. The interannual fluctuations are much smaller, and a general reduction in concentrations is observed. The abovementioned model indicated that for most of the stations the meteorological conditions in 1996 and 1997 favoured higher NO_x concentration than in 1995 and 1994, whereas during the last two years (1998 and 1999) dispersion conditions promoted lower concentrations. Based on the observation to model ratio it becomes clear that the two gradually diverge since the early 1990s, suggesting that the observations have been influenced by emission reductions of the order of 30-40 % since that time (Fig. B11a/b). These developments are at first glance in line with the trends in the reported national NO_x emissions in The Netherlands, Germany and United Kingdom (EMEP, 1999). Only the trend in Belgium deviates from the rest, with much smaller trends in the national emissions.

Changes in NO_x concentrations can result not only from changes in emissions or meteorological conditions, there might also be a contribution by changes in the atmospheric composition. There is enough evidence that over the last 10-15 years emissions of CO, NMVOC and NO_x have been reduced quite substantially in Western Europe. The feedback mechanisms of reactions determining OH in a polluted environment are complicated. The effect of these changes on the OH radical needs to be calculated by a chemical dispersion model. Since CO and NMVOC are the main scavengers of OH in a polluted environment it is plausible however to suppose that OH concentrations have increased over the last 10-15 years. A study of the contribution of changes in atmospheric composition to trends of observed NO_x concentrations requires a series of steps to be taken (removal of meteorological influence in the time series; calculation of trends of OH concentrations,...). Separation of the observations in a summer trend and a winter trend can be seen as part of such an approach. It is expected that changes in OH concentrations are not

the same in winter and summer. Differences in winter and summer trends, especially at the least polluted sites, might reveal (after meteorological and other disturbances have been removed or accounted for) an indication for changes in the chemical removal of NO_x.
This is the idea behind an exploratory study to summer and winter trends. For each month various parameters (averages, percentiles) were calculated under the condition that at least 75 % of all hourly values in a month are present. For the 1987-1998 period a summer trend is determined by simple linear regression through the four (times 12 years) summer months, and in a similar fashion the winter trends are calculated (Table B6a-b).

In the winter the trends are predominantly downward, usually –2% to –3 % per year. At the majority of stations trends of the higher percentiles are more downward than trends of the lower percentiles. At a few stations, in particular the least polluted stations, the lower percentiles show upward trends. A similar pattern is seen in the summer: higher percentiles display more downward trends than the lower percentiles. The number of stations with positive trends (in the lower percentiles) is much higher for the summer than for the winter. In the summer only the most polluted stations show downward NO_x trends in the lower percentiles. Most of the characteristics seen in the Dutch stations are also seen in the German stations, except that the difference between summer and winter trends as seen in the Dutch network is not reflected in the German network. The summer trends of averages in Northrhine-Westphalia are often even more downward the corresponding winter trends.

It seems that in particular for the Dutch sites trends become less downward or even upward when the conditions change from polluted to less polluted. This effect is not only visible in the comparison among stations, but also in the differences between season and between day and night. At the Dutch stations the nighttime (22.00h-06.00h) trends are much more downward than the daytime (12.00h-20.00h) trends. This effect is stronger in the summer than in the winter. This effect is not observed at the German sites. It is plausible to assume that a change in processing the low values might have caused this effect, rather than an atmospheric process.
When instead of NO_x only NO_2 is considered the same features are seen (Table B7). Trends in summer time concentrations of NO_2 demonstrate quite clearly the trend differences in the different segments of the distribution. Now also two Belgian sites are included (Sint-Kruiswinkel and Eupen). Here the tendency is more downward trends at the lowest percentiles, and less downward at the upper percentiles, so opposite to what is found in Germany and especially The Netherlands.
A complication in determining trends of low percentiles under relatively clean conditions is that the time series consists of a row of about 48 values which differ only a few ppb (resolution 0.5 ppb or 1 $\mu g.m^{-3}$). For instance, the time series of the 25-percentile of NO_2 in the summer at Kollumerwaard consists in majority of values which are 1, 2, 3 and 4 $\mu g.m^{-3}$. But also –1 $\mu g.m^{-3}$ appears. Figure B.12 shows

the cumulative distribution of summer time NO_2 for only values below 10 $\mu g.m^{-3}$. Differences amongst years in the lower part of the distribution are large, and more likely a result of operating practices than from a change in the atmospheric distribution. It seems that the instruments are not suited for detection of trends in the low concentration range. The resolution is too insensitive, and at the same time monitoring practices have probably influenced the near zero distribution too much. Trends in the upper percentiles however are more consistent among the stations and much less sensitive to processing of near-zero concentrations.
These statements are primarily based on in-depth analysis of the Dutch stations. However, the findings with regard to the distribution of near zero values in the German and Belgian stations (Table B4 and B5) suggests that trends at the sites are likely to have been influenced by changes in operating practices as well. Given the large portion of near zero values in the distributions (especially the summer distributions) it can be assumed that also the averages are affected. Therefore, it seems safer to restrict trend studies to the upper segments of the distributions.

4.3 Data and data quality of VOC

VOC measurements are more sparse than NO_x measurements. Nevertheless, in the course of time an useful data base of VOC measurements in The Netherlands has been built up (Table 5).

Table 5 *Overview of historic continuous observations of VOC in The Netherlands.*

Location[1]	Type[2]	period	Species[3]	Average and frequency	Remarks[4]	Ref.[5]
Delft	Urb Bkgd	1971-1977	C_2-C_5	Hourly	H.D.L.	A, E,
		1982-1984	C_2-C_5	hourly	L.D.L.	N
Moerdijk MA	Ind.	1976-1980	C_2-C_5	Hourly	H.D.L.	
		1980-1986	C_2-C_5	hourly	L.D.L	B,C
Moerdijk MB	Ind.	1980-1985	C_2-C_5	hourly	L.D.L.	B,C
Moerdijk MC	Ind.	1980-1992	C_2-C_5	Hourly	L.D.L.	B,C,J,N
		1992-1999	$C_2^=$,$C_3^=$,$C_2^{\equiv}$	Daily		P
		1992-1999	C_6-C_{12}	Daily, 90/yr		D, M,Q
Huijbergen	Non-urb	1991-1999	C_6-C_{12}	Daily, 90/yr		K,D,M,Q
Budel	Non-urb	1991-1993	C_6-C_{12}	Daily, 90/yr		D
Houtakker	Non-urb	1991-1993	C_6-C_{12}	Daily, 90/yr		D
Vredepeel	Non-urb	1991-1996	C_6-C_{12}	Daily, 90/yr		D
Ossendrecht	Non-urb	1994-1998	C_6-C_{12}	Daily, 90/yr		K,L
Kollumerwaard	Non-urb	1994-pres.[6]	C_2-C_8	Hourly, D12[7]	V.L.D.L.	F,G,H,I
Biest Houtakker	Non-urb	1992-pres.[6]	C_6-C_{14}	Weekly[8]		O
Maassluis	Non-urb	1997-pres.	C_6-C_{14}	Daily[8]		O
Zegveld	Non-urb	1992-pres.	C_6-C_{14}	Daily[8]		O
Kollumerwaard	Non-urb	1997-pres.	C_6-C_{14}	Weekly[8]		O
Utrecht Univ.	Urb Bkgd	1997-pres.	C_6-C_{14}	Daily[8]		O
Utrecht deJong.	Urb Street	1997-pres.	C_6-C_{14}	Weekly[8]		O
Utrecht Vleut.	Urb Street	1997-pres.	C_6-C_{14}	Daily[8]		O
Utrecht Erzeij.	Urb Street	1992-pres.	C_6-C_{14}	Weekly[8]		O
Apeldoorn	Urb Street	1992-pres.	C_6-C_{14}	Weekly[8]		O

1. First block of stations by TNO, second block of stations by RIVM
2. Urban Background, Industrial, Non-Urban, Urban Street
3. C_2-C_5: ethane, ethene, acetylene, propane, propene, n-butane, isobutane, n-pentane, isopentane; $C_2^=$,$C_3^=$,$C_2^{\equiv}$: ethene, propene, acetylene; other groups consist of 30-50 individual species, see references for specifications
4. High Detection Limit: 1-5 ppb; Lower Detection Limit: 0.1-0.6 ppb; Very Low Detection Limit: 10-100 ppt.
5. For references, see table below.
6. Pres: measurements continue up to today (2001).
7. D12: hourly averages, every two hour.
8. Sampling during a selection of weeks within an eight-week period (see: reference O). Only Zegveld has continuous measurements.

A	Guicherit, 1978	G	Baas and v. Ditshuizen, 1995	M	Thijsse et al., 1999
B	Thijsse and Bijlsma, 1983	H	Beck et al., 1996	N	Roemer et al., 1999
C	Thijsse, 1983	I	Penkett et al., 1996	O	Elzakker and Buijsman, 1999
D	Thijsse, 1993	J	Lindskog et al., 1997	P	Thijsse, 2000a
E	Roemer, 1995	K	Thijsse, 1998	Q	Thijsse, 2000b
F	Baas and Bosman, 1995	L	Thijsse and Wauters, 1999		

In Flanders C_3-C_{11} hydrocarbons were measured near Antwerpen in the period 1994-1998 (Thijsse and Wauters, 1999). An overview of VOC measurements in the three Belgian networks (Flanders, Wallonia, Brussels) is given in IRCELINE (1997). Continuous measurements of non-methane (aromatic) hydrocarbons were performed in 1997 in Berendrecht, Sint-Kruiswinkel and Zelzate. Continuous measurements in 1997 of non-methane hydrocarbons were performed in Brussels, Antwerpen, Borgerhout, Liege (2x), Engis and Charleroi. At a few of these sites the measurements go back to at least 1993 (IRCELINE, 1994).

The most obvious candidate to study long term developments of VOC is Moerdijk MC. First of all because data over a long period of time (October 1980 – December 1999) is available. A second argument for Moerdijk is that the data has been subjected to many studies, resulting in a rather detailed knowledge of the characteristics and peculiarities of the data. A major disadvantage is that the site is located near a large source of hydrocarbons, and that the wind data is rather fragmented. Kollumerwaard and Zegveld are both rural sites; however their time series are much smaller (since 1994 and 1992 respectively), and after validation the data has hardly been evaluated in studies. Serious efforts are required to get familiar to these data before they can be used in trend studies.

Moerdijk is a small village located halfway between Rotterdam and Antwerpen (Fig. B.13a). In the early 1970s a large area of approximately 20 km^2 was made available for industrial activities. For a long period of time there was only one company present at the area with a refinery plant (Fig. B13b). The license reported emissions of various hydrocarbons, and in particular of ethene, acetylene and propene. The administration of the province of Noord-Brabant commissioned TNO to monitor the concentrations in air of the C_2-C_5 hydrocarbons, and, in later years, to estimate the emissions from the refinery. The first 10-15 years after the start of the measurements the attention in reporting the data has been solely on the developments at the local scale. Later attention shifted towards the regional and national scale.

At Moerdijk MC continuous hourly measurements of ethene, acetylene and propene are available over the period October 1980 to April 1992. Over this period the automatic sampling and measurement system has been the same (Thijsse, 1981; Roemer et al., 1999). The monitor was calibrated once a week. After 1991 the species were measured as daily averages on a continuous basis. Air was sampled in canisters and analysed at the laboratory. This method showed excellent agreement with the on-line method with which there was a three-month overlap (Thijsse, 1992). The lower detection limit is 0.1 ppb for ethene and propene, and 0.2 ppb for acetylene. For these species concentrations below the detection limit occur seldom. Data below the detection limit is set at two-third of the detection limit value.

In order to construct time series of these species that can be linked to large scale emission developments a series of steps need to be taken to overcome discontinuities in sampling strategy (hourly versus daily), discontinuities in the wind data, and to remove as much as possible the influence of the nearby industrial complex.

At the Moerdijk sites wind speed and wind direction were measured over the first period (1980-1992). The combination of wind data and hydrocarbon data provided the means to separate influences of the nearby industrial emissions from the larger scale information. However, there are some complications due to the use of different sources of wind data and due to the complicated nature of atmospheric dispersion.
In the first period until April 1986 the wind was measured on a hourly basis in Moerdijk MA (Fig. B13b). This site is free from nearby obstacles. After this site was closed in April 1986 the wind was measured (until April 1992) in Moerdijk MC, about 7 km to the southwest. In the database only wind data of MC in the windsector 350°-150° is included. For the other windsector wind data from Heijningen is used. Heijningen is a RIVM station about 8 km west of MC. The reason to use two sources of information is that MC is covered by a line of trees in the 150°-350° sector. The fact that the Heijningen wind direction data is expressed in tens of degrees, whereas at MC single degrees are used is of less importance than the different positions of the wind stations. Although 8 km distance sounds rather nearby, the near vicinity of a broad waterway (Hollandsch Diep, see Fig. B13b) makes it uncertain to what extent the use of different sets has caused a discontinuity in the wind data.

After 1991 (when the hourly hydrocarbon data are replaced by daily data) a second discontinuity occurs when wind data is retrieved and constructed from three meteorological stations (Volkel, Gilze Rijen and Eindhoven). These stations do not accurately describe the local wind pattern nearby Moerdijk, and must be considered merely as indicative for the large scale advection. Moreover, the daily averaged wind data is based on averaging four hourly data (06.h, 12.00h, 18.00h and 24.00h).
In summary, there are three discontinuities: the transition of wind data in 1986, the transition of hourly to daily hydrocarbon data after 1991, and, at the same time, the transition from local to averaged regional wind.

Hourly data

The most obvious method to remove the influence of the industrial complex is to cut out the associated wind sector. The availability of 5 years of hourly data at two sites (MA and MC) which are located in opposite directions from the source area proved very useful in selecting wind sectors. Based on the wind roses and on the map of the area, the sector 31°-90° was chosen as the "complex sector" viewed from MC, and 221°-260° viewed from MA. After differencing the two stations for the remaining wind sectors, and after creating a subset of data under the condition of wind speeds more than or equal to 3 $m.s^{-1}$ the vast majority of data appeared to fulfill a Gaussian distribution centred closely around 0. A very small number of high values emerged which could be interpreted as air being influenced by the

source area just before a major turn of the wind. These events were discarded by removing data exceeding a certain upper percentile of this subset. The 99.85 percentile showed to be a satisfactory threshold.
The wind-rose of the screened dataset of differences identified a second (and much smaller) source of ethene and propene which initially was overlooked (Fig. B14). Relatively large differences are seen in the 11°-30° sector, viewed from MC. This sector covers a small port where tankers regularly transfer ethene and propene from or to the refinery. Given the Fig. B14, the sector 11°-100° would be more appropriate to exclude most of the refinery influence. Viewed from MA which is at a larger distance from the port, the port almost entirely submerges into the complex sector. After having discarded the 11°-100° sector the remaining differences are on average (1981-1985 period) small, but do contain some structure. For all three species the concentrations at MC in the south sector (Fig. B14) exceed those in MA. In the adjacent southeast sector (101°-150°) it is the opposite: MA exceeds on average MC. For ethene and propene MC exceeds on average MA in the 311°-350° sector, the Rotterdam-Rijnmond sector. Given the distance of about 50 km to the Rotterdam-Rijnmond area it not likely that differences between MA and MC are caused by differences in advected material from this area.

For one windsector (261°-310°) the 1981-1985 differences between MA and MC were studied in more detail by looking at individual data as a function of wind speed. The wind sector 261°-310° is the cleanest sector with the lowest averaged concentrations. In this sector the averages of the MC-MA differences are small, not only the average of all measurements, but also the averages per wind speed class. Per wind speed class the average difference is 0.3 ppb or less. Only for the lowest wind speed class the averaged difference is 0.6-0.7 ppb. Figure B15 shows the distribution per wind class of the individual differences in this sector. It is obvious that air becomes more homogeneous in composition when the wind speed increases. In absolute terms ethene displays the largest differences, acetylene the smallest. When the standard deviation of the differences is expressed in relative terms by dividing through the averaged concentration at MC in the cleanest sector, acetylene shows the smallest differences, followed by ethene and propene with much larger relative differences (Table 6). Similar results are found in the other non-industrial sectors. When the relative differences (in the clean sector) are calculated for individual wind speed classes there appears not much differences among the three species at the lowest wind speed (less than 1 $m.s^{-1}$). At this wind speed the direction of the wind is usually hard to define and variable which means that the influence of the industrial complex in other poorly defined wind sectors might be substantial. With increasing wind speed (and decreasing influence of the industrial complex in the non-industrial wind sectors) the relative MC-MA difference decreases for acetylene, but increases for ethene and propene. Beyond 4 $m.s^{-1}$ the relative MC-MA difference stays at 0.3-0.4 for acetylene, whereas for the other two species the relative differences remain at a level near 0.8-1.2. This suggests that acetylene concentrations at Moerdijk are relatively free from local influences other than the refinery plant. For ethene and propene many more local sources affect concentrations at Moerdijk. Acetylene seems therefore a more suited component for a study of trends at larger scales than ethene and propene.

Table 6 *Standard deviation of MC-MA differences in the 261°-310° sector, average concentration at MC in the sector, for the entire distribution and for wind speed more than or equal to 3 m.s^{-1}. Period: 1981-1985.*

	All data			Wind speed ≥ 3 m.s^{-1}		
	St.dev (ppb)	**Av. MC (ppb)**	**fraction**	**St.dev (ppb)**	**Av. MC (ppb)**	**fraction**
ethene	3.02	3.03	1.00	2.42	2.60	0.93
acetylene	0.77	1.34	0.57	0.52	1.17	0.44
propene	1.14	0.88	1.30	0.91	0.74	1.23

Daily data

The section above describes an approach to identify local influences in the hourly data. Removing the influence of the industrial complex in the data is relatively straightforward. It becomes much more difficult with daily hydrocarbon data. A possibility to partially overcome this problem is to use filters which require hourly wind data. A filter could reject a daily hydrocarbon measurement when the standard deviation of the wind directions on that particular day exceeds a certain value. Or to reject the measurement when more than a certain number of hourly wind direction values on that day were in the sector to be excluded. The 1981-1991 hourly (wind and hydrocarbons) data offer the possibility to test filters. From the MC data set daily values were calculated under the condition that at least 12 hourly hydrocarbon measurements were present. The daily values were then assigned to the daily averaged wind directions. In the no filter case annual averages of the non-industrial sectors were calculated by excluding all daily averaged wind directions in the 11°-100° sector, as in the previous sections. In the case of a filter first the filter was applied, followed by excluding all daily averaged wind directions in the 11°-100° sector. Filters counted the number of occurrences per day of hourly wind directions in the 11°-100° sector. If a certain threshold was exceeded the daily hydrocarbon measurement was rejected. Threshold values of 1, 2, 4 and 8 were tested. Table 7 and Figure B16 show the results for ethene, the reference is the annual average, based on hourly values (without the 11°-100° sector).

Without filtering the annual averaged concentrations are overestimated due to the presence of affected air in the non-industrial sectors. The most stringent criterium (threshold 1) underestimates the reference values. The best approximations come from the threshold 4 and 8 filters. The first 5 years the threshold 8 filter is superior to the other filters. After 1985 the threshold 4 filter performs better. It is not clear yet whether there is a connection with the change of wind data after 1985, moving from MA to MC.

Annual wind roses of filtered data show, not surprisingly, that close to the excluded sector the largest deviations from the reference wind rose occurs. Extending the exclusion sector by adding 20°-30° to both sites would remove most of the deviations. In this case the threshold 8 filter didn't perform satisfactory with occasionally relatively large deviations. A more stringent filter such as threshold filter 4 showed better agreement in the wind rose.

Table 7 *Annual averaged ethene concentrations (without 11°-100° sector) based on hourly values, and based on filtered daily values (see text). Threshold 1: daily value rejected when at least 1 hourly wind direction value is in 11°-100° sector; the hourly column is the reference.*

	Annual Averaged ethene (ppb) of all – (11-100)				
year	**hourly**	**Threshold 1**	**Threshold 4**	**Threshold 8**	**No filter**
1981	3.81	3.32	3.51	3.93	4.27
1982	4.37	3.71	4.01	4.25	4.62
1983	3.67	3.05	3.39	3.70	4.32
1984	4.69	4.19	4.46	4.68	4.90
1985	5.57	4.75	5.12	5.49	5.83
1986	4.05	3.60	3.84	4.31	4.57
1987	3.87	3.40	3.80	4.22	4.32
1988	2.86	2.64	3.02	3.13	3.28
1989	3.82	3.57	3.72	3.92	4.21
1990	2.98	2.85	2.96	3.03	3.17
1991	3.37	2.99	3.23	3.46	3.69

Next

Processing the 1992-1999 data to remove the influence of the industrial complex awaits the delivery of hourly meteorological data over the entire 1981-1999 period. The most nearby meteorological stations are Rotterdam, Woensdrecht and Gilze Rijen, each of them at a distance of about 40-50 km in different directions. A comparison with the local meteorology over the first 11 years is necessary to address the suitability of the more remote wind data. But whether one of these site will be chosen, or that constructed wind data will be used, it is clear that the new wind data set cannot be truly representative of the local conditions. This possibly requires adaptation of the filters. Only after a filter has shown to be able to reproduce the trend characteristics of the reference situation (hourly data, MC, 1981-1991), it can be applied to the entire time series.

4.4 Trends of VOC

1981-1991

The analysis in 4.3 showed that the Moerdijk data suffer from inhomogeneities or local differences in air that is not or not directly influenced by the industrial complex. Although many simultaneous observations in MA and MC revealed large differences, the 1981-1985 averages at both stations did not differ much. The question arises how well the annual averages of the non-industrial sectors in MC correlate to those in MA.

Both data sets are "cleaned" from the industrial complex by first removing the associated sectors, then by removing all data above the 99.85 percentile (for each year), and finally by allowing only wind speed conditions of 3 $m.s^{-1}$ or more. Then annual averages for three sectors are calculated: east (101°-150°), south (151°-210°) and northwest (261°-010°). For propene (Fig. B17c) differences in the interannual variability between MC and MA are not negligible. For ethene the correlation between the two sites is better, although in the northwest sector a large discrepancy is found in 1985 (Fig. B17a). The best agreement between the two sites is found for acetylene (Fig. B17b).
When all non-industrial sectors are merged together and split into a summer (May-August) and winter (Nov.-Feb.) season, it appears that the correlation between the two sites is much better for the winter period than for the summer period (Fig.B18). This holds for all three components. For propene the summer correlation is rather poor.

A rather remarkable feature is that in the summer the acetylene concentrations do not vary much from year to year, whereas for ethene and propene large fluctuations are seen. The winter pattern of interannual variability is quite the same for all three components, with only two exceptions: the year 1985 in the ethene-acetylene comparison, and the year 1982 in the ethene-propene comparison. Meteorology is probably the dominant and common factor in the changes from year to year. Finally, although the fluctuations from year to year are quite large it is apparent from Fig. B18 that in the winter the second half of the time series (1986-1991) is at a lower level than the first half.

1981-1999

In 4.3 it has been shown that at the moment the lack of a consistent meteorological data base does not allow to determine trends in a coherent way. Nevertheless, it is tempting to perform a trend analysis to obtain an idea if and to what extent trends of emissions and concentrations match.

Annual averages over the 1981-1991 period were calculated by excluding the 11°-100° sector, and then to remove all values per year exceeding the 99.85-percentile.

All wind speed conditions were allowed. For the 1992-1999 period annual averages were calculated by excluding the 11°-100° sector (no filtering as in 4.3), and then to remove all values exceeding the annual 99-percentile. This percentile is based on the observation that of the approximately 250 daily values remaining after excluding the complex sector, 2-3 values could be regarded as outliers, and most likely representing air having crossed over the refinery.

Traffic VOC emissions in The Netherlands are split into gasoline, diesel and LPG contributions (CBS, 2000). For each category multiplication factors (VOC profiles) were applied to obtain the emissions of the individual components (Veldt and van der Most, 1993). For ethene and acetylene these factors hardly differ for cars with or without 3-way catalyst. For propene the factors differ more, and two time series of emissions were made. The first is based on the average of the two factors, and the effect of the 3-way catalysts is the reduction of total VOC emissions. In the second time series a gradual shift from the no-catalyst multiplication factor to the catalyst has been applied in line with the penetration of the catalysts in the car fleet. Time series of traffic emissions were used since they are readily available and constructed in a coherent fashion. Acetylene was identified as the most suited component of the Moerdijk species for a trend study, and the vast majority of acetylene emissions come from traffic.

The development in time of the filtered MC observations is compared against the trend of traffic emissions in The Netherlands (Figure B19). It is already pointed out that the current filtering methods have their shortcomings and that more elaborated methods await consistent meteorological data. Another shortcoming in the comparison is that foreign emissions are not considered. For a relatively long-lived component as acetylene a substantial foreign contribution is expected. The German contribution has been reduced severely by cutting out the 11°-100° sector. But important contributions of the United Kingdom, France and especially Belgium are not yet considered. Based on earlier studies their contribution is estimated to be in the order of 30-40 per cent.

Despite all shortcomings and limitations there is an excellent agreement between the emission and concentration trends for acetylene (Table 8; Figure B19b). Also for ethene the agreement is good, for propene the agreement is rather poor, especially over the last ten years. These findings suggest that the order of suitability of components as brought forward in 4.3 is probably correct. It also underlines that there is good evidence that the reduction in traffic emissions as reported by the emission inventories is reflected in the observations. The reduction over the 1981-1999 period is 50% period in the observations (ethene and acetylene), and 60% in the traffic emissions. Figure 19 suggests that the reduction sets in after 1985.

Table 8 Change (% with respect to 1981 values) of annual averages of filtered Moerdijk data, and of Netherlands traffic emissions. Period: 1981-1999.

	Trend (%)	
	Concentrations Moerdijk	**NL traffic emissions**
Ethene	-50	-61
Acetylene	-51	-61
Propene	-8	-61 (-75)[1]

[1] –61%: constant multiplication factor; –75%: including a change of the propene multiplication factor (see text)

The discrepancy in the propene trend is largely caused by the last period (Fig. B19). It is not clear yet whether this is due to deficiencies in the filter method, due to developments in the local propene emissions (other than the complex emissions), due to developments in the industrial propene emissions on a larger scale, or, finally, due to trends in the traffic propene emissions different from those according to the Inventories. In the next phase, first of all attention will be given to improve the filter method. Also information will be collected with respect to trends of the local emissions of the components. If the filter method is known to be robust and if trends of local emissions can be excluded, then the attention can shift to investigate discrepancies in trends on a larger scale.

The study on the Moerdijk data so far has produced a somewhat mixed picture. On one hand it has become clear that local influences are large and that filtering methods require coherent wind data before their results can be accepted as reliable and robust. This is illustrated by the discrepancy in the propene trends which cannot be seen without considering shortcomings in the filter method as a possible explanation. On the other hand, for acetylene and ethene an excellent agreement in trends is found. It is not likely that the agreement is purely coincidental. Also acetylene and ethene are subject to local influences from other nearby sources. But if these other sources are predominantly traffic sources, and if changes in local traffic intensity have kept up with changes in national traffic intensity, then the trend of the local contributions to concentrations at Moerdijk MC is similar to the larger scale trends. It is not unlikely that this has been the case for acetylene and ethene.

5. Discussion and future work

5.1 Discussion

5.1.1 NO_x

The analysis identified that different data-providers use different procedures to process near zero concentrations. The lowest acceptable NO and NO_2 concentrations varied from –5 $\mu g.m^{-3}$ (RIVM) to 0 $\mu g.m^{-3}$ (VMM/ISSEP) and to 3.5 and 5.0 $\mu g.m^{-3}$ (LUA-NRW) for NO and NO_2 respectively. It is obvious that this does not allow for a proper across the border comparison in the low concentrations range. Within a network also temporal changes are seen. This relates to remarkable fluctuations from year to year in the population of near zero concentration classes, but also to changes in threshold values. Monitoring aspects are plausible candidates when an explanation is sought for. It is known that during the period under investigation there have been changes in instruments and in calibration. At the moment most of the instrumental history is not yet disclosed, and a further linking of monitoring aspects to trend discontinuities is postponed to a later stage.
The approach of comparing nearby sites has been applied so far only to a limited set of stations. In at least one case (Vredepeel) it revealed remarkable high NO_2 concentrations during a few months in 1996. In the next phase this method will be applied to a larger set of stations.
Although all stations are non-urban the annual average NO_x concentrations are high: in the order of 20-40 ppb. Sources of NO_x are omnipresent in this part of Europe, and none of the stations are free from local emissions.

Linear regression models indicated that trends in The Netherlands under the least polluted conditions (summer, coastal sites in the north of The Netherlands) are probably affected by instrumental aspects or by changes in the procedures of the near zero values. Under these conditions less downward trends or even upward trends are observed. Trends at the same sites but in higher concentration ranges (winter, higher percentiles) showed much better coherence with the other sites. In general, the German sites showed more consistency in their NO_x trends with less differences between higher and lower percentiles, and between summer and winter. Still, at a few sites remarkable discrepancies in trends were observed, such as Borken (summer) and Nettetal (winter).

The 1985-1992 period showed large interannual fluctuations at nearly all sites, but with little to no change on the long run. After 1992 all sites display a gradual but clear downward trend. (Two exceptions are Rodenkirchen and Eifel in Germany where the reduction in concentrations already sets in in the late 1980s.)

Preliminary calculations with a trajectory model (OPS) which uses 1995 NO_x emissions showed that for nearly all stations the annual average concentration calculated by the model agreed within 10-20% with the average from the observations. The model indicates that the interannual variability is to a large extent due to meteorological variability, especially during the winter since the annual averages are much more determined by winter time than by summer time concentrations. The partitioning of the contributions by variability in circulation (advected material), volume (mixing layer height) and deposition losses will be studied in the next phase.
The model to measurement ratio remains constant during the 1980s and increases by about 30% in the 1990s, equivalent to 3% per year. Since most of the meteorological factors have been accounted for in the model, it suggests that this trend in observations must be due to a reduction of NO_x emissions. The timing and the rate of the concentration decrease coincided quite well with the changes of the reported national emissions of Germany, Netherlands and the United Kingdom. The agreement is much less with the Belgian national emission trends. In the next phase it will be examined if a possible different trend of Belgian emissions can be observed in less reductions of the Netherlands sites close to the border, and at the Belgian sites themselves.

The analysis of NO_x data revealed various monitoring problems on one hand, but on the other hand it identified a striking correlation between NO_x concentration trends and emission trends. The success of the trend study is partly due to the fact that it is based on annual averages which are predominantly determined by polluted conditions (and for which shifts in the near zero data procedures are of less importance), and by the fact that the trends are large. An impact by instrumental changes on the NO_x trends cannot be ruled out, but it seems that they, if present, are overwhelmed by the magnitude of the changes in the atmosphere. The agreement between concentration and emission trends also suggests that trends in local emissions are not markedly different from trends in national emissions.

The problems concerning the near zero procedures make a distinction between summer and winter trends, especially at the cleanest sites, not useful.

5.1.2 VOC

At one location (Moerdijk) trends of ethene, acetylene and propene were examined. There are no problems with processing data near the detection limit. Also there are no indications of instrumental problems. A major problem however is the presence of a large refinery source in the near vicinity of the site, and a few discontinuities in hydrocarbon sampling (hourly versus daily data) and in the wind data. A comparison of data of two stations (Moerdijk MA and MC) for five years of common observations shows that even after filtering (removing the complex sector) the data remains inhomogeneous. On a hour-to hour basis relatively large discrepancies be-

tween MA and MC are often observed. On an (annual) average basis the differences are very small. The differences on a hour to hour basis are likely due to other local sources, although indirect influence of the refinery cannot be ruled out, especially under stagnant conditions. The analysis indicated that acetylene was much less influenced by local sources than ethene and especially propene. The inhomogeneity of propene was rather large.
The transition from hourly to daily sampling which occurred in January 1992 was accompanied by the use of remote wind data instead of local data. Filtering out the refinery influence has become much more difficult. A few filter methods were developed that work on hourly wind data. Application depends on the availability of hourly wind data over the entire 1981-999 period.

A provisional filter has been applied on the daily hydrocarbon data, and both sets (hourly and daily) were combined. Filtered acetylene concentrations show a substantial decrease which sets in approximately after 1985. The decline continues until the end of the time series. On a national scale acetylene is for nearly 90% emitted by traffic. There is an excellent agreement between the 1981-1999 trend of filtered concentrations (-50%) and the trend of The Netherlands traffic emissions (-61%). A similar good agreement is found for ethene. For propene the concentrations indicate hardly any trend, whereas the traffic emissions are reduced by as much as 75%. The discrepancy is for a large part caused by the period after 1991 when the filtered concentrations increase, opposite to the strong decrease of the traffic emissions.
It is not unlikely that an important part of the discrepancy must be attributed to deficiencies in the provisional filter. This can be tested when hourly wind data become available. Apparently, the filter works much better for acetylene and ethene. The filter is designed to filter out the refinery source, but not to exclude other local sources. Propene seems to be more subject to other local influences than the other two components.
Nevertheless, the agreement in acetylene and ethene trends is remarkable, given the fact that both species are also influenced by other local sources near Moerdijk. As with NO_x it is concluded that the similarity in concentration and emission trends suggests that trends in local emissions are not markedly different from trends in national emissions.

5.1.3 Ozone

The analysis revealed various discontinuities and drifts in the ozone data. The comparison of nearby sites from different data providers proved very instrumental and essential in detecting discontinuities. By subtracting the concentrations, most of the natural variation of ozone concentrations that occurs on a daily, synoptical and seasonal scale, is removed. The method amplifies the remaining variations.

The comparison of RIVM data with data from other networks demonstrated a transition in the RIVM ozone at the end of 1990 and in 1991. The transition coincides with a change of the ozone instruments followed by a different calibration procedure. It is concluded that the transition must be attributed to instrumental aspects. This problem can also be seen as the most likely explanation for the downward winter trends (1981-1994; 1988-1995) of ozone in The Netherlands, which are not only opposite to the winter trends in the neighbouring countries, but also in contradiction to the theoretical expectations.
Given the data problems during the late 1970s and early 1980s, and given the transition in 1990/91, the conclusion must be that only post 1991 ozone data can be used for trend detection.

The analysis pointed towards data quality problems in other networks as well, but since less information from the laboratories concerning the history of the instruments and calibration has been received, in this stage of the study the conclusions are less explicit. The pairing of sites indicated a discontinuity at most of the Flemish sites in 1995. The Walloon site Eupen showed a drift after mid-1997, and indications of drifts are also seen for the German site Bielefeld. Various irregularities are seen in the UBA data. Information from UBA confirmed that their sites suffered from various instrumental problems prior to 1995.

A statistical model that links daily maximum ozone concentrations (May-September) to meteorological parameters, seasonal terms and trends explained about 80% of the variance in the ozone time series of Eibergen and Wesel. The interannual variability could be, to a large extent, accounted for by model. At the highest percentiles (90th-percentile and more) of the ozone distribution the model performance became less.
The 1987-1998 ozone trends at two nearby sites (Eibergen and Wesel) differed substantially. In order to couple ozone trends to large scale emission trends the ozone trends need to be free from artefacts and local developments. In this combination, only the last 5-6 years seem useable. Similar trends were found by reducing the time series to the 1993-1998 period. A preliminary analysis of results indicates the developments in different segments of the ozone and oxidant distribution (Table 9). The lower percentiles display upward trends in contrast to the downward trends found at the higher percentiles. By comparing the ozone and oxidant trends, it is clear that there is an effect on ozone of the reduced titration by NO. This is especially the case for the lower ozone concentrations. Still, also the lower oxidant concentrations increase. Whether this is a result of a possible increase of background concentrations, or a result of the chemistry under the influence of emission reductions, is not clear yet.

Table 9 Daily maximum summer trends (%/yr) of ozone and oxidant in different segments of the distribution. Period: 1993-1998.

	Eibergen		Wesel	
	O_3	O_x	O_3	O_x
25-percentile	+2.0	+1.1	+1.3	+0.4
50-percentile	+1.1	+0.8	+0.7	+0.1
90-percentile	-2.7	-2.7	-1.4	-1.7
average	-0.2	-0.4	-0.3	-0.6

The 90th-percentile decreases by 1.5-2.5% per year during 5-6 years that NO_x and VOC emissions are reduced in a rate of about –3% per year. This seems like a rather efficient mechanism of peak scavenging. The model responses for corresponding situations need to be sorted out. In an earlier study with the LOTOS model, percentiles of the daily maximum ozone concentrations over the growing season were presented (Builtjes, 1992). Sensitivity calculations for a scenario with a 30% reduction of anthropogenic NO_x and VOC emissions showed a response of +5% for the 50th-percentile in the corresponding grid cell. For the 99th-percentile a decrease of about –5% was estimated. Although the basis of comparison is not entirely the same, the impression emerges that the sign of the changes in the observations seem to correspond with model results, but that the magnitude of the changes in the observations is much larger than the corresponding response of the model. Assuming a linear response and dividing the model response by ten to obtain a response based on a 3% emission reduction, the increase of 0.5% according to the model is smaller than the 0.7-1.1 % increase in the observations. The 0.5% decrease of the 99th-percentile is much smaller than the 1.4-2.7 decrease in the (90th-percentile of the) observations.

5.2 Future work

In the next phase of the project (2001-2002) the following activities are planned:

NO_x
- extend the analysis by including the years 1999 and 2000;
- extend the set of paired stations;
- collect information from the institutes concerning the history of the NO and NO_2 measurements;
- develop and apply a statistical model for NO_x; This model is different from the ozone model with partially other meteorological parameters; The emphasis in application will probably be on the winter periods;
- perform a few sensitivity runs with the OPS model.

VOC
- collect wind data on a hourly basis for the entire 1981-1999 period;
- develop and apply an extended filter;
- collect information about local emission trends;
- if possible, develop and apply a statistical model for VOC; In principle this could be the same model as for NO_x.
- (elaborate the Kollumerwaard and Zegveld data.) This activity is not planned but highly recommended .

Ozone
- extend the analysis by including the years 1999 and 2000;
- collect (more) information from the institutes concerning the history of the O_3 measurements;
- collect more meteorological data and apply the statistical model for ozone to all sites;
- develop and apply a statistical model for winter time ozone;
- compare the trend results with trend information according to dispersion models.

6. Conclusions

This report describes the first part of an analysis of measurement data of nitrogen oxides, volatile organic compounds and ozone in The Netherlands, Flanders and Northrhine-Westphalia. Additional information comes from Wallonia and two neighbouring German provinces. The following conclusions are drawn.

NO_x

- There are indications that trends of NO_x concentrations in less polluted conditions in The Netherlands are affected by variations in processing the near zero concentrations.
- Trends of NO_x under more polluted situations (winter, higher percentiles) show more consistency amongst the Netherlands and German stations.
- Interannual variability of NO_x concentrations is to a large extent caused by interannual variability during the winter period.
- Model calculations show that a large part of the interannual variability in NO_x concentrations is due to interannual variability of the meteorological conditions.
- The observations indicate little to no long term changes in annual average NO_x concentrations during the 1980s and a 30% reduction during the 1990s. An earlier start of the decrease is seen at two of the German stations.
- The timing and the rate of decrease of the NO_x concentrations correlates very well with the trends of the national NO_x emissions in The Netherlands and Germany.

VOC

- An evaluation of VOC trends is hampered by a lack of sufficient measurement data.
- Propene concentrations at Moerdijk are more influenced by local sources than ethene and especially acetylene.
- The part of the Moerdijk data that is not or little influenced by a large local source shows that acetylene and ethene concentrations have decreased by 50% over the 1981-1999 period. Propene concentrations decreased not more than 8% over the same period. Given the provisional status of a mathematical filter used to overcome a discontinuity in sampling strategy and discontinuities in wind data, the reduction in concentrations need to be regarded as preliminary.
- Traffic emissions in The Netherlands of acetylene and ethene dropped by 61% over the 1980-1999 period. The similarity in emission and concentration trends of ethene and acetylene suggests that the trends in local emissions are not markedly different from trends in national emissions. The cause of the discrepancy in propene trends is not clear.

O_3

- The analysis revealed various discontinuities and drifts in the ozone data of all five networks.
- The analysis shows that the ozone data in The Netherlands have undergone a transition in 1990/91, which is most likely due to the replacement of monitors followed by a change in the calibration. Irregularities in the ozone data in the late 1970s and early 1980s, and the discontinuity in 1990/91 leaves only post 1991 ozone data suitable for trend studies.
- A statistical model based on local meteorological data explains, for the stations Eibergen and Wesel, more than 80% of the variance in summertime daily maximum ozone concentrations over the 1993-1998 period.
- During this period both stations showed downward trends for the higher percentiles of ozone and oxidant, whereas upward trends were seen in the lower percentiles of ozone and oxidant.
- The increase of the lower ozone percentiles is partly due to a reduction of the titration by NO, but partly due to other changes in the chemistry of the atmosphere, or to changes in the background concentrations.
- A preliminary comparison indicated that the sign of the changes in ozone and oxidant (lower percentiles: +; higher percentiles: -) corresponds with results of a chemical dispersion model (30% reduction of anthropogenic emissions of NO_x and VOC), but that the magnitude of the changes is larger in the observations than in the model results.

General

- Trend analyses require a thorough screening and re-examination of the data. Without screening there is a serious chance that the trends are influenced by artefacts.
- Essential in detecting discontinuities in the observations is the intercomparison of data from different data providers.
- Visual inspection of data and examination of trends in different segments of the distribution are instrumental in screening the data sets.
- The striking correlation between emission and precursor concentration trends suggests that the possible impact of instrumental changes is overwhelmed by the magnitude of changes in the atmosphere. It also suggests that, given the presence of local sources at all sites, the trends in local emissions are not markedly different from trends in national emissions.

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9. Authentication

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Annex A Literature Meteorological Variability

Methods that account for the meteorological influence on the observed ozone time series often use fitted relations between ozone and a set of meteorological parameters. The empirical correlation between ozone and for instance temperature does not reveal whether it is through transport, chemistry, deposition, emissions or possibly other processes. A method that offers the possibilities to distinguish between the different contributions and to quantify the processes is by using long term simulations with a three-dimensional high resolution dispersion model that incorporates chemistry, emissions, deposition and transport to calculate the different dependencies. An important condition is that the model is able to simulate the observations at a "sufficient" level of precision to have confidence in its abilities of unravelling the various shares to ozone.

In this section an overview will be given of studies that used the approach of "declimatising" the long-term ozone records by fitting the observations on a set of available meteorological parameters and a trend term. The studies differ in the amount of meteorological parameters that are included, in the periods considered (the whole year; only the summer months) and the sort of statistical procedure employed. Choices are sometimes related to the type of ozone information that is requested. Trends in annual averages require a different approach than a trend in extreme high values or than a trend in the number of exceedances of an air quality threshold value. Most of the studies concern ozone (or the natural logarithm of ozone), a few are based on oxidant. Trends are calculated for individual sites as well as for network values. A network value can be the average or a percentile or a maximum of the ozone concentrations at the sites in the network.

The methods will be briefly described in how they work. Important is to evaluate the performance of the methods in the ability to remove the inter-annual variability. Is the method able to explain to a large extent the variance of the data and to reproduce the observations? Is the method successful in reducing the margins of uncertainty in the regression coefficient?

A.1 Separation of scales

In a series of papers by the State University of New York at Albany (Rao and Zurbenko, 1994; Rao et al., 1995; Rao et al., 1997; Flaum et al., 1996) ozone trend studies are presented which are based on the use of low pass filters to separate different time scales in the observations. The natural logarithm of the daily 1-h maximum ozone concentration is thought to consist of a baseline component and a short-term component. The baseline component is described as the sum of a seasonal component and a trend component. By appropriate filtering of the logarithm of ozone the baseline component is obtained. Subtracting the filter time series from

the original time series gives the short term component. The idea is to consider the short-term component as white noise. This is achieved by working with the natural logarithm of ozone instead of ozone and by choosing an appropriate filter. The filters $KZ_{k,m}$ are defined as the number of iterations (m) performed by a moving average with a window of k days. Filter widths ($KZ_{29,3}$, $KZ_{15,5}$) used in these and other studies (Smith and Adamski, 1998) are in the order of 1-2 months.
The baseline component correlates well with the baseline of the daily maximum temperature which is not surprising since both have rather similar seasonal cycles. Consequently, the temperature correction has no (or not much) relation with synoptic scale temperature influences but accounts for the seasonal cycle of ozone. An improvement in correlation was found by shifting the temperature with 19 days (Rao and Zurbenko, 1994). Surface temperature (filtered) was found to correlate best with filtered ozone (Flaum et al., 1996) followed by dew point temperature. Including meteorological corrections resulted in a reduction of the margins of uncertainty in the regression slopes of ozone by about 20 per cent (Flaum et al., 1996). The addition of dew point temperature did not add to improving the accuracy of the slope lines. It did however affect the slope of the trend lines for sites located in the Carolinas and Georgia which have a more humid climate. The meteorologically corrected trends did not differ significantly from the uncorrected trends for seven of the nine sites.
The short-term or synoptic component in the ozone concentration is well correlated with the synoptic component of neighbouring stations. The e-folding distance of the spatial correlation is about 300-400 km (Rao et al., 1995; Rao et al., 1997).

A similar approach was undertaken by Bosschert and Roemer (1995) in their analysis of oxidant (O_3+NO_2) trends in The Netherlands. Oxidant was chosen rather than ozone due to the abundance of NO_x in this part of Europe, even at the non-urban sites. Trends by linear regression were determined for the logarithm of daily 1-hourly maximum oxidant concentrations (raw data), for temperature corrected data (filtered and unfiltered). Above 15-20° C daily maximum temperature and oxidant are reasonably correlated, at lower temperatures the correlation is much weaker. This relation between oxidant (ozone) and temperature is on a synoptic scale rather than on a seasonal scale as in Rao and Zurbenko (1994).
A filter of $KZ_{7,1}$ was chosen to preserve more synoptical information in the baseline component. Moreover, filters with more iterations and/or larger windows did not change much the distribution of the residuals which was close to random. The raw data for eight of nine sites exhibited significant (at 95 confidence level) downward trends. The temperature corrected trends were slightly more downward (decreasing oxidant in a time of increasing temperatures). The margins of uncertainty of the trends decreased by 20-30% by applying the temperature correction on the unfiltered data. Similar trend results were obtained with the filtered data although the margins of uncertainty increased. The increase is due to the correction for auto-correlation in the data which is much larger in the filtered data.

The correlation between daily maximum temperature and oxidant is positive in the summer because easterlies are associated with warm and polluted air favourable to ozone production. In the winter westerlies are warmer and advect more ozone than easterlies which are depleted of ozone due to dominance of NO titration and deposition in this season. Basically, the method assumes temperature as an indicator for the origin of air. However, in case of a general warming when temperatures increases are observed even within classes of circulation types, it is doubtful whether the method corrects for the proper reasons.
The second year of the time series (1982) is characterised by relatively high ozone concentrations. Leaving out this year reduces the trend of the uncorrected (and unfiltered) data substantially rendering them not significant (95% confidence level) at more than half of the stations. The temperature corrected trends are, however, almost similarly sensitive to omitting this particular year. Summer daily maximum temperatures in 1982 were lower than in 1983 although ozone concentrations were substantially higher indicating that other factors are involved.

A.2 Atmospheric circulation classification

The synoptic-scale atmospheric circulation determines radiation, temperature and moisture and as a result is important in the day-to-day variation of ozone concentrations. In Comrie and Yarnal (1992) pooled network daily 1-h maximum ozone concentrations measured at four locations in the suburban Pittsburgh area were linked to nine synoptic classes. The pooling is to reduce local influences at each of the sites and to obtain more representative data for the whole area.
The interannual variations in annual mean maximum ozone are declimatised by normalising the synoptic-scale frequencies (Comrie, 1992a). The declimatised series of the annual mean of maximum ozone is very close to the original series. The variation within the synoptic classes is large and shifts in frequencies among the different classes explain apparently only a small portion of the variation. The annual means of daily maximum 1-h ozone per synoptic type showed substantial variation from year to year.
Two of the synoptic classes contribute prominently to ozone above 100 ppb. On a monthly and annual basis the distinction between the types is less clear. It is possible that better results might be obtained by applying the technique on summer months only or on the ozone exceedances above thresholds of 100 ppb or more. Comrie (1992b) proposed sequencing techniques to improve the explanatory power of the method.

A similar procedure as in Comrie (1992a) was used by Remijn and Roemer (1996) in their study of oxidant trends in The Netherlands and Germany (1981-1994). Oxidant concentrations were classified into one the 30 Gross Wetter Lage types (Hess and Brezowsky, 1968). Annual statistics were declimatised by normalising on the long term distribution of the Gross Wetter Lage types. The margins of uncertainty of the trend regression lines improved by about 20-30% in the declimatised time series compared to the uncorrected data.

In Pryor et al. (1995) gridded meteorological fields around and above Vancouver were subjected to a Principal Component Analysis (PCA) to yield four principal components. Daily maximum ozone concentrations during five years (1984-1988) were used to test the dependence on synoptic-scale observations. Daily component scores of the four modes were used to construct a multiple least square regression equation of summertime daily maximum ozone. Application of sequencing as in Comrie (1992b) by incorporating previous days in the regression equation did not enhance the explained variance. The method performed rather well in predicting occurrences of exceedance days, but was less accurate in predicting their magnitudes.
The regression equation was then used to predict ozone concentrations during the summers of 1989-1992. It was found that the ozone concentrations were generally overestimated by the regression model. The decrease of ozone concentrations on non-exceedance days could not be explained on the basis of synoptic-scale meteorological variability. It was hypothesised that the downward ozone trends are a response of changing emissions. However, the authors could not exclude inadequacies of the method to properly account for singularly pollution days.
Pryor (1998) extended this study by using eight sites instead of one. Significant (95% confidence level) decreases of ozone were found after accounting for the change in meteorological conditions at six of the eight sites between 1984 and 1991.

In Klein Tank and Können (1996) a principal component analysis was employed on the 1951-1994 daily 500 hPa geopotential height data above Western Europe. The analysis distinguished three modes. In Rijnten and Roemer (1996) daily component scores of the three modes of the atmospheric circulation were linked to daily maximum oxidant concentrations of sites in The Netherlands in the period 1981-1994. The correlation between oxidant and the three modes were rather low; the highest correlation was seen between summertime oxidant and anti-cyclonic circulation. Adjusting the time series for interannual changes in the occurence of the circulation types a small reduction (10-30%) in the margins of uncertainty of the trend lines was achieved.

The development of a classification scheme to describe the relation between ozone in Birmingham, Alabama and meteorology was elaborated by Eder et al., 1994. In the first step the meteorological data consisting of 56 measured and 3 derived parameters per day was decomposed by means of PCA into 5 principal independent components. Meteorological regimes are identified by applying clustering techniques on the five daily principal component scores. A two-stage approach (average linkage plus convergent k means) was adopted to obtain a set of seven clusters with minimum within-cluster variance and large between-cluster variance. The clusters are associated by typical circulation patterns in the Eastern part of the

USA. The Kolmogorov-Smirnov test identified that 19 of 21 pairs of clusters had significantly different ozone characteristics.
The final step is to describe for each of the seven clusters separately the daily 1-h maximum ozone concentration by a linear regression equation linking ozone to a set of meteorological parameters. The parameters were selected in ranking order of their contribution to the explained variance with each cluster. Ranking orders and selected parameters were not similar for the different clusters. The explained variance of the composite of seven clusters was 59% and the root mean square error between model and raw data was 12.8 ppb. A linear regression model on the non-clustered data set yielded an explained variance of 53% and a root mean square error of 13.9 ppb. The segregation by clusters results in an improvement of the performance of the model.

The above mentioned method employed by Eder et al. (1994) was modified in a study by Davis et al. (1998). In the first step a singular value decomposition technique was employed to decompose the meteorological data into 6 principal components. The second step comprised a one-stage approach as well as a two-stage approach of clustering resulting in 7 clusters which were not identical. In the third step the linear regression model by Eder et al. (1994) was replaced by an additive model approach whereby each of the meteorlogical variables was represented by a natural spline (Green and Silverman, 1994). The method was applied on the 1981-1992 daily 1-h maximum ozone data collected in Houston, Texas. Utilisation of the two-stage approach results in a better segregation of clusters than with the one-stage approach. The explained variance within clusters (two-stage) varied between 48% (cluster with highest mean ozone) and 71% (cluster with highest mean ozone). Very remarkably the results are opposite for the two-stage clustering approach. The highest explained variance (73%) corresponds with the cluster with the highest mean ozone, while the lowest variance (54%) is seen in the cluster with the lowest mean ozone.

A.3 Other linear and non-linear regression models

In Bloomfield et al. (1996) a non-linear regression model for network median ozone (based on daily 1-h maximum ozone at 45 sites in the Chicago area) was constructed. The network median was used to be less sensitive to extreme concentrations. Surface as well as upper air meteorological parameters were used to account for changes in the weather patterns. In a step wise procedure linear and polynomial functions describing the relationships between ozone and meteorological parameters were added. Also seasonal terms and a trend term were included. The explained variance by the full model was 80% compared to 30% for the model without meteorological terms. Without the meteorological component the network median ozone displayed an upward trend of 5.3%/decade, including the meteorology a downward trend of -2.7%/decade was found, although in both cases the trends were not significant at the 95% confidence level. Adjusting for meteorology improved the precision of the trend estimate with 30-50%.

A complementary approach was undertaken by Holland et al. (1999) in their analysis of ozone at 35 rural CASTNet sites in the Eastern USA (1989-1995), where, instead of a non-linear model, a generalised additive model (GAM) was used. GAMs model the dependent variable by using non-parametric scatterplot smoothers. The trend model used smoothed functions of meteorology, seasonal variations and trend to describe the logarithmically tranformed weekly ozone concentration at the sites and at clusters of sites. Six clusters were identified by means k-means clustering techniques. For the smoothed functions both smoothing splines and loess functions (local regresssion models) were employed. The authors found their site specific models to predict most concentrations well but that the model tended to underestimate the peak values which might be attributed to the use of weekly averages. The explained variance for the site specific models ranged from 73 to 92%.
The procedure was repeated for daily 1-h and daily 8-h maximum ozone. Explained variance now ranged from 48 to 81% considerably less than the quality of fit with the weekly averages. Trends of the daily maxima were found consistent with the trends of the weekly averages.

A linear regression model was applied on the 1980-1990 ozone data from Windsor in Ontario, Canada (Xu et al., 1996). The logarithm of daily 1-h maximum ozone was described by a trend and a sine and cosine to account for the seasonal variation. A second model was used to include meteorological influences. The second model was linear in the four meteorological variables but distinguished seven categories each of them with different regression lines. The explained variance increased from 57% to 70% by including the meteorology. In the simple model the seasonal variation accounts also for the seasonal variation of the meteorological variables. The margins of uncertainty of the trend by the more advanced model were about 20% more precise than those based on the simpler model. Including the meteorological components in the regression model resulted in a downward shift of the trend at Windsor but also at the other sites in southern Ontario (a shift down to 0.5 per cent per year).

Kuntasal and Chang (1987) have studies trends of ozone (and precursors) in the south coast air basin of California for the period 1968-1984. For ozone they used network average daily 1-h maximum data from the third quarter (July-September). In a polynomial model the 850 mbar temperature and NO_x and NMHC concentrations were linked to the daily maximum ozone concentration. Including the two precursor terms increased the coefficient of correlation between observed and modelled ozone from 0.82 to 0.90. By including the temperature adjustment the correlation between observed and modelled ozone increased somewhat. Depending on the period considered the improvement danged from virtually no improvement to substantial (correlation coefficient increased from 0.46 to 0.67).

A.4 Fixed range and fixed values models

A series of articles is based on the concept of fixed-range and fixed-value criteria. In Chock et al., 1982, followed by Kumar and Chock (1984), exploring trends of oxidant in the California air basin (1971-1979 and 1971-1981 respectively) , three sets of ranges of meteorological parameters were selected corresponding to high, moderate and low oxidant formation potential. Temperature was found to be the primary controlling variable, and in each year the days with the 15 highest temperatures were selected After having determined the means and standard deviations of temperature and other meteorological parameters for a total of 9x15 days the ranges for the meteorological parameters for the three types of oxidant formation potential were determined. According to the fixed-range or meteorological window criteria the days are selected that correspond to for instance the high oxidant category. Trends are determined by linear regression of the annual means of the daily maximum oxidant of one of the three categories. In the fixed-value approach the set of meteorological parameters obtained in the fixed-range approach was used to describe the logarithm of daily maximum oxidant concentration in terms of a background and the selected meteorological parameters for each category and each year separately. The corresponding coefficients varied substantially from year to year. Annual means of daily maximum oxidant (in of the three categories) were constructed by means of the meteorological parameters and coefficients of the corresponding years. Trends followed from linear regression of the so-constructed annual means.

An almost similar procedure was adopted by Korsog and Wolff (1991) in their examination of urban ozone trends in the northeastern U.S. during the summer periods of 1973-1983. Trend lines were calculated by regression of annual statistics of the 75th percentile of daily maximum ozone, and according to the fixed range levels, and the fixed value levels. Initially, distributions of meteorological variables were examined on the basis of days when ozone was greater than 80 ppb. Next the meteorological window was widened to include about 25% of the total data. After applying the fixed-range and fixed-value criteria trends were calculated by simple least square regression and by the Mann-Kendall non-parametric test for trends. At a few sites the correction of data according to the fixed value method resulted in substantially different trends compared to the trend based on the 75th percentile while at other sites both methods produced similar trend lines. At most of the sites the standard error of estimate decreased somewhat by applying the correction method.

A.5 Decision trees

In Stoeckenius (1990) the CART (Classification And Regression Tree) methodology as developed by Breiman et a. (1984) was employed on network data of Philadelphia and Connecticut. The method selects groups of days on the basis of daily meteorological parameters that leaves the variance of ozone within each group as small as possible. In the regression tree analysis the algorithm splits off data into two sub classes (and based on the value of a meteorological predictor variable) in order to maximise the difference between the variance of the initial data group and the sum of variances of the two newly formed sub classes. Since the sum of variances can be decreased by adding more and more sub classes a penalty approach is included to avoid the creation of a large set of sub classes. The daily maximum network ozone of the Philadelphia and Connecticut areas were divided into 15 and 7 sub classes respectively. Due to the interannual variability of the atmospheric circulation the number of days in each sub class varies strongly from year to year. The annual statistics (annual daily maximum, number of exceedance days) are then declimatised by normalising each year on the long term distribution of sub classes. Results show a reduction of the variability from year to year by the meteorology adjusted data set. However, quite a lot of variability remains which is not accounted for by the method.

The same procedure was applied by Dekkers and Noordwijk (1997) on the network average ozone concentrations in the Netherlands for the period 1987-1994. They found a considerable reduction (nearly similar as in Stoeckenius, 1990) in the interannual variability of the number of exceedance days (8-hourly average above 110 $\mu g.m^{-3}$) and a smaller reduction for the interannual variability of growing season averages and number of exceedance days of the 65 $\mu g.m^{-3}$ threshold value of daily averages.

A.6 Extreme values

Several studies have been dedicated to detect trends in the extreme values of ozone. Extreme value theory extended to the largest 10 values (in a year) was applied by Shively (1990) to investigate the presence of a trend in the largest ten annual ozone values at two sites in Texas. To explore whether the probability of the annual ozone maximum exceeding a threshold value is changing in time statistical tests (without meteorology) are used to identify temporal shifts in the extreme value distribution. Trends were determined for the first, fifth and tenth maximum. For both sites it was found that the standard deviation of trends in the fifth and tenth maximum were smaller (in absolute and relative terms) than of the first maximum.
In a second paper by Shively (1991) meteorological parameters are included in the description of the frequency of threshold exceedances. In this study a non-homogeneous Poisson process model was used that links the frequency of high values directly to a trend and to meteorological parameters. The coefficients were determined by maximising the likelihood function. The effect of including the meteorological parameters in improving the precision of the trend estimates can not be inferred from the papers. The first paper presents trends of maxima, the second expresses trends of number of exceedances.

Cox and Chu (1993) developed and applied a probabilistic approach to account for meteorological fluctuations in the ozone data (1981-1991) of 43 urban areas in the US. The method is based on the Weibull probability distribution. Coefficients of trend and meteorological parameters are estimated by the maximum likelihood method. The model was tested in its performance to reproduce the upper percentiles of daily maximum ozone concentrations for each of the eleven years. Results for the Chicago area showed that the modelled 95th and 99th percentiles agreed well with the observed percentiles, except for the 95th percentile in 1984 and the 99th percentile in 1988 which fell outside the error bars. The model has the tendency to slightly underestimate the upper percentiles in ozone rich years, and most particularly in 1988. Meteorologically adjusted ozone percentiles are obtained by normalising each year's meteorology by the long-term average meteorology. The result for the 99th percentile of daily maximum ozone in Chicago is a relatively smooth line. Compared to the uncorrected time series most of the interannual variability has been removed. Taking into account the validity of the model to reproduce the percentiles of the observations the method seems successful in stripping the interannual variability from the annual statistics. The coefficients of correlations between the modelled and observed upper percentiles were 0.78, 0.74 and 0.67 for the 90th, 95th and 99th percentile respectively. Trends below -0.5% per year and above +0.5% per year were found statistically significant at the 95% confidence level, which happened to be at 31 of the 42 sites.

A.7 Time series and intervention analysis (ARIMA)

In Tiao et al. (1975a) trends of ozone (1955-1972) in the Los Angeles basin were studied by means of time series models of the ARIMA type. ARIMA stands for AutoRegressive Integrated Moving Average (Box et al., 1994) and is often used as a tool to make time series analysis. In this study there was no link established with meteorology, a similar study to CO however incorporated a simple relationship with mixing layer height (Tiao et al., 1975b). The authors have examined the time series to the presence of a trend in ozone since 1966, the year when legislation for the reduction of NO_x and HC from mobile sources was adapted. The model describes the change in monthly averages of ozone by incorporating two trend terms (winter and summer) to be effective after 1966. The model furthermore includes a second order moving average and a first order autoregressive term operating on white noise. The model suggests strong evidence of a decrease of ozone in the summer (since 1966) and no change in the winter.

A.8 Conclusions

It can be concluded that the statistical models were successful to explain a certain fraction of the ozone variability. A few studies reported more accurate trends (smaller uncertainty margins) by regression models incorportating meteorological parameters than by models with only trend and seasonal variation terms.
It is not possible to rank the methods in their success rate. The data sets are different, and also different ozone parameters are used. Nevertheless, the impression emerges that models using local meteorology are more successful than those applying synoptic scale parameters. The discriminative power of classification by means of synoptical information is apparently rather limited for ozone, and much ozone variability remains within classes. The approach with local meteorology looks very promising in relatively flat terrain, but it is not certain if the application will be successful under other conditions, such as mountainous terrain.

Table A.1 A selection of trend studies with meteorological correction methods.

Authors	**Sp.**	**Area**	**Period**	**Description**
Bosschert and Roemer, 1995; Roemer and Bosschert, 1997	O_x	Netherlands	1981-1994	daily 1-h maximum; year; temperature correction through Kolmogorov/Zurbenko filter $KZ_{7,1}$
Remijn and Roemer, 1997	O_x	Netherlands, Germany	1981-1994	daily 1-h maximum; year; correction through Gross Wetter Lagen classification
Rijnten and Roemer, 1997	O_x	Netherlands	1981-1994	daily 1-h maximum; year; correction through 500 hPa circulation parameters
Stoeckenius, 1990	O_3	Northeastern USA	1979-1988	daily 1-h maximum; April-October; network average and maximum; decision tree
Dekkers and Noordwijk, 1997	O_3	Netherlands	1987-1994	daily 1-h maximum; network average; decision tree
Zeldin et al., 1990	O_3	California	1981-1989	daily 1-h maximum; June-September; meteo correction for pairs of sites weekdays and weekends;
Shively, 1990	O_3	Texas	1973-1987	annual maximum; extreme value theory; probability of threshold exceedance
Shively, 1991	O_3	Texas	1981-1987	daily 1-h maximum; May-Oktober; non-homogeneous Poisson Processes; probability of threshold exceedance; meteo corrected
Rao et al., 1992	O_3	NJ, NY, C, USA	1980-1989	daily 1-h maximum; June-August; network maximum; extreme value theory; Mann-Kendall np test
Cox and Chu, 1993	O_3	USA	1981-1991	daily 1-h maximum; ozone season[1]; network maximum; fit on various meteo parameters; assumption of Weibull probability distr.
Cox and Chu, 1996	O_3	USA	1983-1993	daily 1-h maximum; ozone season[1]; network maximum; fit on various meteo parameters; assumption of Weibull probability distr.
Chock et al., 1982	O_x	California	1971-1979	daily 1-h maximum; June-Oktober; fit on various meteo parameters;
Kumar and Chock, 1984	O_x	California	1971-1981	daily 1-h maximum; network maximum; June-Oktober;

Authors	Sp.	Area	Period	Description
Korsog and Wolff, 1991	O_3	Eastern USA	1973-1983	daily 1-h maximum; June-August; 75th Percentile; fit on various meteo parameters; Mann-Kendall np-test.
Bloomfield et al., 1996	O_3	Chicago, USA	1981-1991	daily 1-h maximum; April-October; network median; fit on various meteo parameters
Davis et al., 1998	O_3	Texas	1981-1992	daily 1-h maximum; April-October; network median; cluster analysis and fit to meteo parameters
Holland et al., 1999	O_3	Eastern USA	1989-1995	weekly average, daily 1-h and 8-h maximum; generalised additive model
Comrie and Yarnal, 1992	O_3	Pittsburgh, USA	1978-1987	daily 1-h maximum; network pooled mean; correction through synoptic weather classification scheme on annual basis;
Comrie, 1992	O_3	Pittsburgh, USA	1978-1987	as in Comrie and Yarnal (1992) plus sequencing technique.
Eder et al., 1994	O_3	Birmingham, AL, USA	1981-1990	daily 1-h maximum; May-September; PCA, 2-stage clustering....
Pryor et al., 1995	O_3	Vancouver, Canada	1984-1992	daily 1-h maximum; July-September; fit on synoptic circulation parameters.
Pryor, 1998	O_3	Vancouver, Canada	1984-1991	daily 1-h maximum; July-September; fit on synoptic circulation parameters.
Xu et al., 1996	O_3	Ontario, Canada	1980-1991	daily 1-h maximum; year; fit on various meteo parameters.
Rao and Zurbenko, 1994	O_3	New Jersey, USA	1983-1991	daily 1-h maximum; year; fit on daily maximum temperature with $KZ_{29,3}$ filter
Rao et al., 1995	O_3	Eastern USA	1983-1992	daily 1-h maximum; year; fit on daily maximum temperature with $KZ_{365,3}$ filter
Flaum et al., 1996	O_3	Eastern USA	1983-1992	daily 1-h maximum; year; fit on daily maximum temperature and humidity with $KZ_{365,3}$ filter
Smith and Adamski, 1998	O_3	Lake Michigan, USA	1980-1995	daily 1-h and 8-h maximum; April-Oktober; fit on temperature with $KZ_{15,5}$ filter
Kuntasal and Chang, 1987	O_3 HC CO NO_x	California	1968-1985	daily 1-h maximum; July-September; temperature and precursor correction
Tiao et al., 1975a	O_3	Los Angeles	1955-1973	ARIMA
Tiao et al., 1975b	CO	Los Angeles, USA	1955-1972	Mixing layer height correction, Plus ARIMA technique

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Annex B Figures and Tables

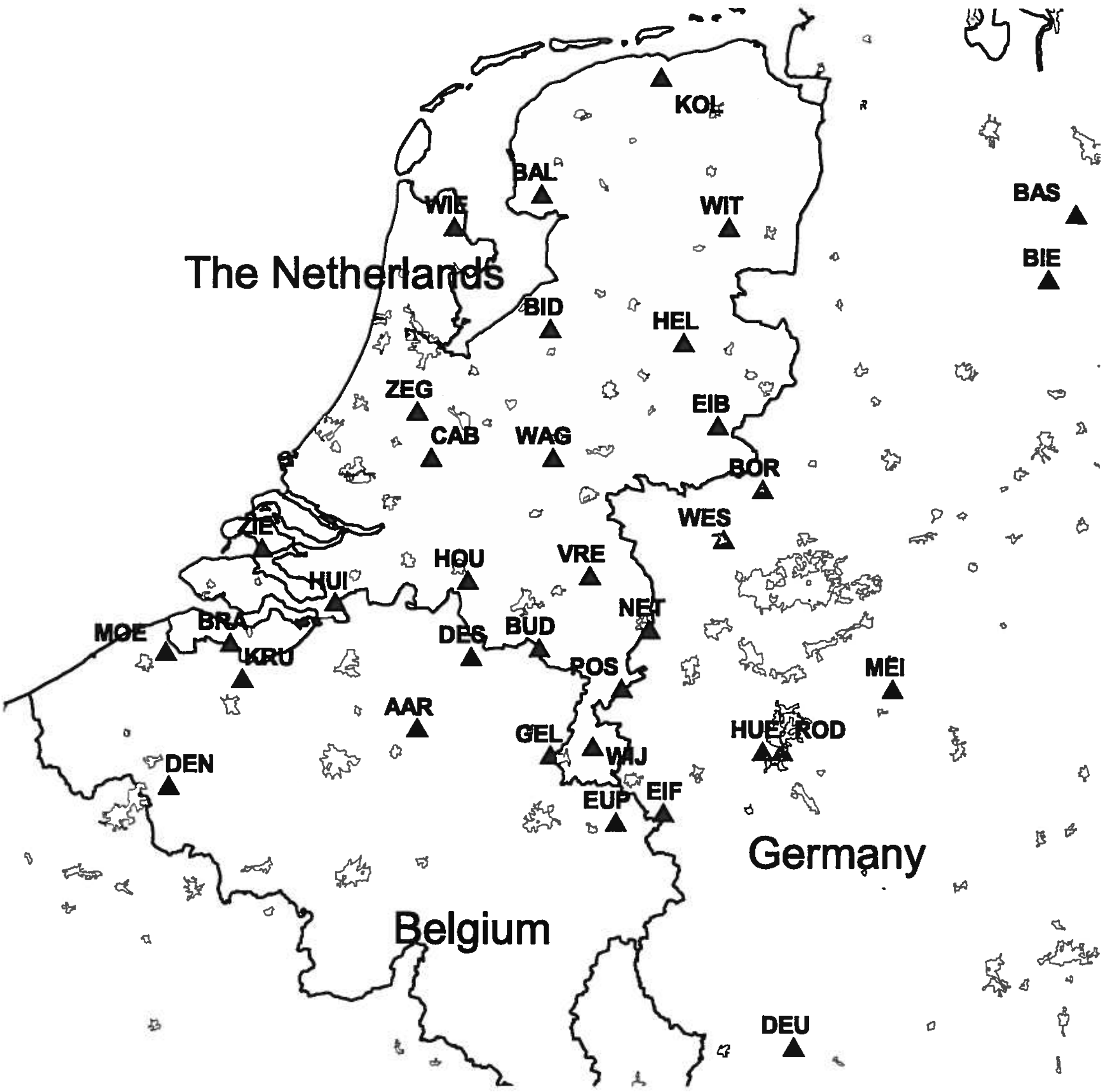
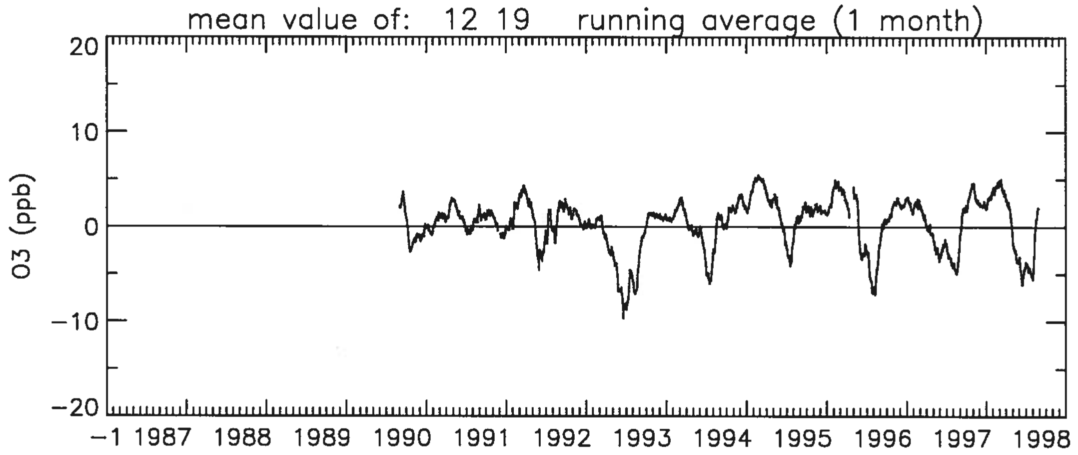
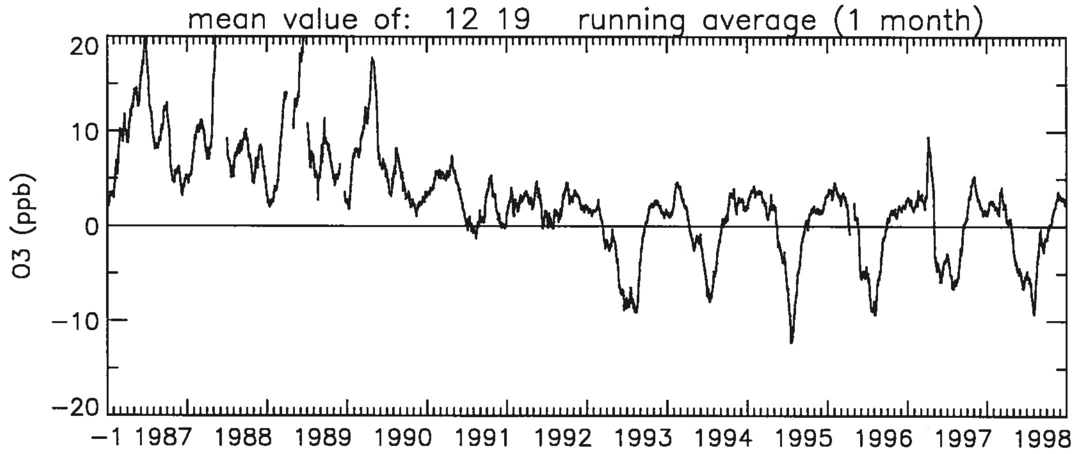


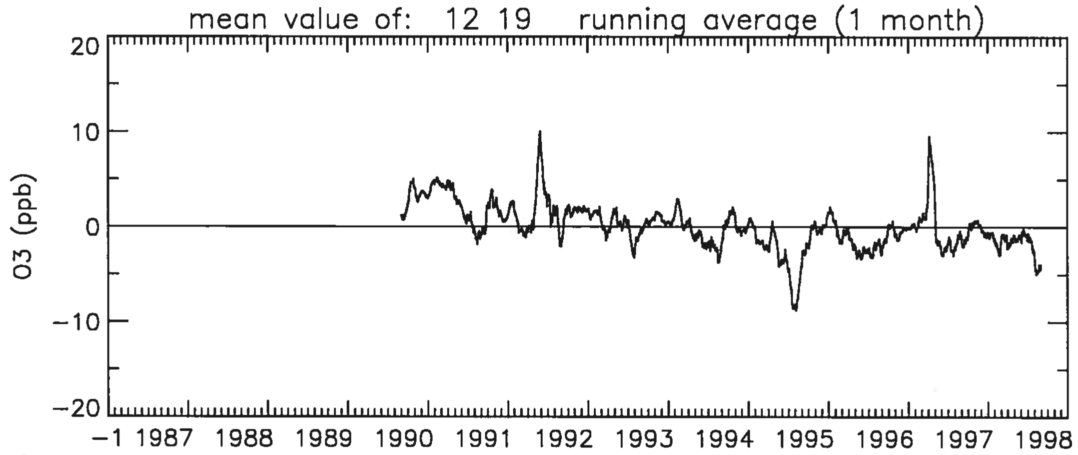
Figure B1 *Location of stations. Stations are abbreviated by the first three characters of station name. Size of the area is approximately 400 x 400 km.*



eibergen – borken

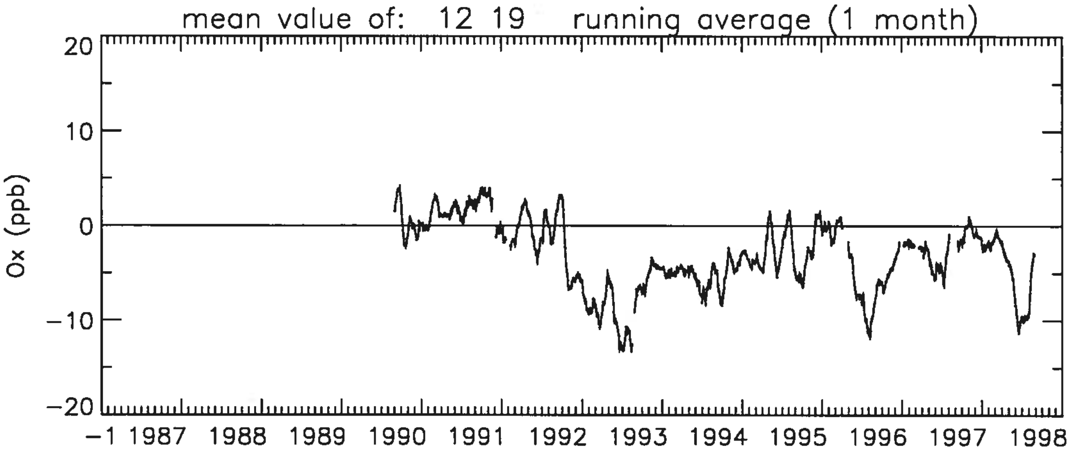


eibergen – wesel

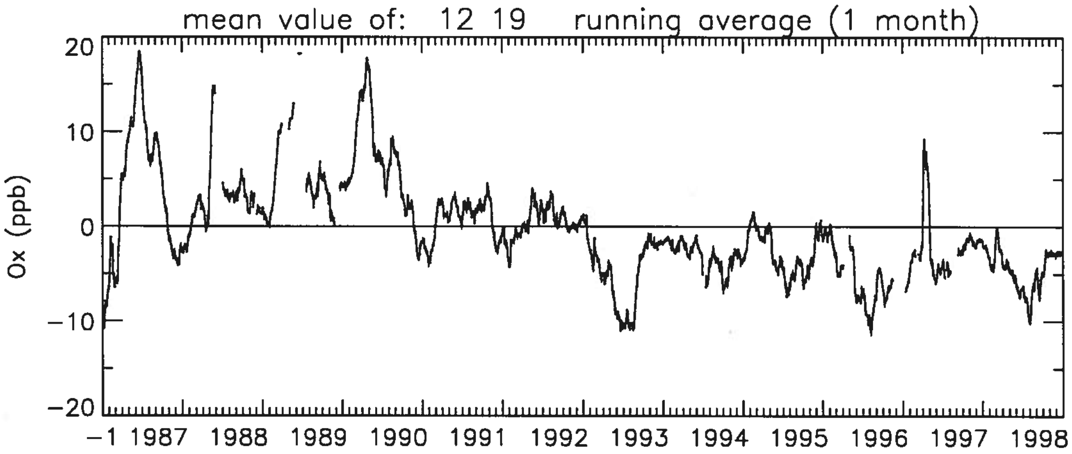


borken – wesel

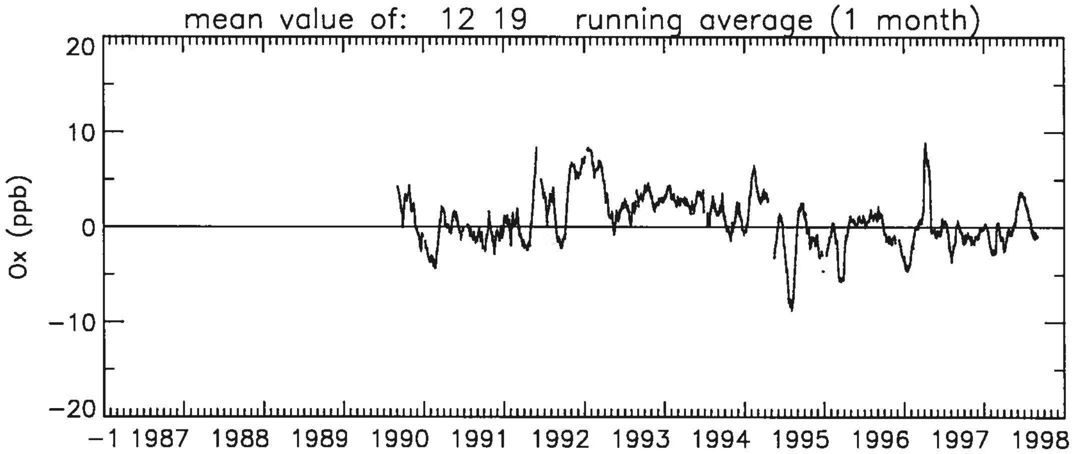
Figure B2a *The monthly running mean of the difference of daily (12-20h) ozone concentrations. Stations: Eibergen, Borken, Wesel. Daily: 75% or more of hourly values required, running average requires at least 50% of daily values present.*



eibergen – borken

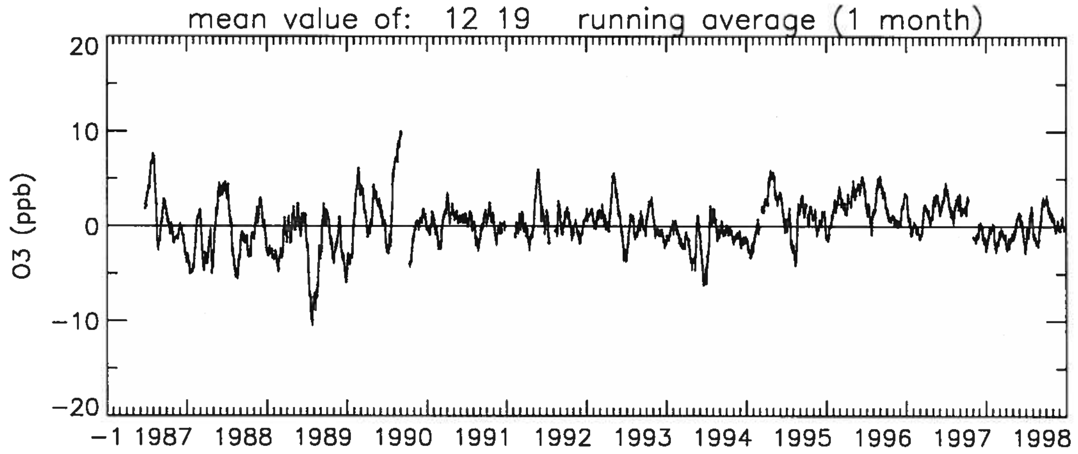


eibergen – wesel

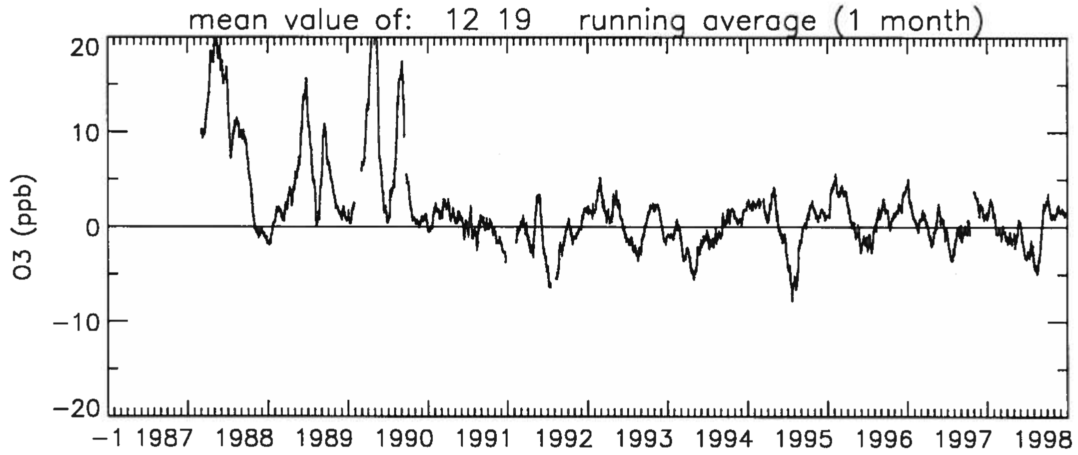


borken – wesel

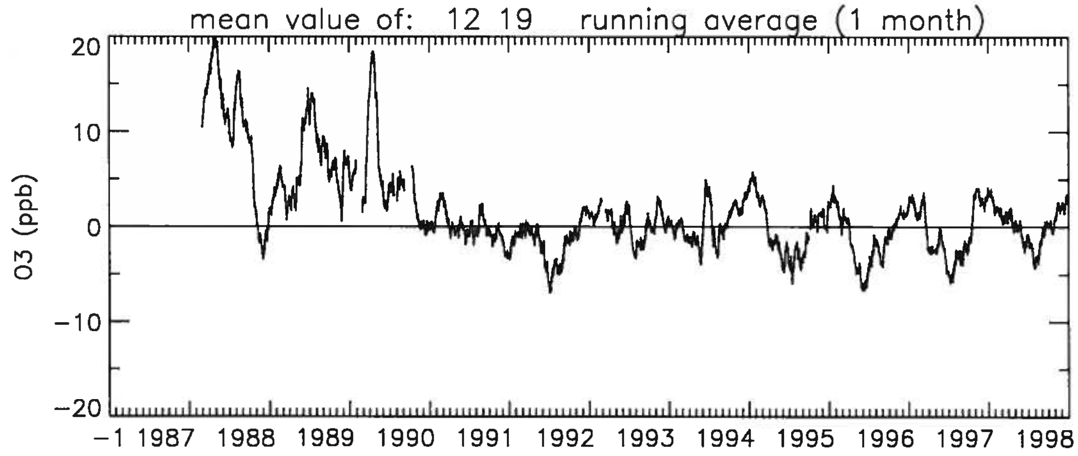
Figure B2b *The monthly running mean of the difference of daily (12-20h) oxidant concentrations. Stations: Eibergen, Borken, Wesel. Daily: 75% or more of hourly values required, running average requires at least 50% of daily values present.*



vredepeel – wijnandsrade

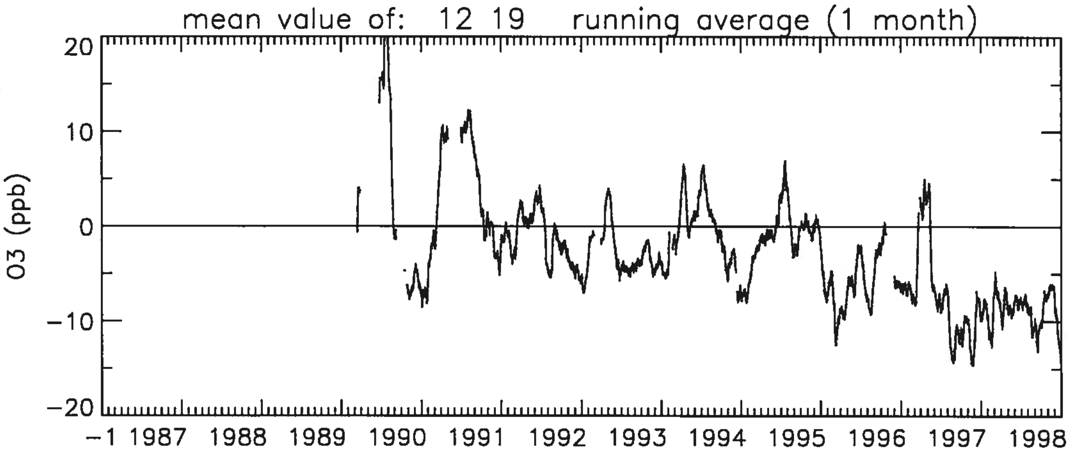


vredepeel – nettetal

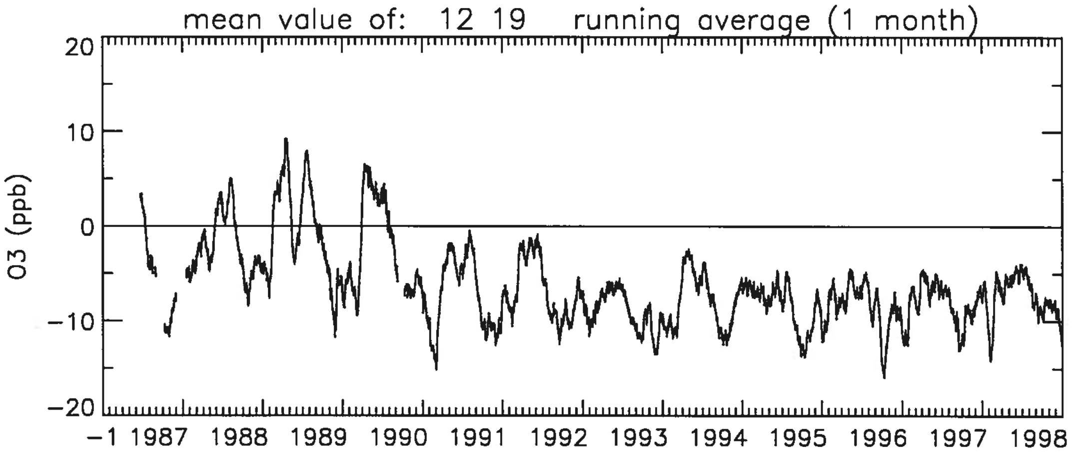


wijnandsrade – nettetal

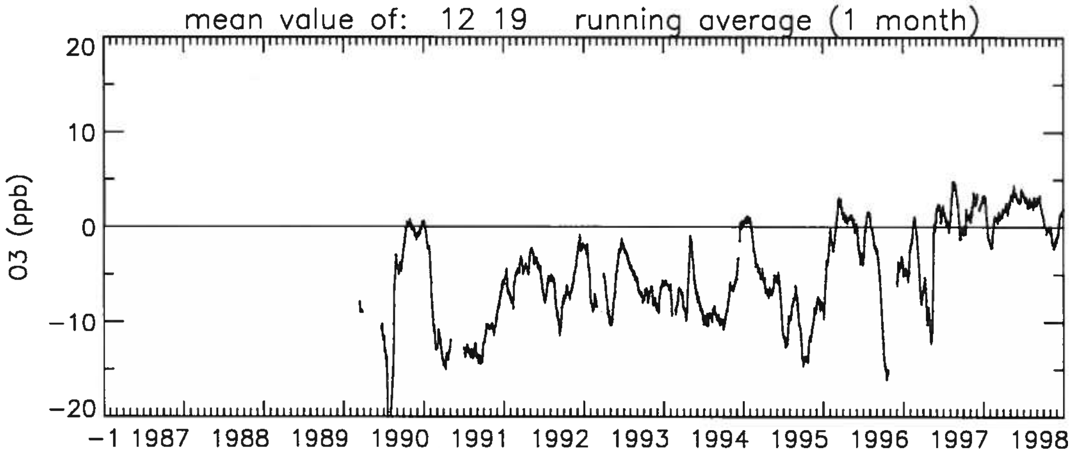
Figure B2c *The monthly running mean of the difference of daily (12-20h) ozone concentrations. Stations: Vredepeel, Wijnandsrade, Nettetal. Daily: 75% or more of hourly values required, running average requires at least 50% of daily values present.*



wijnandsrade – eupen

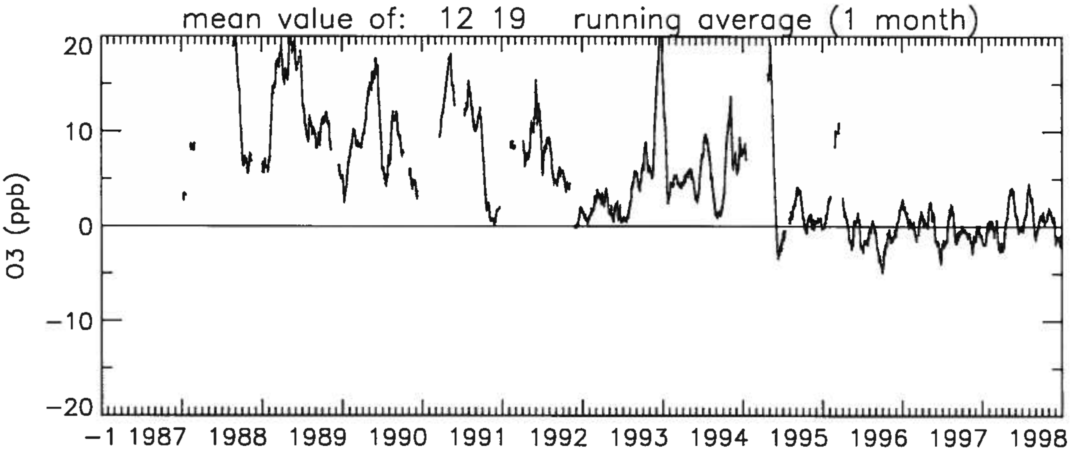


wijnandsrade – eifel

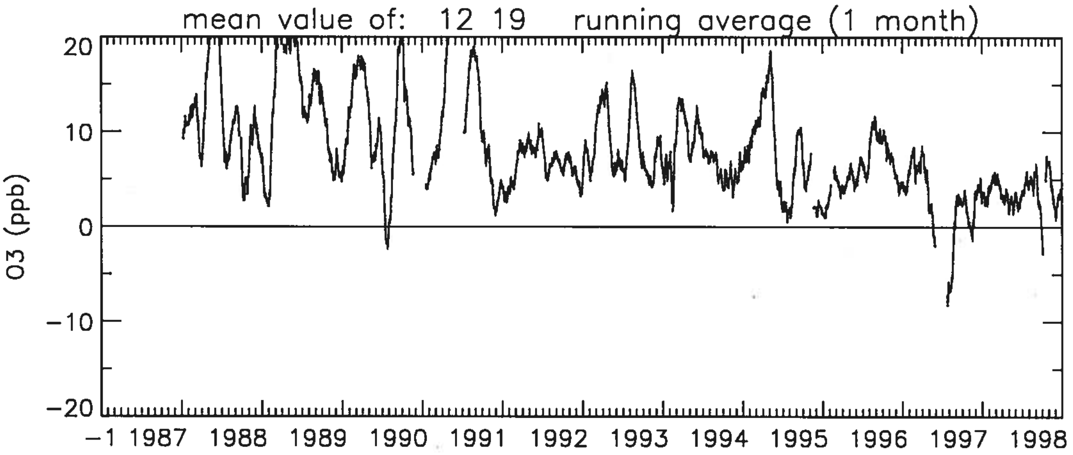


eupen – eifel

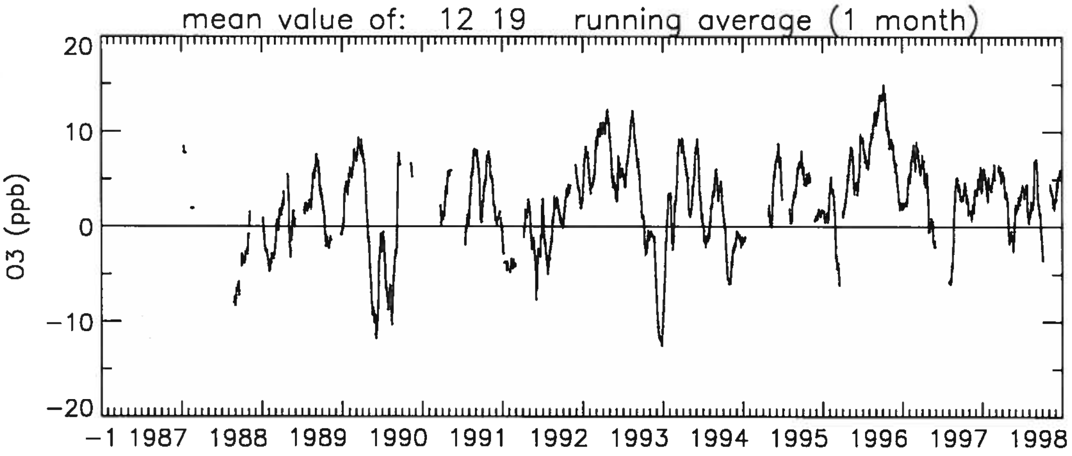
Figure B2d *The monthly running mean of the difference of daily (12-20h) ozone concentrations. Stations: Wijnandsrade, Eupen, Eifel. Daily: 75% or more of hourly values required, running average requires at least 50% of daily values present.*



braakman – moerkerke

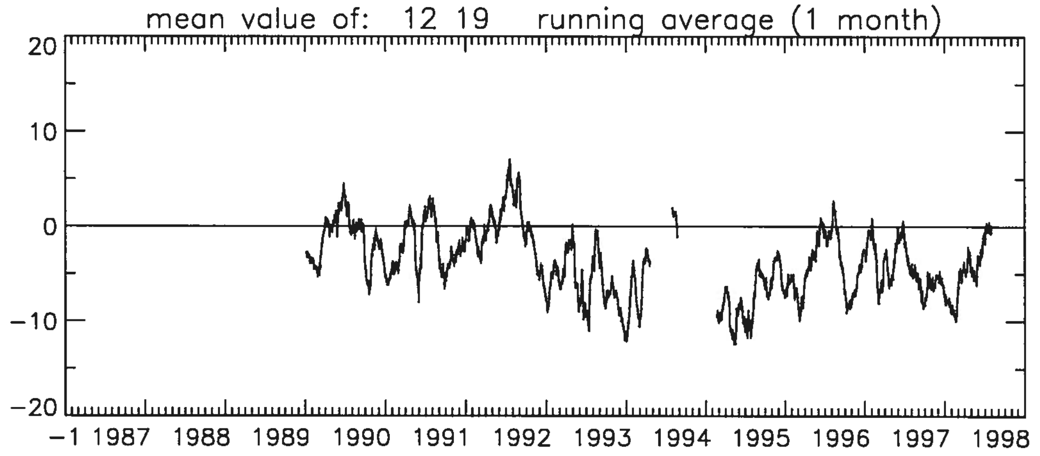


braakman – kruiswinkel–sint

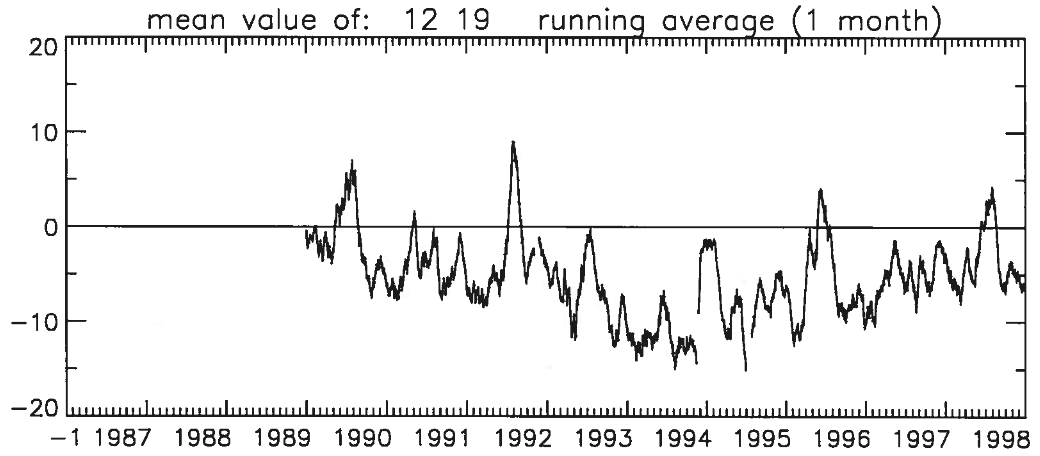


moerkerke – kruiswinkel–sint

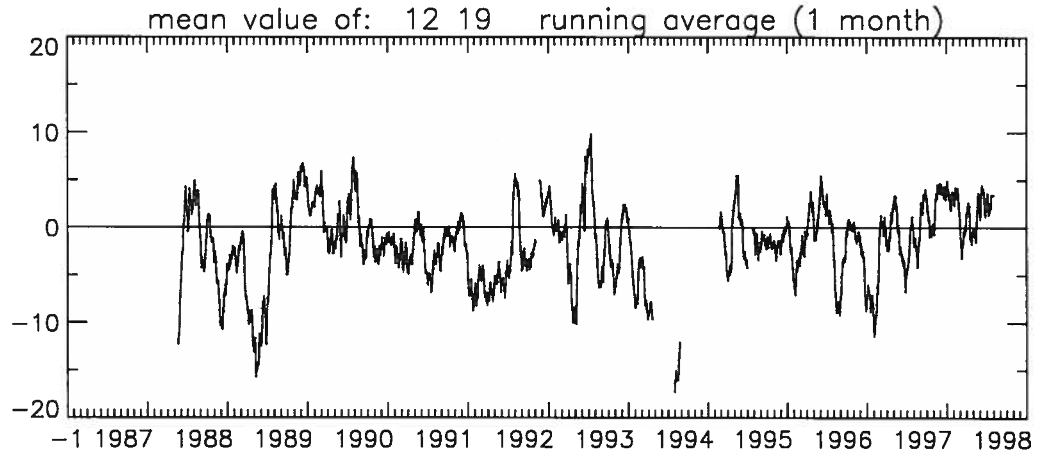
Figure B2e *The monthly running mean of the difference of daily (12-20h) ozone concentrations. Stations: Braakman, Moerkerke, Sint-Kruiswinkel. Daily: 75% or more of hourly values required, running average requires at least 50% of daily values present.*



bielefeld – meinerzhagen

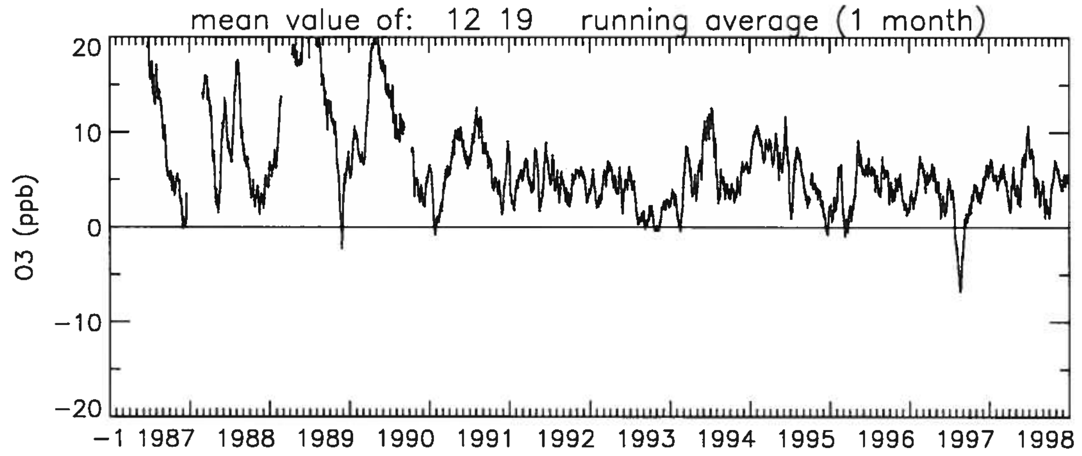


bielefeld – bassum

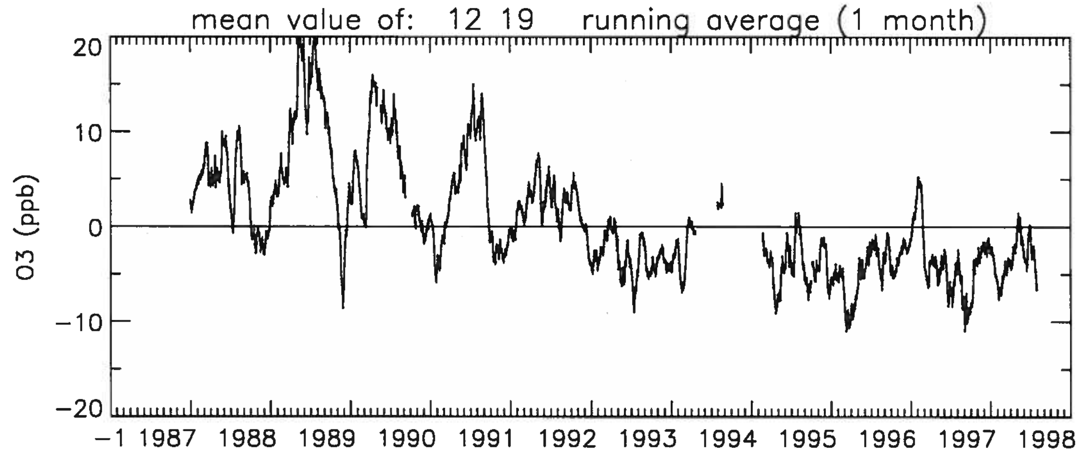


meinerzhagen – bassum

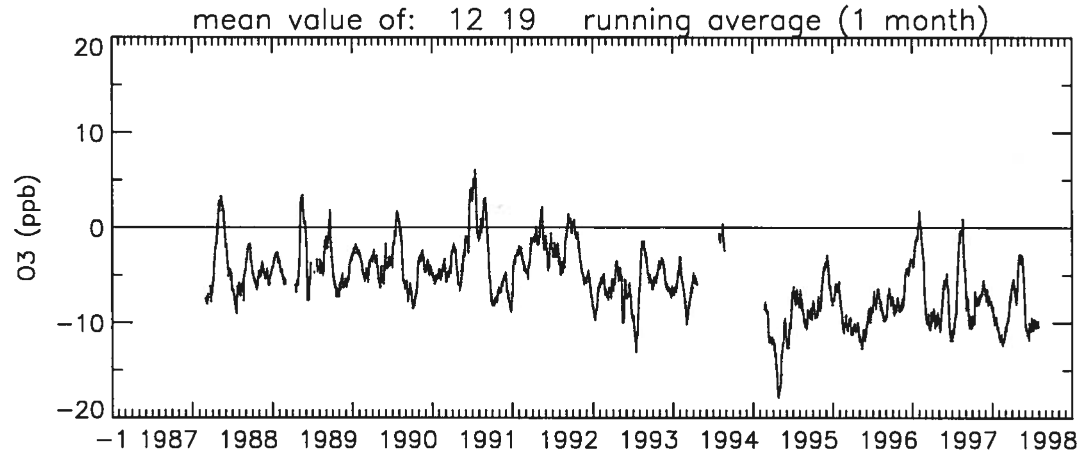
Figure B2f *The monthly running mean of the difference of daily (12-20h) ozone concentrations. Stations: Bielefeld, Meinerzhagen, Bassum. Daily: 75% or more of hourly values required, running average requires at least 50% of daily values present.*



wijnandsrade – rodenkirchen



wijnandsrade – meinerzhagen



rodenkirchen – meinerzhagen

Figure B2g *The monthly running mean of the difference of daily (12-20h) ozone concentrations. Stations: Wijnandsrade, Rodenkirchen, Meinerzhagen. Daily: 75% or more of hourly values required, running average requires at least 50% of daily values present.*

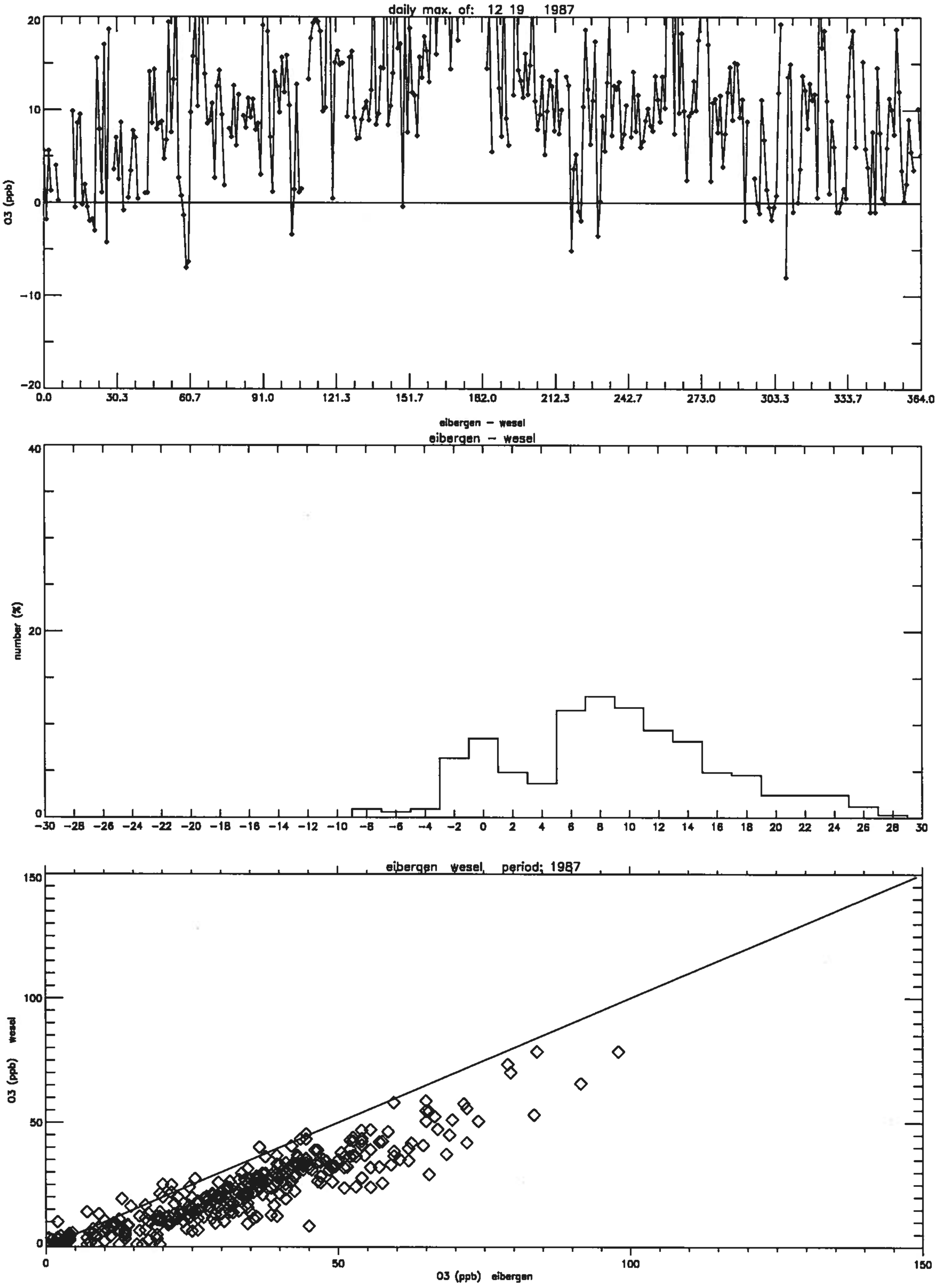


Figure B3a *Difference of daily (12-20h) ozone concentrations: time series, histogram, scatter. Daily: 85% or more of hourly values required. Stations: Eibergen, Wesel. Year: 1987.*

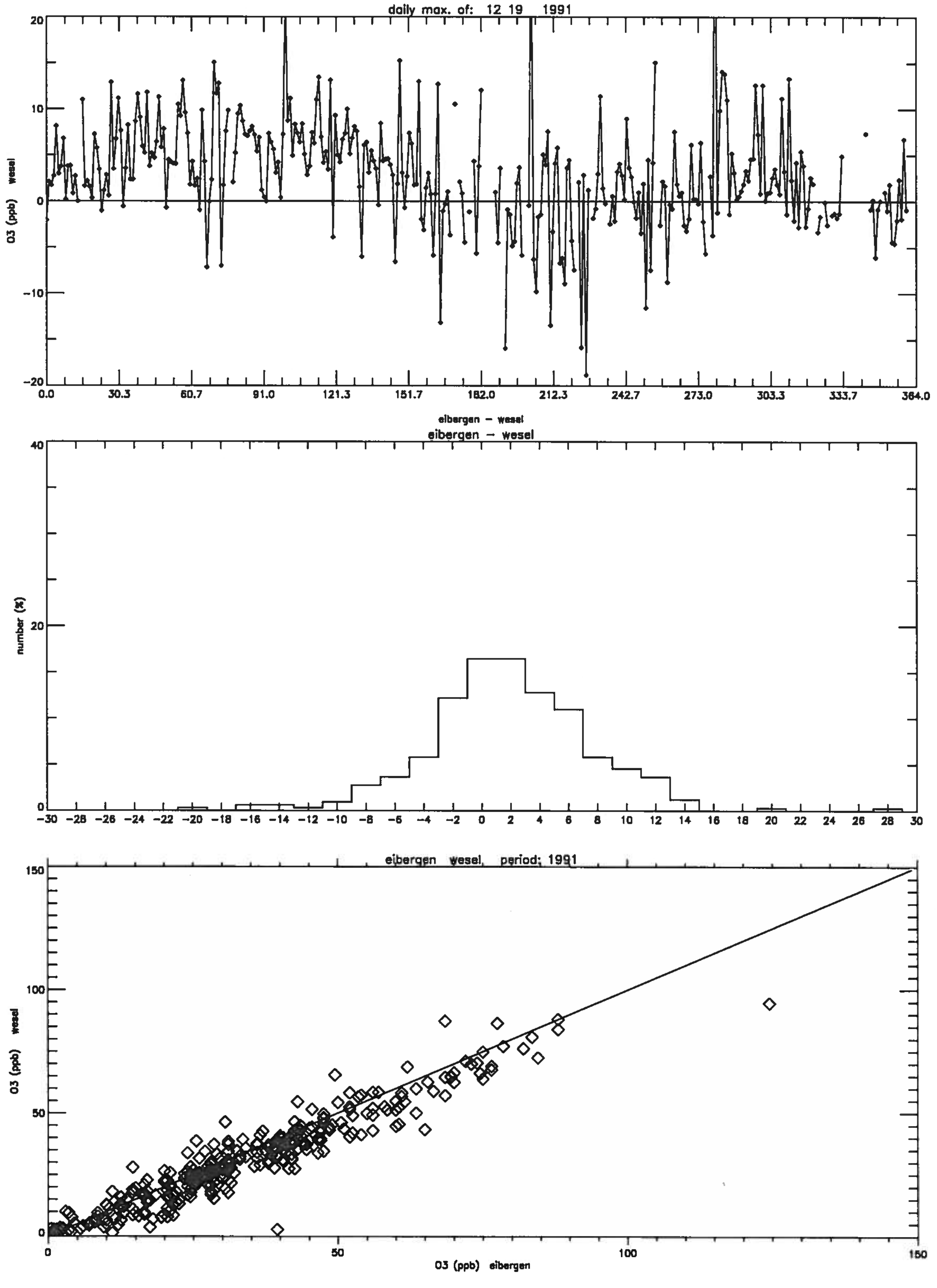


Figure B3b *Difference of daily (12-20h) ozone concentrations: time series, histogram, scatter. Daily: 85% or more of hourly values required. Stations: Eibergen, Wesel. Year: 1991.*

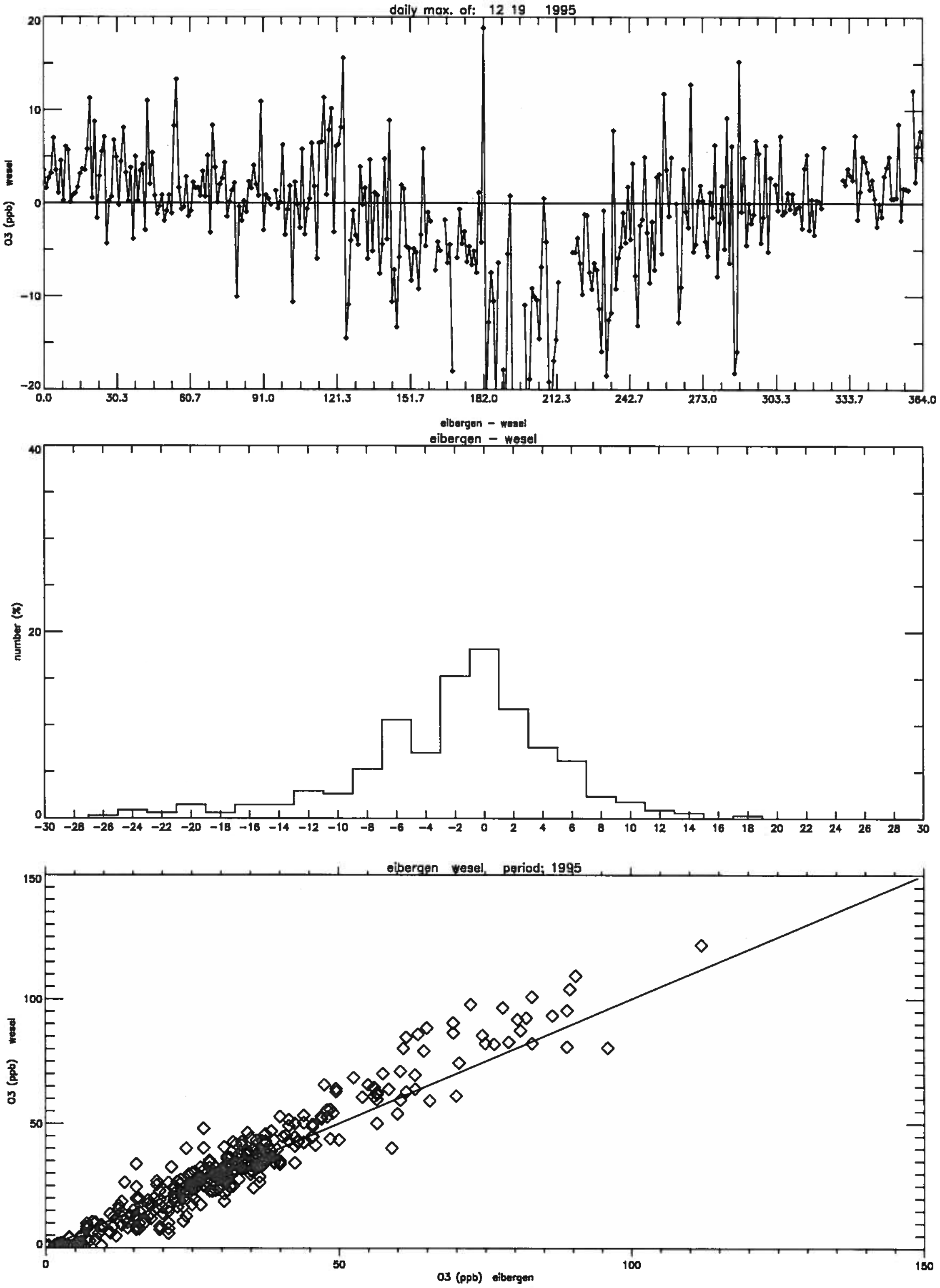
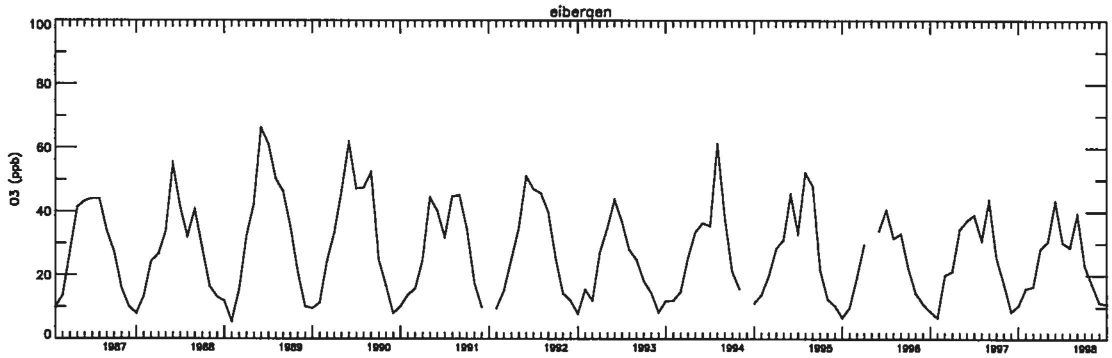
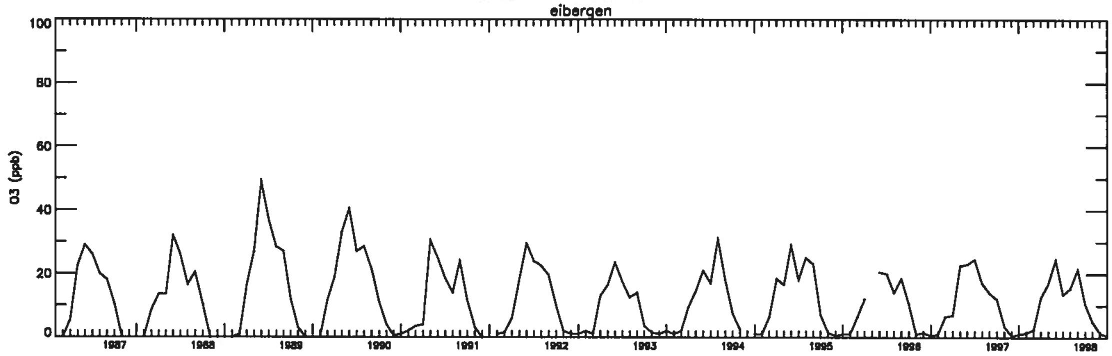


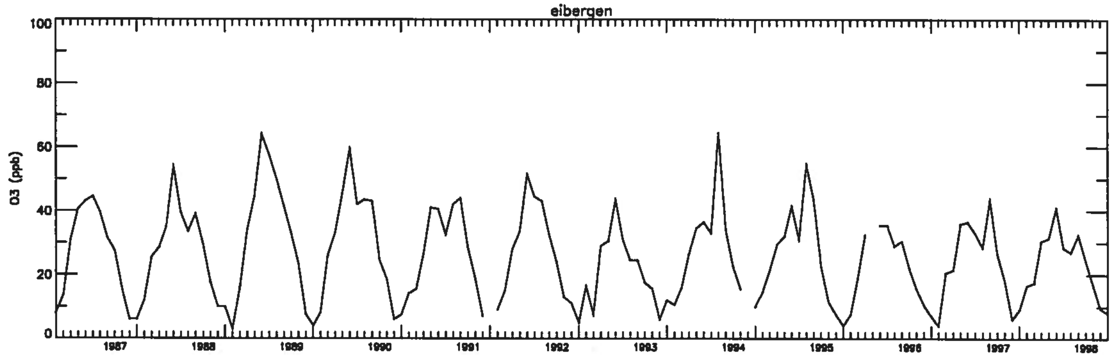
Figure B3c *Difference of daily (12-20h) ozone concentrations: time series, histogram, scatter. Daily: 85% or more of hourly values required. Stations: Eibergen, Wesel. Year: 1995*



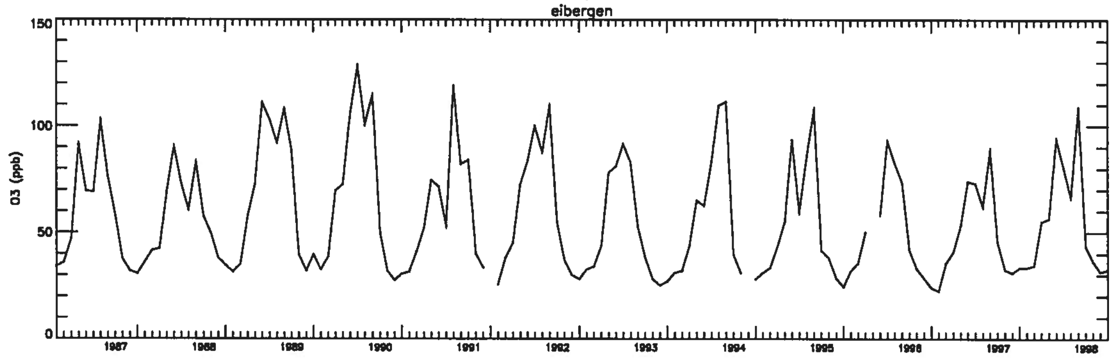
average of hourly values: from12to19



10–percentile of hourly values: from12to19

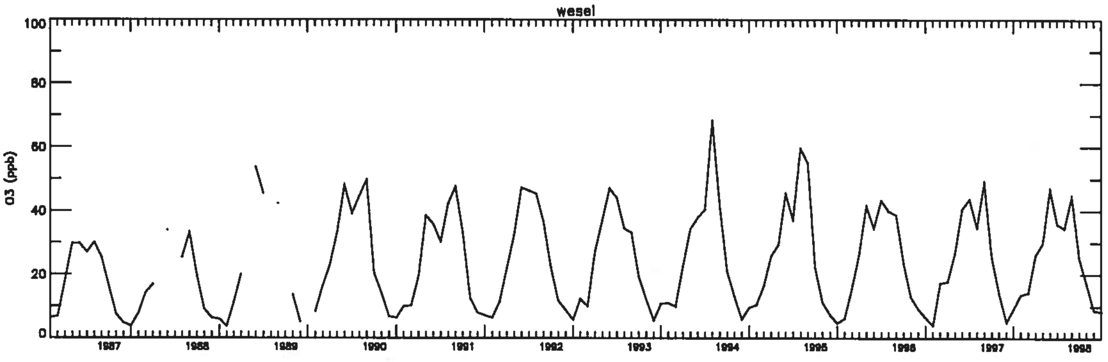


50–percentile of hourly values: from12to19

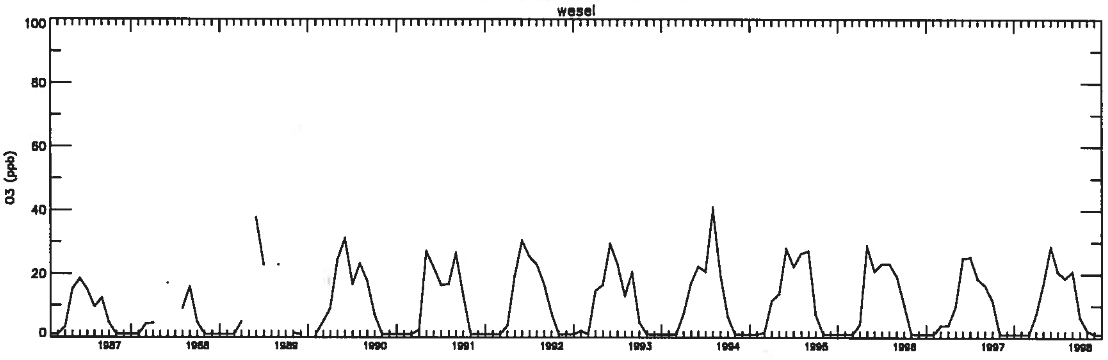


99–percentile of hourly values: from12to19

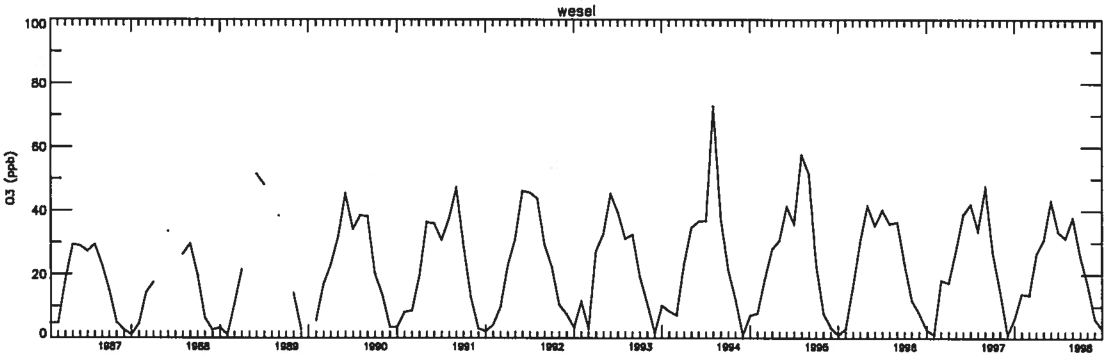
Figure B4a *Time series of monthly parameters (averages, percentiles) based on hourly ozone values in Eibergen between 12 and 20h. Parameters require at least 75% data coverage.*



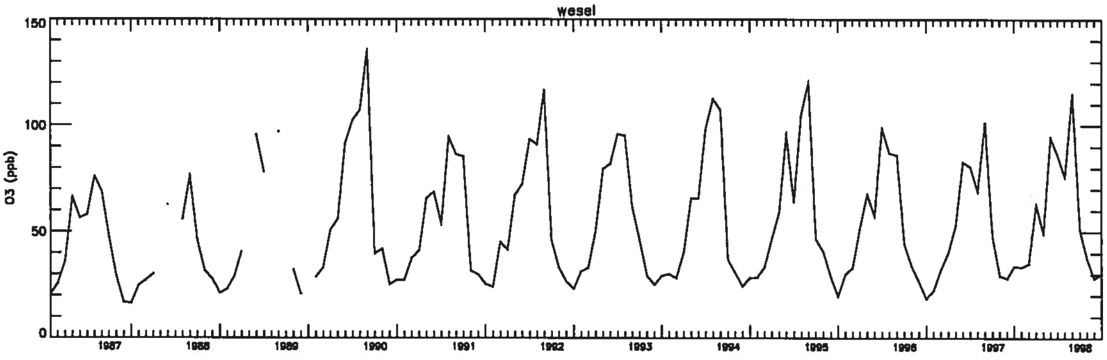
average of hourly values: from12to19



10–percentile of hourly values: from12to19

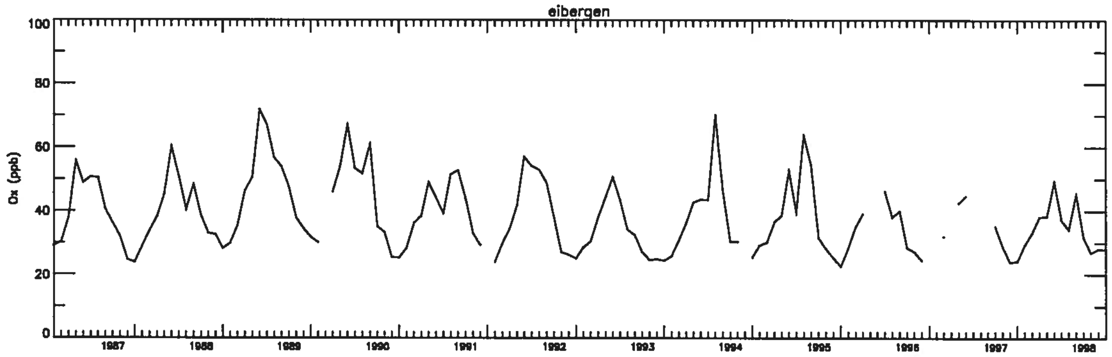


50–percentile of hourly values: from12to19

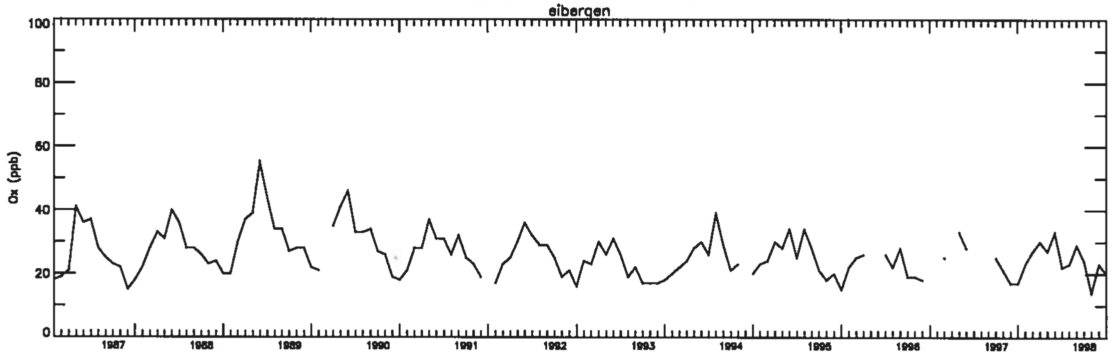


99–percentile of hourly values: from12to19

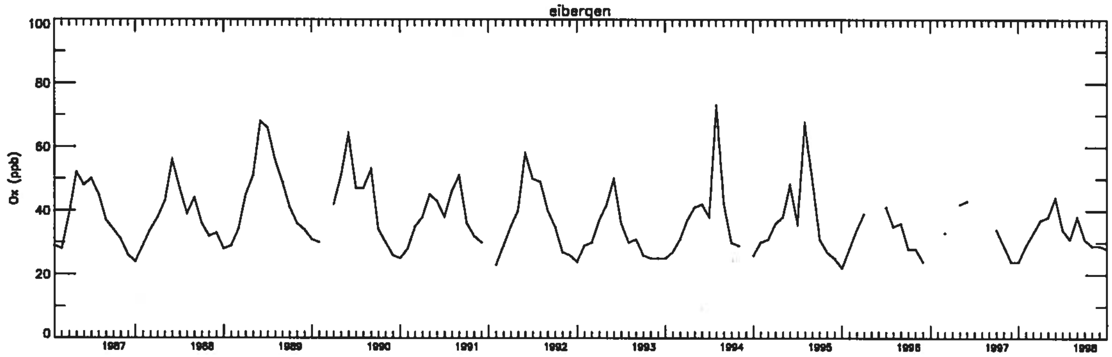
Figure B4b *Time series of monthly parameters (averages, percentiles) based on hourly ozone values in Wesel between 12 and 20h. Parameters require at least 75% data coverage.*



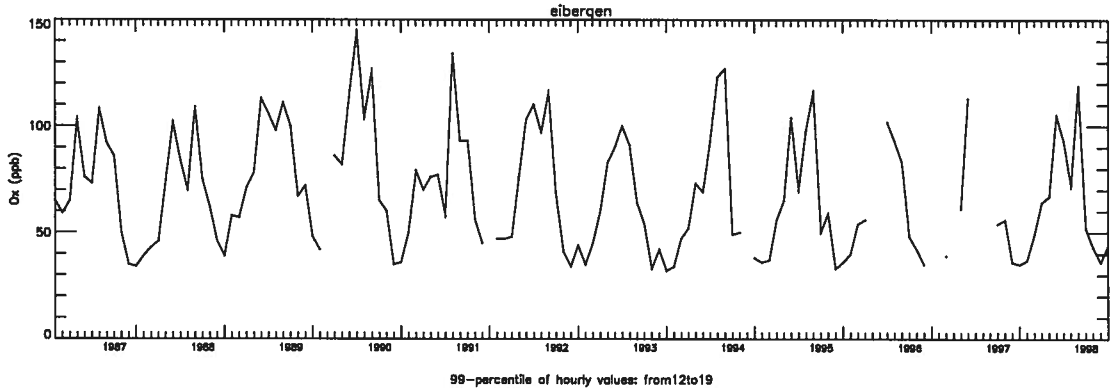
average of hourly values: from12to19



10–percentile of hourly values: from12to19

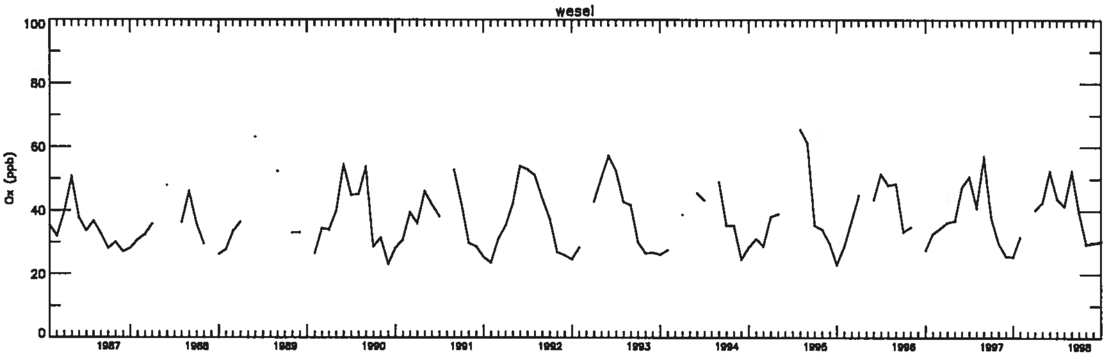


50–percentile of hourly values: from12to19

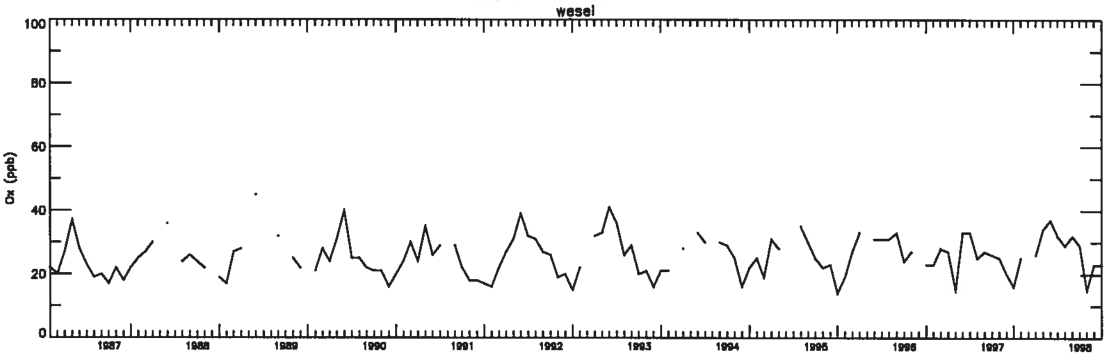


99–percentile of hourly values: from12to19

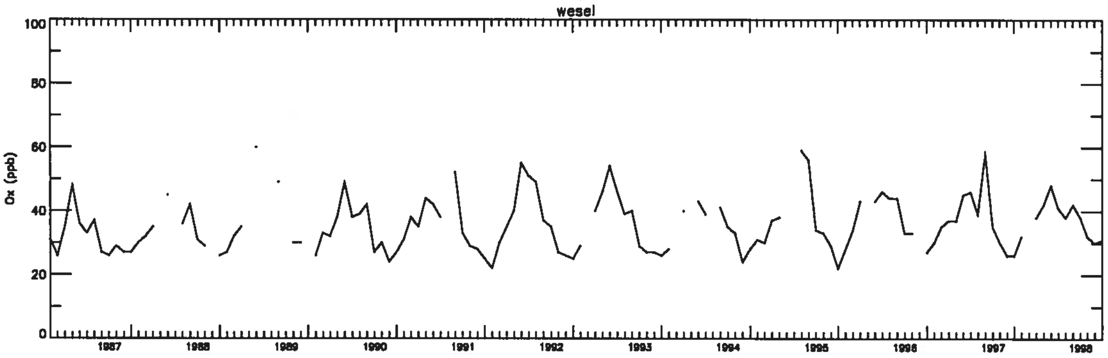
Figure B5a *Time series of monthly parameters (averages, percentiles) based on hourly oxidant values in Eibergen between 12 and 20h. Parameters require at least 75% data coverage.*



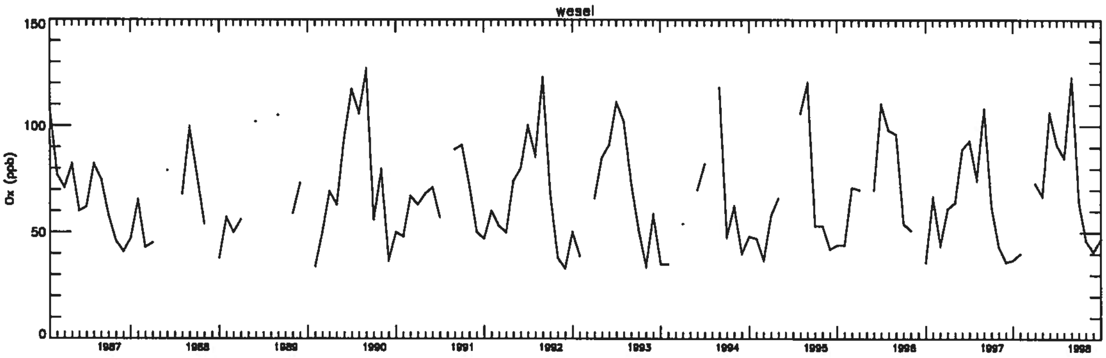
average of hourly values: from12to19



10–percentile of hourly values: from12to19



50–percentile of hourly values: from12to19



99–percentile of hourly values: from12to19

Figure B5b *Time series of monthly parameters (averages, percentiles) based on hourly ozone values in Wesel between 12 and 20h. Parameters require at least 75% data coverage.*

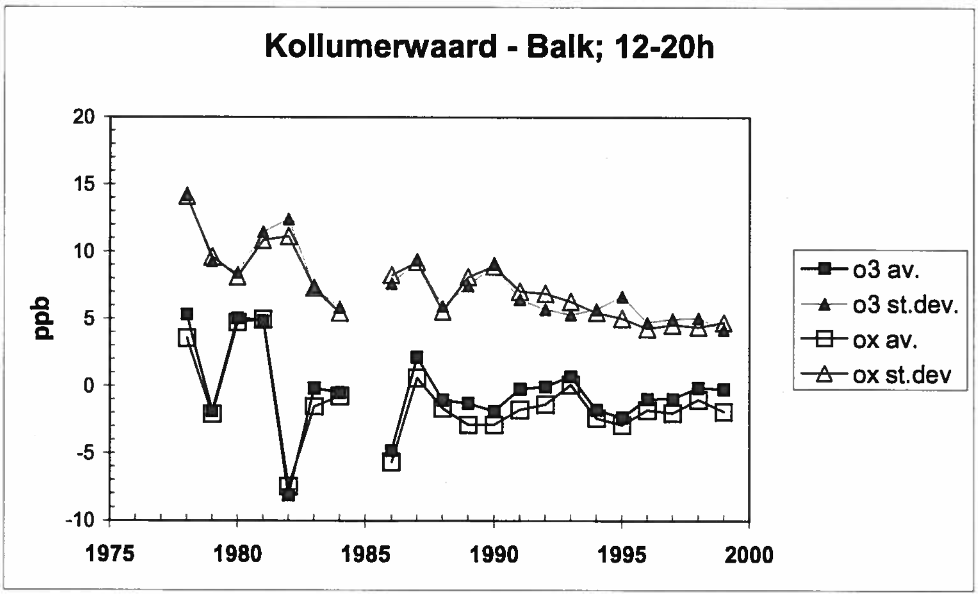


Figure B6a *Annual averages and standard deviations of daily (12-20h) differences of ozone and oxidant between Kollumerwaard and Balk.*

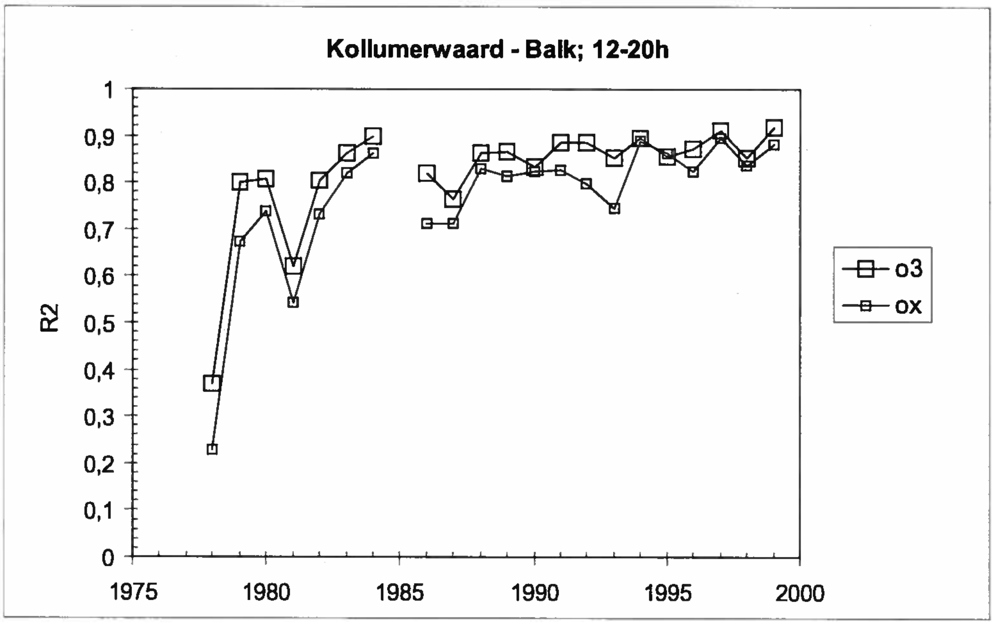


Figure B6b *Correlation coefficient (R^2) of daily (12-20h) averages of ozone and oxidant at Kollumerwaard and Balk.*

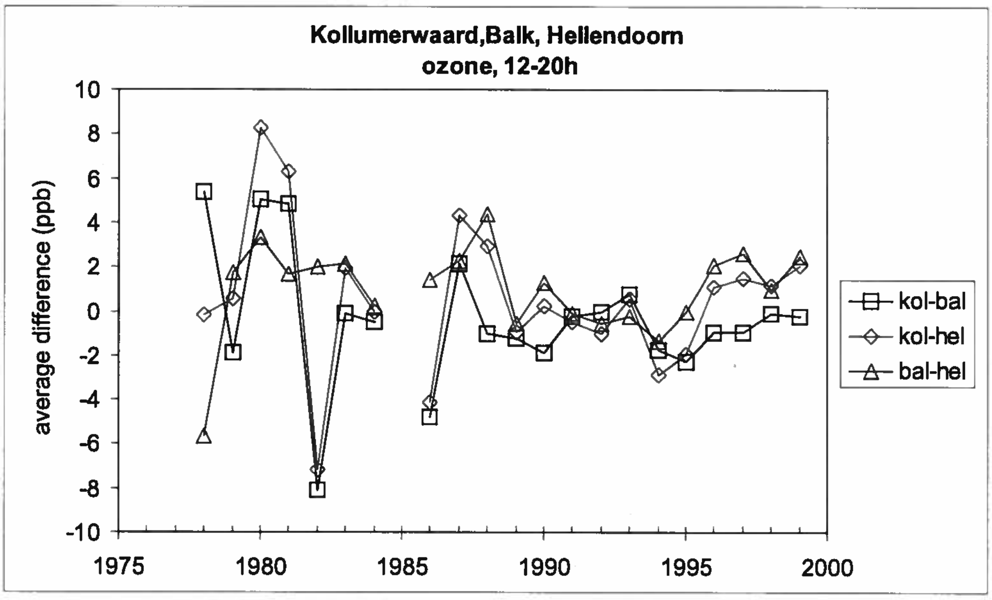


Figure B6c *Annual averages of daily (12-20h) differences of ozone between Kollumerwaard, Balk and Hellendoorn.*

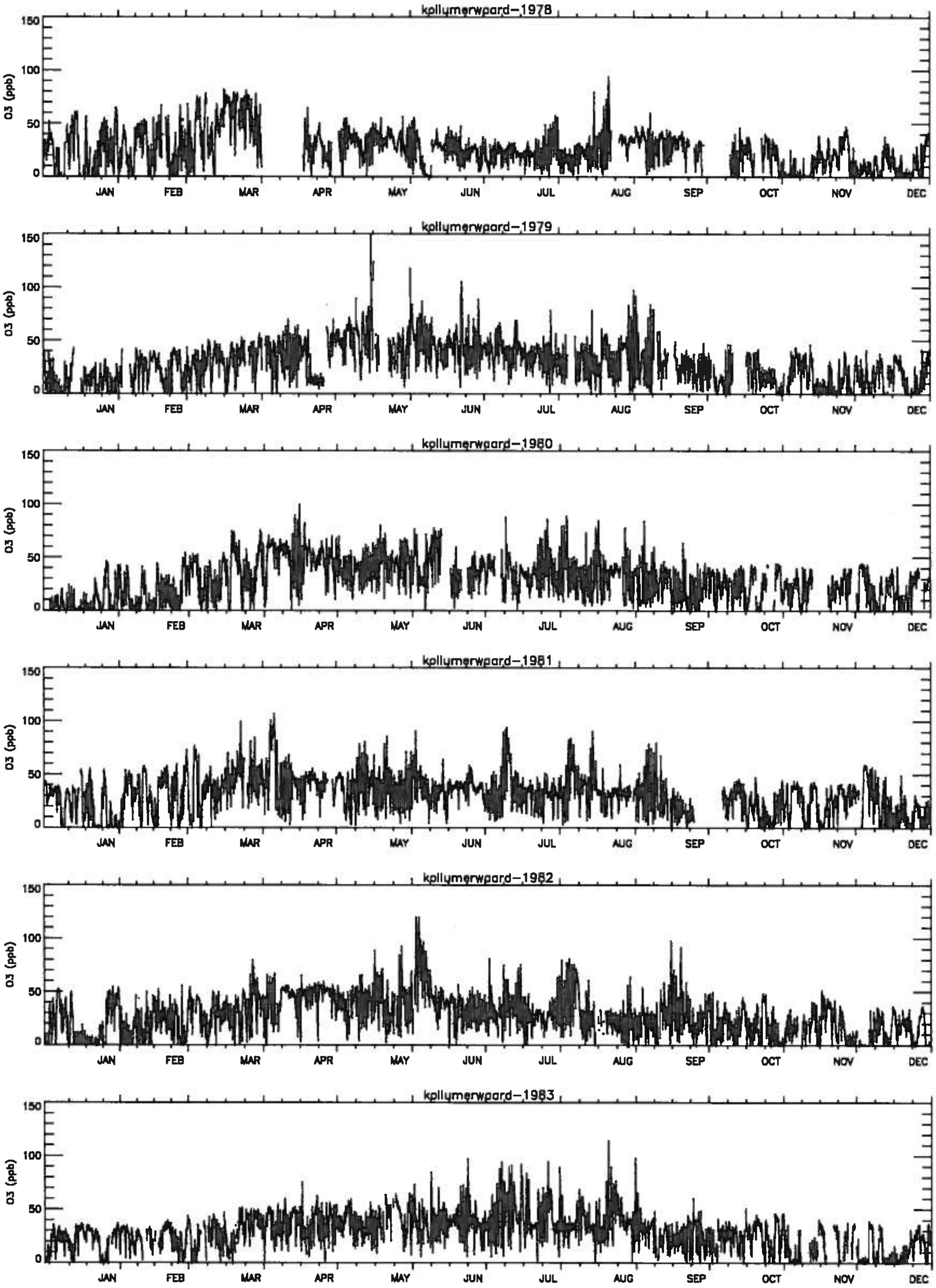


Figure B7a *Time series (1978-1983) of hourly ozone concentrations at Kollumerwaard.*

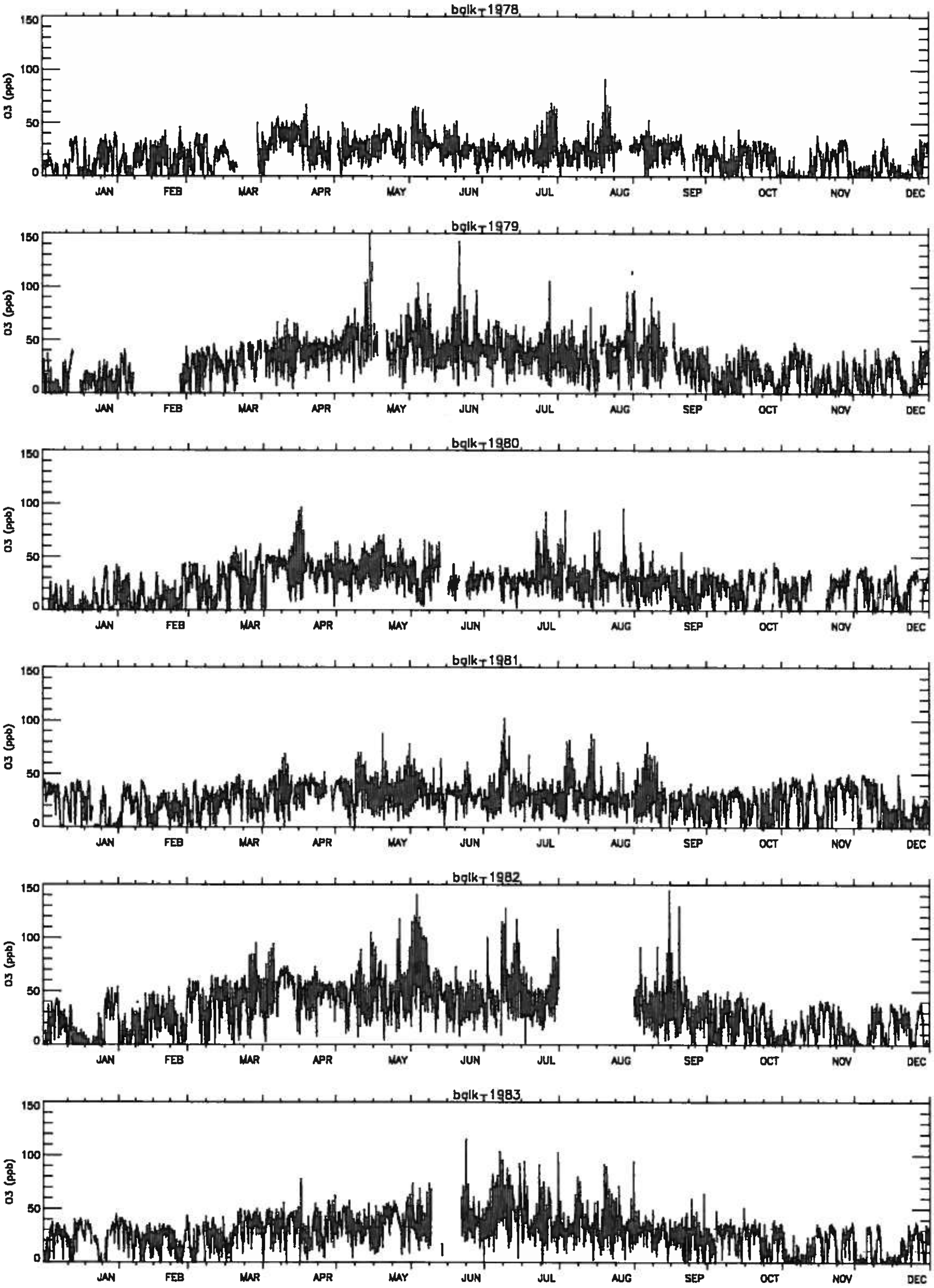


Figure B7b *Time series (1978-1983) of hourly ozone concentrations at Balk.*

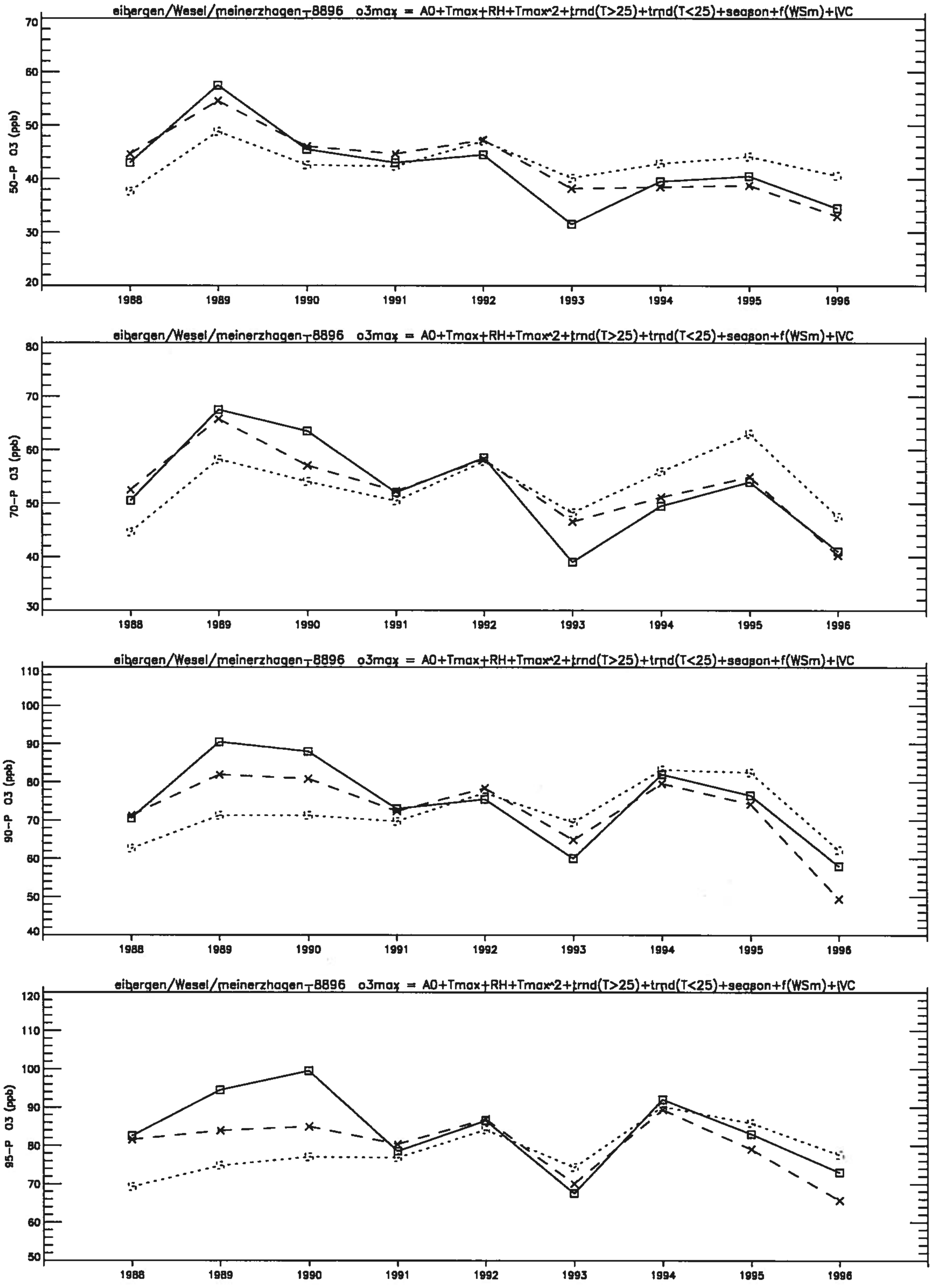


Figure B8a *Percentiles (50, 70, 90 and 95) of daily maximum ozone concentrations in May-September in Eibergen. Solid line: observations, stippled line: statistical fit without trend terms, dashed line: statistical fit with trend terms. Meteo: Wesel; trajectory information: Meinerzhagen.*

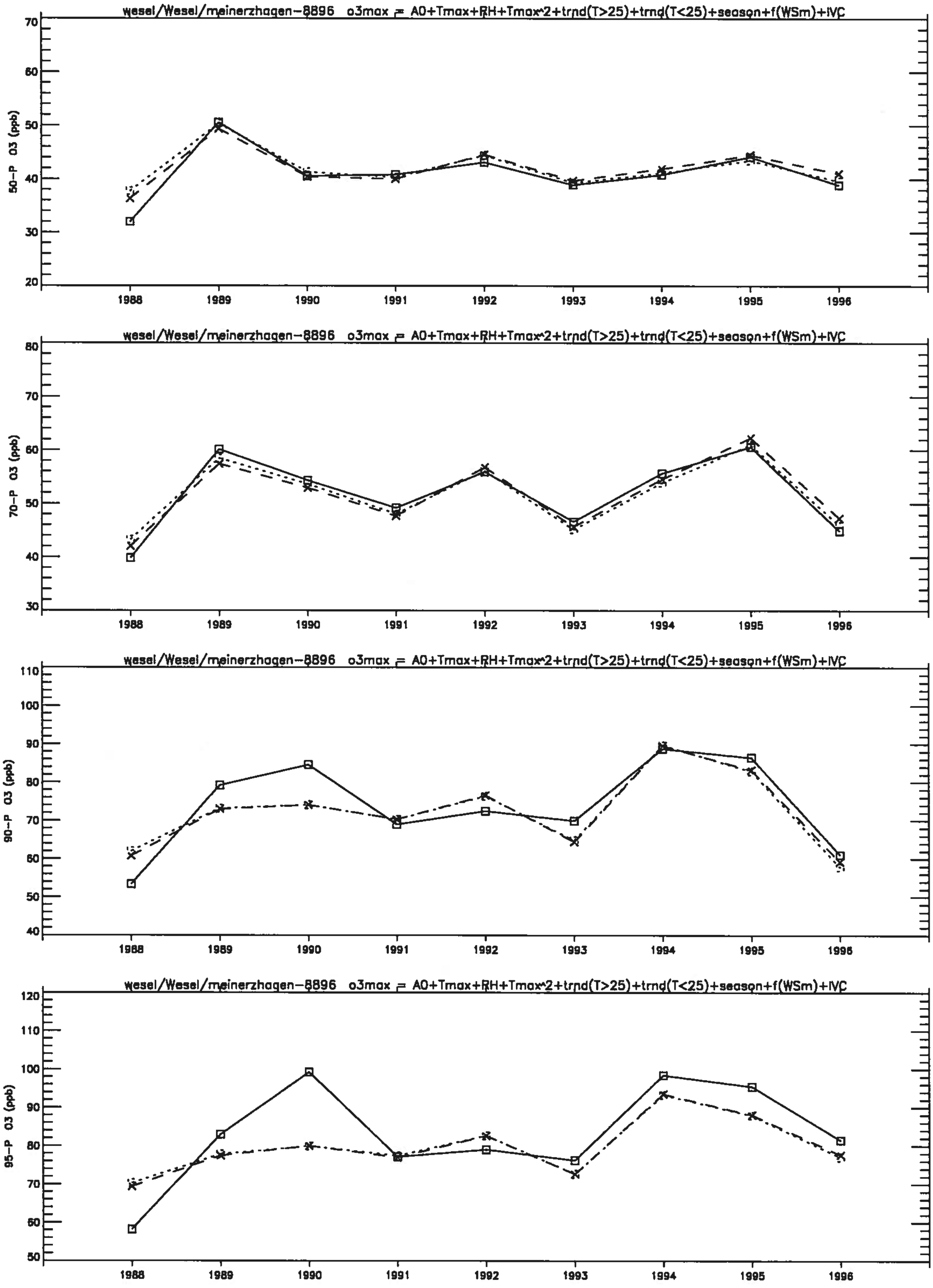


Figure B8b *Percentiles (50, 70, 90 and 95) of daily maximum ozone concentrations in May-September in Wesel. Solid line: observations, stippled line: statistical fit without trend terms, dashed line: statistical fit with trend terms. Meteo: Wesel; trajectory information: Meinerzhagen.*

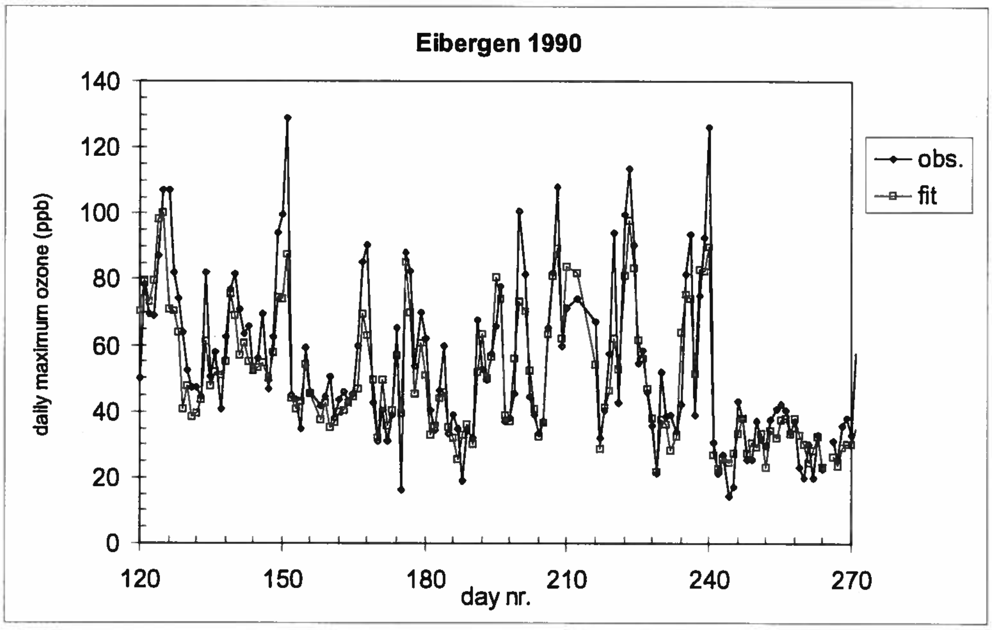


Figure B9a *Daily maximum ozone concentrations in May-September 1990 in Eibergen. Diamond: observations, squares: statistical fit with trend terms.*

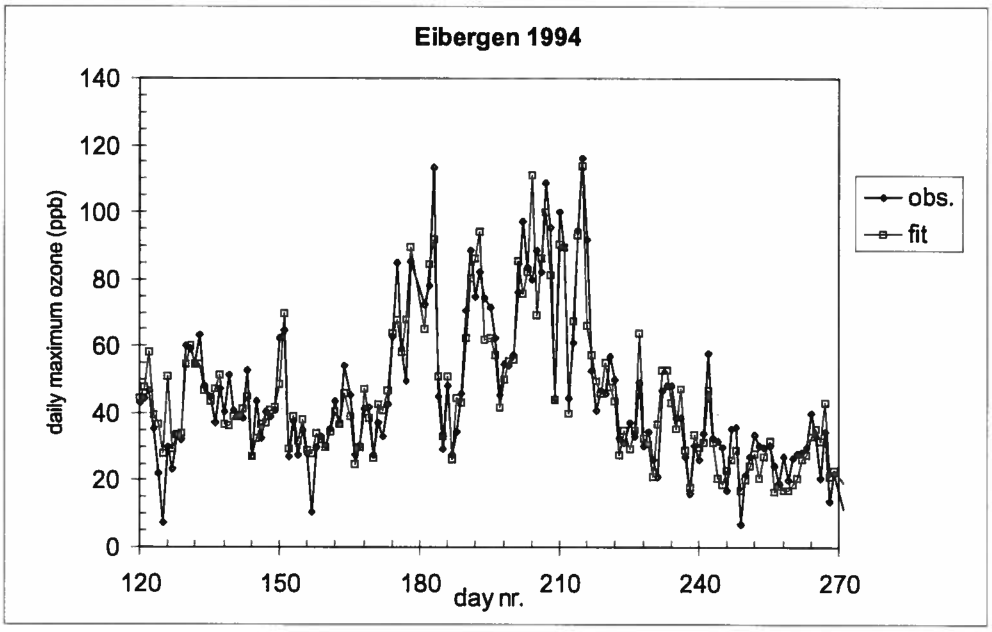


Figure B9b *Daily maximum ozone concentrations in May-September 1994 in Eibergen. Diamond: observations, squares: statistical fit with trend terms.*

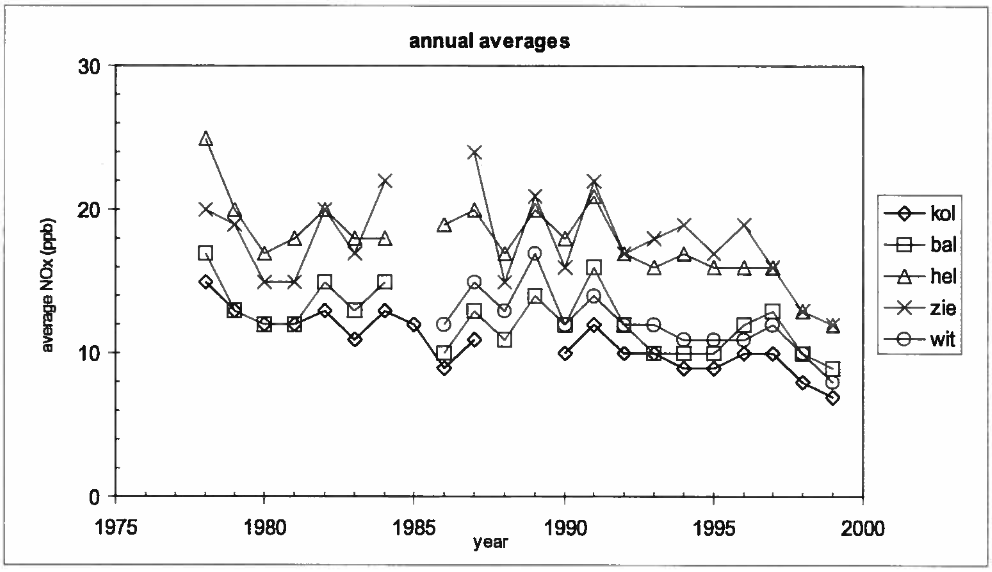


Figure B10a *Annual averages of* NO_x *concentrations: Kollumerwaard, Balk, Hellendoorn, Zierikzee, Witteveen. (Stations are abbreviated by the first three characters of station name.)*

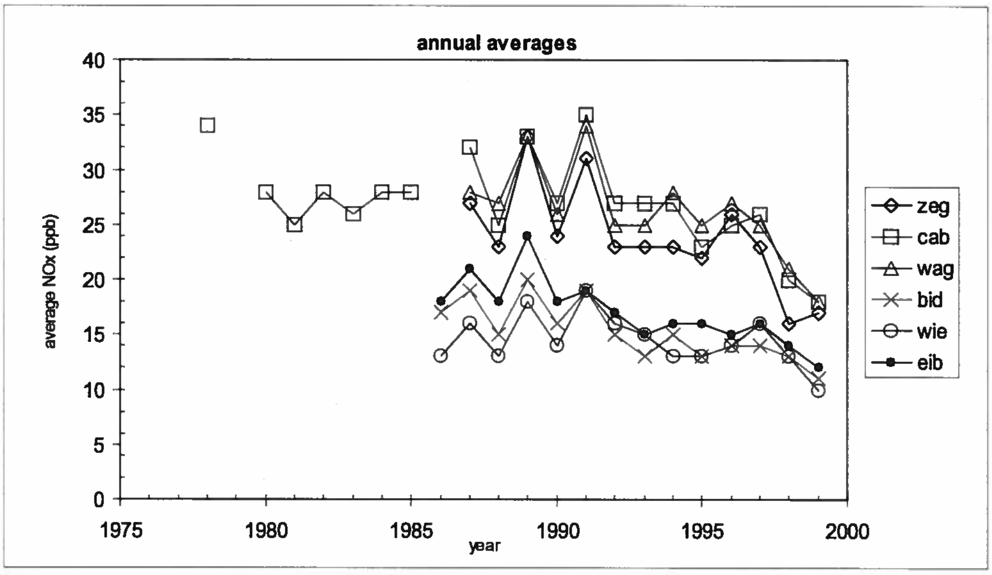


Figure B10b *Annual averages of* NO_x *concentrations: Zegveld, Cabauw, Wageningen, Biddinghuizen, Wieringerwerf, Eibergen. (Stations are abbreviated by the first three characters of station name.)*

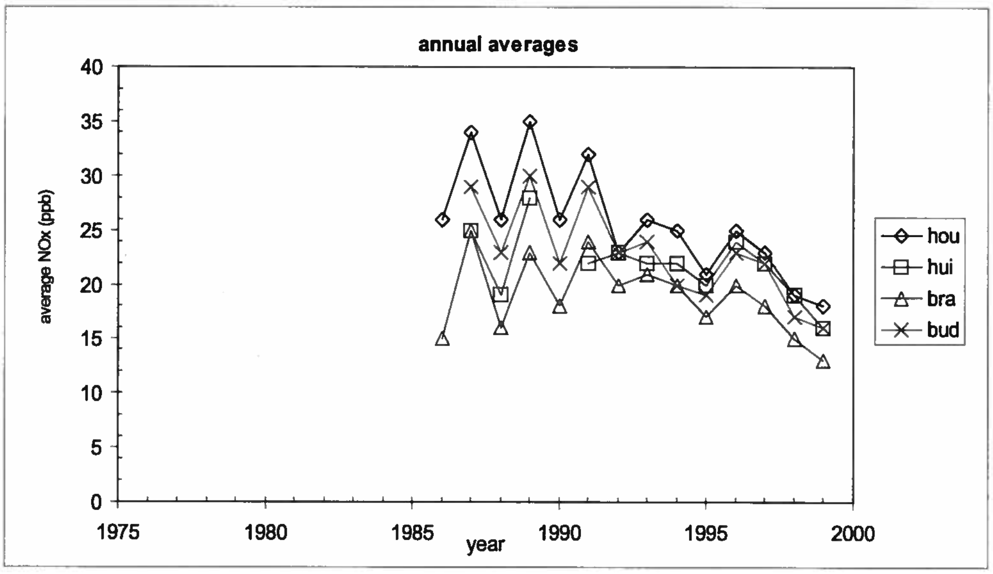


Figure B10c *Annual averages of NO$_x$ concentrations: Houtakker, Huijbergen, Braakman, Budel. (Stations are abbreviated by the first three characters of station name.)*

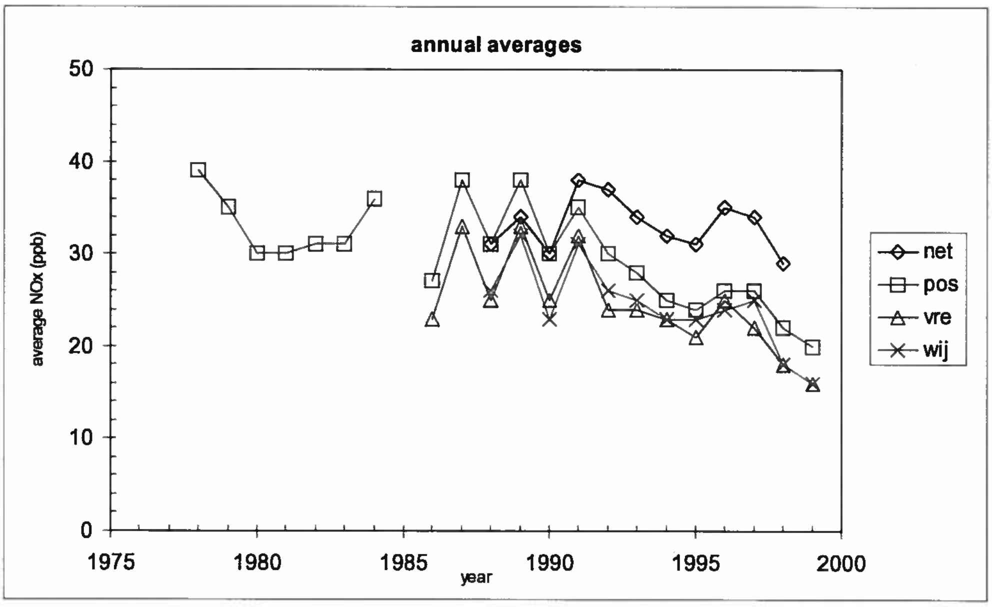


Figure B10d *Annual averages of NO$_x$ concentrations: Nettetal, Posterholt, Vredepeel, Wijnandsrade. (Stations are abbreviated by the first three characters of station name.)*

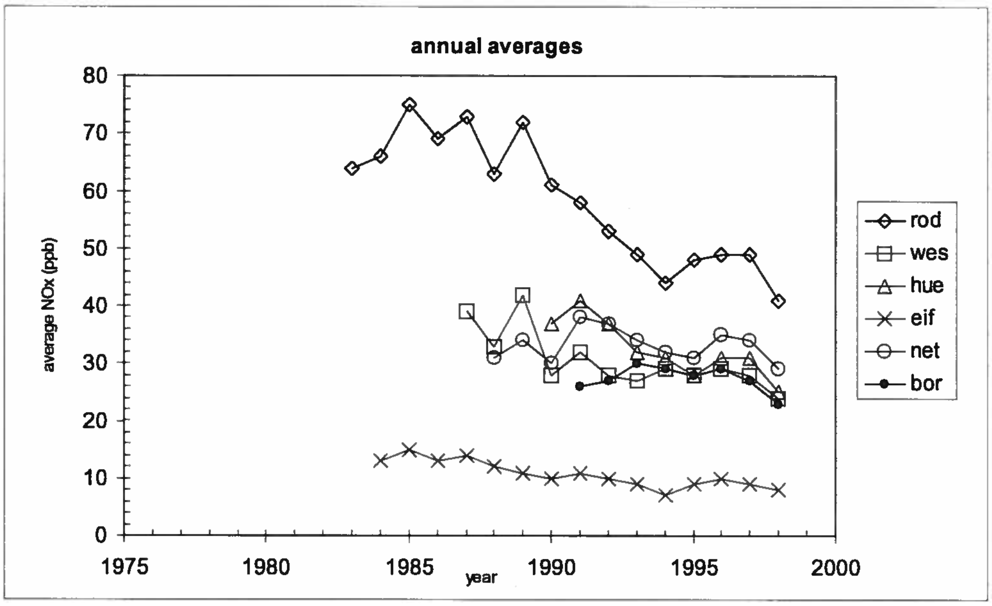


Figure B10e *Annual averages of NO_x concentrations: Rodenkirchen, Wesel, Huerth, Eifel, Nettetal, Borken. (Stations are abbreviated by the first three characters of station name.)*

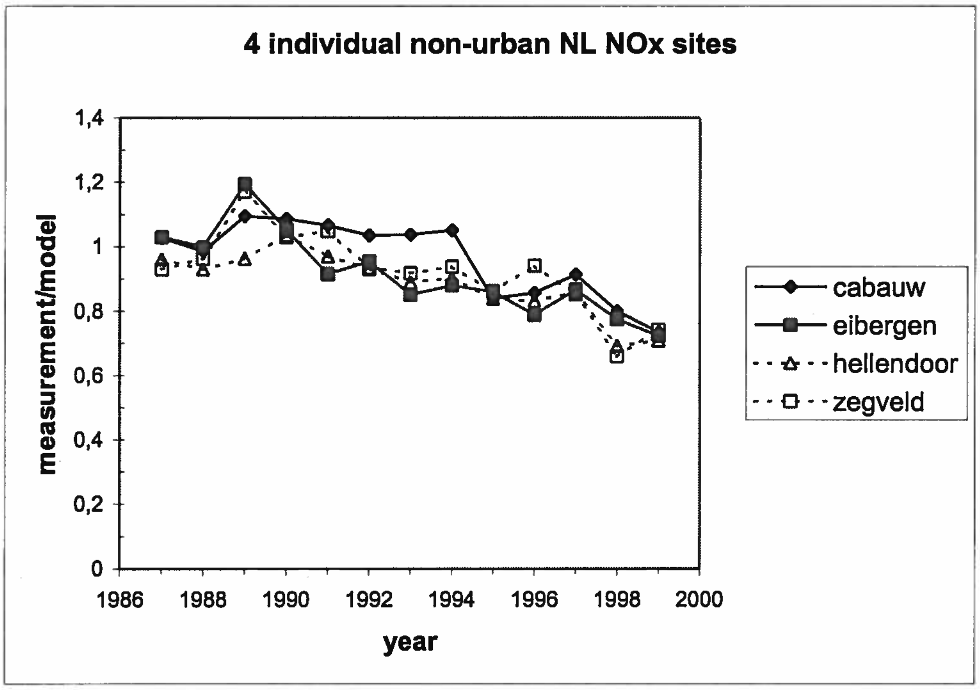


Figure B11a *The ratio of measured versus modelled annual average NO_x concentrations for the 1987-1999 period. Stations: Cabauw, Eibergen, Hellendoorn, Zegveld.*

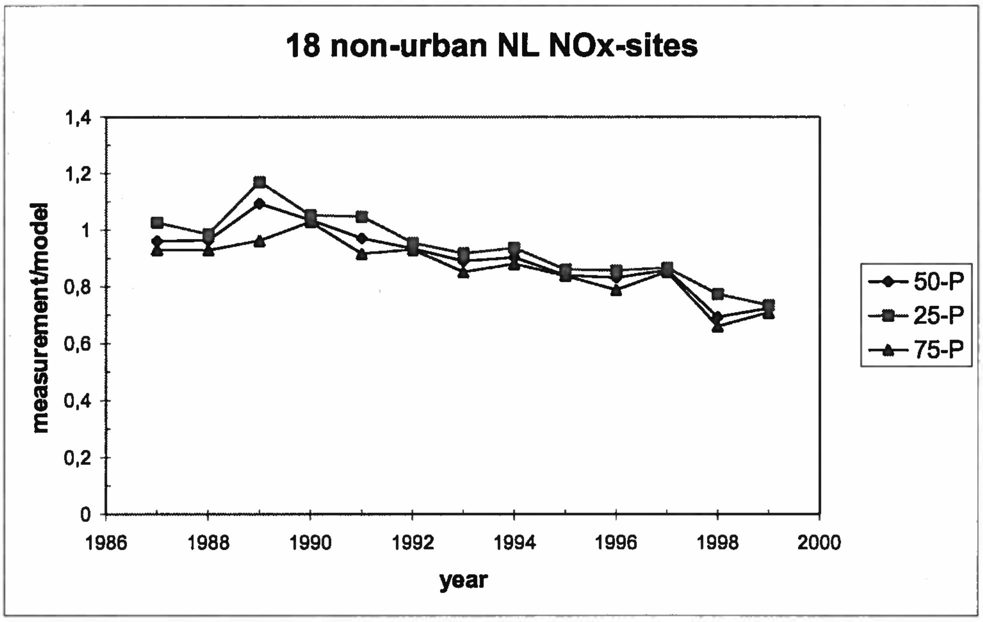


Figure B11b *The ratio of measured versus modelled annual average NO_x concentrations for the 1987-1999 period for 18 Netherlands sites. For each year the 25th-, 50th- and 75th-percentile of the ensemble of 18 stations is given.*

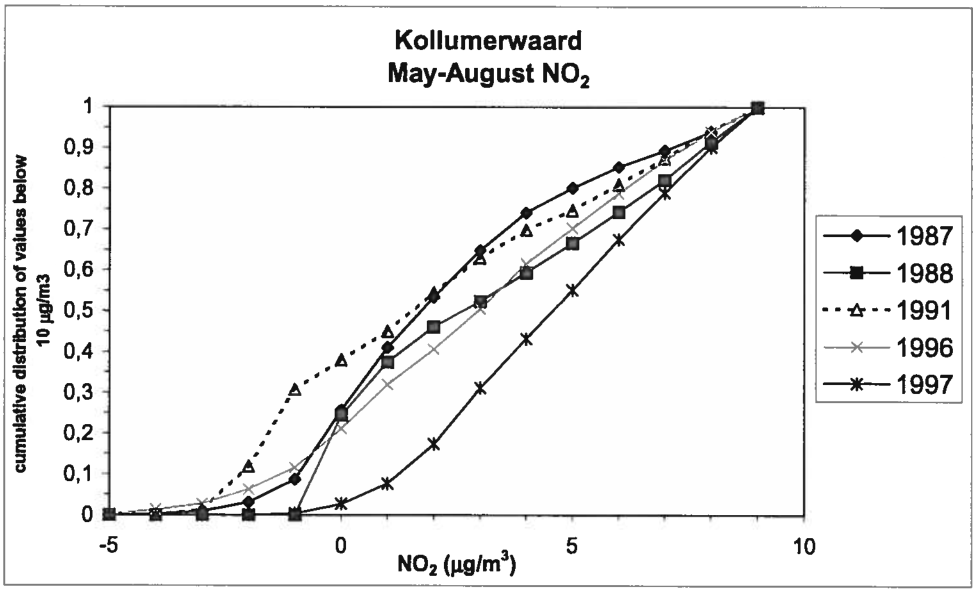


Figure B12 *The cumulative distribution of summer time (May-August) hourly NO_2 concentrations below 10 $\mu g.m^{-3}$ in Kollumerwaard for a selection of years.*

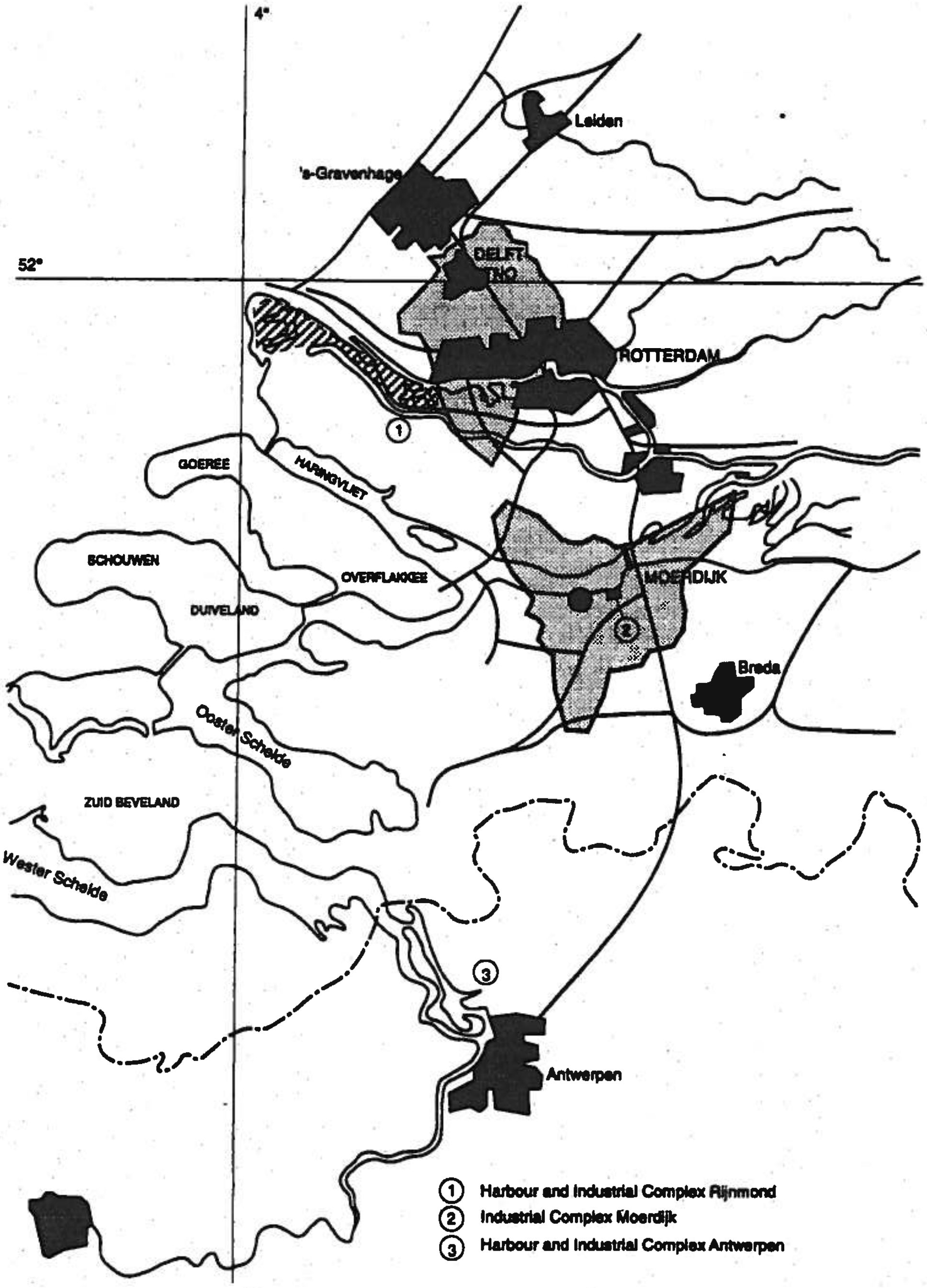


Figure B13a *The location of the site Moerdijk MC (dot west of Industrie Complex Moerdijk). For illustration the average concentration of isobutane per wind sector of 10° at Delft (1982-1984) and Moerdijk (1981-1984) is given.*

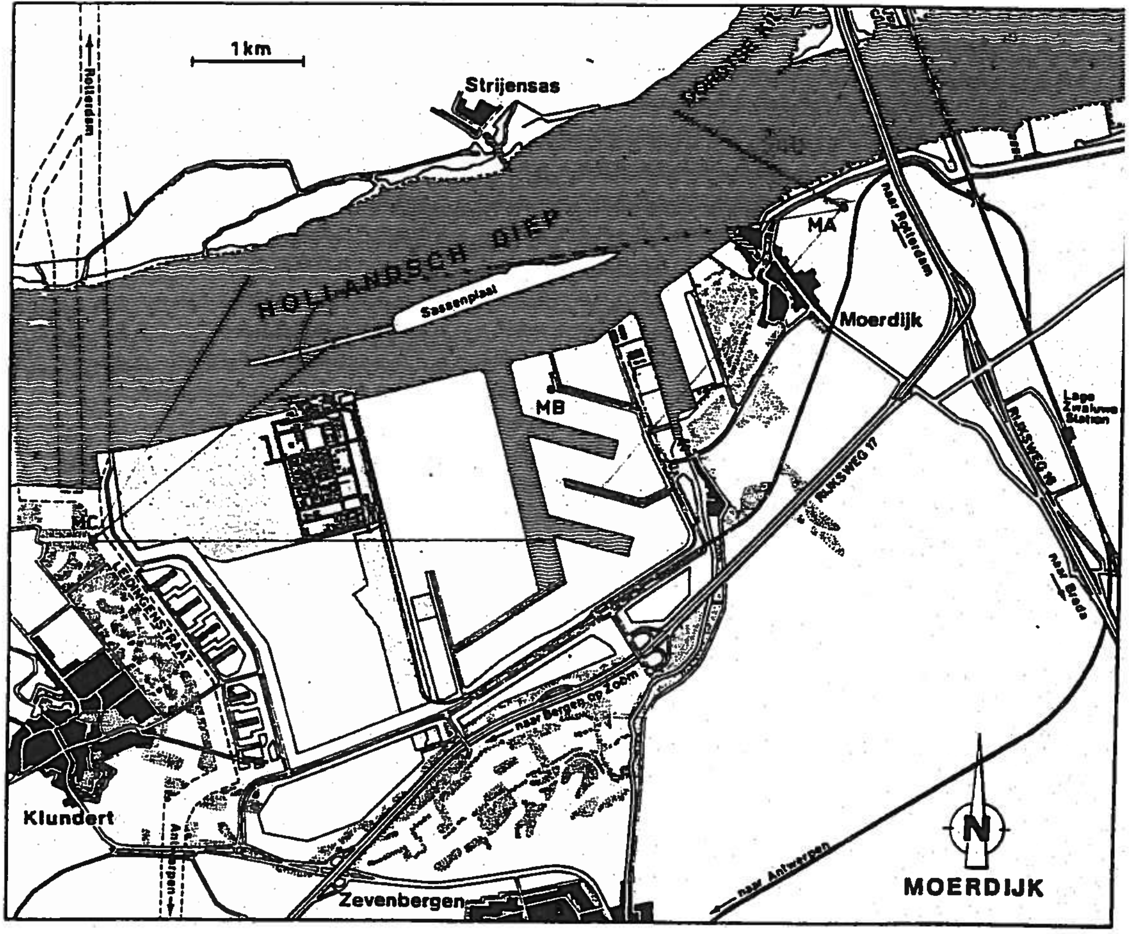


Figure B13b *Location of the measurement sites Moerdijk MA, MB and MC. Situation 1980.*

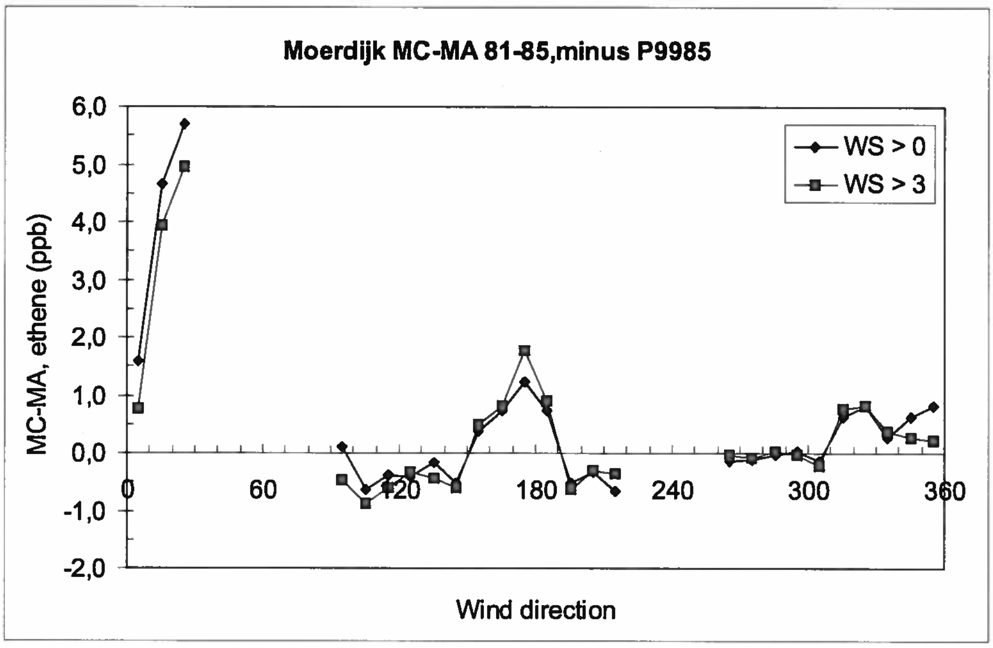


Figure B14a *The average difference, as a function of wind direction and wind speed, between Moerdijk MC and MA over the period 1981-1985 of ethene concentrations (ppb). Values in the industrial sector are removed as well as values above the 99.85th-percentile of the remaining data set.*

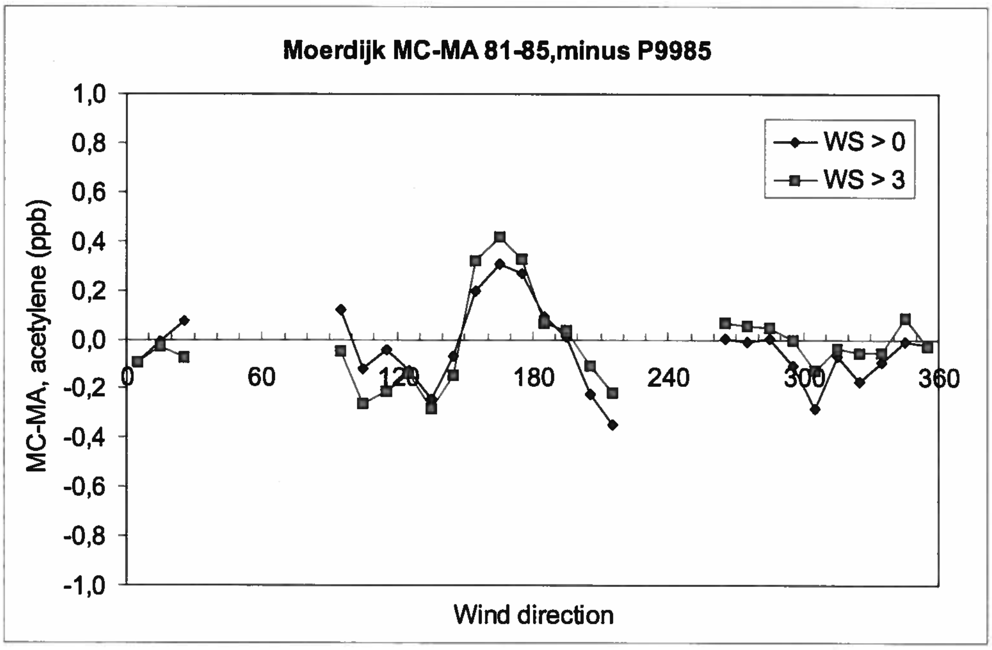


Figure B14b *The average difference, as a function of wind direction and wind speed, between Moerdijk MC and MA over the period 1981-1985 of acetylene concentrations (ppb). Values in the industrial sector are removed as well as values above the 99.85th-percentile of the remaining data set.*

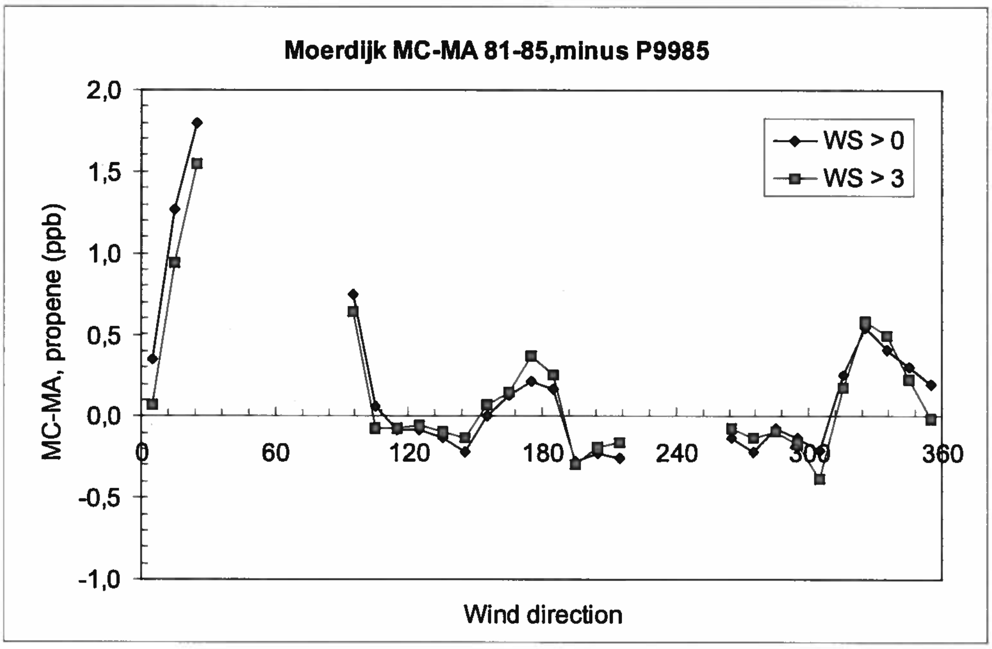


Figure B14c *The average difference, as a function of wind direction and wind speed, between Moerdijk MC and MA over the period 1981-1985 of propene concentrations (ppb). Values in the industrial sector are removed as well as values above the 99.85th-percentile of the remaining data set.*

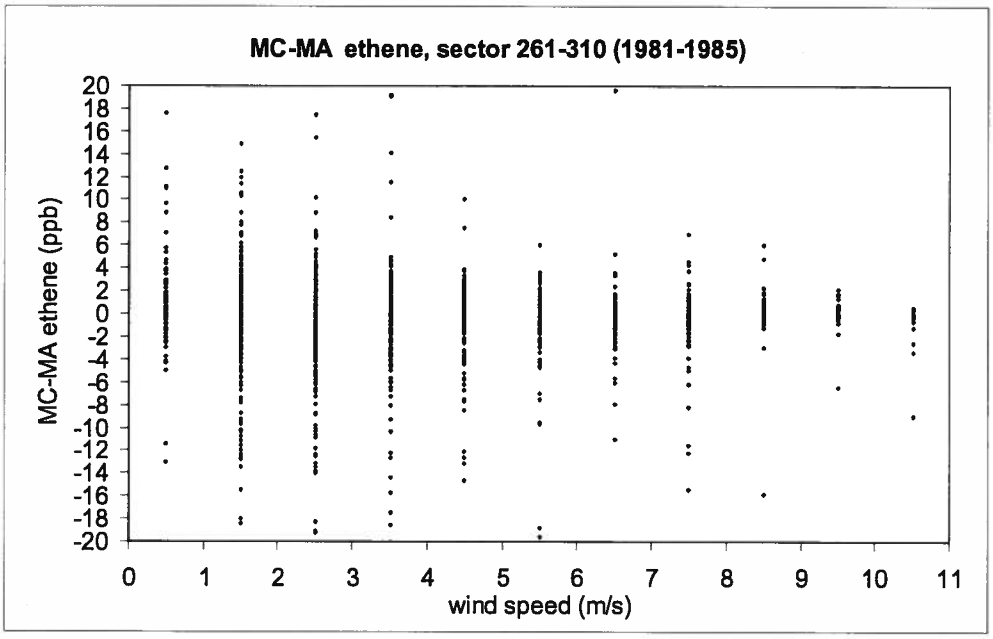


Figure B15a *The differences in the 261°-310° wind sector on a hourly basis over the 1981-1985 period between Moerdijk MC and MA of ethene concentrations (ppb) as a function of wind speed.*

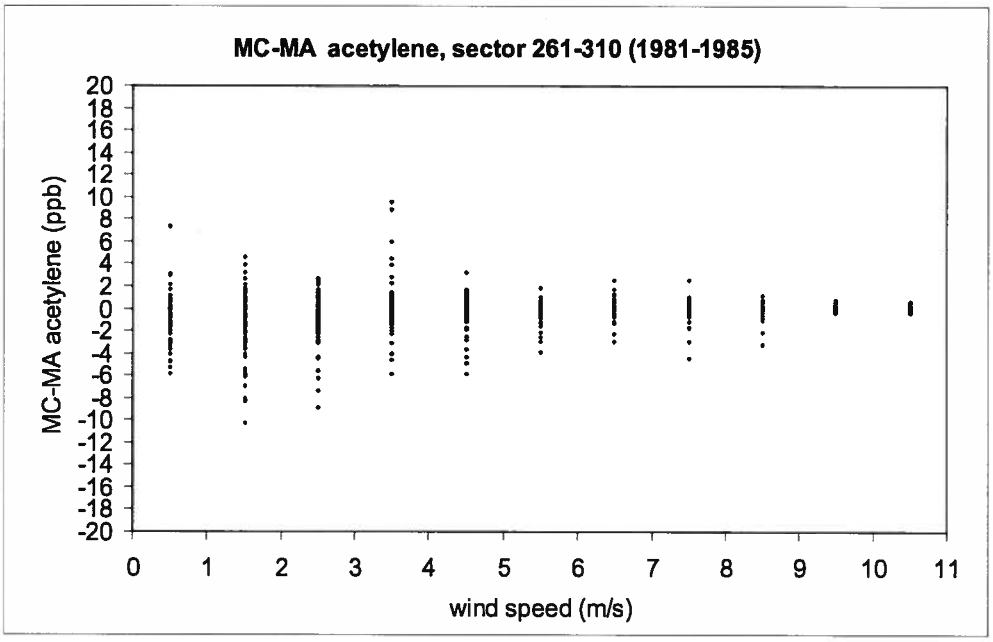


Figure B15b *The differences in the 261°-310° wind sector on a hourly basis over the 1981-1985 period between Moerdijk MC and MA of acetylene concentrations (ppb) as a function of wind speed.*

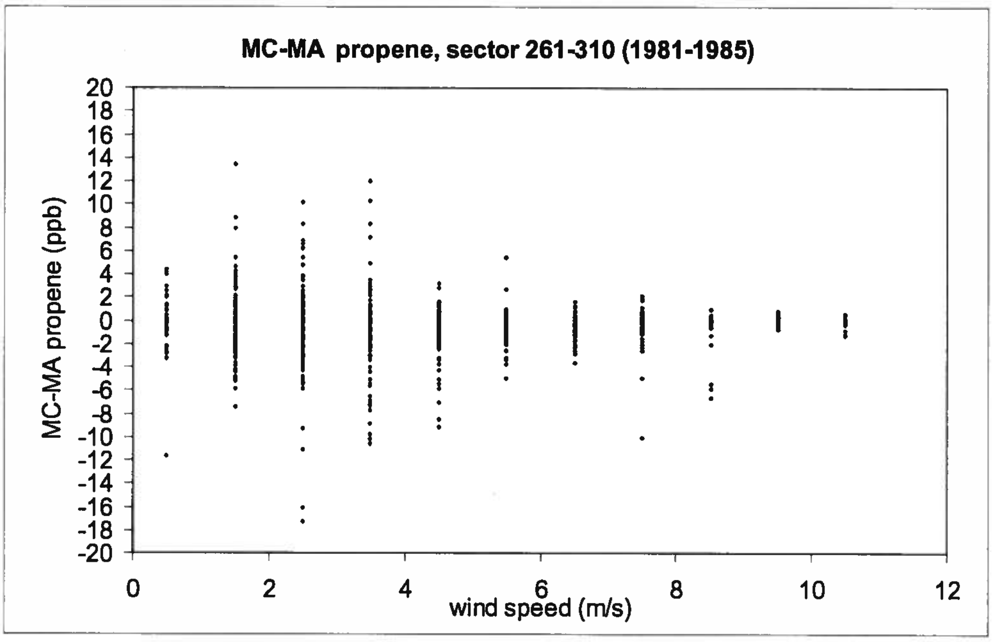


Figure B15c *The differences in the 261°-310° wind sector on a hourly basis over the 1981-1985 period between Moerdijk MC and MA of propene concentrations (ppb) as a function of wind speed.*

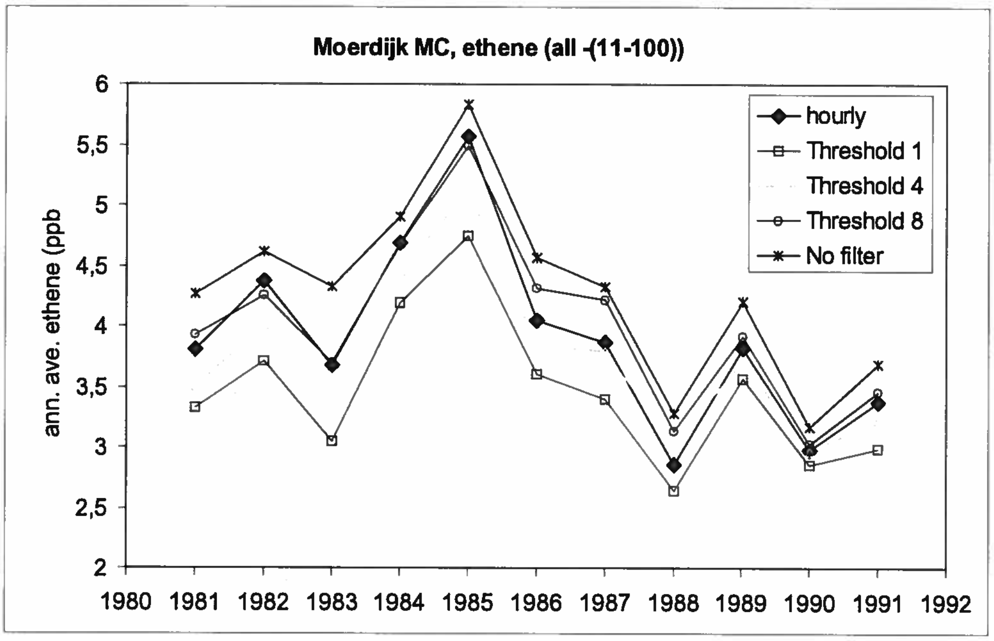


Figure B16 *Annual average ethene concentrations (ppb) of the non-industrial sector acccording to hourly values, and according to filtered and non-filtered daily values. Threshold 1/4/8: filter rejects daily values when at least one/four/eight of the 24 hours has(have) been in the industrial sector.*

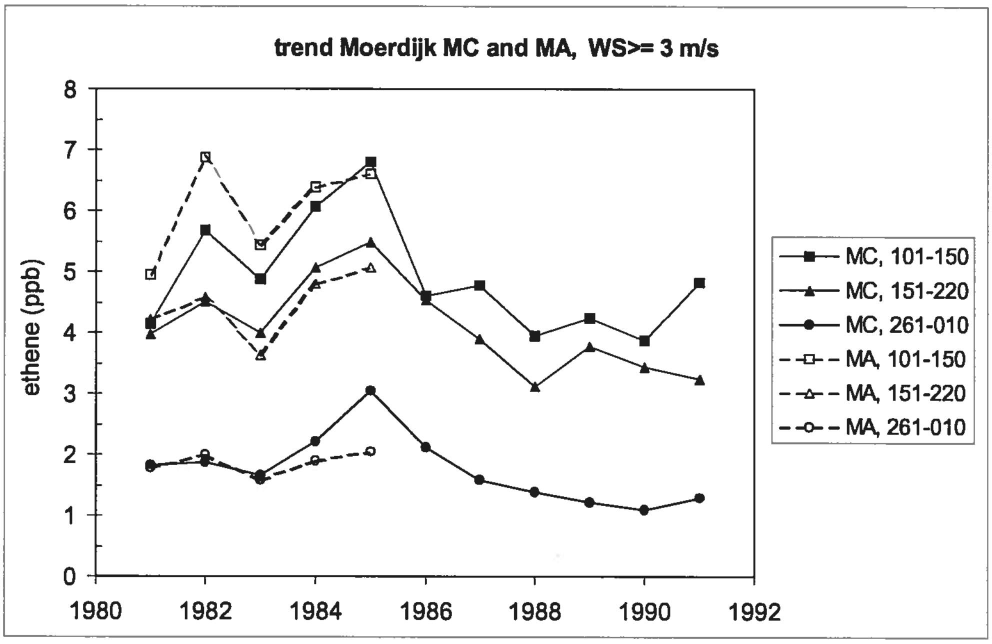


Figure B17a *Trends of annual average ethene concentrations (ppb) at Moerdijk MA and MC for a selection of wind sectors and wind speed of 3 ms^{-1} or more.*

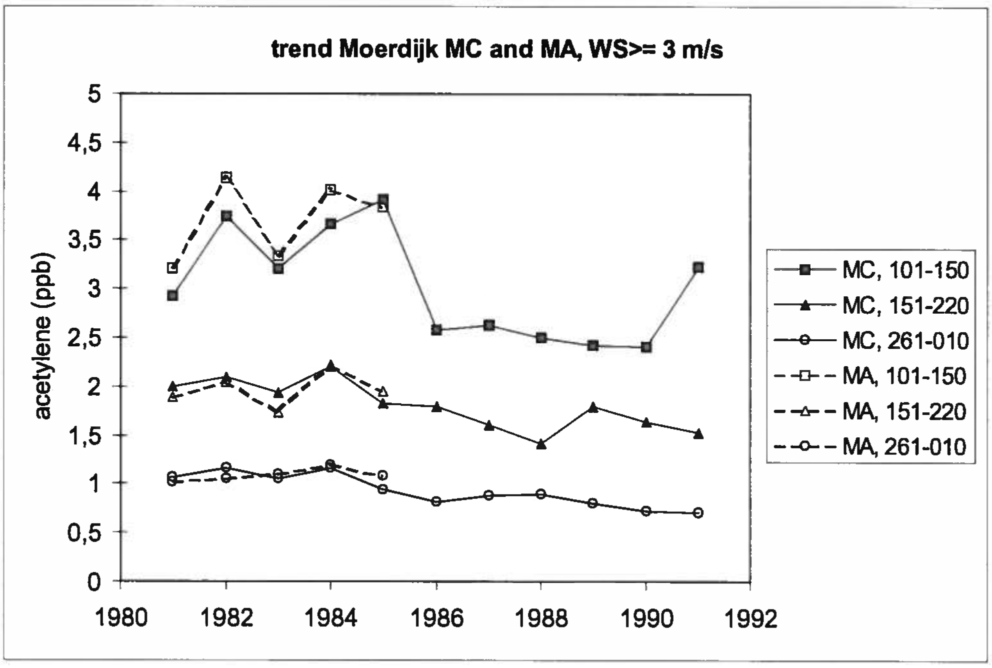


Figure B17b *Trends of annual average acetylene concentrations (ppb) at Moerdijk MA and MC for a selection of wind sectors and wind speed of 3 ms^{-1} or more.*

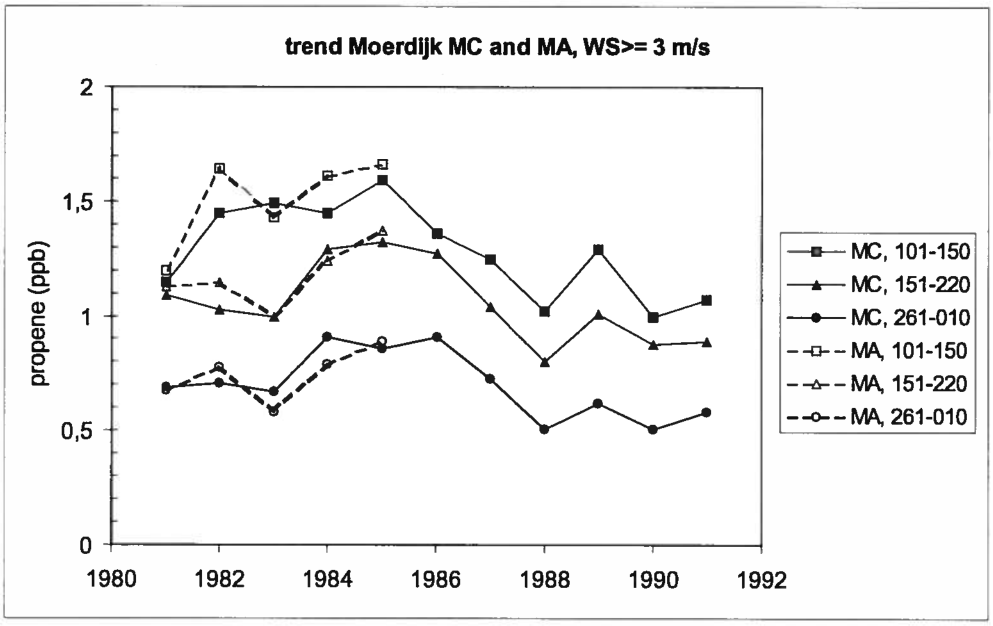


Figure B17c *Trends of annual average propene concentrations (ppb) at Moerdijk MA and MC for a selection of wind sectors and wind speed of 3 ms^{-1} or more.*

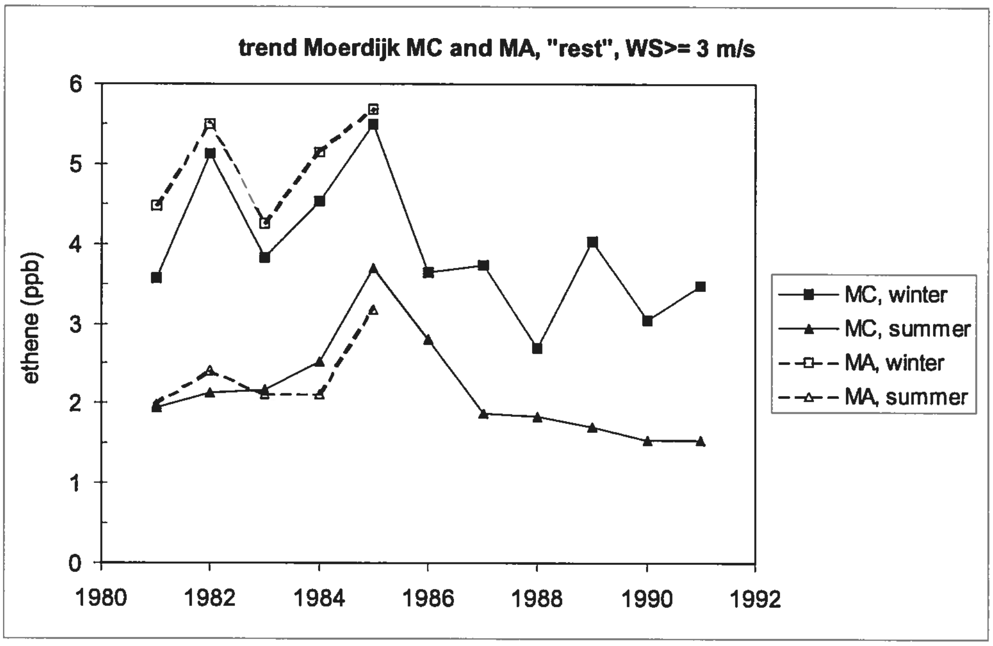


Figure B18a *Trends of summer (May-Aug.) and winter (Nov.-Feb.) average ethene concentrations (ppb) at Moerdijk MA and MC for the non-industrial wind sector and wind speed of 3 ms^{-1} or more.*

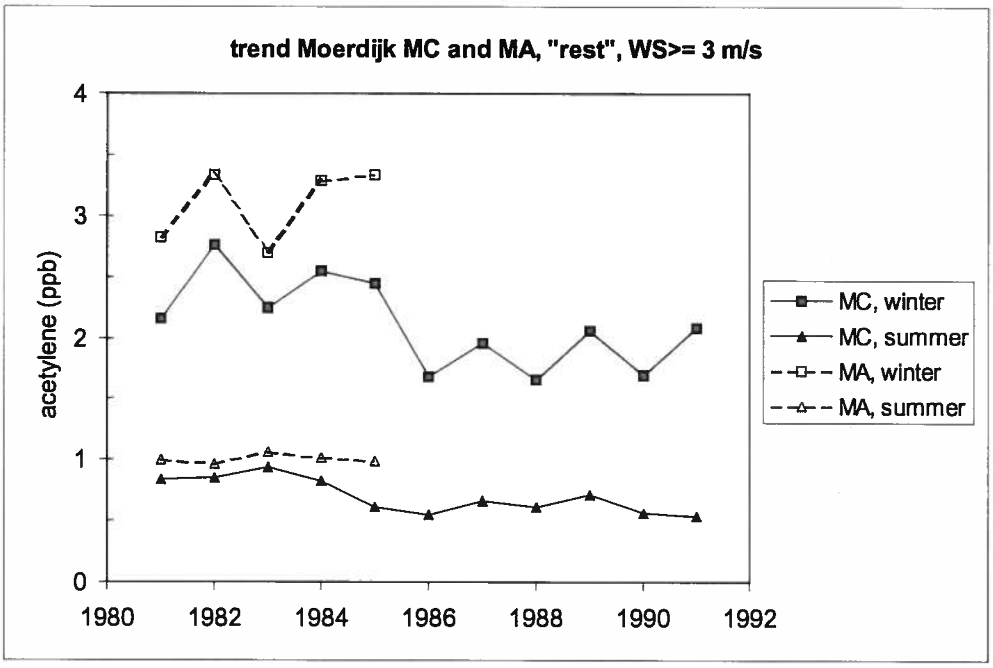


Figure B18b *Trends of summer (May-Aug.) and winter (Nov.-Feb.) average acetylene concentrations (ppb) at Moerdijk MA and MC for the non-industrial wind sector and wind speed of 3 ms^{-1} or more.*

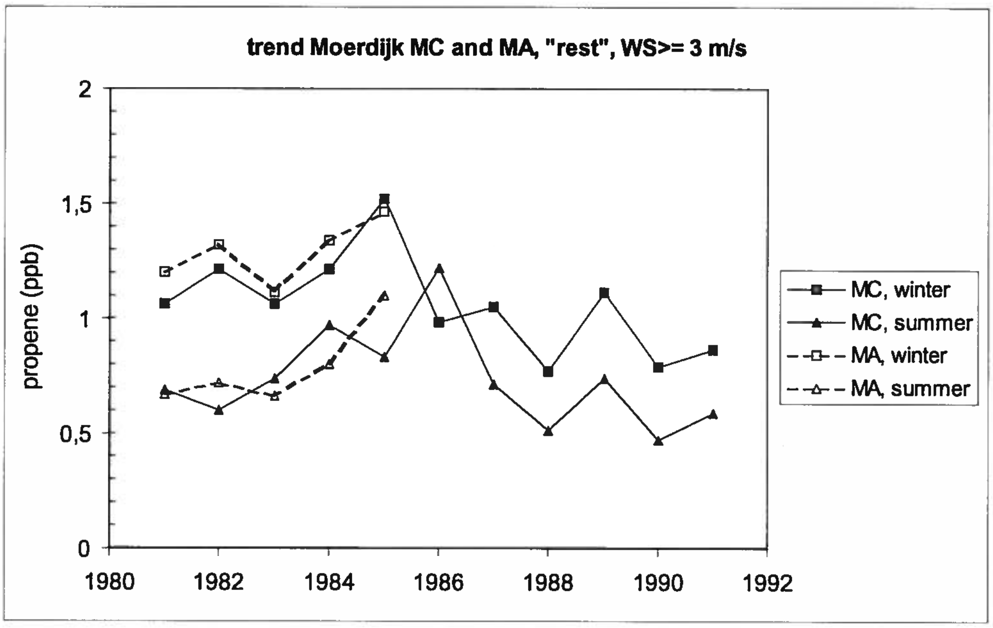


Figure B18c *Trends of summer (May-Aug.) and winter (Nov.-Feb.) average propene concentrations (ppb) at Moerdijk MA and MC for the non-industrial wind sector and wind speed of 3 ms*$^{-1}$ *or more.*

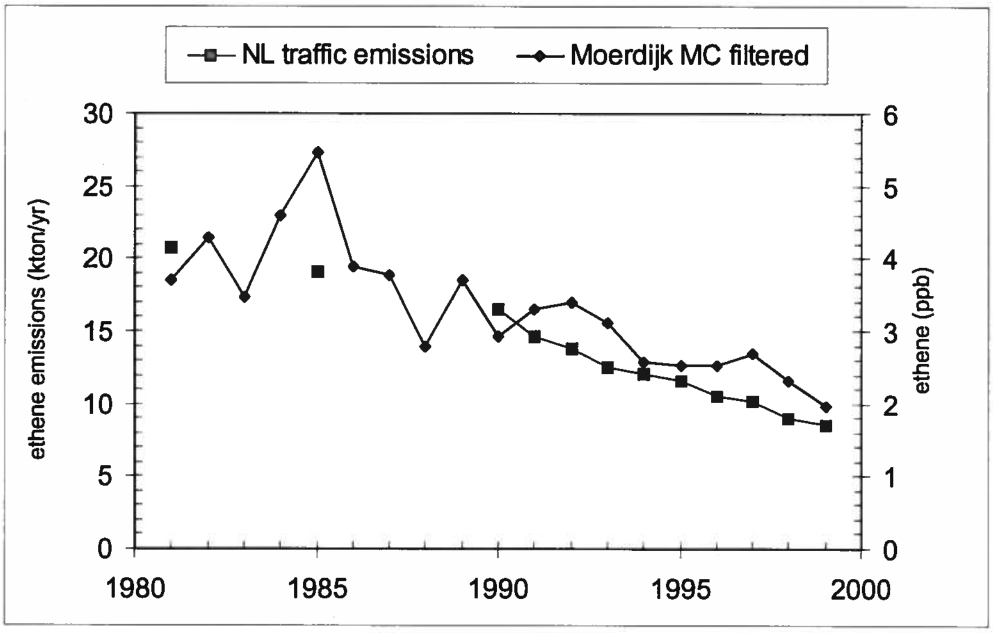


Figure B19a *Trend of filtered Moerdijk MC ethene concentrations (ppb) and trend of the Netherlands traffic ethene emissions (kton/yr) over the 1980-1999 period.*

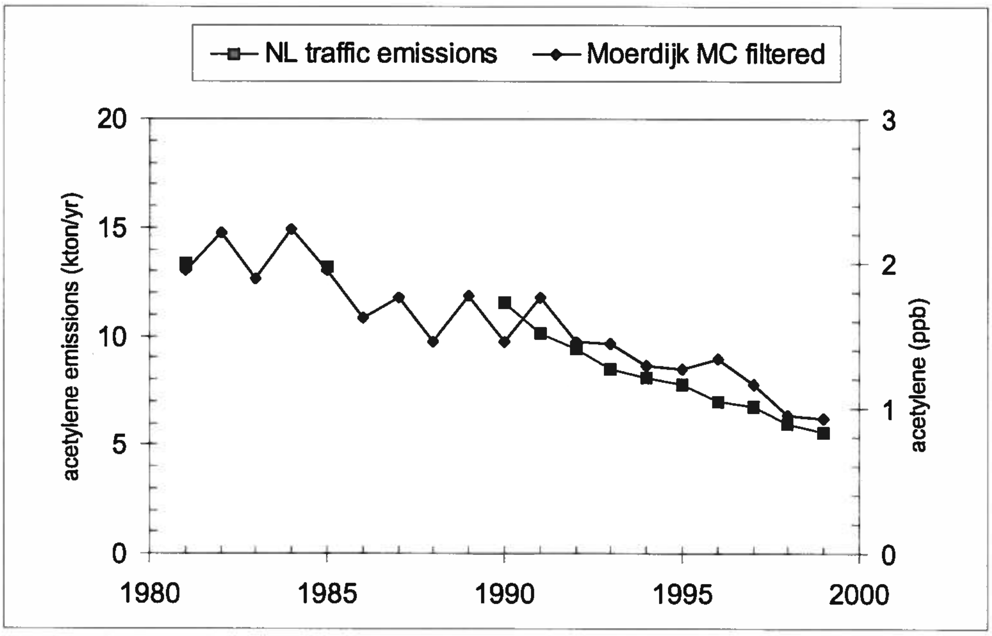


Figure B19b *Trend of filtered Moerdijk MC acetylene concentrations (ppb) and trend of the Netherlands traffic acetylene emissions (kton/yr) over the 1980-1999 period.*

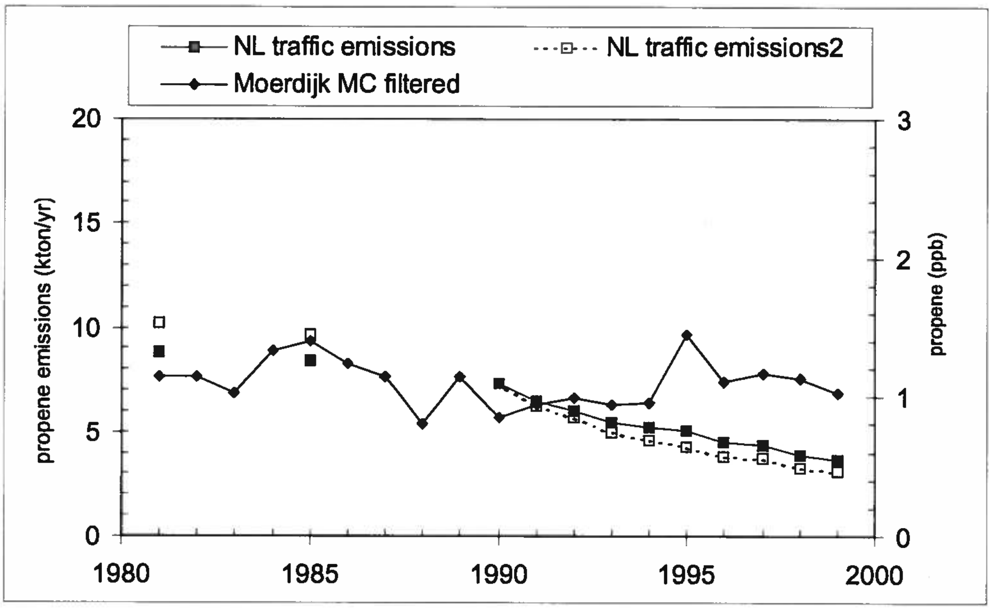


Figure B19c *Trend of filtered Moerdijk MC propene concentrations (ppb) and trend of the Netherlands traffic propene emissions (kton/yr) over the 1980-1999 period. NL traffic emissions2: including a shift in propene propertion in VOC emissions (see text)*

Table B.1 *Overview of O_3 sites used in the study; RIVM, NRW and a few Belgian sites have NO_2 and NO. For NO and NO_2 the available period is sometimes shorter than for O_3.*

station	area	code	Latitude (north)	Longitude (east)	Altitude (masl)[9]	EMEP grid cell	Period available	A'frts[7] W-E	A'frts[7] N-S
Aarschot	VL[1]	N035	50° 58'	4° 50'	55	2014	95-98	1161	3308
Moerkerke	VL	N012	51° 15'	3° 21'	3	1914	86-98	0128	3642
St-Kruis-Winkel	VL	R740	51° 09'	3° 48'	5	1914	83-98	0439	3523
St.-Denijs	VL	N050	50° 45'	3° 22'	42	1914	86-98	0124	3085
Gellik	VL	N046	50° 52'	5° 37'	70	2015	95-98	1711	3196
Dessel	VL	N016	51° 14'	5° 09'	30	2015	95-98	1384	3604
Eupen	WAL[2]	N066	50° 37'	6° 00'	295	2015	90-98	1983	2919
Kollumerwaard	NL[3]	934	53° 20'	6° 16'	~ 2	1916	78-99[8]	2143	5944
Balk	NL	918	52° 55'	5° 34'	~ 2	1916	78-99	1675	5478
Wieringerwerf	NL	538	52° 48'	5° 03'	~ 2	1916	86-99	1323	5352
Witteveen	NL	928	52° 48'	6° 40'	~ 10	2016	86-99	2414	5369
Biddinghuizen	NL	631	52° 26'	5° 37'	~ 2	1916	86-99	1708	4957
Hellendoorn	NL	807	52° 23'	6° 24'	~ 20	2016	78-99	2242	4894
Eibergen	NL	722	52° 05'	6° 36'	~ 20	2016	86-99	2385	4566
Wageningen	NL	724	51° 58'	5° 38'	~ 20	2016	86-99	1729	4427
Zegveld	NL	633	52° 08'	4° 50'	~ 2	1915	86-99	1174	4612
Cabauw	NL	620	51° 58'	4° 55'	~ 2	1915	86-99	1233	4425
Zierikzee	NL	301	51° 38'	3° 55'	~ 2	1915	86-99	0532	4061
Braakman	NL	318	51° 17'	3° 44'	~ 2	1914	86-99	0408	3685
Huijbergen	NL	235	51° 26'	4° 21'	~ 5	1915	86-99	0836	3833
Houtakker	NL	230	51° 31'	5° 08'	~ 10	2015	86-99	1384	3922
Budel	NL	227	51° 16'	5° 33'	~ 20	2015	89-99	1671	3642
Vredepeel	NL	131	51° 32'	5° 51'	~ 30	2015	86-99	1873	3947
Posterholt	NL	107	51° 07'	6° 02'	~ 30	2015	91-99	2009	3480
Wijnandsrade	NL	133	50° 54'	5° 52'	~ 60	2015	86-99	1898	3237
Nettetal	NRW[4]	NETT	51° 20'	6° 12'	49	2015	88-98	2116	3718
Eifel	NRW	EIFE	50° 39'	6° 17'	572	2115	84-98	2183	2958
Huerth	NRW	HUE2	50° 53'	6° 52'	90	2115	90-98	2591	3225
Rodenkirchen	NRW	RODE	50° 53'	6° 59'	45	2115	83-98	2673	3226
Wesel	NRW	WESE	51° 40'	6° 38'	25	2015	87-98	2412	4093
Borken	NRW	BORK	51° 51'	6° 52'	42	2016	90-98	2569	4299
Bielefeld	NRW	BIEL	52° 37'	8° 33'	102	2116	90-98	3691	5189
Deuselbach	RP[5]	DE04 [6]	49° 46'	7° 03'	480	2114	84-98	2748	1986
Meinerzhagen	NRW[5]	DE14	51° 07'	7° 38'	510	2115	87-98	3122	3498
Bassum	NS[5]	DE12	52° 51'	8° 43'	52	2017	87-98	3792	5454

1. VL: Vlaanderen, data provided by VMM, through IRCEL
2. WAL: Wallon, data provided by ISSEP, through IRCEL
3. NL: Nederland, data provided by RIVM
4. NRW: Nordrhein-Westfalen, data provided by LUA
5. data provided by UBA to EMEP; RP: Rheinland-Pfalz, NS: Niedersachsen
6. EMEP codes
7. Amersfoortse coordinates; a rectangular system in units of 100 m. W-E: west-east; N-S: north-south
8. 1978-1988 data is from Kloosterburen, a few km's away from Kollumerwaard
9. M.a.s.l. of the ground level; RIVM altitudes estimated from the map by author.

Table B.2 Results of visual inspection of ozone data 1988-1998

Station	Area	Remarks
Aarschot	VL	-
Moerkerke	VL	Few outliers in 88
St-Kruis-Winkel	VL	Offset (2.5 ppb) Dec.97-Dec.98; peak values Jul-Aug 1990 above 150 ppb[1]
St.-Denijs	VL	-
Gellik	VL	very few low values (0-1 ppb) in Dec.96 -Jan.97
Dessel	VL	-
Eupen	WAL	very few low values (0-1 ppb) in Dec.96 -Jan.97
Kollumerwaard	NL	High values (>50 ppb) in Nov.90; 2 high (>50 ppb) values in Feb.97
Balk	NL	-
Wieringerwerf	NL	-
Witteveen	NL	High values (>50 ppb) in Jan.90; peak values Jul.1990 above 150 ppb
Biddinghuizen	NL	-
Hellendoorn	NL	-
Eibergen	NL	-
Wageningen	NL	very few low values (0-1 ppb) in Feb-Oct.91
Zegveld	NL	-
Cabauw	NL	-
Zierikzee	NL	peak values Jul.1990 above 150 ppb
Braakman	NL	Outlier (100 ppb) in Jan.96
Huijbergen	NL	-
Houtakker	NL	Outlier (90 ppb) in Mar.91; very few low values (0-1 ppb) in Feb-Oct.91
Budel	NL	-
Vredepeel	NL	very few low values (0-1 ppb) in Jan.-Mar.91
Posterholt	NL	-
Wijnandsrade	NL	very few low values (0-1 ppb) in Dec.90 -Aug. 91
Nettetal	NRW	No values below 2.8 ppb in Jan. 91 – Feb. 92
Eifel	NRW	-
Huerth	NRW	Offsets in periods of 91 and 92; peak values above 150 ppb in Jun.-Aug. 90
Rodenkirchen	NRW	No values below 1.8 ppb Jan.-Apr. 91
Wesel	NRW	
Borken	NRW	Offsets Sep.90 – Nov. 91
Bielefeld	NRW	-
Deuselbach	RP	Jun.-Jul.88 factor 1.6 too low[2]
Meinerzhagen	NRW	Offsets 88, Oct.89 - Jan.90, Dec.92
Bassum	NS	Offsets Dec.90 - Nov.91, Oct.93 – Nov.94

1. peak values: no outliers
2. factor 1.6 according to UBA (Uhse, 1997)

Table B3 Distribution of lowest ozone values for a selection of sites.

Station	Year	Max. num.	Number missing	Number greater equal than threshold1 (µg.m^{-3}) and less than threshold2 (column next right)										
				0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
kollumerwaard	1987	8760	1172	510	0	75	0	36	0	38	0	43	0	43
kollumerwaard	1988	8784	568	384	0	62	0	48	0	54	0	45	0	38
kollumerwaard	1989	8760	1460	532	0	63	0	63	0	53	0	44	0	33
kollumerwaard	1990	8760	727	309	0	38	0	129	0	96	0	52	0	50
kollumerwaard	1991	8760	51	10	0	22	0	96	0	93	0	112	0	120
kollumerwaard	1992	8784	537	91	0	173	0	265	0	117	0	97	0	61
kollumerwaard	1993	8760	254	29	0	120	0	210	0	188	0	151	0	74
kollumerwaard	1994	8760	1354	42	0	174	0	202	0	95	0	65	0	71
kollumerwaard	1995	8760	491	43	0	263	0	205	0	99	0	83	0	74
kollumerwaard	1996	8784	350	132	0	283	0	179	0	108	0	77	0	66
kollumerwaard	1997	8760	657	66	0	219	0	199	0	106	0	97	0	55
kollumerwaard	1998	8760	38	138	0	196	0	87	0	57	0	49	0	41
kruiswinkel-sint	1987	8760	8760	0	0	0	0	0	0	0	0	0	0	0
kruiswinkel-sint	1988	8784	2163	567	0	122	0	123	0	122	0	143	0	213
kruiswinkel-sint	1989	8760	2551	684	0	181	0	137	0	129	0	196	0	245
kruiswinkel-sint	1990	8760	2316	553	0	145	0	113	0	105	0	157	0	159
kruiswinkel-sint	1991	8760	3086	1050	0	211	0	157	0	122	0	112	0	215
kruiswinkel-sint	1992	8784	1358	586	0	224	0	199	0	164	0	153	0	250
kruiswinkel-sint	1993	8760	1470	960	0	154	0	102	0	108	0	110	0	169
kruiswinkel-sint	1994	8760	1285	291	0	46	0	164	0	278	0	134	0	317
kruiswinkel-sint	1995	8760	1945	1017	0	116	0	115	0	84	0	80	0	103
kruiswinkel-sint	1996	8784	1475	1381	0	98	0	109	0	98	0	75	0	119
kruiswinkel-sint	1997	8760	2504	1033	0	101	0	80	0	76	0	85	0	248
kruiswinkel-sint	1998	8760	1530	0	0	0	0	0	0	0	0	0	0	894
moerkerke	1987	8760	8760	0	0	0	0	0	0	0	0	0	0	0
moerkerke	1988	8784	5899	415	0	161	0	64	0	68	0	77	0	84
moerkerke	1989	8760	2608	620	0	272	0	213	0	141	0	101	0	83
moerkerke	1990	8760	2522	83	0	183	0	162	0	108	0	117	0	84
moerkerke	1991	8760	3979	167	0	315	0	241	0	152	0	110	0	60
moerkerke	1992	8784	2856	285	0	359	0	219	0	144	0	124	0	113
moerkerke	1993	8760	1244	713	0	564	0	377	0	256	0	157	0	83
moerkerke	1994	8760	1354	799	0	291	0	230	0	253	0	202	0	106
moerkerke	1995	8760	3714	821	0	149	0	99	0	83	0	81	0	61
moerkerke	1996	8784	1440	938	0	183	0	96	0	89	0	68	0	85
moerkerke	1997	8760	1664	804	0	187	0	118	0	102	0	86	0	92
moerkerke	1998	8760	1565	171	0	123	0	111	0	75	0	59	0	38

Table B3 *Distribution of lowest ozone values for a selection of sites (continued).*

Station	Year	Max. num.	Number missing	Number greater equal than threshold1 ($\mu g.m^{-3}$) and less than threshold2 (column next right)										
				0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
eupen	1987	8760	8760	0	0	0	0	0	0	0	0	0	0	0
eupen	1988	8784	8784	0	0	0	0	0	0	0	0	0	0	0
eupen	1989	8760	8760	0	0	0	0	0	0	0	0	0	0	0
eupen	1990	8760	4146	9	0	26	0	27	0	29	0	54	0	102
eupen	1991	8760	2316	392	0	210	0	114	0	89	0	88	0	88
eupen	1992	8784	1205	63	0	101	0	130	0	159	0	134	0	117
eupen	1993	8760	1647	3	0	86	0	158	0	195	0	124	0	89
eupen	1994	8760	1808	95	0	66	0	72	0	61	0	67	0	56
eupen	1995	8760	765	465	0	140	0	108	0	138	0	88	0	91
eupen	1996	8784	1941	188	0	49	0	92	0	119	0	93	0	91
eupen	1997	8760	1473	0	0	0	0	42	0	142	0	97	0	101
eupen	1998	8760	1064	0	0	0	0	0	0	0	0	45	0	116
rodenkirchen	1987	8760	868	0	0	0	3101	0	102	107	103	97	70	86
rodenkirchen	1988	8784	1804	0	0	0	65	0	26	9	25	31	52	72
rodenkirchen	1989	8760	1823	0	0	0	1095	0	275	129	378	161	173	159
rodenkirchen	1990	8760	180	0	0	0	1846	0	166	140	238	161	176	146
rodenkirchen	1991	8760	496	0	0	0	1773	0	88	57	124	165	325	154
rodenkirchen	1992	8784	371	0	0	0	2396	0	131	150	108	109	132	115
rodenkirchen	1993	8760	326	0	0	0	1329	0	160	160	144	214	182	207
rodenkirchen	1994	8760	532	0	0	0	2054	0	31	134	92	95	93	76
rodenkirchen	1995	8760	597	0	0	0	1049	1717	12	108	87	78	80	71
rodenkirchen	1996	8784	603	0	0	0	0	2790	0	86	103	80	59	85
rodenkirchen	1997	8760	637	0	0	0	0	2716	0	90	92	61	56	67
rodenkirchen	1998	8760	428	0	0	0	0	2364	0	109	69	82	62	66
meinerzhagen	1987	8760	8760	0	0	0	0	0	0	0	0	0	0	0
meinerzhagen	1988	8784	713	0	0	2	0	0	0	2	3	7	5	33
meinerzhagen	1989	8760	827	0	0	66	28	33	58	77	77	57	52	66
meinerzhagen	1990	8760	1000	0	0	190	45	53	47	42	34	40	46	80
meinerzhagen	1991	8760	811	0	0	58	33	30	46	68	111	104	61	40
meinerzhagen	1992	8784	555	0	0	409	44	44	51	39	32	37	54	66
meinerzhagen	1993	8760	410	0	0	208	11	19	35	29	31	16	42	62
meinerzhagen	1994	8760	5646	0	0	55	21	21	16	10	11	14	25	15
meinerzhagen	1995	8760	1593	0	0	345	31	31	31	35	30	24	29	26
meinerzhagen	1996	8784	381	0	0	372	0	97	0	77	0	84	0	55
meinerzhagen	1997	8760	534	0	0	400	0	115	0	91	0	68	0	83
meinerzhagen	1998	8760	3922	0	0	64	0	13	0	14	0	23	0	10

Table B4 *Distribution of lowest NO_2 values for a selection of sites.*

Station	Year	Max. num.	Number missing	Number greater equal than threshold1 ($\mu g.m^{-3}$) and less than threshold2 (column next right)										
				-5.0	-4.5	-4.0	-3.5	-3.0	-2.5	-2.0	-1.5	-1.0	-0.5	0.0
kollumerwaard	1987	8760	215	0	0	5	0	23	0	68	0	191	0	515
kollumerwaard	1988	8784	403	0	0	0	0	0	0	0	0	0	0	763
kollumerwaard	1989	8760	1387	0	0	0	0	0	0	0	0	0	0	402
kollumerwaard	1990	8760	546	7	0	11	0	30	0	73	0	178	0	472
kollumerwaard	1991	8760	80	3	0	0	0	41	0	259	0	451	0	378
kollumerwaard	1992	8784	789	1	0	8	0	9	0	26	0	117	0	379
kollumerwaard	1993	8760	349	1	0	3	0	1	0	13	0	45	0	233
kollumerwaard	1994	8760	1517	1	0	2	0	3	0	20	0	72	0	321
kollumerwaard	1995	8760	827	0	0	0	0	0	0	3	0	56	0	364
kollumerwaard	1996	8784	1059	10	0	26	0	40	0	94	0	158	0	259
kollumerwaard	1997	8760	902	2	0	1	0	2	0	1	0	19	0	91
kollumerwaard	1998	8760	40	0	0	0	0	0	0	0	0	16	0	162
balk	1987	8760	321	0	0	3	0	8	0	83	0	267	0	407
balk	1988	8784	252	1	0	13	0	13	0	36	0	78	0	217
balk	1989	8760	913	6	0	13	0	32	0	82	0	238	0	479
balk	1990	8760	359	26	0	49	0	58	0	148	0	309	0	362
balk	1991	8760	388	0	0	0	0	0	0	12	0	55	0	204
balk	1992	8784	906	0	0	2	0	6	0	11	0	57	0	280
balk	1993	8760	648	7	0	10	0	19	0	26	0	103	0	309
balk	1994	8760	283	10	0	27	0	26	0	61	0	156	0	333
balk	1995	8760	657	3	0	15	0	27	0	51	0	136	0	295
balk	1996	8784	625	0	0	4	0	5	0	13	0	38	0	154
balk	1997	8760	975	0	0	1	0	16	0	38	0	54	0	117
balk	1998	8760	994	0	0	5	0	11	0	28	0	65	0	201
wieringerwerf	1987	8760	459	0	0	0	0	0	0	0	0	0	0	297
wieringerwerf	1988	8784	276	0	0	0	0	9	0	23	0	136	0	329
wieringerwerf	1989	8760	585	5	0	11	0	22	0	42	0	132	0	271
wieringerwerf	1990	8760	151	6	0	11	0	14	0	60	0	245	0	430
wieringerwerf	1991	8760	89	1	0	0	0	1	0	38	0	110	0	407
wieringerwerf	1992	8784	755	19	0	20	0	27	0	25	0	30	0	115
wieringerwerf	1993	8760	135	0	0	0	0	0	0	0	0	4	0	85
wieringerwerf	1994	8760	935	0	0	0	0	0	0	0	0	8	0	71
wieringerwerf	1995	8760	563	8	0	5	0	11	0	14	0	39	0	138
wieringerwerf	1996	8784	1595	0	0	0	0	0	0	0	0	12	0	30
wieringerwerf	1997	8760	1623	0	0	0	0	0	0	0	0	20	0	25
wieringerwerf	1998	8760	636	0	0	0	0	0	0	0	0	6	0	23

Table B4 *Distribution of lowest NO_2 ozone values for a selection of sites (continued).*

Station	Year	Max. num.	Number missing	Number greater equal than threshold1 ($\mu g.m^{-3}$) and less than threshold2 (column next right)										
				0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
moerkerke	1987	8760	8760	0	0	0	0	0	0	0	0	0	0	0
moerkerke	1988	8784	8784	0	0	0	0	0	0	0	0	0	0	0
moerkerke	1989	8760	8760	0	0	0	0	0	0	0	0	0	0	0
moerkerke	1990	8760	2477	45	0	116	0	118	0	127	0	146	0	131
moerkerke	1991	8760	3965	47	0	21	0	47	0	73	0	64	0	68
moerkerke	1992	8784	2239	41	0	13	0	17	0	51	0	147	0	199
moerkerke	1993	8760	1097	204	0	149	0	143	0	160	0	178	0	247
moerkerke	1994	8760	2219	76	0	24	0	73	0	134	0	192	0	307
moerkerke	1995	8760	3350	124	0	48	0	56	0	125	0	183	0	225
moerkerke	1996	8784	839	77	0	56	0	93	0	194	0	273	0	336
moerkerke	1997	8760	1206	2	0	13	0	38	0	83	0	160	0	241
moerkerke	1998	8760	1789	0	0	0	0	8	0	55	0	101	0	222
eupen	1987	8760	8760	0	0	0	0	0	0	0	0	0	0	0
eupen	1988	8784	8784	0	0	0	0	0	0	0	0	0	0	0
eupen	1989	8760	8760	0	0	0	0	0	0	0	0	0	0	0
eupen	1990	8760	2022	25	0	24	0	28	0	30	0	60	0	102
eupen	1991	8760	1912	33	0	17	0	41	0	50	0	53	0	63
eupen	1992	8784	1919	422	0	316	0	267	0	314	0	304	0	300
eupen	1993	8760	1872	177	0	437	0	446	0	355	0	330	0	251
eupen	1994	8760	1252	342	0	338	0	407	0	445	0	403	0	363
eupen	1995	8760	1123	554	0	395	0	406	0	514	0	453	0	385
eupen	1996	8784	1960	718	0	197	0	219	0	209	0	220	0	183
eupen	1997	8760	1071	0	0	0	0	0	0	0	0	0	0	0
eupen	1998	8760	1288	0	0	0	0	0	0	0	0	0	0	0
				4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0
wesel	1987	8760	647	0	0	987	0	0	0	0	94	66	47	35
wesel	1988	8784	1232	0	0	464	0	0	0	0	90	63	37	22
wesel	1989	8760	1496	0	0	499	0	0	0	0	124	36	29	11
wesel	1990	8760	873	0	0	1779	0	0	0	0	145	84	57	42
wesel	1991	8760	1060	0	0	1294	0	0	0	0	161	69	34	32
wesel	1992	8784	597	0	0	1213	0	0	0	0	78	94	61	50
wesel	1993	8760	1304	0	0	657	0	0	0	0	80	81	42	38
wesel	1994	8760	1451	0	0	790	0	0	0	0	98	74	49	31
wesel	1995	8760	1821	0	0	936	0	0	0	0	121	78	48	34
wesel	1996	8784	1547	0	0	529	0	0	0	0	71	59	35	16
wesel	1997	8760	1059	0	0	651	0	0	0	0	105	78	50	18
wesel	1998	8760	809	0	0	691	0	0	0	0	151	72	46	30

Table B5 *Distribution of lowest NO values for a selection of sites.*

Station	Year	Max. num.	Number missing	Number greater equal than threshold1 ($\mu g.m^{-3}$) and less than threshold2 (column next right)										
				-5.0	-4.5	-4.0	-3.5	-3.0	-2.5	-2.0	-1.5	-1.0	-0.5	0.0
kollumerwaard	1987	8760	215	0	0	1	0	4	0	212	0	1154	0	4248
kollumerwaard	1988	8784	8784	0	0	0	0	0	0	0	0	0	0	0
kollumerwaard	1989	8760	8651	0	0	0	0	0	0	0	0	1	0	75
kollumerwaard	1990	8760	534	1	0	21	0	99	0	249	0	594	0	2620
kollumerwaard	1991	8760	80	0	0	5	0	0	0	47	0	644	0	3053
kollumerwaard	1992	8784	720	0	0	0	0	1	0	5	0	55	0	4194
kollumerwaard	1993	8760	348	0	0	4	0	2	0	15	0	192	0	3589
kollumerwaard	1994	8760	1499	0	0	1	0	3	0	8	0	38	0	4011
kollumerwaard	1995	8760	818	4	0	11	0	24	0	68	0	208	0	3922
kollumerwaard	1996	8784	912	3	0	18	0	22	0	47	0	193	0	4260
kollumerwaard	1997	8760	238	4	0	12	0	41	0	193	0	1023	0	3743
kollumerwaard	1998	8760	40	0	0	0	0	4	0	2	0	323	0	4794
wageningen	1987	8760	3499	0	0	3	0	19	0	71	0	455	0	1584
wageningen	1988	8784	878	11	0	12	0	32	0	138	0	613	0	2021
wageningen	1989	8760	270	13	0	32	0	68	0	124	0	423	0	1360
wageningen	1990	8760	65	3	0	5	0	23	0	91	0	524	0	2021
wageningen	1991	8760	312	1	0	17	0	46	0	128	0	396	0	1769
wageningen	1992	8784	68	0	0	0	0	0	0	0	0	38	0	2799
wageningen	1993	8760	526	0	0	0	0	0	0	0	0	2	0	2028
wageningen	1994	8760	725	4	0	6	0	23	0	37	0	82	0	2590
wageningen	1995	8760	279	0	0	10	0	51	0	36	0	105	0	3113
wageningen	1996	8784	659	0	0	0	0	3	0	18	0	171	0	2146
wageningen	1997	8760	665	19	0	21	0	54	0	118	0	400	0	1368
wageningen	1998	8760	256	0	0	0	0	1	0	17	0	257	0	2818
balk	1987	8760	311	16	0	24	0	103	0	283	0	809	0	3422
balk	1988	8784	200	1	0	6	0	45	0	93	0	781	0	2984
balk	1989	8760	911	0	0	0	0	1	0	27	0	716	0	2489
balk	1990	8760	320	0	0	2	0	22	0	148	0	755	0	2359
balk	1991	8760	387	2	0	2	0	15	0	54	0	272	0	2782
balk	1992	8784	853	0	0	0	0	0	0	0	0	4	0	4300
balk	1993	8760	481	1	0	5	0	12	0	41	0	225	0	3824
balk	1994	8760	181	0	0	0	0	0	0	30	0	33	0	3883
balk	1995	8760	649	0	0	13	0	32	0	66	0	292	0	4514
balk	1996	8784	499	1	0	4	0	40	0	88	0	364	0	3226
balk	1997	8760	114	14	0	35	0	63	0	191	0	739	0	3020
balk	1998	8760	886	2	0	17	0	34	0	114	0	535	0	3352

Table B5 *Distribution of lowest NO values for a selection of sites (continued).*

Station	Year	Max. num.	Number missing	Number greater equal than threshold1 ($\mu g.m^{-3}$) and less than threshold2 (column next right)										
				2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0
rodenkirchen	1987	8760	1019	0	0	0	1883	0	0	59	81	67	55	54
rodenkirchen	1988	8784	1619	0	0	0	2141	0	0	70	88	79	59	47
rodenkirchen	1989	8760	1616	0	0	0	2001	0	0	93	76	74	49	46
rodenkirchen	1990	8760	630	0	0	0	2628	0	0	108	113	123	52	61
rodenkirchen	1991	8760	1197	0	0	0	2418	0	0	73	104	79	60	58
rodenkirchen	1992	8784	534	0	0	0	3362	0	0	0	0	0	76	134
rodenkirchen	1993	8760	772	0	0	0	3507	0	0	0	0	0	82	123
rodenkirchen	1994	8760	455	0	0	0	3981	0	0	0	0	0	71	130
rodenkirchen	1995	8760	811	0	0	0	3313	0	0	43	91	78	58	87
rodenkirchen	1996	8784	778	0	0	0	3038	0	0	95	148	81	57	66
rodenkirchen	1997	8760	701	0	0	0	3068	0	0	99	146	86	77	65
rodenkirchen	1998	8760	436	0	0	0	3578	0	0	91	133	147	77	61
wesel	1987	8760	617	0	0	0	4231	0	0	132	112	82	62	76
wesel	1988	8784	1232	0	0	0	4247	0	0	151	122	75	53	85
wesel	1989	8760	1189	0	0	0	3665	0	0	155	74	67	35	72
wesel	1990	8760	643	0	0	0	4772	0	0	163	106	80	38	71
wesel	1991	8760	878	0	0	0	4675	0	0	116	85	64	25	61
wesel	1992	8784	513	0	0	0	5612	0	0	0	0	0	58	90
wesel	1993	8760	818	0	0	0	5523	0	0	0	0	0	55	93
wesel	1994	8760	791	0	0	0	5515	0	0	0	0	0	45	85
wesel	1995	8760	825	0	0	0	5203	0	0	42	88	47	50	47
wesel	1996	8784	1054	0	0	0	5071	0	0	73	118	68	43	50
wesel	1997	8760	734	0	0	0	5104	0	0	88	97	66	43	37
wesel	1998	8760	557	0	0	0	5758	0	0	67	90	81	47	47
borken	1987	8760	8760	0	0	0	0	0	0	0	0	0	0	0
borken	1988	8784	8784	0	0	0	0	0	0	0	0	0	0	0
borken	1989	8760	8760	0	0	0	0	0	0	0	0	0	0	0
borken	1990	8760	6226	0	0	0	648	0	0	36	41	21	14	15
borken	1991	8760	1203	0	0	0	3129	0	0	109	135	74	61	75
borken	1992	8784	950	0	0	0	4069	0	0	0	0	0	86	130
borken	1993	8760	616	0	0	0	4071	0	0	0	0	0	99	149
borken	1994	8760	390	0	0	0	4448	0	0	0	0	0	88	176
borken	1995	8760	633	0	0	0	3428	0	0	70	110	73	79	94
borken	1996	8784	378	0	0	0	3485	0	0	121	223	122	81	83
borken	1997	8760	878	0	0	0	3698	0	0	121	197	128	83	64
borken	1998	8760	3283	0	0	0	2908	0	0	63	121	91	69	46

Table B6a *NO_x trends (% per year) of monthly NO_x parameters for summer (May-August) period; monthly values require 75% or more of hourly values present. Bold: significant at 95% confidence interval including correction for autocorrelation; period: 1987-1998.*

		Trend (% per year)						
station	**area**	**Avg.**	**P25**	**P50**	**P75**	**P90**	**P98**	**P99**
Aarschot	VL[1]							
Moerkerke	VL							
St-Kruis-Winkel	VL							
St.-Denijs	VL							
Gellik	VL							
Dessel	VL							
Eupen	WAL[2]							
Kollumerwaard	NL[3]	+0.4	+3.8	+1.0	-0.4	-0.2	-0.9	-1.3
Balk	NL	-0.6	+4.3	+0.5	-0.7	-1.6	-1.4	-1.8
Wieringerwerf	NL	+1.1	**+5.6**	+0.6	-0.7	-0.6	+5.2	+6.0
Witteveen	NL	-1.2	+0.2	-1.5	-1.4	-1.8	-2.8	-3.2
Biddinghuizen	NL	-1.0	+2.4	-0.2	-1.2	**-2.0**	**-2.5**	**-2.6**
Hellendoorn	NL	-1.9	-1.1	-1.4	-2.1	-2.4	-2.5	-2.3
Eibergen	NL	**-2.2**	+0.4	-0.9	**-2.6**	**-3.5**	**-4.2**	**-3.8**
Wageningen	NL	-1.0	+0.2	-0.4	-1.2	-1.6	-1.5	-1.4
Zegveld	NL	**-2.8**	**-1.4**	**-2.3**	**-2.9**	**-3.4**	**-3.4**	**-3.5**
Cabauw	NL	**-2.0**	**-2.1**	-1.6	**-2.0**	-2.2	-2.2	-2.2
Zierikzee	NL	-0.8	+3.0	+0.6	-0.7	-1.1	**-2.3**	**-4.3**
Braakman	NL	-0.6	+1.4	+0.2	-0.8	-1.0	-1.6	-2.3
Huijbergen	NL	-0.2	**+2.4**	+0.7	-0.8	-1.2	-1.8	-2.1
Houtakker	NL	-2.2	-0.7	-1.5	-1.9	**-2.6**	**-3.7**	**-3.7**
Budel	NL	-1.8	+0.2	-1.2	-21.	**-2.7**	**-2.8**	**-2.8**
Vredepeel	NL	-1.8	-0.8	-0.6	-1.3	-2.3	-3.4	-4.2
Posterholt	NL	**-3.0**	**-2.4**	**-2.9**	**-3.1**	**-3.2**	**-3.7**	**-3.9**
Wijnandsrade	NL	**-2.5**	**-1.5**	**-2.2**	**-2.4**	**-3.0**	**-3.5**	**-3.5**
Nettetal	NRW[4,6]	-1.8	-1.3	-1.8	-1.7	-1.6	-2.0	-2.2
Eifel	NRW	**-3.2**	-0.8	**-3.1**	**-3.3**	**-3.8**	**-5.1**	**-5.3**
Huerth	NRW[5]	**-4.1**	**-3.3**	**-4.1**	**-4.5**	**-4.3**	**-4.1**	**-3.9**
Rodenkirchen	NRW	**-4.4**	**-3.4**	**-4.4**	**-4.5**	**-4.5**	**-5.0**	**-4.9**
Wesel	NRW	**-2.3**	+1.9	-0.7	**-2.4**	**-3.7**	**-3.8**	**-3.3**
Borken	NRW[7]	+3.0	+11.1	+6.2	+3.2	+1.3	-0.2	-1.1
Bielefeld	NRW[5]	**-4.0**	**-4.0**	**-3.8**	**-3.7**	**-4.0**	**-4.4**	**-4.6**

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5. Period: 90-98
6. Period: 88-98
7. Period: 91-98

Table B6b *NO_x trends (% per year) of monthly NO_x parameters for winter (Jan-Feb, Nov-Dec) period; monthly values require 75% or more of hourly values present. Bold: significant at 95% confidence interval including correction for autocorrelation; Period: 1987-1998.*

Station	Area	Trend (% per year)						
		Avg.	P25	P50	P75	P90	P98	P99
Aarschot	VL[1]							
Moerkerke	VL							
St-Kruis-Winkel	VL							
St.-Denijs	VL							
Gellik	VL							
Dessel	VL							
Eupen	WAL[2]							
Kollumerwaard	NL[3]	-1.5	**+8.2**	+1.0	-1.2	-2.2	**-3.9**	**-3.7**
Balk	NL	-1.2	+4.2	+1.4	-1.2	-2.2	-2.6	-2.6
Wieringerwerf	NL	-1.3	+3.4	+1.4	-1.2	-2.2	-2.8	-3.3
Witteveen	NL	**-2.9**	-0.1	-1.7	**-2.9**	**-3.7**	**-3.8**	**-3.8**
Biddinghuizen	NL	**-2.5**	-0.4	-1.9	**-2.6**	**-2.7**	**-3.2**	**-3.2**
Hellendoorn	NL	**-2.3**	-0.8	-1.6	**-2.2**	**-2.9**	**-2.9**	**-2.9**
Eibergen	NL	**-3.0**	-1.3	-1.9	**-2.7**	**-3.4**	**-4.5**	**-4.3**
Wageningen	NL	-2.1	-1.4	-2.0	-2.6	-2.1	-2.7	-2.8
Zegveld	NL	-2.4	-0.8	-1.7	-2.7	-2.8	-2.8	**-2.9**
Cabauw	NL	-1.8	+0.6	-0.8	-2.2	-2.3	-2.4	-1.9
Zierikzee	NL	-2.8	+0.4	-1.3	**-3.6**	-3.5	-3.2	-3.1
Braakman	NL	-2.9	-2.1	-2.3	-3.5	-3.1	-2.8	-2.8
Huijbergen	NL	-2.0	+0.4	-0.5	-2.0	**-2.8**	**-4.0**	**-3.6**
Houtakker	NL	**-3.7**	**-3.2**	**-3.7**	**-4.1**	**-3.8**	**-3.6**	**-3.4**
Budel	NL	**-3.3**	-1.6	-2.7	**-3.7**	**-3.4**	**-3.8**	**-3.6**
Vredepeel	NL	**-3.0**	-1.9	-2.1	**-3.2**	**-3.0**	**-3.9**	**-3.9**
Posterholt	NL	**-3.6**	-2.6	**-3.2**	**-3.7**	**-3.8**	**-4.4**	**-4.4**
Wijnandsrade	NL	-2.3	+0.4	-1.7	-2.7	-2.8	-2.7	-2.6
Nettetal	NRW[4,6]	+0.0	+1.9	+0.9	+0.7	-0.4	-1.1	-1.7
Eifel	NRW	-3.6	-1.8	-3.8	-4.3	-4.2	-3.5	-3.3
Huerth	NRW[5]	-2.6	-1.6	-3.2	-3.0	-2.6	-2.4	-2.2
Rodenkirchen	NRW	**-3.0**	**-2.6**	**-3.6**	**-3.3**	**-3.3**	-2.2	-1.5
Wesel	NRW	**-2.8**	-1.3	-2.3	**-2.8**	**-3.3**	**-3.7**	**-3.9**
Borken	NRW[7]	-1.7	+2.0	-0.9	-2.2	-2.3	-3.3	-3.3
Bielefeld	NRW[5]	-2.0	-1.5	-1.1	-1.8	-1.5	-2.7	-3.5

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5. Period: 90-98
6. Period: 88-98
7. Period: 91-98

Table B7 *NO_2 trends (% per year) of monthly NO_2 parameters for summer (May-August) period; monthly values require 75% or more of hourly values present. Bold: significant at 95% confidence interval including correction for autocorrelation. NO_2 (ppb) value of average 25-percentile (P25) in the summer. Period: 1987-1998*

Station	Area	P25 (ppb)	Trend (% per year)						
			Avg.	P25	P50	P75	P90	P98	P99
Aarschot	VL[1]								
Moerkerke	VL								
St-Kruis-Winkel	VL	12.8[5]	-1.6	**-2.9**	**-1.8**	-0.9	-0.4	+0.0	-0.5
St.-Denijs	VL								
Gellik	VL								
Dessel	VL								
Eupen	WAL[2]	9.5[5]	**-6.6**	-7.4	**-7.2**	**-6.4**	**-6.1**	**-5.4**	**-5.4**
Kollumerwaard	NL[3]	1.0	-0.3	**+6.1**	+0.1	-1.0	-1.5	**-2.5**	**-2.6**
Balk	NL	1.4	-0.9	+5.2	+0.2	-1.4	**-2.0**	**-2.2**	-1.9
Wieringerwerf	NL	1.5	+0.1	**+6.4**	+0.8	-0.5	-1.2	-0.8	-1.0
Witteveen	NL	3.7	-1.4	-0.1	-1.6	-1.7	**-2.2**	**-2.7**	**-3.1**
Biddinghuizen	NL	1.9	-0.6	**+5.0**	+0.5	-1.3	**-2.0**	**-2.5**	**-2.6**
Hellendoorn	NL	4.4	-1.8	-0.5	-1.6	-2.2	**-2.3**	**-2.5**	**-2.3**
Eibergen	NL	4.5	**-1.6**	+0.9	-0.9	**-2.2**	**-3.0**	**-3.1**	**-3.3**
Wageningen	NL	6.0	-0.9	+0.7	-0.5	**-1.4**	**-1.6**	**-1.4**	-1.1
Zegveld	NL	5.4	**-2.2**	-0.8	**-1.8**	**-2.6**	**-2.9**	**-2.8**	**-2.7**
Cabauw	NL	6.6	**-1.6**	**-1.8**	-1.4	-1.7	-1.7	-1.6	-1.3
Zierikzee	NL	2.6	-0.5	+3.8	+0.4	-0.9	-1.4	**-1.8**	**-1.9**
Braakman	NL	3.6	-0.1	+2.1	+0.4	-0.7	-1.0	-0.6	-0.7
Huijbergen	NL	5.4	-0.2	+1.9	+0.4	-0.9	-1.2	-1.8	-1.5
Houtakker	NL	7.5	-1.7	-0.3	-1.5	-1.9	-2.1	**-2.5**	**-2.8**
Budel	NL	5.8	-1.3	+1.0	-1.0	-1.9	**-2.1**	**-1.8**	**-1.7**
Vredepeel	NL	6.8	-0.5	+0.2	-0.6	-0.7	-0.7	-0.6	-0.7
Posterholt	NL	9.3	**-2.5**	**-1.7**	**-2.6**	**-2.8**	**-2.8**	**-2.8**	**-3.0**
Wijnandsrade	NL	7.8	-1.9	-1.2	**-1.8**	**-2.2**	**-2.2**	**-2.3**	**-2.3**
Nettetal	NRW[4]	7.0[6]	-1.9	-0.8	-1.7	**-2.1**	-2.3	-1.6	-1.6
Eifel	NRW	3.0	**-3.8**	**-1.2**	**-4.1**	**-4.1**	**-4.3**	**-5.0**	**-5.1**
Huerth	NRW	12.6[5]	**-3.7**	**-3.4**	**-4.0**	**-3.7**	**-3.3**	**-3.4**	**-3.7**
Rodenkirchen	NRW	16.1	**-2.7**	**-2.5**	**-2.7**	**-2.9**	**-2.9**	-2.3	-2.3
Wesel	NRW	4.5	-1.2	+2.6	-0.5	-1.3	**-2.0**	**-2.3**	**-2.3**
Borken	NRW	2.1[7]	+6.4	+24.1	+13.0	+6.7	+2.7	+0.7	+0.5
Bielefeld	NRW	14.9[5]	**-4.3**	**-4.7**	**-4.4**	**-4.2**	**-3.8**	**-3.6**	**-3.5**

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Annex C Questionnaire

(This questionnaire was sent to data providers.)

SURVEY of METHODS for SAMPLING, MONITORING and CALIBRATION OF OZONE

Network and Monitoring site identification:			
1. SAMPLING	**tick off by entering period / details**		
1.1 Primary sampling tube			
1.1.1 use of filters: filter type			
1.1.2 residence time: calculated			
1.1.3 cleaning routines: filters/tube frequency			
1.2 Secondary sampling tube			
1.2.1 use of filters: filter type			
1.2.2 residence time: calculated			
1.2.3 cleaning routines: filters /tube frequency			
1.3 Instrument inlet			
1.3.1 inlet filters: filter type			
1.3.2 cleaning routines: filters frequency			
1.4 Siting of monitoring station and air inlet			
1.4.1 monitoring site surrounding macro scale			
1.4.2 air inlet surrounding micro scale			
1.4.3 air inlet height (above ground level)			
1.4.4 station elevation (topographic height)			
1.4.5 changes in surroundings			
1.4.6 changes sampling height			
1.4.7 relocation, displacement: distance			
2. MONITORING PRINCIPLE	**tick off by entering period / type**		
2.1 Chemical method: name method			
2.2 Gas Phase Chemiluminescence			
2.3 Solid Phase Chemiluminescence			
2.4 UV absorption Instrument: manufacturer and type			
2.5 Other methods: name method			
2.6 Interference studies: moisture, others			
2.7 Intercomparisons of methods in field			

SURVEY of METHODS for SAMPLING, MONITORING and CALIBRATION OF OZON (continued)

Network and Monitoring site identification:			
3. CALIBRATION PRINCIPLE	**tick off by entering period / frequency**		
	UV	**GPT**	**CHEM**
3.1 Primary or reference laboratory standard 3.2 Transfer or secondary laboratory standards 3.3 Periodic calibration in field: method 3.4 Calibration frequency 3.4.1 Laboratory 3.4.2 Field: zero / span; to be applied for performance check or data correction 3.5 Intercomparisons of (primary) standards			
4. DATA PROCESSING	**tick off by entering period / details**		
4.1 Data storage: averaging time 4.1.1 time base: local, MET, UT (GMT) 4.1.2 time label: begin/end of averaging time 4.2 Digitiser precision (ppb or µg/m^3) 4.3 Unit conversion and P, T, RH-corrections 4.4 Data validation 4.4.1 technical validation: auto / manual 4.4.2 validation at data processing stage rejection, correction, interpolation 4.5 Data statistics 4.5.1 Data statistics available 4.5.2 Data aggregation criteria (% available): 8-hour, day, month, quarter, year Comments: Reports and publications of interest:			

Explanation of the survey

In studying ozone trends it is important to make sure that changes observed in concentration time series do not result from changes in monitoring and (reference) calibration methods. Similar, when combining time series from several monitoring networks, comparability should not be corrupted by differences in monitoring practice and calibration methods.

In 1980 EPA published its findings of the evaluation of ozone calibration methods (Rehme et al., 1980). The UV absorption method emerged as the least variable and most accurate one and was therefore chosen to replace the former reference method (NBKI). To day the UV reference standard has generally been accepted, also in Europe (EU directive), but older monitoring data may be based on the other calibration methods mentioned.
As a result of the variability studies EPA concluded that the Gas Phase Titration (GPT) method was more variable (due to differences in apparatus) and showed a significant positive bias (8 %) with respect to the UV-method. It was, however, also recognized that previous work had shown one-to-one agreement between GPT and UV methods. Reasons for the disagreement between the EPA comparison and those reported in literature were not readily apparent and specific reasons remained obscure (and have so).
Wet chemical methods (a variety of KI-based methods and may be a few others) for the primary calibration of ozone are also known to suffer variability and bias.
More recent and in Europe, comparisons have been carried out by JRC-ERLAP and UMEG. These studies also result in different conclusions with respect to comparability of the UV, GPT and KI (reference) calibration methods: ERLAP fair agreement and UMEG (cited in ERLAP) differences up to 10%. Apart from that, the ERLAP study noted significant water vapour interferences for several analysers, which is not always found confirmed in literature.
Therefore and based on the fact that we did find sudden "jumps" in time series of differences between stations, we thought it necessary to inquire on the monitoring and calibration methods and practice used to establish the time series communicated to us.

We are aware of the fact that many more factors may influence the concentration data as obtained from a monitoring station. These relate importantly to the siting of the monitoring stations, both on a macro and micro scale, sampling heights and the whole process of sampling and sample conditioning. Moreover monitoring stations may have been re-sited during their operational life.
In our experience, there is also some divergence in the practice of time labelling and the time base used with the stored data (MET, GMT (now UT)) and may be summer and winter times), as well as criteria used in aggregation of data. Therefore we have added some questions on those aspects to the survey, which originally was limited to monitoring and calibration methods. In some cases it might be very difficult to recollect the required information.

By now we have obtained a long list. Structuring the list, we thought, would save you valuable time, but on the other hand you might find it inconvenient. We would be most grateful if you would spent some time in completing the survey, but do not hesitate to remark: “not applicable” and report separately or in a different (matrix) form what you think is important.
We would like to come back to you, in case it appears that valuable information, which is heavily required, is still missing.

Rehme K., Puzak J., Beard M., Smith C. and Paur J. (1980). Evaluation of ozone calibration procedures. EPA technical report EPA 600/4-80-050, EPA, Research Triangle Park, North Carolina, USA.