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Tropospheric Ozone Research:
Monitoring and modelling of photo-oxidants over Europe

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Abstract

The Dutch activities contributing to the EUROTRAC-TOR programme were set up to study and quantify the underlying chemical and transport processes important to the occurrence of photochemical oxidants in Europe. The project involved establishing an advanced monitoring site at Kollumerwaard, monitoring for a number of years and evaluating the data, which included a modelling effort. This report contains the technical and scientific documentation of the observatory, a documentation of the TOR database, an evaluation of the O_3, NMVOC, CO, CO_2, CH_4 and PAN data, both from Kollumerwaard and the international TOR network, and a description of the modelled European O_3 budget.

SAMENVATTING

Probleemstelling

De concentratie van ozon (O_3) in de atmosfeer verandert, vooral op het noordelijk halfrond. Een vergelijking van metingen, uit de pre-industriële periode met recente data, heeft uitgewezen dat de concentraties, via een trend van ongeveer 1% per jaar, intussen meer dan verdubbeld zijn. Gedurende het laatste decennium is de concentratietrend afgenomen en op enkele locaties in Europa zelfs negatief geworden.

Veranderingen in het atmosferisch gehalte aan O_3 zijn van belang omdat de component een bepalende rol speelt in het klimaatprobleem en in de chemische samenstelling van de atmosfeer. Voorts resulteert blootstelling aan O_3 in schadelijke effecten op de biosfeer. Modelberekeningen wijzen uit dat het gestegen ozonniveau in de troposfeer op het noordelijk halfrond tot een positieve stralingsforcering van ongeveer 0.4 W m^{-2} geleid heeft. Dit aandeel is gelijk aan ongeveer 15% van de totale forcering ten gevolge van langlevende broeikasgassen.

In atmosferisch-chemische zin is O_3 een oxyderende stof en de primaire bron van hydroxyl (OH) radicalen. Deze worden 'het wasmiddel van de atmosfeer' genoemd en initiëren de meeste afbraakreacties van vervuilende componenten zoals koolwaterstoffen (NMVOC), methaan (CH_4) en koolstofmonoxyde (CO).

Inkadering en uitvoering van het onderzoek

Het EUROTRAC-TOR programma is opgezet om chemische- en transportprocessen, die van belang zijn voor het optreden van foto-oxidantia in Europa te bestuderen. Kernvraag is: "welke rol spelen emissies in Europa en welke resultaten kunnen beleidsmatig maximaal behaald worden?".

In het kader van TOR is een meetnet van kwalitatief hoogwaardige meetstations opgezet, enkele jaren intensief gemeten en heeft analyse van de metingen plaatsgevonden onder andere met behulp van modellen. Dit rapport geeft de technische en wetenschappelijke documentatie van het Nederlandse TOR station Kollumerwaard (aan het Lauwersmeer, op de grens tussen Friesland en Groningen). Verder omvat het de documentatie van de TOR database, een evaluatie van de koolwaterstof metingen in het Europese TOR netwerk en een beschrijving van het O_3-budget in Europa. Voor het laatste onderdeel zijn ook modellen toegepast.

Ontwikkelde infrastructuur

Data van TOR stations, uit het internationale netwerk, worden verstuurd naar de centrale database, die beheerd en verzorgd wordt door het RIVM in Bilthoven. Door de centrale opslag zijn data goed beschikbaar voor andere TOR deelnemers. De toegang verloopt via het World Wide Web.

Het Nederlandse TOR station werd opgezet tijdens het project. Het observatorium bekleedt een strategische positie in het TOR meetnet omdat het zich bevindt aan de 'rand' van het Europese continent. Deze locatie maakt het mogelijk om de grootschalige troposferische achtergrondconcentratie van veel stoffen vast te stellen. Verder kan de klimatologie vergeleken worden met meer 'vervuilde' data, waardoor inzicht ontstaat in het effect van emissies en chemische productie van vervuilende stoffen in Europa. De huidige set van gemeten parameters omvat O_3, NO, NO_2, CO, CO_2, CH_4, PAN, individuele koolwater-stoffen, $j(NO_2)$ en meteorologische parameters.

Analyse van metingen uit het TOR netwerk

De O_3-data over de jaren 1989 - 1993 van meer dan 70 meetstations in de Europese TOR en EMEP meetnetten zijn geëvalueerd. Over het algemeen wordt in de zomer in Europa een van het noordwesten tot zuidoosten stijgend concentratieveld geconstateerd. De gemeten waarden lopen uiteen van 30 - 40 ppb in het noordwesten tot 60 - 70 ppb in het zuidoostelijke deel van het meetnet. In de winter is er juist een dalende gradiënt (van NW naar ZO) in het meetnetgebied aanwezig.

De O_3 concentratie in de vrije troposfeer bedraagt 's winters 25 tot 29 ppb, terwijl deze 's zomers ongeveer 35 ppb is. Via vergelijking van de dagverlopen in de O_3 concentratie is een schatting gemaakt van de regionale produktie van O_3 uit emissies in Europa. Deze analyse leidde tot een geschatte produktie van 0-5 ppb in het noordwesten van het meetnet tot ongeveer 10-15 ppb in centraal-Europa. In de winter werd juist een O_3-put geconstateerd. Deze data schetsen in groffe streken de concentratiereducties, die via emissie-beperkingen van de 'precursors' NMVOC en NO_x in Europa bereikt kunnen worden.

De UN-ECE drukt haar norm ('critical level') voor de bescherming van gewassen tegen blootstelling aan O_3 uit in de eenheid ppb.uur. Deze wordt bepaald uit het produkt van de residu concentratie boven de drempel van 40 ppb en de blootstellingsduur gedurende daglicht uren in de maanden mei, juni en juli. De norm van 5300 ppb.uur wordt op bijna alle stations (95%) in het netwerk overschreden. Blootstelling aan meer dan 10 000 ppb.uur werd waargenomen in de tijdreeksen van verschillende stations in midden-Europa.

De advectie van in Europa geproduceerd O_3 naar Kollumerwaard bedraagt 's zomers 2 ~ 5 ppb. Het Europese continent zorgt 's winters voor een O_3-put ten gevolge van droge depositie en titratie met stikstofoxyde (NO) emissies. De NO_x (= NO + NO_2) klimatologie op het station laat een substantiële invloed zien van NO_x emissies op het continent. Een vergelijking met de NMVOC data van Europese achtergrondstations wijst uit dat Kollumerwaard als relatief 'schoon' beschouwd mag worden voor langlevende componenten zoals ethaan. Er zijn echter aanwijzingen dat (lokale) verkeersemissies van acetyleen en benzeen de fenomenologie van deze stoffen op het station voor een belangrijk deel bepalen. Tabel 0.1 geeft geeft de klimatologie van foto-oxidantia en gerelateerde componenten op het station weer.

De NMVOC klimatologie van het hele TOR netwerk laat een concentratie maximum zien in Nederland, België en het zuidoostelijk deel van het Verenigd Koninkrijk. Enkele stoffen (ethaan, acetyleen, benzeen, tolueen) hebben 's winters een concentratie-maximum in het oostelijk deel van Duitsland, het westen van Polen en de Tsjechische republiek. Dit winter-maximum is vermoedelijk gerelateerd aan emissies van verkeer en aan gaslekken. Dit patroon is in overeenstemming met het beeld dat emissie-inventarisaties van NMVOC laten zien.

De trend in de ozonconcentratie in Nederland

De trend in de langjarige meetreeksen van O_3 en oxidant (O_x = O_3 + NO_2) van diverse Nederlandse stations was licht neerwaarts in de jaren '80 voor zowel O_3 als O_x. Een statistisch significant dalende trend van ongeveer 1% per jaar voor de jaargemiddelde oxidant concentratie is berekend uit de gecombineerde Kloosterburen[1] / Kollumerwaard meetreeks. Hoewel deze veranderingen een relatie zullen hebben met gedaalde emissies, kan de neerwaartse O_3 trend niet volledig aan verminderde emissies worden toegeschreven. Gedurende de jaren '80 zijn in west Europa de emissiefactoren van CO en NMVOC door verkeer aanzienlijk gedaald en iets afgenomen voor NO_x. Dit wordt bevestigd door analyse van de NMVOC data van het station Moerdijk[2]; in de data-reeks (1981 - 1991) van dit station is een afname van ongeveer 30% in de acetyleen concentratie geconstateerd.

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[1] Het meetstation Kloosterburen is in 1989 gesloten. De lokaties Kloosterburen en Kollumerwaard liggen ongeveer 10 km van elkaar en gezien de gelijke karakteristieken van beide stations kunnen de meetreeksen gecombineerd worden.

[2] Het station Moerdijk is gesitueerd bij het Rijnmond gebied en de A16 / A17 snelwegen. Door het lokaal beïnvloede karakter, levert analyse van metingen van dit station gegevens op over emissies in het Rijnmond-gebied en van verkeer op snelwegen.

Acetyleen wordt over het algemeen beschouwd als een indicator voor verkeersemissies. Echter, modelberekeningen wijzen uit dat emissiereducties in Europa de neerwaartse O_3 en O_x trend niet volledig kunnen verklaren. De invloed van andere factoren zoals een verandering in de meteorologische circulatie boven Europa zouden hiervoor onderzocht kunnen worden.

Tabel 0.1 De zomer- en winter-gemiddelde concentraties van componenten gemeten op Kollumerwaard in 1) de schone marine wind sector (voor NMVOC's tussen 315-350°) en voor de andere stoffen tussen 320-030° en 2) de vervuilde continentale wind sector (voor NMVOC's tussen 030-210°) en voor de andere gassen de oost en zuid sectoren (tussen 030-210°). NMVOC's in ppt, andere componenten in ppb of ppm.

	Marine wind sector		Continentale wind sector	
component	zomer	winter	zomer	winter
O_3 (ppb)	35	25	34	8
O_x (ppb)	36	27	42	23
PAN (ppb)	0.5	0.2	0.9	0.3
NO_x (ppb)	2	3	7	25
CO (ppb)	210	210	250	380
CH_4 (ppb)	1880	1850	2000	2080
ethaan (ppt)	1222	1544	1681	2778
etheen (ppt)	60	128	291	1417
acetyleen (ppt)	298	495	491	1829
propaan (ppt)	442	928	844	2285
propeen (ppt)	38	19	106	495
i-butaan (ppt)	113	210	258	824
n-butaan (ppt)	214	459	533	1552
i-pentane (ppt)	93	94	328	597
n-pentaan (ppt)	40	110	131	502
hexane (ppt)	22	62	52	259
benzeen (ppt)	143	159	223	602
tolueen (ppt)	54	83	245	737
ethylbenzeen (ppt)	10	5	67	147
m,p-xyleen (ppt)	17	17	139	298

Het gemodelleerde Europese O_3 budget

Het O_3 budget in de Europese grenslaag in de jaren 1985 en 1990 is tevens onderzocht middels een modelexercitie. De simulatie van het jaar 1990 laat in de onderste 2 km van de atmosfeer een netto chemische produktie van O_3 zien over geheel Europa (afgezien van IJsland) van 21 Tg per maand gedurende de zomer (juli - augustus). In centraal Europa leidt dit tot een concentratieverhoging van ongeveer 10 ppb ten opzichte van de Atlantische achtergrondwaarde. Een vergelijking tussen dit getal en de uit data-analyse geschatte Europese produktie (10-15 ppb) leert dat beide methoden gelijkwaardige resultaten opleveren. Het belangrijkste destructieproces (17 Tg per maand) is depositie; een aandeel ter grootte van 60 à 90% van het chemisch geproduceerde O_3. Netto transport uit het Europese model-domein bedraagt ongeveer 4 Tg per maand.

De intensiteit van de netto chemisch produktie is het hoogst in west Europa. Hoewel dit gebied slechts 6% van het totale continent uitmaakt, leiden de emissies tot ongeveer 13% van de netto chemische produktie. Per eenheid van oppervlakte bedraagt de intensiteit van de chemisch produktie in noord en zuid Europa respectievelijk 30 en 60% van de intensiteit in west Europa.

's Zomers wordt er een netto flux van O_3 uit Europa naar andere gebieden gemodelleerd. Tevens draagt Europa bij tot O_3-vorming elders via transport van NO_y (10% van de emissies) in de vorm van NO_x (5%) en peroxy-acetyl-nitraat (PAN: 5%). In de orde van 40% van de emissies van het, relatief lang-levende, CO wordt uit Europa geadvecteerd. 's Winters is de situatie omgekeerd: het aandeel van depositie is groter dan de chemische vorming en wordt er dus O_3 geïmporteerd.

SUMMARY

Background

Ozone (O_3), an important species in the atmosphere, is changing in its tropospheric concentration, particularly in the Northern Hemisphere. Comparisons of pre-industrial O_3 data with modern data have shown that surface O_3 in Europe has more than doubled, via a trend of about 1% per year, over the past century. However, recent reports indicate that the rate of increase over Europe has levelled off during the last few years.

Changes of O_3 are of concern, because of the important role O_3 plays in the climate issue and in controlling the chemical composition of the troposphere. Furthermore, exposure to O_3 has adverse effects on vegetation and human health. Model calculations indicate that the increased tropospheric O_3 concentrations in the Northern Hemisphere have resulted in a positive radiative forcing. This forcing is estimated to be about 0.4 Wm^{-2} (15% of that from the long-lived greenhouse gases).

Apart from being an oxidant itself, O_3 is the primary source of hydroxyl (OH) radicals, which initiate the oxidation pathways of many chemical and radiative active species. Because O_3 is one of the products of the photochemical oxidation of air pollutants (e.g. NMVOCs, CH_4, CO) this is a positive feedback effect.

Framework of the research

The EUROTRAC-TOR programme was set up to study and quantify the underlying chemical and transport processes of importance for the occurrence of photochemical oxidants in Europe. The project involves establishing advanced monitoring sites, monitoring for a number of years and evaluation of the data, including a modelling effort.

This report contains the technical and scientific documentation of the Dutch TOR station, Kollumerwaard, in the north of the Netherlands, a documentation of the TOR database, an evaluation of the O_3, NMVOC, CO, CO_2, CH_4 and PAN data from the international TOR network, and a description of the modelled European O_3 budget.

Infrastructure developed during the project

Data from the individual TOR stations are submitted to the central database, hosted by RIVM in Bilthoven, from where they are made available to other TOR participants for analysis in the context of the European O_3 budget. The TOR data set is available via the Internet on the World Wide Web (http://torwww.rivm.nl:8000).

The Dutch TOR site of Kollumerwaard, established during the project, has gradually developed into a high quality tropospheric monitoring station. The observatory has a strategic position in the network because it is located on the coastal fringe of the European continent. This location enables us to establish the large-scale tropospheric background concentration of many species, on the one hand, and the internal European production of pollutants on the other. The current set of variables measured at the site consist of O_3, NO, NO_2, CO, CO_2, CH_4, PAN, speciated NMVOCs, $J(NO_2)$ and meteorological parameters.

Analysis of measurements from the TOR network

The O_3 data from more than 70 sites in the TOR and EMEP networks from 1989-1993 were evaluated. In summer, this showed a gradient in the average diurnal maximum ozone concentration, with lower concentrations (30 - 40 ppb) in the northwestern part and higher values (60 - 70 ppb) towards the southeastern part of the networks. In winter, a decreasing gradient was exhibited from the northwest to the southeast.

The data set indicates that the free tropospheric background value of O_3 is 25 - 29 ppb in winter and about 35 ppb in summer. An estimate of the European internal production and destruction of ozone was made by analyzing the diurnal variation in ozone at European boundary layer background 'reference' and 'polluted' sites. The assessment led to a summer mean internal production of 0 - 5 ppb in the northwest to 10 - 15 ppb in some areas in central Europe, while during winter an ozone sink was found.

The current UN-ECE critical level for the prevention of vegetation damage is expressed as the product of the residual ozone concentration above a threshold (40 ppb) value and exposure duration in the daylight hours of the months May, June and July. The provisional O_3 exposure limit of 5,300 ppb.h was exceeded at nearly all monitoring sites (95%). Concentrations over 10,000 ppb.h were calculated for several sites in central Europe.

The summertime internal European production of O_3 in air advected to the observatory is about 2 - 5 ppb. The continent acts as an O_3 sink in winter due to dry deposition and titration of O_3 with emissions of NO. The contribution of European NO_x emissions to the NO_x climatology at the site is substantial. The NMVOC measurements indicate that the site acts as a relatively clean location for long-lived components (e.g. ethane), but they reveal polluted 'fingerprints' from shorter lived components in local emissions from particularly traffic (e.g. acetylene, benzene). Table 0.1 shows some basic features of the pollutant climatology at the observatory.

Table 0.1 The average concentration of species measured at Kollumerwaard during summer and winter in: 1) the clean background sector (marine) which is 315-350° for NMVOC and 320-030° (northern sector) for other species and 2) the continental (polluted) sector which is 030-210° for all species.

	Marine sector		Continental Sector	
component	summer	winter	summer	winter
O_3 (ppb)	35	25	34	8
O_x (ppb)	36	27	42	23
PAN (ppb)	0.5	0.2	0.9	0.3
NO_x (ppb)	2	3	7	25
CO (ppb)	210	210	250	380
CO_2 (ppm)	361	359	365	371
CH_4 (ppb)	1880	1850	2000	2080
ethane (ppt)	1222	1544	1681	2778
ethene (ppt)	60	128	291	1417
acetylene (ppt)	298	495	491	1829
propane (ppt)	442	928	844	2285
propene (ppt)	38	19	106	495
i-butane (ppt)	113	210	258	824
n-butane (ppt)	214	459	533	1552
i-pentane (ppt)	93	94	328	597
n-pentane (ppt)	40	110	131	502
hexane (ppt)	22	62	52	259
benzene (ppt)	143	159	223	602
toluene (ppt)	54	83	245	737
ethylbenzene (ppt)	10	5	67	147
m,p-xylene (ppt)	17	17	139	298

NMVOCs in ppt, other species in ppb and ppm.

The NMVOC climatology from the whole TOR network shows a spatial maximum over the Netherlands, Belgium and the southeastern part of the UK. Some components show a winter maximum over the eastern part of Germany, the western part of Poland and the Czech Republic. This winter maximum may be related to emissions of motor-driven vehicles and gas leaks. This combined large-scale pattern is not in disagreement with the pattern shown in emission inventories.

The trend in O_3 in the Netherlands

The O_3 and oxidant ($O_x = O_3 + NO_2$) time-series from several sites in the Netherlands were analysed. This shows a slightly downward trend in the 1980s for ozone and oxidant in the Netherlands. A statistically significant downward trend of about 1% per year for the annual average oxidant concentrations is found at the Kollumerwaard / Kloosterburen[3] stations. These changes are unlikely to be related to changes in emissions of O_3 precursors alone for several reasons. In Western Europe the emission factors for traffic have dropped considerably for CO and NMVOC and have decreased slightly for NO_x during the 1980s. This is confirmed by analysis of the Dutch Moerdijk[4] data. These data indicate a downward trend of -30% in, traffic-related, acetylene concentrations over the period 1981 - 1991. However, theoretical considerations based on model calculations indicate that the emission changes which may have occurred in Western Europe during the 1980s are by far not sufficient to explain the rather strong downward trend of oxidant concentrations in the Netherlands. Other factors such as possible changes in the general circulation over Europe need to be considered as well.

Modelling the European O_3 budget

The boundary layer ozone budget during the 1985 and 1990 summer periods was also modelled with the LOTOS model. Apart from extensive work on emission inventories, this also required a major overhaul operation on the model itself. The 1990 simulation indicates a net chemical production of ozone over the entire European area (Iceland excluded), and in the lowest 2 km of the troposphere, of about 21 Tg ozone per month for

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[3] The Kloosterburen site closed in 1989. However, Kloosterburen and Kollumerwaard are situated less than 10 km apart and therefore we use the O_3 time series in connection to each other.

[4] The Moerdijk site is located closely to the industrial Rijnmond area and two motorways. These local influences facilitate conclusions regarding developments in the emissions of the Rijnmond area and the motorways.

the summer (July-August). In central Europe this caused an increase in the concentration of O_3 of about 10 ppb relative to the Atlantic background modelled. A comparison between this result and the estimate of 10-15 ppb production from data analysis shows that both methods produce comparable results. Most of the ozone is lost by dry deposition (17 Tg per month), i.e. 60 - 90% of the O_3 produced chemically. Net transport out of Europe accounts for about 4 Tg per month.

The intensity of the (net) chemical production of ozone (oxidant) is highest in Western Europe. Covering only 6% of the European area, it is responsible for almost 13% of the net chemical production of ozone. If scaled per unit area the intensity of the chemical ozone production in northern and southern Europe is about 30% and 60%, respectively, of that in Western Europe.

In summer there is a net direct outflux of ozone to other areas. In addition, Europe contributes to the production of ozone elsewhere by a net transport of precursors. In summer the net transport of the sum of NO_x and PAN out of Europe is about 10 % of the emitted NO_x, with 5% in the form of NO_x and 5% in the form of PAN. About 40% of the emissions of longer lived gases (e.g. CO) is transported out of the European area

In winter the situation is reversed: the amount of ozone lost by dry deposition exceeds the chemically produced ozone, and consequently, there is a net import of ozone from elsewhere. Analysis of measured data supports this finding.

1 INTRODUCTION

1.1 General scientific background

The troposphere is composed of the atmospheric boundary layer and the free troposphere. Ozone (O_3) is present in both layers. The tropospheric O_3 budget consists mainly of three terms: transport from the stratosphere, photochemical production and destruction processes, and deposition at ground level. The magnitude of these terms is difficult to quantify and is therefore subject of many scientific studies. The Northern Hemispheric downward flux from the stratosphere to the troposphere is estimated at about $3 \sim 8 * 10^{10}$ molecules cm^{-2} s^{-1} (Danielsen, 1968; Danielsen and Mohnen, 1977; Husain *et al.*, 1977; Johnson and Viezee, 1981; Murphy *et al.*, 1993). Fishman (1985) and several model studies report estimates of the Northern Hemispheric sink of about $10 \sim 17 * 10^{10}$ molecules cm^{-2} s^{-1} due to destruction of ozone at the earth's surface; a factor of $2 \sim 5$ larger than the supply from the stratosphere. The ozone balance is made up from net chemical production. This term is estimated at about $10 * 10^{10}$ molecules cm^{-2} s^{-1} in the northern hemisphere (Liu *et al.*, 1987; Crutzen, 1993).

The photochemical production term includes O_3 formation, both in the boundary layer and in the free troposphere, where O_3 is photochemically generated by the oxidation of anthropogenic and biogenic non-methane volatile organic compounds (NMVOCs), methane (CH_4) and carbon monoxide (CO) in the presence of oxides of nitrogen (NO_x) and sunlight (Seinfeld, 1986). Another indicator of photochemical activity is the occurrence of PAN (peroxy acetyl nitrate). There is an exchange of air masses between the boundary layer and the free troposphere; therefore a separate budget may be drawn up for these two atmospheric layers.

The tropospheric O_3 concentration is changing, in particular, in the Northern Hemisphere. Comparisons of pre-industrial O_3 data with modern data have shown that surface O_3 has more than doubled over the past century (Volz and Kley, 1988). Concentrations of O_3 in the middle troposphere (about 3 - 5 km) over Europe and North America appear to have increased at a rate of about 1% per year over the last two decades (Logan, 1985, 1994; Penkett, 1988). Low *et al.* (1991) report that the rate of increase over Europe has levelled off during the last few years. Anthropogenic emissions in the Northern Hemisphere's heavily industrialised areas are expected to play an important role in the increase of the O_3 concentration and possibly in its changing climatology (Isaksen and Hov, 1987; Hough and Johnson, 1990).

1.2 Policy making and the ozone problem

Increases in O_3 are of concern because of the important role O_3 plays in controlling the chemical composition of the troposphere (Crutzen, 1993) and climate (IPCC, 1994). Calculations with models indicate that the increased tropospheric O_3 concentrations in the Northern Hemisphere have resulted in a positive radiative forcing. This forcing is estimated to be about 0.4 Wm^{-2} (15% of that from the long-lived greenhouse gases). Furthermore, exposure to O_3 has adverse effects on vegetation and human health. For this reason, several international organizations and conventions like the World Health Organization (WHO), United Nations Economic Commission for Europe (UN-ECE) and the Commission of the European Union (CEU) have proposed or set guide values for the protection of ecosystems, human health and/or vegetation. These guide values indicate concentrations and exposure times below which no adverse effects are expected (Zierock, 1991).

Every summer large parts of Europe are exposed to O_3 concentrations above those affecting agricultural crops, forests and possibly also human health. Peak concentration levels of 100-150 ppb are monitored over large areas, in particular, during stable high pressure situations with intense sunshine and high temperatures (Guicherit and Van Dop, 1977; Grennfelt and Schjoldager, 1984). These episodic concentrations occurring in the boundary layer are superimposed on tropospheric background O_3 values. This leads to the intertwining of O_3 problems on the continental and global scales, both in a spatial and temporal sense.

The O_3 problem has been given attention within the UN-ECE Convention on Long-Range Transboundary Air Pollution, which, in 1991, decided on a protocol to reduce the emissions of NMVOCs by approximately 30% before 1999 (UN-ECE, 1991). A European monitoring and evaluation programme (EMEP) was set up to facilitate the work within the UN-ECE convention using monitored and modelled data. Since 1988, O_3 monitoring has been requested as a part of the monitoring programme.

1.3 The EUROTRAC-TOR programme

The photochemical oxidant problem has also been the focus of an international research project, EUROTRAC (European Experiment on the Transport and Transformation of Environmentally Relevant Trace Constituents in the Troposphere over Europe), functioning under EUREKA (European Research Coordination Agency). The photochemical oxidant and O_3 issues within EUROTRAC are primarily dealt with within the Tropospheric Ozone Research (TOR) project. This project uses both short-term and long-term models to study the underlying chemical and transport processes of importance for the occurrence of photochemical oxidants in Europe. The project involves establishing advanced monitoring sites, monitoring for a number of years, evaluating the data and model studies.

Basic issues posed by the project include the following questions (Kley *et al.*, 1987):

1- How much higher is the mean O_3 concentration in the boundary layer over Europe than that averaged over northern mid-latitudes, and what is the seasonal latitudinal and vertical variation of ozone with the adjacent troposphere?
2- What are the emissions and distribution of the precursor molecules responsible for that excess of O_3?
3- Can we measure how much of the excess O_3 in the boundary layer over Europe spills over into the background atmosphere?
4- Is there a secular trend in the concentrations of O_3 and precursor molecules in the boundary layer or in the background atmosphere?
5- Which exchange processes take place in the troposphere, especially between the surface layer and the free troposphere?
6- Can we model the observations, and how well do the model calculations agree with the observations?
7- How much O_3 and its precursors are transported across regional boundaries?

Thirty measuring stations in 13 countries have been set up to address these issues. The variables measured at the TOR sites include O_3, NO_x, NMVOCs, CH_4, CO, PAN, oxidized nitrogen (NO_y), CFCs and meteorological parameters. Vertical profiles of O_3 are determined at four sites, either by balloon soundings or lidar. Several intercalibration experiments have been carried out. A full technical description of the TOR measurements, including monitoring strategy, data handling, specifications of monitors and calibration procedures is given in Cvitas and Kley (1994). The TOR and EMEP project staff have agreed to exchange data, since it was realized that their mutual objectives would benefit from this.

1.4 The current report and earlier results of the project

The Dutch contribution to the international EUROTRAC-TOR programme consists of four parts: (a) setting up and operating a TOR monitoring site in Kollumerwaard in the north of the Netherlands, (b) developing and hosting the international TOR database, (c) interpreting the measured data and (d) modelling photo-oxidants over Europe. The latter two activities were performed with respect to TOR's basic issues listed above. Earlier results of the project are reported in several papers and reports (including Baas and

Bosman (1995); van den Beld and Veldkamp (1995); Beck and Grennfelt (1994); Beck *et al.*, (1994); Vosbeek, 1994).

Chapters 2 and 3 of this current report discuss, respectively, the technical issues concerning the Kollumerwaard observatory and the database. The photochemical climatology at Kollumerwaard, along with interpretation of this observatory's data set are described in Chapters 4 and 5. The latter text section of Chapter 5 puts the NMVOC measurements at the site in a European perspective. In Chapter 6 the trends of O_3 and photo-oxidants are analysed. Finally, in Chapters 7 and 8 the measurement and modelling efforts are combined and put in a global perspective. Conclusions are listed in the final and ninth Chapter.

2 MEASUREMENTS

2.1 The Kollumerwaard observatory

The international TOR programme has provided for an extensive measurement network over Europe. The network consists of more than 30 high-quality ground-based and vertical sounding stations for accurate and compatible measurements of ozone and its related species. Figure 2.1 shows the locations of the TOR sites in Europe. Their site names and geographical coordinates are listed in Appendix A. This appendix also shows the EMEP stations (see section 3.1). The technical documentation on all TOR field stations is given in Cvitas and Kley (1994). In this report we will summarise some necessary information on the Dutch TOR site Kollumerwaard.

2.1.1 General information

The measurements are taken at TOR station number 9, which is situated in an agricultural area in the northern part of the Netherlands at Kollumerwaard (Figure 2.2). The observatory is located in a relatively unpolluted part of the country. In order to give an idea of the pollution climatology of the site, the concentrations of O_3, NO_2, SO_2, ethane and acetylene, averaged yearly, and for the summer and winter seasons, are presented in Table 2.1.

Figure 2.3 illustrates a 'wind rose' of NO_2 concentrations for 1990. It is obvious from this figure that the site 'sees' clean air only from the north.

2.1.2 Description of the site

Originally, the station consisted of one accommodation that was part of the Netherlands National Air Quality Monitoring Network (LML), owned and managed by RIVM. In 1993 the accommodation became too small and a second porta-cabin was built next to the existing station. The new accommodation became available in June 1993. In Figure 2.4 a picture of the site with the old and the new accommodation is shown.

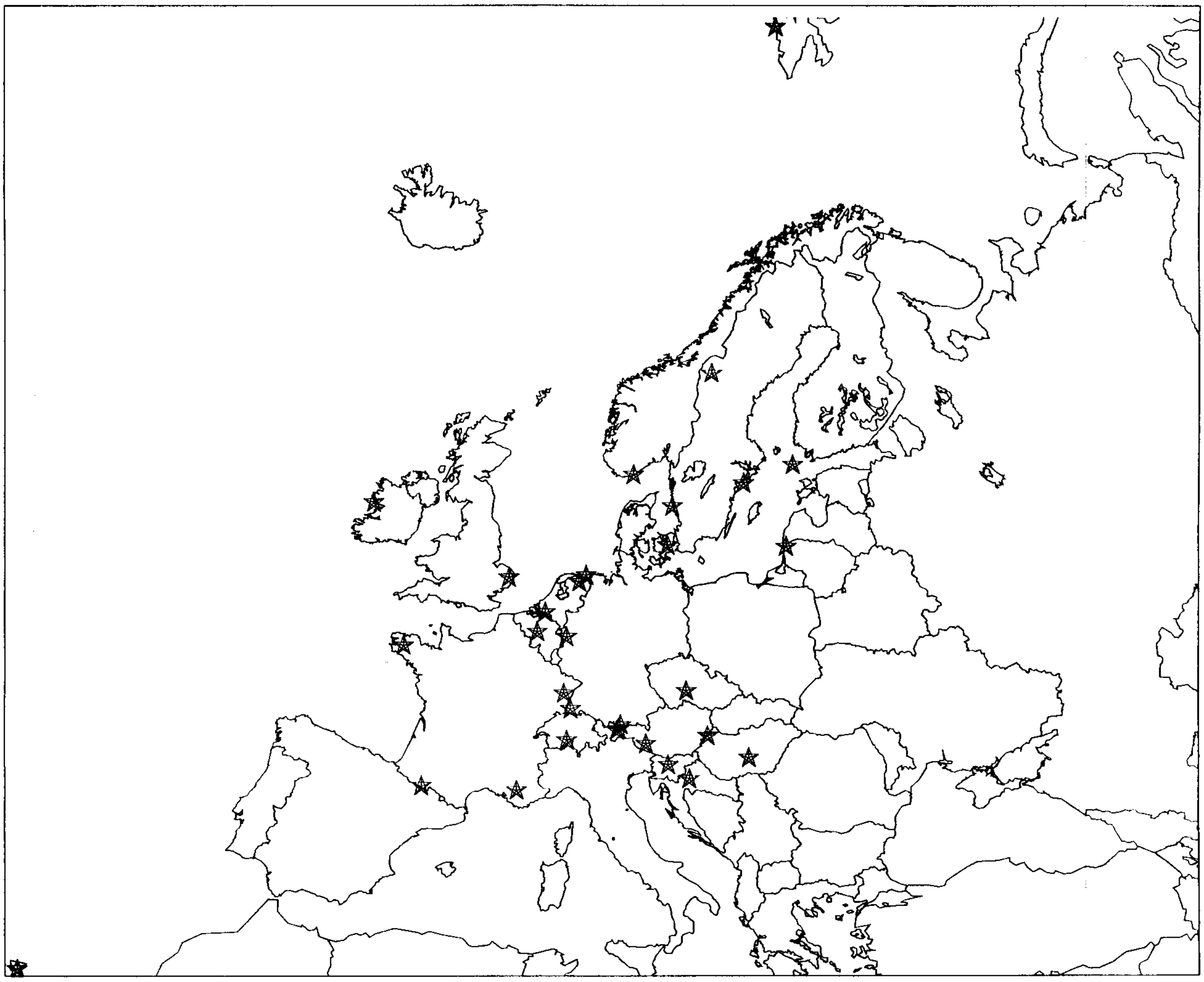

Figure 2.1 Locations of TOR sites in Europe.

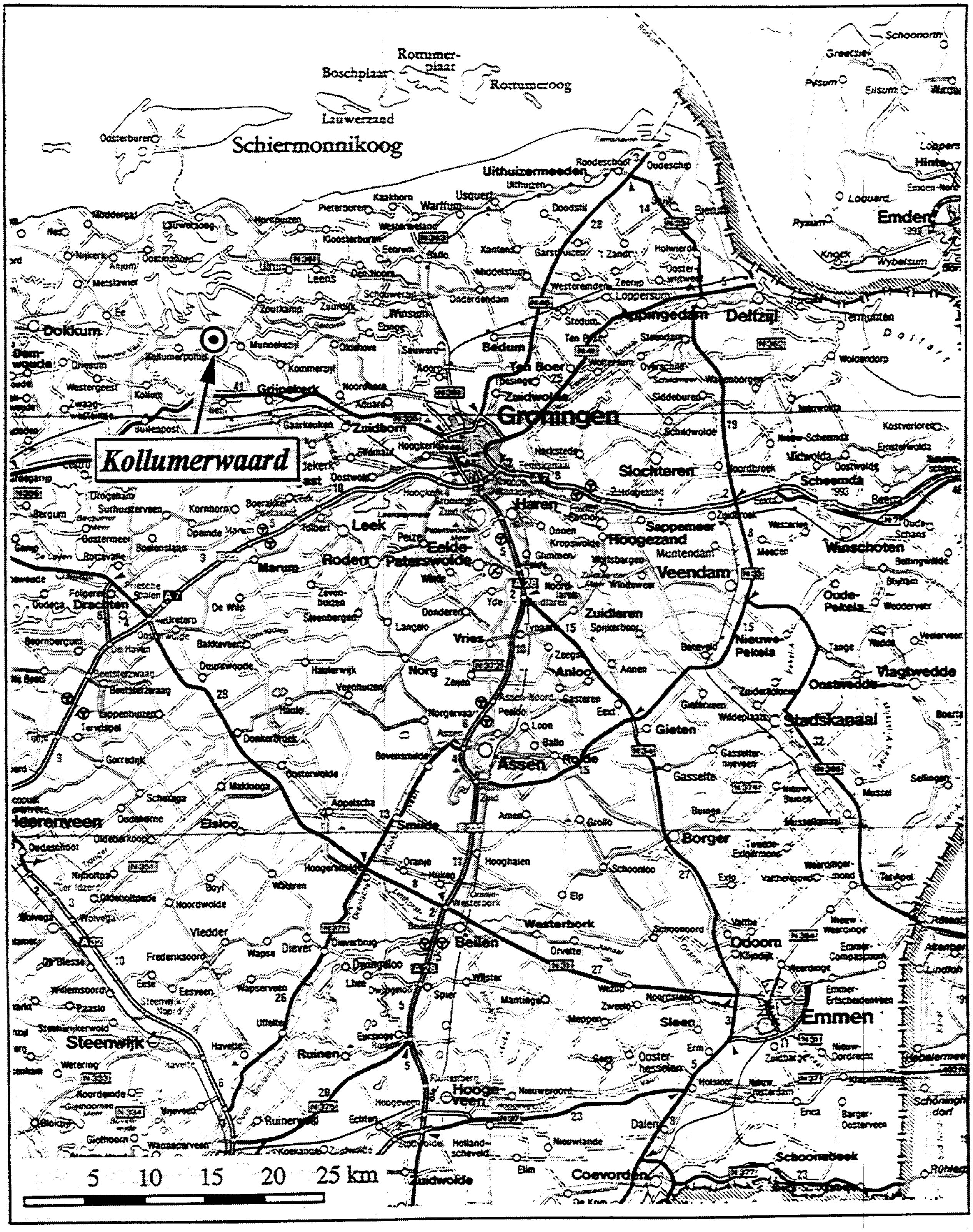

Figure 2.2 Map showing the site of the Kollumerwaard station in the northern part of the Netherlands.

Table 2.1 Concentrations (in ppb) of O_3, NO_2, SO_2, PAN (1993 data), CO, CO_2, CH_4, ethane and acetylene, averaged yearly and for summer and winter, at Kollumerwaard (1994 data). The climatology of other components measured is given in Chapter 4.

Component	Year	Winter (Dec, Jan, Feb)	Summer (Jun, Jul, Aug)
O_3	22	17	26
NO_2	8	11	3
SO_2	2	2	1
CO	260	280	230
CO_2	372×10^3	373×10^3	371×10^3
CH_4	1980	1990	1980
PAN	0.47	0.27	0.48
ethane	1.9	2.2	1.4
acetylene	0.8	1.3	0.4

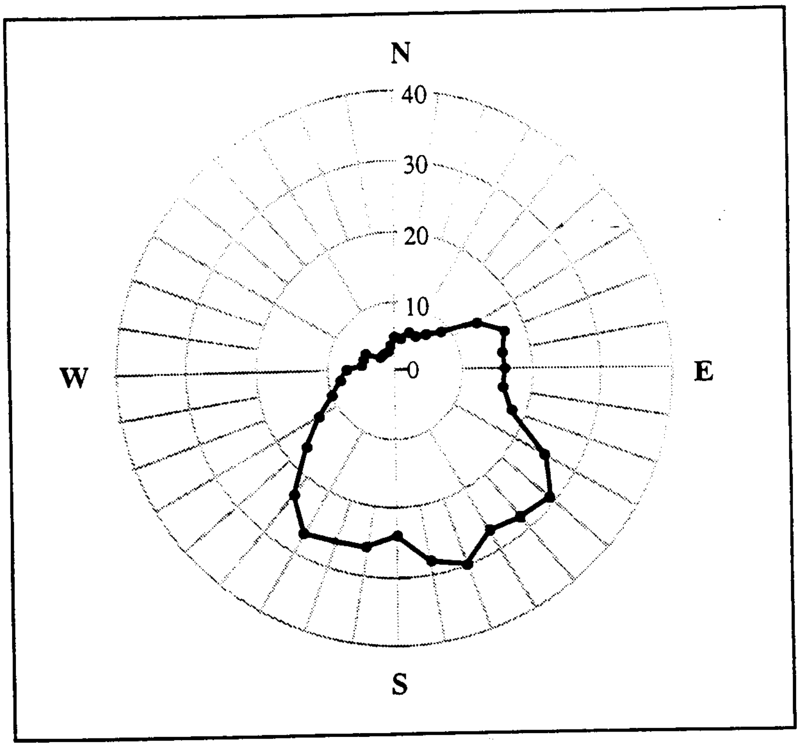

Figure 2.3 Wind rose of the NO_2 concentration in µg m^{-3} per wind sector of 10° in 1990 (1 µg m^{-3} of $NO_2 \approx 0.53$ ppb).

Figure 2.4 The Kollumerwaard observatory (53°20'02" N; 6°16'38" E; 0 m asl)

2.2 Instruments and measurements

Table 2.2 shows from which compounds / parameters the ambient air concentrations are measured at the site. The RIVM[5] measurements at Kollumerwaard have been operational since January 1989; the KEMA[5] and TNO[5] activities commenced mid-1991. The data are reported to the TOR, ECE-EMEP and WMO-WDCGG programmes and databases. A detailed description of the measurement methods for the components measured within the TOR framework is given in Appendix B.

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[5] National Institute of Public Health and Environment (RIVM); Netherlands Organization for Applied Scientific Research (TNO); Electricity Production Sector (KEMA).

Table 2.2 Components measured at Kollumerwaard

component	measurement method	measurement frequency	institute
O_3	CRANOX system	continuously	RIVM
NO	CRANOX system	continuously	RIVM
NO_2	CRANOX system	continuously	RIVM
PAN	gaschromatograph (ECD)	1x/2 hours	TNO
NMVOC	gaschromatograph VOC-AIR	1x/15 minutes	TNO
$J(NO_2)$	$J(NO_2)$ Radiometer	1x/15 minutes	TNO
CO	gaschromatograph (FID)	1x/15 minutes	KEMA
CO_2	gaschromatograph (FID)	1x/15 minutes	KEMA
CH_4	gaschromatograph (FID)	1x/15 minutes	KEMA
wind speed	cup anemometer	1x/5 seconds	RIVM/KEMA
wind direction	weather vane	1x/5 seconds	RIVM/KEMA
aerosols	MVS-LVS	phys. properties 1x/ minute chem. composition 1x/ day	RIVM
wet deposition	Van Essen, wet only type ECN	1x/ day	RIVM
chemical composition		1x/ day	
air pressure	vacuum membrane	1x/5 seconds	KEMA
temperature	PT-100 sensor	1x/5 seconds	KEMA
rel. humidity	solid state sensor	1x/5 seconds	KEMA
global radiation	pyranometer	1x/5 seconds	KEMA

2.3 Round robin experiments

In joint research projects such as TOR, the required data compatibility can only be attained by an intercomparison of the analytical methods employed by the various participating laboratories and subsequent data harmonisation. The Dutch TOR group has participated in NMVOC, CO, CO_2, CH_4, PAN, NO_x, O_3 and $J(NO_2)$ intercalibration experiments (Hahn, 1993) organised within EUROTRAC-TOR, EU and IGBP frameworks. The results are summarised in Appendix B section 4.

3 The TOR database

3.1 Introduction

Since the objectives of the international TOR project require evaluation of the measurements from all sites (30), it is essential to have a central database providing controlled exchange of data. Such a database should enable collection of all data from the project, regular correspondence with the owners of the data and support for its users. This section describes the TOR database (developed and hosted by RIVM), its contents and access facilities. Since there is a formal connection between the TOR and UN-ECE-EMEP programmes, the data of both projects are interchangeable. Therefore, the TOR database at RIVM also consists of the data from the EMEP NMVOC and O_3 network.

3.2 General description

The data archive contains data with a multiform character, resulting from the diverse nature of the sites within the networks. This situation calls for storage and exchange of data designed to accommodate the non-uniform structure of the data. Ground-based data exchange is performed through the ISO 7168, NASA/Ames 1010 and spread-sheet formats.

Incoming new data files require extensive quality control on correct formatting. It is our general principle to have TOR PIs retain responsibility for the quality assurance of the data. Clarifying ambiguities and suspicious values by TOR PIs was necessary, in particular, at the beginning of the project. Later on, the number of necessary contacts with the PIs decreased under the influence of a mutual learning process.

3.3 Database access, consultation and publication rights

The current database access facilities are designed to make it easier for users to request data. The archive is accessible via a Web site ((http://torwww.rivm.nl:8000) and e-mail (tor@rivm.nl). By sending an e-mail to tor@rivm.nl, database users can go through the system at their convenience. The system scans the subject field of incoming e-mail messages. Depending on the keyword found in the subject field of a message, specific applications are started. e.g. the keyword *help* in the subject field causes the system to echo a help file to the sender. Other keywords cover requests about the table of contents (Table 3.2), data requests, information on the sites connected to the database and components measured.

The high scientific value of the observations made in the network and the necessary validation procedures result in the necessity of some time lapse between the actual measurements, submission to the database and, finally, use of the data by other TOR and/or non-TOR participants. RIVM has offered to host the database for another two years after EUROTRAC-1 has ceased to exist (closure planned for December 1995). Table 3.1 shows the access scheme to be used during this period (minutes, 9th TOR workshop).

Table 3.1 Access to the TOR database in the period 1996 - 1998

Period	Status of data in the release schedule
1-1-1996 to 30-6-1997	Data open to TOR and non-TOR PIs; however, co-authorship should be offered if a scientific paper originates from the data
From 1-7-1997	Public access with proper acknowledgement of the owners of data; the data will be released on a CD-ROM or WWW

The TOR database is currently integrated in the data archive of the Dutch National Air Quality Network. This is a relational database with an SQL interface and has the advantage that all the logistic procedures, like back-up facilities, maintenance and administration used, are applied to the TOR archive as well. Note that TOR data carry the 'TOR' label, implying that any guideline for the release of data coupled to TOR will be respected.

Table 3.2 Summary of the contents of the database (an extensive summary can be requested via an e-mail message to tor@rivm.nl with the keyword *full* in the subject field of the message)

Site no.	Site name / component	O_3	NO_x	NO_y	PAN	NMVOCs	CH_4	CO	CFCs	meteo	O_3 profile	Meteo profile
1	Ny Ålesund (N)	x	x									
2	Birkenes (N)	x	x			x	x		x	x		
3	Utö (SF)	x	x		x	x				x		
4	Areskutan (S)	x	x							x		
5	Rörvik (S)	x	x		x	x				x		
7	W-Beckham (GB)	x	x			x						

Site No.	Site name / component	O_3	NO_x	NO_y	PAN	NMVOCs	CH_4	CO	CFCs	meteo	O_3 profile	Meteo profile
8	Mace Head (EI)	x					x					
9	Kollumerwaard (NL)	x	x		x	x	x	x	x	x		
10	Porspoder (F)	x	x			x						
11	Schauinsland (D)	x	x	x		x				x		
12	Garmisch-P. (D)										x	x
13	Sonnblick (A)	x										
14	Pic du Midi (F)	x										
15	K-Puszta (H)	x	x			x						
16	RBI (CR)	x										
17	Izaña (E)	x			x	x				x		
18	Lille Valby (DK)	x	x									
19	Aspvreten (S)	x	x	x	x	x				x		
20	Donon (F)	x	x			x						
21	Wank (D)	x	x	x						x		
22	Zugspitze (D)	x	x							x		
23	Ukkel (B)										x	x
24	Jülich (D)										x	x
25	OHP (F)										x	x
27	Zeppelinfjellet (N)	x	x		x	x	x					
51	Puntijarka (Cr)	x										
66	Krvavec (Slo)	x										
70	Kloosterburen (NL)	x	x									
71	Moerdijk-c (NL)					x				x		
213	Tänikon (CH)	x										
222	Waldhof (D)	x				x						
344	Col du Donon (F)	x	x			x						
345	Kosetice (CZ)					x						
346	Rucava (LIT)					x						

4 CONCENTRATION MEASUREMENTS IN KOLLUMERWAARD

4.1 Introduction

In order to provide answers to the basic questions cited in Chapter 1, measurements of ozone and its related species were performed along with model calculations. This section deals with the analysis of the concentration measurements of O_3, NO_x, O_x, PAN, NMVOCs, CO and CH_4 performed at the Dutch TOR observatory Kollumerwaard. In addition, Chapter 5 describes the climatology of the other NMVOC stations in Europe. Several analyses were performed to discuss different terms acting on the boundary layer ozone budget. Final sections focus attention on the interaction between O_3 and its precursors.

4.2 The ozone budget

The boundary layer ozone budget over a certain domain is determined by four chemical, physical and meteorological processes, given the emissions of precursors:

1) Photochemical production and destruction;
2) Deposition at ground level (dry deposition);
3) Vertical exchange processes (between the boundary layer and the free troposphere);
4) Advection (large-scale meteorology).

ad 1. Ozone is photochemically generated by the oxidation of anthropogenic and biogenic NMVOCs (non-methane volatile organic compounds), methane (CH_4), carbon monoxide (CO) in the presence of oxides of nitrogen (NO_x) and sunlight. Destruction of O_3 takes place by reaction with unsaturated NMVOCs and peroxyradicals, and as a result of heterogeneous processes. The photostationary state between NO, NO_2 and O_3 provides fast cycling of NO, NO_2 and O_3. Both chemical chains, production and destruction, occur simultaneously. Which of the two determines the sign of the chemical term on the budget is generally controlled by the ambient NO_x concentration. At NO_x concentrations larger than about 30 ppt ozone is usually produced while at levels smaller than 30 ppt, destruction of ozone prevails. NO_x concentrations smaller than 30 ppt are seldom observed at the Kollumerwaard station;

ad 2. Physical quenching of ozone is a major destruction process during transport over relatively unpolluted areas (Guicherit and Van Dop, 1977). Due to the removal of ozone by dry deposition, ground-level ozone concentrations will always be lower than those a few metres aloft. The vertical concentration profile shows a stronger gradient during the night in fair weather conditions due to the lack of replenishment with fresh free tropospheric air;

ad 3. The effectiveness of vertical exchange processes depends on the thermal stability of the actual air mass and the wind speed. Fast (≈hours) decreasing ground-based O_3 levels can be found in stably stratified air due to deposition and the small inflow of O_3-rich air from aloft. On the other hand, when the air mass is in a turbulent state (sunny summer day) there is an efficient vertical overturning. In addition clouds and frontal passages establish exchange between the boundary layer and the free troposphere. The boundary layer will experience the direct influence of stratospheric air only occasionally;

ad 4. Transport (advection) of air masses from their origin is established by the general circulation. The original properties of air can be drastically modified by the underlying surface. An air mass with a low precursor level can pick up a major quantity of emissions when it is advected over polluted urban or industrialised areas. The general characteristics of air masses can therefore be very different.

4.3 The climatology of photo-oxidants at Kollumerwaard

4.3.1 Introduction

Four different types of analyses have been performed to study the climatology of photo-oxidants at the site. The rationale behind these is listed below.

Diurnal cycle

The degree of influence of local sources on the Kollumerwaard data set was studied by means of the summertime and wintertime diurnal cycles of O_3 and its precursors. A differentiation of the diurnal cycles in four wind-direction sectors was performed i.e. North: 321°-030°; East: 031°-130°; South: 131°-210° and West: 211°-320°. By studying longer periods (more than 1 year) each sector will contain enough data.

Seasonal cycle

An examination of the seasonal variation of O_3 and its precursors at Kollumerwaard provides information on the extent to which the site experiences the influences of springtime or summertime production of ozone, wintertime build-up of precursors and stratosphere - troposphere exchange or other factors listed in section 4.2.

Wind speed and wind direction

The climatology and processes in the free troposphere aloft can be studied using the data set from the Kollumerwaard site, even though the station is located at sea level. We assume that the site experiences air with a fresh free-tropospheric origin during occasions with high wind speed in particular when air is advected from the north. The boundary layer and the free troposphere during high wind speed are seen as follows:

- The depth of the boundary layer will increase under higher wind speed conditions so that a larger part of the troposphere is in a state of efficient mixing and is connected to the lowest layers of the atmosphere;
- The nocturnal inversion layer will not build up under strong wind speed conditions;
- Very often there is a vertical sheer in the wind speed which results in additional mechanical mixing of the air involved.

Consequently, an increasing wind speed causes a larger free tropospheric fingerprint. In the case of O_3 a more efficient downward transport of O_3 from aloft leads to a higher ground-level concentration.

Dry deposition will still play a role in the boundary layer ozone budget during occasions of high wind speed. We may therefore call the air ’pseudo free tropospheric air’ on windy days. The site experiences relatively little influence of dry deposition in air advected from the north, since the deposition velocity of ozone at water surfaces is small or negligible. A final consideration for the proposition that O_3 and precursor levels measured at the highest wind speed will be close to that in the free troposphere, is that during these conditions the contribution of nearby sources of precursors to the measured concentrations will be reduced, thereby bringing the precursor concentrations closer to background values.

Correlation coefficients

Correlation coefficients between hourly averaged concentrations of species measured at the site provides information on the extent to which compounds have similar sources and sinks. The correlations calculated for the summer and winter data sets show whether photo-oxidants find their source in the oxidation of shorter or longer lived components, or are a result from transport phenomena.

4.3.2 The diurnal cycle of ozone and related compounds

Phenomenology

In the summer season the concentrations of O_3 and O_x (= $NO_2 + O_3$) show a clear diurnal pattern with a minimum in the morning and a maximum in the afternoon. The diurnal pattern of PAN, a tracer of photochemical activity, is similar to that of O_3 and O_x, only the

PAN maximum occurs about two hours earlier than the O_3 maximum (Appendix C, Figure 1c). This difference is caused by the differing relative importance of the source and sink terms on the boundary layer budgets of the two components. Both O_3 and PAN are photochemically formed from the oxidation of NMVOCs in the presence of NO_x and sunlight. The free troposphere is an important source of boundary layer O_3, but it is a sink of PAN due to the lower PAN concentrations in the free troposphere. The deposition sink of PAN is smaller relative to that of O_3 due to the deposition velocity of PAN which is about one fifth of that of O_3. Furthermore, PAN is thermically destroyed while O_3 is not.

The precursors of ozone (NO_x, CO and CH_4) show a small diurnal variation. In summer the NO_x and CO curves reveal small increases between 6:00 and 10:00, possibly as a result of emissions from traffic (Appendix C, Figures 2a, b, c). The daily variation in the concentration of these components also reflects the larger depth of the mixing layer during the afternoon hours. During winter diurnal variation is absent in the pattern of these three components (Appendix C, Figures 4a, b, c). This pattern shows some inconsistencies which are not understood so far. There is no clear signature of both the effect of the mixing layer and the effect of local emissions.

The diurnal cycle in relation to the wind direction and period of the year

The concentrations of the precursors NO_x, CO, CH_4, and also of PAN, are clearly higher in the southern wind sector than they are in the northern sector. Figures 1c and 2a, b and c of Appendix C illustrate this for the summer diurnal cycles. Nitrogen oxide concentrations, in summer, in the south, are about five times higher than in the north. Figures 3c and 4a, b and c (Appendix C) illustrate the higher southern concentrations for the winter season.

Ozone shows the opposite pattern: low concentrations from the south and higher concentrations from the north. The higher precursor concentrations in the southerly wind sector find their origin in the emissions at the continent, whereas the lower O_3 levels from the south are probably an effect of a sink from deposition to the earth's surface and a quenching of NO.

The diurnal variation of CO and CH_4 is almost absent during the winter months, though higher absolute concentrations are observed compared to the summer situation (Appendix C, Figure 4b and c). Wintertime accumulation of precursors stems from the lower photochemical destruction during this period of the year. Furthermore, the mixing layer has a shallower depth during the winter season. This results in trapping of emissions in a much smaller volume, and thus in higher concentrations.

The diurnal cycle in relation to the influence of emissions of O_3 precursors on the continent

Figures 1 to 4 in Appendix C illustrate that air from the northerly sector contains the lowest concentrations of O_3 precursors. We therefore characterise the north as the 'cleanest' sector at the observatory. The southern and eastern sectors show an apparent signature of emissions in polluted regions of the European continent.

If one assumes that air masses from the northerly sector represent the large-scale hemispheric boundary layer background, estimates of the contribution of European emissions, or chemical production inside Europe, to the photo-oxidant climatology at the observatory may be derived. Table 4.2 shows the estimated continental contribution of different components (between 9:00 and 21:00) calculated by subtracting the background northerly concentration from the levels occurring during advection from the east and south. The 9:00 to 21:00 values were selected since these are, during summer, representative of a relatively well-mixed boundary layer, with small influence of local sources.

The summertime internal European production of O_3 in air advected to the observatory is estimated at about 3 ppb. This is in agreement with the estimates from Beck and Grennfelt (1994). Table 4.2 shows that during winter the European continent is a sink of O_3 (-16 to -18 ppb). Most of this effect is due to a shift in the photostationary state to the NO_2 side, since only -3 to -5 ppb wintertime destruction arises from the O_x data. The remaining -3 to -5 ppb are probably a result of dry deposition, a combination of removal by nighttime and heterogeneous chemistry or due to different advection, resulting in a different climatology.

It is interesting to note that O_3 shows a net concentration decrease with southerly winds compared to the background concentration, however, not in the east. This may be due to an important local source of NO in the vicinity of the site in the south. This is also illustrated by the high concentration of NO_x in the southerly sector, in particular in winter. In summer and winter, concentrations are increased by a factor of 4 to 8 relative to the background, respectively. It is currently unclear whether this is a result of local or remote sources.

Air with a continental origin acts as a source of PAN of about 0.3 to 0.4 ppb in summer and about 0.1 to 0.3 ppb in winter at Kollumerwaard. The wintertime values of PAN are typically about 40% of the summertime concentrations, both in the northerly background and in the polluted southerly and westerly sectors. Winter PAN concentrations are often reported higher than summer concentrations. Cox and Roffey (1977) and Brice *et al.* (1984) argue that this is due to the effect of a smaller sink, i.e. slower thermal decomposition (being dominant over the smaller source) and thus slower formation of the species during winter. The Kollumerwaard data, however, seem to indicate the opposite.

The concentrations of CO are relatively high, even in the background air from the north (about 210 ppb). Simmonds (1993) reports an annual unpolluted average of about 130 ppb and an annual polluted average of about 200 ppb in polluted air at the Mace Head background site. It is interesting to note that there is no difference between the summer and winter averaged values in the north (210 ppb) at Kollumerwaard, while there is an annual amplitude of about 100 ppb in the polluted sectors. A CO source from decomposition of NMVOCs and direct emissions of CO on the continent contribute 30 to 55 ppb in summer and 150 to 190 ppb in winter (Table 4.2).

Table 4.2 The average concentration of O_3, O_x, PAN, NO_x, CO and CH_4 in the northerly, easterly and southerly sectors during summer and winter at the Kollumerwaard observatory (ppb). The northerly sector is assumed to represent the large-scale boundary layer background. The last two columns represent the European contribution, which is calculated by subtracting the 9:00 to 21:00 northerly sector concentrations from the easterly and southerly sector concentrations between 9:00 and 21:00.

	Large-scale boundary layer background; northerly sector (ppb)		Average concentration in easterly wind sector (ppb)		Average concentration in southerly wind sector (ppb)		Estimate of the European contribution easterly sector (ppb)		Estimate of the European contribution southerly sector (ppb)	
Component	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
O_3	35	25	38	9	30	7	3	-16	-5	-18
O_x	36	27	43	22	39	24	7	-5	3	-3
PAN	0.5	0.2	0.9	0.35	0.82	0.29	0.4	0.15	0.32	0.09
NO_x	2	3	6	18	8	31	4	15	6	28
CO	210	210	265	360	240	400	55	150	30	190
CH_4	1880	1850	1980	2060	2020	2100	100	210	140	250

Averaged concentrations of CH_4 in the background sector are about 1880 and 1850 ppb in summer and winter, respectively. This is relatively high compared to the data of other CH_4 sites at similar latitudes, since these report 50 to 100 ppb lower averaged values. In the polluted sectors wintertime concentrations are about 100 to 150 ppb higher than the summer concentrations, which is explained by the boundary layer and larger photochemical sink during summer. The relatively high concentrations in the northerly sector may be the result of a local source of CH_4 e.g. at the continental shelf.

Table 4.3 shows the average concentration of some NMVOCs in the marine and continental sectors during winter and summer. In addition, Table 4.3 also shows the European contribution, which is calculated by subtracting the continental and marine sector concentrations (0-24 h). Note that 24-h concentrations are involved here so differences in mixing layer height and chemistry are included. Therefore the 'Estimate of the European contribution' column in Table 4.3 should be considered with caution.

Table 4.3 The average concentration of some NMVOCs in the marine (315-350°) and continental (030-210°) sectors during summer and winter at Kollumerwaard (ppt) The estimate of the European contribution is calculated by subtracting the continental and marine sector concentrations (0-24h).

	Marine sector		Continental sector		Estimate of the European contribution	
component	summer	winter	summer	winter	summer	winter
ethane	1222	1544	1681	2778	459	1234
ethene	60	128	291	1417	231	1289
acetylene	298	495	491	1829	193	1334
propane	442	928	844	2285	402	1357
propene	38	19	106	495	68	476
i-butane	113	210	258	824	145	614
n-butane	214	459	533	1552	319	1093
i-pentane	93	94	328	597	235	503
n-pentane	40	110	131	502	91	392
hexane	22	62	52	259	30	197
benzene	143	159	223	602	80	443
toluene	54	83	245	737	191	654
ethylbenzene	10	5	67	147	57	142
m,p-xylene	17	17	139	298	122	281

4.3.3 Seasonal variations; influence of larger scale pollution

Table 4.4 shows the monthly averaged concentrations of the components measured at Kollumerwaard for the period 1991-1993. The table illustrates that maximum O_3 and O_x concentrations occur in spring (April-May-June); in July, concentrations are generally lower. This is also illustrated in Figures 5a and b in Appendix C. The minimum in the annual cycle occurs in November and December. An O_3 maximum in spring rather than in summer illustrates that the site shows some 'rural behaviour'. Minimum O_3 concentrations in winter point to chemical destruction, a less efficient replenishment of boundary layer air by free tropospheric air and persisting dry deposition. The concentrations of ozone precursors (NO_x, CO and CH_4) at Kollumerwaard show much higher values in winter than in summer due to the low photochemical activity during the winter season and due to the decrease in the mixing height (Figures 6a, b and c, Appendix C).

Table 4.4 Monthly averaged concentrations for 1991-1993 (in ppb)

Month	O_3	O_x	NO_x	PAN	CO	CH_4
January	15.5	25	14.5	.24	290	1940
February	15	27	15	.35	340	1920
March	19.5	29	12.5	.51	310	2010
April	28.5	34	8	.80	265	2040
May	33.5	37	6	.76	300	1980
June	30.5	33	5	.63	270	1985
July	26	30	5.5	.66	210	1975
August	25	24.5	6	.52	180	1970
September	20	27	9	.42	200	1950
October	16	25	11	.30	260	1960
November	12	25	22	.32	340	2020
December	13	26	14	.22	300	2020

The concentration of PAN (Figure 5c, Appendix C) shows a maximum in April, whereas O_3 and O_x have their maximum in May. The earlier annual maximum in PAN in comparison to that of O_3 originates from the stronger thermal decomposition of PAN as the atmospheric temperatures continue to rise from spring to summer. Ozone is not exposed to thermal decomposition as a major sink process.

Tables 4.5 and 4.6 show monthly averaged concentrations for NMVOCs over 1994 and 1995, respectively. The annual variation of all NMVOCs, except for isoprene, is qualitatively equivalent to the variation of other primary pollutants such as NO_x and CO (Table 4.4). The highest monthly mean concentrations are found during the winter months and the lowest concentrations in the summer months, which is caused by the annual variations of mixing-layer height and chemical decay rates. The emissions of most species vary as well over the year (about 20%), but to a much lesser extent than the meteorological and chemical terms. Isoprene is an exception. The isoprene concentrations are higher in summer than in winter, although it is a very reactive component and therefore sensitive to the annual variation of the chemical decay term. This clearly shows that isoprene emissions predominantly occur in the summer (warm) season. Figures 7a-k (Appendix C) illustrate the seasonal cycle of several NMVOCs.

Table 4.5 Monthly averaged concentrations of NMVOC for 1994 (ppt)

	July	August	September	October	November	December
ethane	1446	1389	1544	2054	2502	2176
ethene	202	261	395	863	1081	974
acetylene	338	363	547	1028	1347	1338
propane	676	683	822	1504	1744	1848
propene	43	95	196	345	324	428
i-butane	233	207	286	602	745	686
n-butane	456	482	530	1054	1284	1254
cyclopentane	4	10	7	12	18	22
i-pentane	266	246	197	372	418	549
n-pentane	86	89	69	182	368	415
cyclopentene	-	-	-	6	7	21
2-methyl-2-butene	1	5	4	13	15	29
methylcyclopentane	28	33	37	79	97	97
cyclohexane	0	0	0	13	34	37
2-methylpentane	61	75	91	148	154	141
3-methylpentane	0	0	0	45	225	232
isoprene	129	55	20	15	-	-
hexane	32	25	21	123	193	207
2-methyl-2-pentene	-	-	-	7	9	18
2-,3-methylhexane	27	24	34	109	140	133
heptane	13	16	16	41	50	54
benzene	215	184	220	368	481	426
octane	0	15	0	5	10	20
toluene	164	189	201	429	560	583
nonane	-	-	-	-	-	-
ethylbenzene	37	55	47	92	115	125
m-,p-xylene	97	137	12	165	243	256
o-xylene	24	27	157	76	104	110

0: below detection limit; -: no measurement

Table 4.6 Monthly averaged concentrations of NMVOC for 1995 (ppt)

	January	February	March	April	May	June
ethane	2190	2186	2225	1736	1699	1236
ethene	872	535	481	221	168	150
acetylene	1362	1007	951	567	563	359
propane	1727	1542	1343	846	736	538
propene	280	215	183	91	86	96
i-butane	494	445	358	223	188	151
n-butane	1113	1010	745	427	355	314
cyclopentane	17	7	7	4	7	6
i-pentane	361	333	277	163	179	207
n-pentane	351	245	195	102	101	85
cyclopentene	12	5	1	0	0	0
2-methyl-2-butene	24	15	7	8	11	1
methylcyclopentane	83	46	3	1	2	2
cyclohexane	30	37	48	37	33	24
2-methylpentane	115	47	0	62	58	48
3-methylpentane	190	209	205	30	35	30
isoprene	-	20	19	12	17	18
hexane	172	129	97	61	59	38
2-methyl-2-pentene	13	10	12	16	16	0
2-,3-methylhexane	108	81	69	29	28	21
heptane	40	33	29	12	15	10
benzene	427	347	338	211	190	130
octane	7	6	6	1	4	2
toluene	444	350	279	136	128	170
nonane	-	89	67	22	50	107
ethylbenzene	93	72	52	25	31	23
m-,p-xylene	193	150	105	47	63	45
o-xylene	78	55	38	16	24	17

0: below detection limit

-: no measurement

4.3.4 Wind speed; The climatology of the free troposphere aloft

The fingerprint of air from the free troposphere on the Kollumerwaard data set is studied by analysis of the relation between observed concentrations and wind direction, and wind speed (Table 4.7). The table shows that differentiation by both wind direction and wind speed ($\geq$ 4 m.s^{-1}) gives rise to similar precursor concentrations for the northerly wind sector. If one assumes that concentrations occurring at higher wind speeds show a larger influence of the free troposphere, the above findings may imply that the boundary layer and the free troposphere are in equilibrium in the northerly sector even at lower wind speeds. It is interesting to note that the precursor NO_x, CO, CH_4 levels in the north are not only indifferent to the wind speed but also to the time of the year.

In the southerly sector the precursor concentrations during higher wind speeds are lower than those occurring at all wind speeds. The latter carry the signature of ground-based emissions on the European continent.

Ozone and O_x show increasing concentrations with increasing wind speed, both in the northerly and in the southerly sector. This is due to a reduced influence of deposition and a more efficient mixing with free tropospheric air at higher wind speeds. The analysis implies that the free troposphere background value of ozone is about 29 ppb in winter and about 35 ppb in summer.

Table 4.7 Concentrations of precursors in the north and south (in ppb), for all wind speeds and for wind speeds of 4 m s^{-1} or higher

Component	Season	North (360°, all wind speeds)	North (360°, ≥ 4 m s^{-1})	South (180°, all wind speeds)	South (180°, ≥ 4 m/s)
NO_x	winter	2	2	33	25
	summer	2	2	8	8
CO	winter	210	210	420	370
	summer	210	210	240	240
CH_4	winter	1820	1820	2100	2040
	summer	1850	1850	2120	2020
O_3	winter	25	29	7	8
	summer	33	35	20	24
O_x	winter	27	30	26	26
	summer	32	35	26	31
PAN	winter	0.38	0.38	0.54	0.60
	summer	0.20	0.26	0.32	0.28

In winter NMVOC concentrations (except isoprene) are higher than in summer. In the continental sector this winter to summer ratio is more pronounced than in the marine sector, partly due to the fact that the annual variation of the mixing layer height is fairly moderate in the marine sector, and partly due to the slower chemistry in the winter.

In the marine sector the winter to summer ratio varies from 1.3 (ethane) to 2-3 for the other more abundant species (Table 4.8). For a few components with concentrations usually below the 20-30 ppt level, the picture is not very consistent. Further study will identify whether this is due to artefacts such as the occurrence of a few observations with unusual high concentrations or that variations of source strengths are involved.

The averages of these species are possibly affected due to the fact that for these species the observed concentrations were (very) often below the detection limit.

Table 4.8 Concentrations of NMVOC as a function of wind sector and season, July 1994-June 1995 (ppt); marine: 315-350°, continental: 030-210°

	Winter		Summer	
	Marine	Continental	Marine	Continental
ethane	1544	2778	1222	1681
ethene	128	1417	60	291
acetylene	495	1829	298	491
propane	928	2285	442	844
propene	19	495	38	106
i-butane	210	824	113	258
n-butane	459	1552	214	533
cyclopentane	0	29	3	11
i-pentane	94	597	93	328
n-pentane	110	502	40	131
cyclopentene	0	20	0	0
2-methyl-2-butene	4	32	5	6
methylcyclopentane	22	120	7	26
cyclohexane	14	49	17	12
2-methylpentane	29	170	31	87
3-methylpentane	63	300	7	21
isoprene	7	27	59	58
hexane	62	259	22	52
2-methyl-2-pentene	6	19	6	13
2-,3-methylhexane	28	177	7	39
heptane	15	64	4	22
benzene	159	602	143	223
octane	1	15	0	5
toluene	83	737	54	245
nonane	23	180	9	188
ethylbenzene	5	147	10	67
m-,p-xylene	17	298	17	139
o-xylene	3	127	5	38

In the continental sector the winter to summer ratio varies from 1.7 (ethane) to values of 3-5 for most of the other components. It will be clear that concentrations in the continental sector are (much) higher than in the marine sector. The direct influence of emissions from continental Europe is more prominently visible during winter than during summer (Table 4.8), again due to differences in mixing layer height and chemistry. In winter the continental to marine ratio of concentrations range from 1.8 (ethane) to more than 10 for the very reactive components. In summer the continental to marine ratio is smaller than in winter, varying from 1.4 (ethane) to more than 5 for most of the very reactive species.

4.3.5 Correlation coefficients

The relation between photo-oxidants and their precursors can be further clarified by correlations within their concentrations. Table 4.9 shows correlation coefficients based on hourly averaged data during various conditions (time of year, day or night).

The results of the correlation between CO and NO_x demonstrate that the concentrations of these species in the winter season are highly correlated in air masses from polluted sectors (east, south, west) and uncorrelated in the north, the latter possibly explained by the low detection limit. The polluted air masses obviously carry the fingerprint of the coinciding CO and NO_x emissions from traffic. In summer, however, correlation coefficients are small in all sectors. This may indicate that the time scale of the relevant chemical and physical processes is smaller (e.g. chemical conversion) than the time needed for transport between the main CO and NO_x sources and the observatory.

In summer the hourly values of CO and O_x have very small correlation coefficients, except for the southerly sector during the afternoon. The increase in the southerly sector summer coefficient from 0.11 to 0.65, caused by the selection of those samples with lower NO_x values, illustrates the effect of the elimination of data which were influenced by very local, and possibly large, sources of NO_x. High correlation coefficients between CO and O_3 summer data are found at Mace Head (Simmonds, 1993), Izaña (Schmitt, 1994), Zugspitze (Sladkovic *et al.* 1994) and over the North Atlantic (Fehsenfeld, 1994). In winter O_3 and CO are negatively correlated at these sites due to the role of CO as an indicator of pollution, leading to O_3 removal. During winter the close relationship between CO and O_3 is less pronounced at Kollumerwaard. Emissions of CO will not result in a direct decrease of ozone. The negative correlation between the winter values of CH_4 and O_3 may have a similar reason.

Concentrations of ozone and PAN have a small correlation in the northerly and the largest in the southerly sector. The small coefficient in northerly air masses indicates that in that sector ozone results from other sources than PAN. Oxidation of CH_4 and CO and intrusions from the stratosphere are main sources of northerly O_3 , whereas the source of PAN is purely photochemical, resulting from the oxidation of higher NMVOCs. In air masses from polluted sectors, however, the high correlation between O_3 and PAN indicates that O_3 is much more a result of oxidation of NMVOCs.

Table 4.9 Correlation coefficients between components measured at Kollumerwaard under different circumstances (period 1991-1993; based on hourly values)

CO-NO_x	Winter, 13h-17h	Winter, 1h-24h	Summer, 13h-17h
north east south west all	0.01 0.61 0.69 0.43 0.66	0.03 0.64 0.65 0.58 0.66	0.02 0.14 0.08 0.09 0.11
O_3-PAN	Summer,13h-17h		
north east south west all	0.25 0.44 0.70 0.41 0.50		
O_x-PAN	Summer, 13h-17h		
north east south west all	0.37 0.53 0.71 0.53 0.61		
CO-O_x	Summer, 13h-17h all NO_x	Summer, 13h-17h $NO_x \leq 5$ ppb	Summer, 1h-24h $NO_x \leq 5$ ppb
north east south west all	0.04 0.11 0.11 0.09 0.13	0.03 0.003 0.65 0.15 0.09	0.08 0.02 0.25 0.02 -
O_3-CO	Summer (July)	Winter (December)	
all	0.186	-0.652	
O_3-CH_4	Summer (July)	Winter (December)	
all	0.223	-0.744	

4.4 Kollumerwaard: background station

An important question is to what extent the Kollumerwaard observatory can be considered a European background site. From the analysis of the ozone data described in the above sections one may conclude that some sections of the Kollumerwaard climatology show a background signature. The data from the northerly wind sector, in particular at higher wind speeds, show an almost flat diurnal curve and a spring maximum in the annual cycle. A summer minimum distinctive of a real background site is not observed. The Mace Head site (facing the Atlantic in Ireland) still observes an annual minimum in July of 5 to 10 ppb from the annual average in its 'unpolluted' selection of data (Simmonds, 1993). The unpolluted yearly averaged O_3 concentration at Mace Head is about 31 ppb, whereas it is

33 ppb at Kollumerwaard. It may well be possible to create a better 'unpolluted' data set from the Kollumerwaard climatology using the distinctive capacities of trajectories and tracer species.

The NO_x data set presented in this chapter is collected using an analyser with a limited resolution of 0.7 ppb and a lower detection limit of 1 ppb. The NO_x concentration in air masses from the north is 2 ppb, which indicates relatively clean air. However, this number is of tentative value only, due to the constrained applicability of the NO_x analyser used in this work. The NO_x instrument in now replaced by a Cranox type, with a lower detection limit of 15 ppt.

The data on the precursor species CH_4 and CO indicate that the site is not a background site for these components even with winds from the north. The concentrations measured in the northerly sector are relatively high and an unexpected summer maximum in the case of CH_4 is observed. At Mace Head North-Atlantic background values of 1810 ppb CH_4 and 70 ppb CO were observed in 1990 (Simmonds *et al.*, 1993). The average CO concentration in the Northern Hemisphere is about 90 to 120 ppb (Khalil and Rasmussen, 1994). At Kollumerwaard the lowest concentrations measured in the northerly sector reach about 1820 ppb CH_4 and 210 ppb CO. These high values may be related to a local source e.g. on the nearby continental shelf. A local source of CO and CH_4 is not necessarily shown in the phenomenology of photo-oxidants at Kollumerwaard because of the long atmospheric lifetime of these species. This is illustrated by the low correlations of about 0.02 between CO and NO_x , and CO and O_x , in air masses from the north (Table 4.9).

The concentrations of the NMVOCs in Kollumerwaard in the 'clean' marine sector show that Kollumerwaard is a background site for this sector. As already shown, concentrations of NMVOCs in the continental sector are higher than in the marine sector. The direct influence of emissions from continental Europe is more prominent visible during winter then during summer due to differences in mixing height and chemistry. In Chapter 5 NMVOC data from other stations in Europe are studied.

5 AN NMVOC CLIMATOLOGY OVER EUROPE

Table 5.1 shows an NMVOC (non-methane volatile organic compound) climatology collected from TOR and EMEP sites across Europe for 12 different compounds. The sites listed are arranged from north to south, with the data presenting the annual average mixing ratio and, in parentheses, the values averaged over the summer (June, July, August) and winter months (December, January, February), respectively. The species are arranged from left to right according to their reactivity with the hydroxyl radical (OH), with the least reactive component in the first column. The molecules listed were selected because of their relevance to the formation of photo-oxidants and, for benzene, due to the concern over its carcinogenity. The NMVOC profiles of some sites are fairly well-established because air samples have been taken and analysed several times per day for a number of years there. Other averages, only representative for a short time interval, are calculated from a limited number of spot samples. The data in the table should therefore be considered with caution.

The character of the sites is variable due to the extent to which sites are exposed to nearby anthropogenic sources. The elevation above sea level plays an important role in this respect; sites at higher altitudes often sample air from the free troposphere. In some cases the meteorology associated with the location of a station determines its NMVOC climatology to an important degree (e.g. the small number of occasions in which polluted air is transported to the Zeppelin site due to the polar front). Note that the data in Table 5.1 is generally unfiltered. Only for the Moerdijk clean site a wind rose selection has taken place.

Lindskog *et al.* (1993, 1996) evaluated a similar data set for the seasonality in the advection of clean and polluted air; they used the data in emission inventories for validation purposes. A subset of the data consisting of the NMVOCs measured in the EMEP network was analysed by Solberg *et al.* (1995).

5.1 Phenomenology: the seasonal cycle in the NMVOC mixing ratios

Many chemical, meteorological, biogenic and anthropogenic factors may induce a seasonal cycle in NMVOC mixing ratios. These factors include seasonalities in chemical sinks (OH, NO_3, O_3), the mixing volume of emissions (boundary layer depth), and anthropogenic and biogenic emissions. These influences, varying from very obvious to very concealed, cast their signature on the observed NMVOC concentration patterns and profiles. At many sites the seasonal cycle of most slowly reacting NMVOCs (ethane, acetylene, propane, i-, n-butane and n-pentane) shows a summer minimum and a winter maximum. This seasonality partly reflects the annual variation in the concentration of hydroxyl radicals (OH), providing a maximum sink of NMVOCs in summer and a build-up of concentrations during the colder months. An OH-initiated chemistry signature on winter to summer ratios in the NMVOC climatology is described for Porspoder (continental air), Schauinsland (southwest sector), Zeppelin (clean sector), Izaña and several other sites (Boudries *et al.*, 1994; Volz-Thomas *et al.*,1992 and Lindskog *et al.*,1996). In the current database the correlation coefficient between the winter/summer concentration ratio of long-lived molecules and the winter/summer ratio in the OH reaction rate for each individual species is larger than 0.8 in the Zeppelin, Utö, Rucava and Great Dun Fell data. The correlation coefficient was also found larger than 0.5 at Weybourne and Izaña. The more reactive shorter lived compounds (toluene, n-hexane, ethene, propene, isoprene) and, in some cases benzene as well, do not show a correlation with the OH reaction rate. A very small or negative correlation for all components was calcuated at most of the remaining sites, pointing to other mechanisms playing a role in the seasonal cycle of NMVOCs as well. In particular, the unfiltered data from sites situated in source regions (e.g. Moerdijk, Kollumerwaard, West-Beckham, Tänikon) exhibit winter/summer concentration ratios of between 2 and 4 for both long and short-lived components. The data from the Moerdijk-polluted site show a remarkably stable winter/summer concentration ratio of 1.5 to 2 for all species measured. Since this station is located close to one of Europe's major source areas, this merely demonstrates a dominant influence of the annual cycle in the boundary layer depth rather than a seasonality in OH. In winter the depth of the mixing layer is about half that of the summer depth. This results in doubled winter concentrations compared to the summer situation.

The magnitude of many anthropogenic and biogenic emission sources shows a distinct seasonal cycle as well. The winter/summer ratio in the emission pattern of commercial and residential combustion sources adds up, as averaged over Europe, to a factor of 4. Utility and industrial combustion sources are about 1.2 times larger in winter compared to summer (Berdowski and Zandveld, pers.comm.). The combined seasonal oscillation in all anthropogenic source categories leads to a winter/summer ratio of about 1.2 ~ 1.3 in the emissions of ethane, propane, ethene, propene, acetylene and benzene. Anthropogenic emissions of butanes, pentanes, hexanes and toluene have a winter/summer emission ratio of about 1.1. (Berdowski and Zandveld, pers.comm.). On average, the biogenic sources of isoprene show a summer maximum which is about a factor of 13 to 15 higher than during winter (winter/summer ratio 0.07). Emissions of biogenic non-isoprene species (propene, ethene) exhibit a winter/summer ratio of circa 0.7.

The chemical sinks of NMVOCs other than OH (e.g. due to reaction with O_3 and NO_3) displays a seasonality of importance to the climatology of ethene, propene and isoprene. The NO_3 sink is expected to be more evident in winter when the OH chemistry is less dominant, whereas removal by O_3 is maximal in spring and summer.

Table 5.1 Annually averaged mixing ratios (ppt) of NMVOCs at TOR and EMEP sites, with numbers in parentheses indicating the seasonal variation (June, July, August average - December, January, February average)

Site, Network	Location	ethane (ppt)	acetylene (ppt)	propane (ppt)	benzene (ppt)	i-butane (ppt)	n-butane (ppt)	n-pentane (ppt)	toluene (ppt)	hexane (ppt)	ethene (ppt)	propene (ppt)	isoprene (ppt)	Comments, References
Zeppelin (N) TOR F.Stordal	78°55'N 11°54'E 474 m asl	1754 (866-2482)	441 (91-798)	708 (82-1402)	186 (133-228)	153 (24-330)	293 (30-646)	105 (13-242)	199 (175-235)	80 (65-121)	196 (102-423)	64 (81-77)	5 (5-8)	Ann.rep.TOR '91 Database
Utö (SF) TOR T.Laurila	59°47'N 21°23E 7 m asl	1513 (713-2098)	558 (180-921)	734 (191-1276)		173 (43-323)	344 (95-623)	134 (51-218)		56 (27-78)	409 (138-727)	55 (34-82)		Ann.rep.TOR '92 Fin.rep.TOR '95 Database
Aspvreten (S) TOR P.Oyola	58°48'N 17°39'E 20 m asl	2620 (1720-2920)	1080 (410-1360)	1160 (380-1640)		710 (310-790)	1160 (500-1230)	420 (260-410)			1130 (1240-1170)	660 (940-600)		Ann.rep.TOR '91 Database
Birkenes (N) TOR F.Stordal	58°23'N 08°15'E 116 m asl	1972 (1125-2449)	626 (209-880)	804 (302-1172)	289 (200-386)	347 (194-415)	651 (322-811)	225 (115-299)	479 (636-650)	105 (114-155)	530 (301-726)	136 (114-156)	23 (59-11)	Ann.rep. '90, '91 EMEP rep. Database
Rörvik (S) TOR A. Lindskog	57°23'N 11°55'E 0 m asl	1707 (817-2620)	769 (184-1191)	732 (215-1316)		313 (145-492)	545 (236-867)	241 (96-428)			598 (213-995)	95 (34-172)		Ann.rep. TOR '92 Database
Rucava (LIT) EMEP J.Schaug	56°13'N 21°13'E 18 m asl	2070 (1072-2710)	1099 (312-1754)	937 (245-1390)	383 (214-527)	279 (65-408)	529 (137-775)	237 (54-410)	357 (206-463)	144 (59-185)	890 (256-1547)	185 (81-290)	32 (64-22)	EMEP rep. Database
Kollum (NL) TOR J.Beck	53°20'N 06°17'E 0 m asl	1869 (1413-2176)	835 (351-1337)	1240 (679-1872)	314 (197-426)	473 (233-685)	872 (502-1254)	255 (130-414)	413 (209-584)	143 (59-207)	687 (259-1014)	284 (126-446)	107 (128-.)	Database
Great Dun Fell (GB) TOR S.Penkett	54°51'N 02°27'W 844 asl	2097 (1400-2800)	779 (200-1600)	857 (200-1850)	343 (100-450)	335 (100-600)	708 (100-1700)	192 (80-500)	501 (50-700)	90 (10-30)	986 (130-1800)	162 (50-400)	25 (10-40)	Ann.rep.TOR '91 PORG '93
West-Beckham (GB) TOR S.Penkett	52°54'N 01°10'E 9 m asl	2816 (2025-3250)	1407 (669-2010)	1316 (719-1830)	707 (403-978)	681 (386-873)	1498 (906-1773)	413 (233-515)	987 (504-1399)	141 (88-180)	1541 (837-2169)	272 (126-416)	26 (36-17)	Ann.rep.TOR '91 PORG '93 Database
Wey-bourne (GB) TOR S.Penkett	52°57'N 01°o7'E 15 m asl	(1741-2772)	(225-1130)	(477-1193)	(131-302)	(119-491)	(233-1203)	(60-259)	(97-284)	(28-11)	(230-1264)	(48-206)	(2-9)	Proc.symp. '94
Waldhof (D) EMEP J.Schaug	52°48'N 10°45'E 74 m asl	2473 (1185-3235)	1594 (391-2313)	1264 (456-1805)	501 (213-671)	377 (140-537)	727 (264-1027)	306 (113-385)	504 (265-684)	141 (77-190)	1448 (308-2238)	287 (78-453)	21 (36-13)	EMEP rep. Database

Site	Location	ethane	acetylene	propane	benzene	i-butane	n-butane	n-pentane	toluene	hexane	ethene	propene	isoprene	Comments
Moerdijk-clean (NL) TOR M.Roemer	51°41'N 04°32'E 1 m asl	2200 (1840-2500)	600 (400-820)	930 (600-1260)		290 (240-340)	530 (370-690)				1200 (1160-1260)	430 (400-460)		Atm.Env.paper **clean sector data** Database
Moerdijk-polluted (NL) TOR M.Roemer	51°41'N 04°32'E 1 m asl	4000 (2500-5300)	2600 (1500-3800)	2900 (1900-3900)		900 (700-1200)	1900 (1400-2400)	900 (800-900)			6300 (4600-7500)	2200 (2100-2200)		Atm.Env.paper **10 years data** Database
Kosetice (CZ) EMEP J.Schaug	49°35'N 15°05'E 633 m asl	2264 (1142-2773)	1465 (464-2313)	992 (369-1372)	463 (245-645)	308 (137-450)	568 (243-793)	233 (116-309)	471 (276-578)	165 (97-203)	1253 (344-2149)	262 (161-385)	27 (52-15)	EMEP rep. Database
Porspoder (F) TOR G.Toupance	48°30'N 04°46'W 20 m asl	1541 (980-2289)	385 (224-696)	621 (352-1181)	209 (170-252)	243 (166-465)	307 (260-473)	95 (76-143)	310 (248-370)	47 (32-27)	314 (223-647)	189 (139-315)	78 (105-107)	Ann.rep.TOR '92, '93 Database
Schauinsland (D) TOR A.Volz-Thomas	47°54'N 07°48'E 1220 m asl	2200 (1410-2548)	562 (352-630)	873 (467-1129)		219 (177-236)	503 (419-543)	118 (111-107)			503 (299-607)	102 (77-107)		Ann.rep.TOR '91 Database
Wank (D) TOR E.Scheel	47°31'N 11°09'E 1776 m asl	1150-	425-	350-	200-	350-		350-	160-	130-		100-		Proc.symp. '92 **summer data only**
Tänikon (CH) EMEP J.Schaug	47°29'N 08°54'E 540 m asl	2116 (1143-2881)	2207 (793-3862)	987 (419-1478)	607 (321-953)	436 (209-667)	1070 (642-1508)	359 (228-475)	1043 (564-1589)	155 (102-217)	1756 (567-3030)	400 (131-694)	45 (70-17)	EMEP rep. Database
Zugspitze (D) TOR E.Scheel	47°25'N 10°59'E 2962 m asl	1100-	275-	325-	225-	195-		195-	175-	110-	350-	90-		Proc.symp. '92 **summer data only**
K-Puszta (H) TOR L.Haszpra	46°58'N 19°33'E 125 m asl	5500 (500-8500)	500 (250-3000)	1533	750 (267-1333)	550	750 (500-1000)	800 (400-1200)	833 (333-1335)	750 (417-1167)	3000 (1000-5000)			Ann.rep.TOR '90, '91, '93 Proc.symp. '94
Izaña (E) TOR R.Schmitt	28°18'N 16°30'W 2368 m asl	968 (691-1198)	134 (51-232)	159 (50-350)	43 (16-81)	24 (8-52)	45 (24-100)	17 (14-26)	27 (36-30)	13 (21-15)	26 (27-30)	7 (6-12)	98 (186-313)	Ann.rep.TOR '93. Fin.rep.TOR '95 Database

As stated above, propene, ethene and isoprene have both biogenic and anthropogenic sources. The relative influence of these emission categories is clearly reflected in the absolute values and the winter/summer concentration ratios of these molecules. A summer maximum observed at some sites (e.g. Izaña, Zeppelin) demonstrates the dominance of biogenic emissions. However, even at these remote sites, there is very little seasonal variation. This may imply that the higher biogenic emissions are partly compensated by higher summer removal rates. The relatively high mixing ratios and the winter maximum of propene and ethene at Tänikon, Kosetice, Moerdijk, Waldhof and West-Beckham may indicate that these sites are exposed to sources from traffic. This is thought true since propene and ethene are strongly linked to petrol and diesel exhaust. Other traffic-indicator species are acetylene, benzene and toluene. The concentration ratios of toluene to benzene, and ethene to acetylene, can be used qualitatively to assess whether a site is generally exposed to fresh emissions from traffic. Toluene/benzene and ethene/acetylene concentration ratios of 1.78 (= 114 ppbv / 64 ppbv) and 0.41 (= 217 ppbv / 531 ppbv), respectively, were measured in a London street (Penkett *et al.*, 1993). The ethene/acetylene ratio is, however, is strongly influenced by the average speed of vehicles and may differ between about 0.5 in an urban environment to about 1.9 at an average speed of 110 km h^{-1} on a motorway (Eggleston, 1993). Table 5.2 shows the above concentration ratios for the TOR and EMEP sites measuring all four components.

Table 5.2 The toluene/benzene and ethene/acetylene concentration ratios calculated from annually averaged unfiltered data at 10 TOR/EMEP sites

Site	Toluene / benzene concentration ratio based on annual averaged data	Ethene / acetylene concentration ratio based on annual averaged data
Izaña	0.63	0.19
Rucava	0.93	0.81
Waldhof	1.01	0.91
Kosetice	1.02	0.86
Zeppelin	1.07	0.44
Kollumerwaard	1.32	0.82
West-Beckham	1.40	1.10
Porspoder	1.48	0.82
Birkenes	1.66	0.85
Tänikon	1.72	0.80

Since these ratios of hydrocarbons are determined by both photochemistry and transport processes, caution is needed in drawing conclusions on photochemical ages of airmasses by examining ratios of hydrocarbons (McKeen and Liu, 1993). A comparison of the toluene / benzene ratios observed at the TOR and EMEP sites, and in a London street, suggests a consistent picture. However, apart from traffic emissions, toluene also arises from the evaporation of solvents and this may disturb the labelling of fresh emissions from traffic. Inconsistencies are apparent in the two lists of ratios. These may also be related to analytical difficulties e.g. the quantification of acetylene has a detector dependency (Romero, 1995). Further work is obviously needed to derive the signature of vehicular and other emission sources on the NMVOC climatologies.

5.2 The spatial pattern of NMVOCs over Europe

It is no easy, if not impossible, task to draw up a general overview of the spatial distribution of NMVOCs over Europe from the current database. This is caused by a lack of sites and data coverage, in general. However, over southern Europe, in particular, this is due to the often unknown spatial representativeness of sites, and causes related to different measurement strategies and instrumentation. However, if one considers the data from the low-level sites in northwestern Europe (Utö, Aspvreten, Birkenes, Rörvik, Rucava, Kollumerwaard, West-Beckham, Weybourne, Waldhof, Moerdijk, Kosetice and Porspoder), the database seems to indicate a similar pattern for several components. From the annual, summer and winter averaged data there are some indications that all species exhibit a spatial maximum over the Netherlands, Belgium and the southeastern part of the UK. In addition, the winter averaged data of ethane, acetylene, benzene, toluene and ethene suggest somewhat higher values over the eastern part of Germany, the western part of Poland and the Czech Republic as well. This winter maximum may be related to emissions of motor-driven vehicles and gas leaks. From their clean-sector data Lindskog *et al.* (1996) concluded the winter concentrations north of 50°N to show a very smooth pattern, which may indicate that meridional mixing is efficient and photochemical degradation is slow during winter. This combined large-scale picture is not in disagreement with the pattern shown in emission inventories (Figure 5.1).

The CORINAIR/LOTOS inventory of anthropogenic NMVOC emissions in Europe consists of the sum of all NMVOC species from 11 source categories (Figure 5.1). The total 1990 Pan-European emissions of anthropogenic NMVOCs are estimated at 25,820 ktonnes y^{-1}, with shares in percentages from Finland (0.8%), Sweden (2.1%), Norway (1.0%), Poland (4.7%), Denmark (0.6%), France (9.3%), Ireland (0.8%), UK (10.1%), Germany (11.7%), Luxemburg (0.1%), Belgium (1.5%) and the Netherlands (1.7%) (EEA, 1995). Unfortunately, no data are available on the speciation within the emissions from each source category nor data on temporal behaviour. A detailed speciated emission inventory is available from the UK (PORG, 1993); however, nine source groups are defined here and time profiles from this inventory are not readily available. In the GENEMIS project, work is currently being carried out on a speciated emission inventory with an hourly temporal resolution (Friedrich *et al.*, 1993).

A preliminary evaluation of the TOR/EMEP NMVOC data combined with the CORINAIR (EEA,1995) and PORG (1993) inventories, and emission time profiles (Berdowski and Zandveld, pers.comm.) has proven that the available information is currently not entirely consistent (e.g. the relative concentration ratios at the sites in relation to speciation and time profiles of emission sources). Due to the shortcomings in knowledge on emissions this is not unexpected, and possibly also to the limited intercomparison of field instrumentation and subsequent data harmonisation (Hahn, 1993). An iterative process between measurements, model calculations and speciated emission inventories is expected to provide the best mechanism to establish the spatial pattern of NMVOCs over Europe. Solberg *et al.* (1995) in comparing measured with modelled data were able to reproduce measured values to a fair extent; in particular, for those components linked to engine combustion.

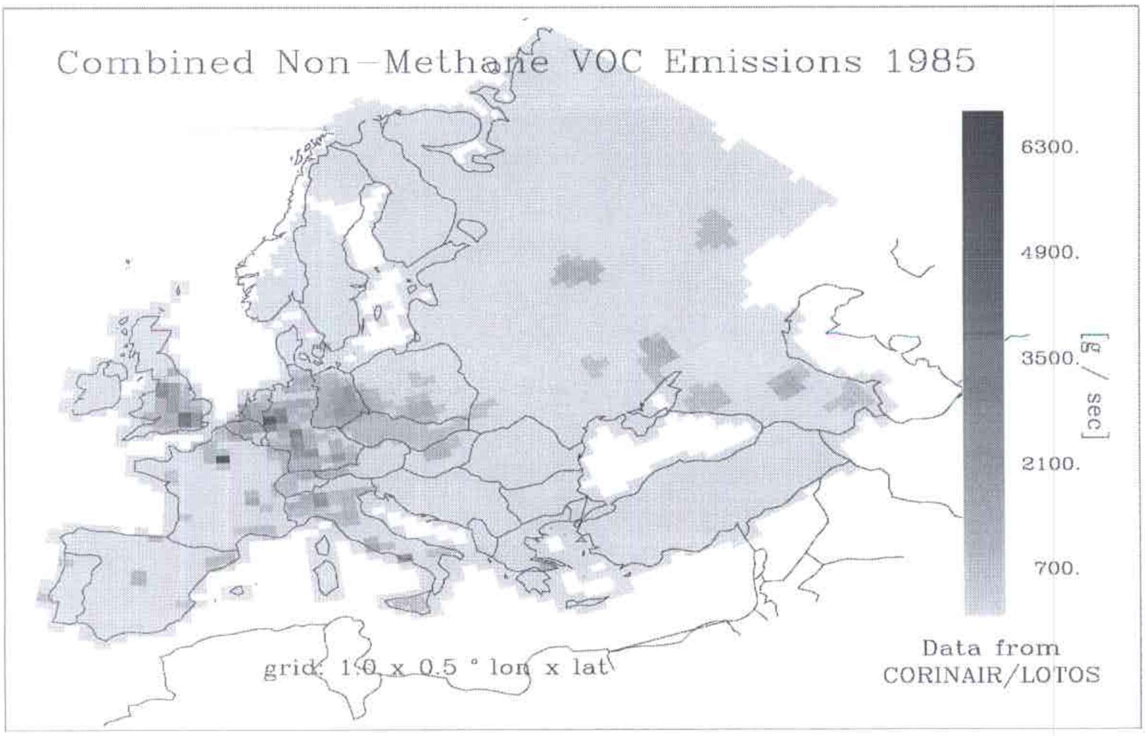

Figure 5.1 Spatial distribution of anthropogenic emissions of NMVOCs in 1985; data from CORINAIR and LOTOS.

5.3 Ozone production from individual NMVOCs

Although the basic mechanisms in the process of ozone formation are well understood, the quantitative share of individual NMVOCs in different chemical regimes is still plagued with uncertainties. Only for a small number of sites connected to the network is it possible to evaluate the relation between the levels of NMVOCs, NO_x and photo-oxidants occurring. An important question in this respect is whether the production of O_3 in various regions in Europe is NMVOC- or NO_x-limited. Volz-Thomas *et al.* (1991, 1992) and Flocke *et al.* (1994) evaluated the above relation from measurements of O_3, NO_x, NO_y, HO_2 and organic peroxy radicals at Schauinsland, comparing their findings with modelled results. The Schauinsland data indicate that the photochemical production of O_3 is NO_x-limited, even in freshly polluted air. It was found that at Schauinsland about four molecules of O_3 are produced per emitted molecule of NO_x in summer, whereas in winter emissions of NO_x did not appear to lead to a net formation of O_3. Due to a lack of similar data at other locations, it is currently impossible to check whether the NMVOC, NO_x and O_3 relation established at Schauinsland is supported elsewhere in Europe.

The mean summertime West-Beckham data were used to calculate instantaneous O_3 production rates for each individual NMVOC (PORG, 1993). The overall impact on ozone production of the average concentration of NMVOCs resulted in a production potential of 2 ppbv.h^{-1} (OH=5 x 10^6 cm^{-3}). A value of 958 ppt of ethene, 64 ppt of isoprene and 741 ppt of toluene appeared to account for 7.6, 6.0 and 4.1% of the O_3 production rates, respectively. It is worth noting that about 25% of the ozone production in this calculation resulted from the oxidation of CH_4 and CO. The importance of isoprene as a precursor of photo-oxidants during episodic conditions was also put forward by Poppe *et al.* (1993). In a combined evaluation of modelled EURAD results and measured data, they concluded that about 30% of the episodic ozone resulted from oxidation of isoprene and its degradation products.

The concept of the photochemical ozone creation potential (POCP) is a widely used modelled approach to estimate the relative importance of individual NMVOCs for the production of O_3 (Derwent and Jenkin, 1991; Heupel, 1995; Simpson, 1995). The definition of POCP is subject to some discussion because it does not refer to: (1) the transport time scales versus the photochemical reaction time scales, (2) the levels of HO_2, RO_2 and NO_x required during the production of O_3 and (3) the question of NMVOC or NO_x limitation. This has led to considerable variation in the POCP values calculated for individual NMVOC species in different modelled studies. However, a combination of calculated POCP values with estimates of man-made emissions may lead to a qualitative assessment of a 'photochemical importance' ranking of individual NMVOCs. Such an evaluation points to toluene, ethene, butane and propene as the most efficient short-term (48 hours) O_3 producers of those listed in Table 5.1. However, if one evaluates POCP values on longer time frames (e.g. 96 hours), the slow reacting alkanes become increasingly important.

5.4 Trends

At only few sites were NMVOC time-series collected long enough to allow for trend analysis. At the Moerdijk (NL) site C_2-C_5 data over the period 1981-1991 were collected and analysed for trends by Roemer *et al.* (1995). Solberg *et al.* (1994) have evaluated more than six years' NMVOC data from the Birkenes (N) site.

In the most polluted wind sector of the Moerdijk site (direct advection from the industrial Rijnmond area) a downward trend of -2.3±1.7 % y^{-1} for ethane and -5.9±3.2 % y^{-1} for ethene was observed. The other compounds analysed (acetylene, propane, propene, i- and n-butane) showed downward trends within the above range and, except for propane and i-butane, these trends were significant at the 2σ level. The trend in acetylene supports estimates of decreasing NMVOC emissions from traffic at a similar rate over the same period. In the cleanest sector of the Moerdijk site the concentrations of all C_2-C_4 NMVOCs decreased, with significant downward trends of -2~-4 % y^{-1} for ethane, acetylene and propane (Roemer *et al.*, 1995).

Linear regression analysis of the data series from Birkenes, shows, however, that there is a statistically significant (95% confidence level) upward trend in the concentrations of acetylene, propane, butane and the C_2-C_5 sum. In the concentrations of ethene and propene a downward trend was derived. Solberg *et al.* (1994) reported that their Birkenes trend analysis was not entirely free from meteorological bias because a significant year-to-year variability in large-scale transport patterns was detected. Furthermore, the sampling frequency at Birkenes over the period analysed, in combination with wind sector analysis, may lead to difficulties with respect to representativeness of the data set in each sector.

The two trend studies indicate that the composition of the hydrocarbon mix at Moerdijk and Birkenes is changing. The results can hardly be generalised because the sites experience a very different mix of emission sources and meteorology. It will probably take more time and effort to establish the relation between emissions and the NMVOC climatology at individual sites.

6 TRENDS IN OZONE AND OXIDANT CONCENTRATIONS

6.1 Introduction

There are indications that ground-level ozone concentrations in Europe might have tripled over the last 100 years. The Montsouris time-series from 1876-1910, recently re-examined by Volz and Kley (1988), points towards annually averaged ozone concentrations of about 10 ppb. During the last decade many historical ozone time series have been re-examined; most of them indicate ozone concentrations of about 10 ppb at the turn of the century (Bojkov, 1986). Virtually all of these ancient records were measured by applying Schönbein's measurement method, a method well-known to be inaccurate and subject to many disturbances. Indeed some of the ancient records do show higher concentrations of ozone which then are usually attributed to the inaccuracy of the method.

In the 1950s measurements of ozone at ground level and of ozone profiles at more remote sites were started. From these time-series it was concluded that background ozone concentrations over Europe increased by as much as 1-2 per cent per year (Bojkov, 1988). Interference with trends in the concentrations of other species (SO_2) cannot be excluded (Low, 1991). There are several indications that in the 1980s the concentration of background ozone above Europe ceased to increase and that ozone concentrations stabilised. However, increasing ozone concentrations are still reported from sites often located on mountain tops (Scheel, 1994).

Generally, proper statistically meaningful trend analysis can be established from time-series of at least ten years long. The time horizon of the current TOR database is too small for trend analysis. The time horizon of the Air Quality Monitoring Network of RIVM is 15 years old, which allows for an analysis of the trend of ozone and oxidant (O_3 + NO_2) in the Netherlands from 1979 onwards.

In areas such as the Netherlands it is preferred to analyse trends of oxidant as opposed to ozone to minimise the disturbing effects of titration of O_3 by NO. Most NO_x is emitted as nitrogen monoxide (NO), which reacts very fast with O_3, resulting in conversion to NO_2. The photostationary equilibrium of O_3, NO_2 and NO is usually established on a minutes time scale, implying that each molecule of ambient NO_2 is actually a molecule of O_3 in disguise.

The contribution of directly emitted NO_2 to oxidant concentrations at rural areas in the Netherlands is only a few per cent. We therefore expect that a slight downward trend of NO_x emissions, including emissions of NO_2, since the beginning of the 1990s will have a negligible effect on the trends in concentrations of oxidant.

In this chapter a brief overview will be presented of the trends of ozone and oxidant at several sites connected to the Dutch Air Quality Monitoring Network managed by RIVM. Section 6.2 briefly discusses the trend in oxidant at 11 stations in the Netherlands; section 6.3 presents aspects of trends in oxidant and ozone at Kloosterburen/Kollumerwaard in more detail.

A study is currently underway to address filtering the data set of the disturbances caused by year-to-year meteorological fluctuations (Bosschert and Roemer, 1995). This study aims at solid statistically meaningful trends. Such trends, or absence of them, then need to be interpreted on the basis of presumed changes in precursor emissions and concentrations in Western Europe.

6.2 Oxidant trends in the Netherlands

Table 6.1 Trend of oxidant concentrations in the Netherlands; 1980-1992

Station	Missing years	Trend (% a^{-1}) annual av.[1]
Kloosterburen-Kollumerwaard (NL)	-	-1.1 ± 1.0
Balk (NL)	85	-0.5 ± 1.4
Hellendoorn (NL)	85	-0.1 ± 1.5
Biddinghuizen (NL)	-	-1.2 ± 1.0
Cabauw (NL)	86	-1.1 ± 1.0
Huybergen-Waarde (NL)	80,85,86,90	-1.5 ± 1.3
Braakman-Axel (NL)	83,85	-0.4 ± 1.2
Vreedepeel-Afferden (NL)	80,85	-0.1 ± 1.4
Wijnandsrade-Oost Maarland (NL)	85,86,87	-0.1 ± 0.8
Wieringerwerf-Den Helder (NL)	85	-1.1 ± 1.1
Eibergen-Winterswijk (NL)	85,88	-0.3 ± 1.0

1) Uncertainty range at the 95% confidence interval

It appears from Table 6.1 that the trend of ozone and oxidant in the Netherlands in the 1980s is slightly downward, though for most stations not significant at the 95% confidence interval. The table shows that statistically significant downward trends of about -1% per year for the annual average oxidant concentrations are found for Kloosterburen / Kollumerwaard, Biddinghuizen, Cabauw and Huybergen/Waarde. The trends at the other sites range from -0.1 to - 0.5% per year and these are not significant.

A recent analysis by Bosschert and Roemer (1995) on trends of daily maximum oxidant concentrations and on hourly oxidant concentrations showed that for all sites, except one, significant (at the 95% confidence interval) downward trends of -1.0 % per year were found.

6.3 Ozone and oxidant trends at Kollumerwaard

Ozone and oxidant trends over the 1979-1993 period at Kloosterburen/Kollumerwaard were examined for the whole data set and for subsets. Subsets were defined for three seasons (winter, summer and transition) and for a particular wind sector (315°-350°) at wind speeds greater than 5 m s^{-1}.

The ozone trend from all data is -1.2% per year and that for the oxidant is -1.2% per year (Appendix D6., Figure 1a and 1b; the statistical analysis is explained in Appendix D). It appears that the downward trend occurs primarily during the summer and transition periods and that particularly the ozone levels over the winter period remained constant (Appendix D6, Figure 2a and 2b).

A similar downward feature is observed from the whole data set in the 'clean' wind sector in the north (Appendix D6, Figure 3a and 3b). However, the negative annual trend in this sector is smaller (-0.6 and -0.9% per year for ozone and oxidant, respectively) than the trend averaged over all wind sectors (-1.2% per year for both O_3 and O_x). The analysis of the clean sector data in each of the three seasons (Appendix D6, Figure 4a and 4b) reveals a smaller downward trend to what is shown in Appendix D6, Figure 2a en 2b from the whole data set. The curve representing the winter data shows a fairly constant level over the 14 years of data.

The figure for Appendix D6.5 shows the (forward) 12 months moving average in the entire data set for O_3 and O_x. The curves reveal a similar downward feature to that presented above.

6.4 Trends in precursors of ozone and oxidant over Europe

The reasons for the downward trend in the Netherlands are not yet clear (Bosschert and Roemer, 1995). The NMVOC emissions in the Netherlands and Germany have decreased by approximately 30% since 1980 (Roemer *et al.*, 1995), mainly from the late 1980s onwards, but in other West European countries no significant reduction of NMVOC emission has occurred. The NO_xemissions have been reduced by approximately 10% since 1980 in some West European countries, mainly since the late 1980s (Van Jaarsveld, 1995).

According to model calculations these reductions are by far too insufficient to explain the observed trends.

Furthermore, there is no indication that background ozone levels have decreased. Measurements at Hohenpeissenberg show a slight increase during the 1980s until 1991 and a slight decrease in the last few years. The consequences of the changing of the ozone monitors (in the winter of 1990-1991) are not yet fully known, but until now there are no indications of any systematical influence on the observed trends (Uiterwijk *et al.*, 1990).

Finally, a long-term change in circulation patterns, which may have contributed to a change in the climate, may also have had an influence on ground-level ozone concentrations and thereby may have caused a certain downward oxidant trend. However, this aspect has not yet been fully explored.

7 MODELLING AND ANALYSIS OF THE TOR/EMEP DATA SET

7.1 Introduction

The distribution of trace gases in the boundary layer over Europe is determined by a complex set of physical and chemical processes interacting on various temporal and spatial scales. Over the last 20-30 years tremendous progress has been made in our understanding of the chemical and physical state of the lowest troposphere. Nevertheless our knowledge is still limited and many aspects of the chemistry of the atmosphere are not sufficiently known. This study - embedded in the international TOR project - is a contribution to further progress.

From the analysis of the measurements at Kollumerwaard and other sites certain characteristics emerge from which a few chemical and physical processes can be quantified. A proper understanding of the contributions of the different processes to the concentration levels of the trace gases over Europe is not only a scientific challenge, it also is required to formulate a sound abatement strategy with the objective of reducing ambient air concentrations of those species which are believed to have environmentally adverse effects at their current levels.

The ozone budget (i.e. the balance between sources and sinks) over Europe is determined by many processes. The main terms used in model simulations are: chemistry, dry deposition and transport. The latter usually consists of different terms describing convection, other forms of vertical transport and horizontal advection. The importance of these subterms may vary strongly from place to place, depending on the concentration gradients.

In this chapter the issue of determination and quantification of processes to (mainly) the ozone budget will be addressed. This is done by analyses of the TOR and EMEP measurement data set, as well as by calculations with models describing the supposedly main physical and chemical processes.

7.2 The ozone budget over Europe; data analysis

7.2.1 Estimate of the production of ozone in Europe

Chemical production of O_3 from primary pollutants in the European boundary layer contributes substantially to ambient levels of O_3. During discussions on abatement strategies it is relevant to know to what extent O_3 levels are expected to decrease when emission reduction measures are implemented. First of all, we will address the issue of how much O_3 is currently produced in the European boundary layer. This is performed by analysis of the diurnal variation of O_3 in the TOR and EMEP data sets.

The ratio between the mean maximum and minimum O_3 values (O_3max/O_3min) in the summertime and wintertime diurnal curves was calculated for all O_3 stations connected to the TOR/EMEP database. At some stations a mean O_3max/O_3min of more than 5 was calculated, while there were stations showing almost no variation. Those stations showing the highest O_3max/O_3min ratios, both in summer and winter, were the Swiss valley stations, and some urban and suburban sites. The stations showing the smallest variations, summarised in Table 7.1, are either situated on mountains or remote coastal locations.

Table 7.1 Characteristics of O_3 monitoring stations showing an O_3max/O_3min ratio of less than 1.2 for the mean daily variation from April - September and less than 1.1 averaged over October-March

No.	Station	Height above sea level (m)	Type	Ratio O_3max/O_3min		Number of monitored hours		Network
				Summer	Winter	Summer	Winter	
13	Sonnblick (A)	3112	mountain	1.04	1.04	1992	2042	TOR
4	Areskutan (S)	1240	mountain	1.06	1.02	2605	3178	TOR
1	Ny Ålesund (N)	40	coastal	1.07	1.04	3913	2069	TOR & EMEP
17	Izaña (E)	2368	mountain	1.12	1.06	3956	4029	TOR
3	Utö (SF)	6	coastal	1.12	1.09	3359	3838	TOR & EMEP
8	Mace Head (IR)	20	coastal	1.12	1.03	3804	4177	TOR & EMEP
11	Schauinsland (D)	1100	mountain	1.16	1.04	3814	2421	TOR
223	Schauinsland (D)	1205	mountain	1.16	1.06	4018	4329	EMEP

There are 14 European lowland stations connected to the TOR database where increased O_3 concentrations (e.g. above the EU guide value of 75 ppb) are seldom observed. These stations all show similar afternoon concentrations, with the mean daily summer maximum ranging from 32 to 42 ppb. If only the stations with a small diurnal variation (O_3max/O_3min < 1.4) are selected, the number decreases to 4 and the means of the daily summer and winter maxima become 36 (± 1.3) ppb and 30 (± 2.8) ppb, respectively. The summertime daily mean for these four stations is 32 (± 2.6) ppb, while the daily mean during the winter months is 31 ppb (± 2 ppb). We have assumed that these four stations, (Mace Head, IR; Svanvik, N; Jergul, N; Strath Vaich, UK), with their specific O_3 values and diurnal patterns, represent the European boundary layer background of O_3. Herewith they will be referred to by 'reference sites'. The four reference sites are all located on the western and northwestern fringe of Europe. We expect these sites to exhibit trace gas concentrations from the Northern Hemisphere background in a wide wind sector ranging, at least, from southwest to northeast and where the air has travelled more than several thousand kilometres over the Atlantic Ocean. Table 7.2 shows characteristic levels for these four sites. We have also assumed that O_3 regionally produced or destroyed from European emissions occurring at lowland 'polluted stations' is superimposed on the boundary layer background. Thus internal production and destruction of O_3 can be determined by comparing O_3 levels at polluted sites with respect to the four reference sites.

Table 7.2 Characteristic O_3 levels observed at the four boundary layer background sites in 1989

No.	Station	Maximum monthly mean (ppb)	Minimum monthly mean (ppb)	Number of hours with O_3 values > 75 ppb	Maximum average hourly O_3 value (ppb)	Number of daily maxima below 20 ppb	Ratio O_3max/O_3min	
							Summer	Winter
8	Mace Head (IR)	44 (±10)	21 (±10)	11	99	17	1.1	1.03
265	Svanvik (N)	38 (±9)	23 (±9)	6	86	5	1.4	1.05
270	Jergul (N)	40 (±8)	27 (±7)	0	75		1.4	1.04
41	Strath Vaich (UK)	42 (±8)	27 (±7)	5	80	6	1.3	1.06

The numbers in parentheses represent standard deviations.

A comparison of the daily variations at some lowland stations in continental Europe to the reference diurnal cycle averaged from the four reference stations as defined above reveals that European sources contribute to the regional O_3 concentrations mainly during the afternoon. During this time the contribution may, at some stations, be in the range of 20 - 25 ppb. More specifically concentrations at polluted sites are higher and the diurnal patterns more pronounced from 9:00 - 21:00. This coincides with the period during which photochemical formation of O_3 occurs.

The diurnal curves also show lower O_3 concentrations during nighttime at the polluted stations. This effect may be caused by a shifted photostationary state due to titration of O_3 with oxides of nitrogen and dry deposition. The photostationary state, however, reaches a new equilibrium during daylight hours. In order to exclude the titration effect during nighttime the 12-h interval between 9:00 and 21:00 was used and (sub)urban sites were excluded. Also, to avoid the dominant influence of air from the free troposphere at elevated sites (e.g. Izaña (E), Areskutan (S)) and of local influences at elevated valley stations, sites above 500 m above sea level were excluded from this analysis.

The summertime mean of the amount of O_3 exceeding the reference values over the 9:00 to 21:00 interval was calculated for all stations except the (sub)urban and elevated sites. The analysis generally shows an increasing gradient from the northwest to the southeast of the TOR network area. European internal production ranges from 0 - 5 ppb in Scandinavia, Scotland and Ireland to 5 - 10 ppb at the coastal fringe of the continent to 10 - 15 ppb in central Europe. The pattern shows a minimum discrepancy on the negative side in the Ruhr, Antwerp, Rotterdam and London industrial belts. Furthermore, maxima appear in the north of Germany and across the French / German border. We note that the contribution represents the mean for the period April - September (9:00 - 21:00) and that substantially higher contributions due to 'internal production' during periods favourable for O_3 formation are to be expected.

As derived in section 4.3.2 the summertime internal European production of O_3 in air advected to the Kollumerwaard observatory is about 3 ppb of O_3. This estimate is found at the lower end in comparison to the number calculated from the total database; this is because of Kollumerwaard's location in the '5 - 10 ppb belt'. In a previous estimate of the regional contributions of O_3 Grennfelt and Schjoldager (1984) came to the conclusion that episodic O_3 at Rörvik (S) contributed overall less than 5 ppb as a mean for the summer. The corresponding figure in this work is 3 ppb, proving that these methods of estimating continental contribution give comparable results.

A similar analysis was performed comparing averaged diurnal cycles of polluted and reference sites for the October to March period. Again, a gradient from the northwestern to southeastern part of the network area can be distinguished, however, it is a decreasing gradient. Here is shown a destruction of 0 to 5 ppb at the coastal fringe of the continent to about 10 ppb, with an occasional minimum of 20 ppb in central Europe, probably due to scavenging of O_3 with oxides of nitrogen. So the unreacted primary pollutants act as a sink for O_3 in winter. At Rörvik (S) the wintertime destruction was estimated at about 3 ppb in a previous work (Grennfelt and Schjoldager, 1984), which is in agreement with the present results.

The estimate of the summertime production of O_3 in Europe (ranging between 0-15 ppb) indicates the boundary condition of the *maximum* effectiveness of reductions of emissions of relatively short-lived species (NMVOC, NO_x) in Europe. The UN-ECE Convention on Long-Range Transboundary Air Pollution decided on a protocol to reduce the emissions of NMVOCs by approximately 30% before 1999 (UN-ECE, 1991). With respect to NO_x emissions, the UN-ECE requires that parties stabilise their emissions at the 1987 level.

It is important to note that the relation between emission reductions of NMVOC, NO_x and the resulting O_3 is very non-linear. Generally, emission reductions of NMVOC are more effective in decreasing O_3 levels than an equal percentage of emission reductions of NO_x. A reduction in NO_x emissions in Europe is expected to lead to decreasing O_x concentrations, but in the Netherlands the O_3 concentrations will increase (De Leeuw *et al.*, 1990). This is mainly due to a shift in the photostationary state.

7.2.2 Excess ozone; data analysis

The WHO, UN-ECE and EU have defined several guide values for the protection of human health and/or vegetation. In this section the number of hours exceeding the 40 ppb UN-ECE guide value will be discussed. This 40 ppb guide value is called the 'critical level[6]' in UN-ECE terminology. Except for Ny Ålesund (N) at Spitzbergen and at two other Norwegian sites, the 40 ppb critical level was exceeded frequently at all stations in both networks.

The frequent exceedance of the 40 ppb concentration illustrates that vegetation damage may be expected in large areas of Europe. This parameter, however, does not provide information on the magnitude of the peaks and the duration of exposure. This is important with respect to plants because when the total exposure (product of O_3 concentration and exposure duration) is kept constant, the amount of leaf damage rises progressively with rising O_3 concentrations (Davis and Wood, 1973).

The critical levels agreed upon in 1988 (75 ppb) were then already considered to be provisional; it was pointed out that they should be re-evaluated. A revision of the concept and critical levels took place in the UK in 1992 and in Switzerland in 1994 and a new concept for the critical levels for O_3 based on an 'excess ozone' parameter was introduced. The new critical levels are directed towards the protection of agricultural crops and forests but may also take into account effects to other ecosystems. According to this concept the effect parameter will be the O_3 exposure of the vegetation above a certain threshold value, calculated by subtracting the threshold value from each hourly average concentration and adding the residuals together. The excess O_3 is expressed as the number of ppb.h above the threshold value and should be related to the daylight hours during the vegetation season. The critical level was set at 5300 ppb.h above the threshold concentration of 40 ppb in May, June and July during daylight hours only (Führer and Achermann, 1992).

In Figure 7.1 the number of ppb.h above the threshold level of 40 ppb is presented (1990 data). The critical level is exceeded at all monitoring sites in central Europe and the excess ppb.h often amounts to more than 10,000 in this area. Surely it is important to

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[6] 'Critical level' is defined as the concentrations of pollutants in the atmosphere above which direct adverse effects on receptors, such as plants, ecosystems or materials may occur according to present knowledge (Ashmore and Wilson, 1988).

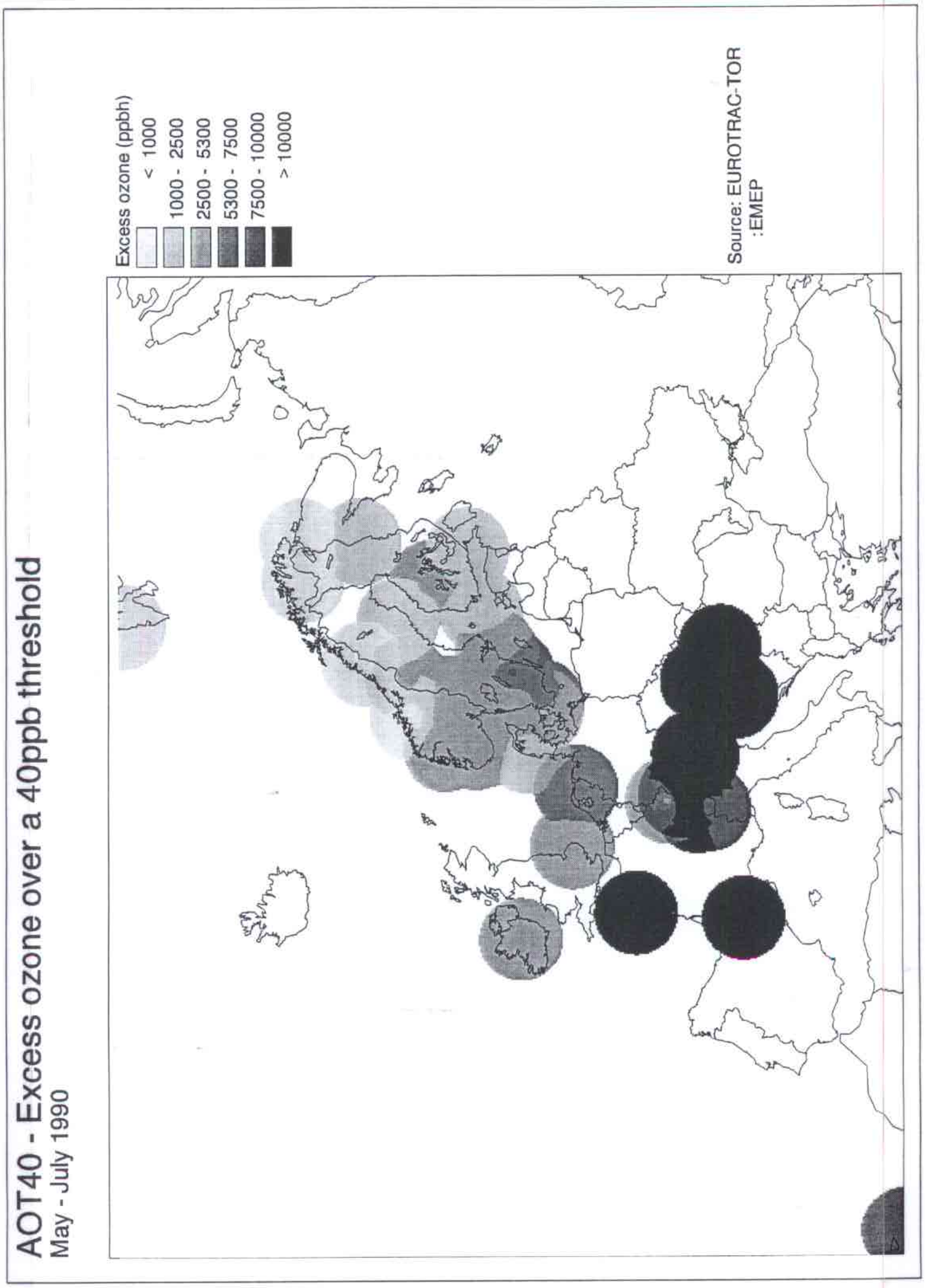

Figure 7.1 Excess O_3 above the threshold level of 40 ppb.

evaluate the relation between measured exceedances of the critical level and emissions of ozone precursors in Europe causing the excess. This issue will be addressed using a model approach in section 7.3.

7.2.3 Analysis of the importance of vertical exchange processes between the boundary layer and the free troposphere

Pollutants emitted by European sources have a wide range of atmospheric lifetimes depending on many physical and chemical characteristics. Some components,e.g. CH_4 and CO, can easily reach the free troposphere and affect the budgets from these species at a long distance from the original sources. In the case of secondary pollutants like O_3 the situation is more complex. This compound has its sources both in the stratosphere and the troposphere, whereas its main sinks are deposition to the earth's surface and chemical destruction. We addressed the issue of O_3 budgets in the troposphere by making a distinction between the *boundary layer* and the *free troposphere* budgets. In this section we analyse the transfer of O_3 between these atmospheric layers.

Jacob *et al.* (1993) calculated in a mesoscale model study that the summertime direct export of ozone from the U.S. boundary layer to the free troposphere adds up to about -4 Gmol day^{-1} (*[7]). In addition, the equivalent of another -4 Gmol day^{-1} of ozone is exported in the form of ozone precursors. These two sources correspond to a flux of about $-4 * 10^{10}$ molecules cm^{-2} s^{-1} (= -0.3 ppb h^{-1}) to the Northern Hemispheric free troposphere from U.S. emissions only. Pickering *et al.* (1992) analysed the effect of strong convective mixing in a thunderstorm. This process provides a 'fast transport track' of ground-based emissions to the free troposphere. Simmonds (1994) investigated the 1987 to 1992 ozone time-series from the Mace Head (Ireland) site and reported that the continent of Europe would provide a small net sink of ozone of 2.6 ppb for all occasions when air with a continental origin was flowing out over Mace Head into the North Atlantic.

To address the issue on vertical exchange mechanisms we started the development of a data analysis model (DAM) to study the exchange processes between the atmospheric boundary layer and the free troposphere (Beck and Van Pul, 1993; Beck *et al.*, 1994; Kirchner, 1995). The model integrates several data sets (the ground-based TOR data, vertical profiles of O_3 and meteorological parameters, land use information and synoptical information) and evaluates the transfer of air from the boundary layer to the free troposphere, and vice versa, induced by convective activity. The model was run for the full year of 1989 to study the exchange processes at the location of Uccle (B). For the summer

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(* [7])A negative sign indicates a flux from the boundary layer to the free troposphere, whereas a positive sign indicates flow from the free troposphere to the boundary layer.

months of June, July and August the results reveal a net boundary layer to free troposphere flux of $O_{3,=}$, with a magnitude of -0.43 * 10^{-3} mol m^{-2} day^{-1} (= -0.2 ppb h^{-1}).

Memmesheimer *et al.* (1994) and Flatøy and Hov (1995) performed model calculations of photosmog episodes from which the importance of exchange processes can be studied. Both model exercises were aimed at the investigation to determine which processes are important for ozone and its precursors in areas characterised by different chemical, dynamical and emission regimes. A summary of their and our results from the data analysis model is shown in Table 7.3.

Table 7.3 Summary of the tendency in the boundary layer O_3 concentration (ppb.h^{-1}) as a result of exchange processes between the boundary layer and the free troposphere from several studies. In order to give an impression of complete budgets, the chemistry, deposition and net result terms are listed as well.

Term contributing to boundary layer O_3 budget	Flatøy and Hov (1995)		Memmesheimer *et al.*, (1994)		Polluted area Europe; boundary layer with a varying depth (Beck *et al.*, (1994))
	Polluted area Europe (lowest 1200 m)	Less polluted area Russia (lowest 1200 m)	Polluted area Europe (lowest 1050 m)	Polluted area Europe (lowest 1550 m)	
Net result	+0.1	+0.025	+0.06	+0.1	
Chemical formation	+0.7	-0.005	+1.09	+1.24	
Dry deposition			-0.45	-0.45	
Convection	-0.15	+0.05	-0.05	-0.01	-0.2
Vertical advection	-0.25	+0.33	+0.61	+0.75	
Horizontal advection	-0.20	-0.35	-1.15	-1.43	
Cloud effects			-0.002	-0.002	-0.015

Although the periods modelled and studied (Table 7.3) were different, some general conclusions from this work may be drawn. The model and data analysis efforts show that vertical advection (subsidence) is a more important process for the vertical redistribution of O_3 than convection, even over continental Europe. However, when it occurs, convection represents an important redistribution process of ozone in the troposphere. Due to the little spatial and temporal extent of convective processes, they are of little importance in a total area-averaged budget. The model studies of Flatøy and Hov (1995) and Memmesheimer *et al.*, (1994) show that over the European region the concentration of ozone in the boundary layer is so high that the tendency in contribution of convection to the ozone concentration is negative near the ground. Less episodic conditions demonstrate that the net effect of convective transport is to increase the boundary layer concentration, which is consistent with a stratospheric source and a ground sink of O_3. The latter situation is expected to occur more frequently than the former since severe photochemical episodes as modelled by Flatøy and Hov (1995) and Memmesheimer *et al.* (1994) are only occasional. Caution is advised if the aim is to make an overall assessment of the contributions from different vertical redistribution processes on the boundary layer and free tropospheric ozone budgets from the results presented in this section. On the one hand, the analysis presented using chemistry and transport models covered typical periods of about 10 days, for which the temporal representativeness is not yet fully assured (Flatøy and Hov, 1995; and Memmesheimer *et al.*, 1994). On the other, TOR data-set analysis yielded findings covering longer time periods; but then the spatial representativeness of these results could be limited (Beck *et al.*, 1994). Furthermore, all exchange mechanisms addressed are so intermingled and co-located in time and place that it is virtually impossible to examine each topic individually. A long-term simulation with a fully coupled and validated climate and chemistry model may enable a full evaluation of the importance of transfer. Such a model evaluation is currently not feasible. Therefore we prefer to present our results in an 'order of magnitude atmosphere' rather than 'certified final data'.

7.3 The ozone budget over Europe: A modelled approach

7.3.1 General; the LOTOS model

LOTOS (LOng Term Ozone Simulation) is a three dimensional Eulerian model that calculates the distribution of ozone and related species in the lowest 2.0-2.5 km of the troposphere over Europe (Builtjes, 1992). The horizontal resolution is 0.5° latitude x 1.0° longitude, which is about 60x60 km^2. In vertical direction three layers are used. The lowest layer follows the diurnal variation of the mixed layer, the other two layers are so-called reservoir layers.

The concentrations are calculated by solving the continuity equation for all processes involved. These processes are: advective and diffusive transport in horizontal direction, vertical transport by diffusion and entrainment/detrainment, chemistry, wet and dry deposition, and emissions. Transport is accounted for by the use of analysed windfields received from the Norwegian Meteorological Institute (DNMI). Calculations have been performed for a specific year (1985 and 1990).

Boundary and initial conditions are set by the calculated concentrations from the two-dimensional global TNO-Isaksen model (Roemer and Van den Hout, 1992). The boundary concentrations vary as a function of height, latitude and month. The description of the chemistry is based on the CBM-IV mechanism. The current LOTOS model uses 17 long-lived (transportable) species and 7 short-lived (radical) species reacting with each other in 52 reactions.

Dry deposition is determined by three sequential resistances, an atmospheric turbulent resistance, an atmospheric laminar resistance and a surface resistance. The surface resistance is a function of land use and species.

Emissions are used in the model as annual averages. Temporal variation is obtained by applying time and temperature functions. A more detailed description of the emissions in the model is given in section 7.2.2.

7.3.2 Emissions

For the emissions the primary information entering the LOTOS model are the annual average emission data per component. Prior to this project the basic reference year in LOTOS was 1985, not only for meteorology but for emissions as well (Builtjes, 1992). The spatial resolution with which the 1985 emissions in LOTOS were used was 1.0° latitude x 2.0° longitude, which is approximately 120x120 km^2. An overview of the 1990 emissions per country for each of the six main species (SO_x, NO_x, NMVOC, CO, CH_4, N_2O) is given in Table 7.4.

With respect to the 1985 emission database, the LOTOS 1990 emission database has been modified fairly substantially (Berdowski, 1996). To start with, the basic information on which the emission figures were based was updated according to developments between 1985 and 1990. Secondly, the spatial resolution of the whole system was doubled to 60x60 km^2. And finally more species were added. The original database included NO, NO_2, SO_2, SO_4, CO and speciated NMVOCs. In the 1990 emission database CH_4 and N_2O were added.

As far as the EC countries are concerned, the LOTOS 1990 emission database is not based on CORINAIR data, simply because at the time the 1990 database was designed no official CORINAIR emission data existed. The LOTOS 1990 emission database starts from basic information such as energy and traffic statistics (EC-CORINAIR-COPERT, manuals, IEA, UN, EUROSTAT), technological characteristics (capacity, efficiency, reduction technologies) and land-use data.

Sources are distinguished into point and area sources. Only the largest point sources are selected; the remaining sources are aggregated with the area sources. Important parameters of the largest point sources are: (effective) stack height, emissions and the temporal and temperature profile. The LOTOS 1990 contains 10 industrial and 3 natural source categories. With the addition of CH_4 and N_2O four extra source categories were added, making a total of 17 categories. For natural NMVOC emissions the concept of biomass factors is used. Per source category different NMVOC specifications are given as well as time- and temperature dependencies.

Table 7.4 Emissions (ktonne per year) in the LOTOS 1990 emission database

	SO_x	NO_x	NMVOC	CO
Great Britain	3726	2435	2413	9085
France	1122	1522	2577	8965
Belgium	360	375	290	1709
Luxembourg	22	22	16	246
Netherlands	188	489	488	1619
Denmark	213	232	193	613
Norway	53	161	502	583
Sweden	104	332	1715	1239
Poland	2780	1040	1488	4889
Czech and Slovakian Reps.	2097	468	1011	2750
Austria	172	221	566	1195
Hungary	637	217	338	1367
USSR	25215	8515	18061	47991
Ireland	192	103	137	499
Switzerland	66	169	234	854
Finland	214	243	1236	738
Romania	1397	453	1048	1703
Bulgaria	1502	312	514	1625
Greece	581	288	439	1130
Italy	2281	1578	2154	5814
Portugal	266	173	374	618
Spain	1398	952	2041	3401
Yugoslavia	937	503	874	2102
Albania	111	39	79	160
Germany	5412	2813	3736	11844
Total	51057	23666	42537	112752

7.3.3 Evaluation of results.

Results of calculations for two summer months (July and August 1990) will be presented. Emphasis is on a 7-day period at the end of July and the beginning of August 1990, the so-called core-period. During this period high concentrations of ozone were observed in Western Europe.

This period was analysed within the framework of a model intercomparison in which model groups for four models participated: 1. EMEP (EMEP Centre-West; Simpson, Berge), 2. EURAD (University of Cologne; Hass, Memmesheimer), 3. REM3 (University of Berlin; Stern) and 4. LOTOS (TNO, Builtjes, Roemer). Objective of the intercomparison was to evaluate the results of the four models in terms of model specifics. Each model describes the innumerous aspects of dispersion, emission and transformation in its own way. Input is used in most cases in an unique way. An attempt was made to restrict the comparison to a few important variables and parameters. Where possible, the comparison included measurements as well. Time-series during the core period were made for several sites but the comparison focused on only four of them: Sibton (UK), Kollumerwaard (NL), Waldhof-Langenbruegge (D) and Lindenberg (D). The species and parameters included O_3, NO, NO_2, O_x, PAN, H_2O_2, HNO_3, OH, J_{no2}, $V_{dep,o3}$ and ground-level temperature. Furthermore, anthropogenic and biogenic emissions of NMVOC and NO_x for several countries (Netherlands, Germany and Poland) were compared as well as trajectories. Next to this analysis, several additional runs were performed to study the sensitivity of the model with respect to changes in NO_x, biogenic and anthropogenic emissions, and to changes in the dry deposition rate of ozone. A brief summary of the findings of the intercomparison will be given in the next section. An extensive discussion can be found in Hass *et al.*, (1996).

The calculated ozone concentrations of the four models are most of the time found within a range of 20-30 ppb from each other, but occasionally larger discrepancies are found (Appendix E, Figures 7.2-7.5). The figures show that the diurnal cycle as such in the model results agree with those in the observations. The measured ozone concentrations are generally within the range of model results. Though this can be regarded as encouraging, it nevertheless demonstrates that agreement between measured and calculated ozone in a time-series nearer than 20 ppb is hard to achieve. Causes for discrepancies between measurements and model results are manifold and often different for different models. Moreover, previous studies have shown that the concentrations of ozone and species at several stations within a grid cell of about 100x100 km^2 show deviations of 10-20% (Esser, 1994; Roemer *et al.*, 1993). This phenomenon is expected to be most prevalent in industrialized areas, such as Western Europe, where the assumption of homogeneity of the air in a grid cell is often violated.

It turns out that the agreement of the model results with measurements and with each other is best for ozone. For species like PAN, NO, NO_2 and OH the discrepancies are often large. This is not surprising since the models were designed for ozone calculations. The number of measurements available across Europe is probably the highest for ozone.

Key elements determining the ozone budget are the dry deposition velocity of ozone and the concentration of the OH radical, a radical which initiates many reactions. The noon values of the OH radical in the LOTOS calculations are generally 0.5 ppt for the period concerned. In REM3 and EURAD OH concentrations are calculated which are 20-50% lower. The EMEP model computes the lowest OH concentrations, about 0.1 ppt.

Large differences are also found in the dry deposition velocities of ozone. Noon values in LOTOS are about 1 cm s^{-1}; in REM3 and EURAD they are about 0.6-0.7 cm s^{-1} and in EMEP 0.5 cm s^{-1}. The nighttime dry deposition values of ozone in EMEP and EURAD are close to zero, whereas in REM3 and LOTOS a minimum value of about 0.2-0.3 cm s^{-1} seems to be maintained.

The sensitivity runs show that though model results may differ fairly substantially with respect to the absolute levels of the calculated species, the differences between models in terms of relative changes when, for instance, emissions are altered, are generally small. This gives some confidence in the results obtained for abatement strategies, at least when they are interpreted in relative terms.

7.3.4 Budgets

Ozone concentrations above Europe are determined by transport in and out of the European area, by deposition and by local chemistry. The effect of local chemistry strongly depends on local emissions. A combination of a global two-dimensional model and a three dimensional European model (LOTOS) is used to calculate the contributions of different processes, not only to the concentrations of ozone but also of PAN and precursors.

Budgets for all species were calculated as a function of time during the July-August period. Four regions were distinguished. Northern Europe (Norway, Sweden, Finland, Denmark and the Baltic States), Western Europe (Germany, Benelux, northern France and England), Southern Europe (Europe south of the Alps from Portugal to Greece) and Europe as a whole. The main results for oxidant, PAN, NO_x, CO and SO_2 are summarised in Table 7.5.

Table 7.5 Budgets O_x, NO_x, CO, PAN and SO_2 in Europe; NO_x in NO_2 equivalents

	North	West	South	Europe
	54.5-69N; 05E-26E; 0-2 km	47°-54.5°N; 04°W-14°E; 0-2 km	36°-47°N; 09°W-26°E 0-2 km	35.5°-69°N; 09°W-58°E; 0-2 km
Area (10^6 km^2)	2.6	1.0	3.6	16.7
Ox (Tg month^{-1})				
emissions	0.0	0.0	0.0	0.1
chemistry	2.2	2.7	5.5	21.3
dry depos.	-1.9	-1.6	-3.4	-16.8
wet depos.	-0.0	-0.0	-0.0	-0.0
net trans.	-0.3	-1.1	-2.1	-4.2
NOx (Gg month^{-1})				
emissions	114	523	400	1742
chemistry	-124	-377	-356	-1526
dry depos.	- 19	- 62	- 56	- 235
wet depos.	- 0	- 0	- 0	- 0
net trans.	12	- 79	- 6	- 81
CO (Tg month^{-1})				
emissions	0.5	2.2	1.6	7.8
chemistry	-0.4	-0.4	-0.9	-4.0
dry depos.	-0.0	-0.0	-0.0	-0.0
wet depos.	-0.0	-0.0	-0.0	-0.0
net trans.	0.1	-1.7	-0.6	-3.0
PAN (Gg month^{-1})				
emissions	-	-	-	-
chemistry	18	84	33	194
dry depos.	-	-	-	-
wet depos.	0	0	0	0
net trans.	-15	-80	-31	-179
SO2 (Gg month^{-1})				
emissions	132	785	660	3514
chemistry	- 99	-207	-338	-1620
dry depos.	- 69	-161	-202	-1044
wet depos.	- 6	- 5	- 6	- 39
net trans.	45	-404	-106	- 739

Calculations with the LOTOS model for the year 1990 indicate a net chemical production of ozone over the entire European area (Iceland excluded) and in the lowest 2 km of the troposphere of about 21 Tg ozone (oxidant) per month in the summer (July-August), see Table 7.5. Most of the ozone is lost by dry deposition (17 Tg month^{-1}). Net transport out of Europe accounts for about 4 Tg month^{-1}.

The intensity of the (net) chemical production of ozone (oxidant) is highest in Western Europe. Covering only 6% of the European area it is responsible for almost 13% of the net chemical production of ozone. Consequently, also the contribution of dry deposition and net transport out of the domain is disproportionally higher. If scaled per unit area, the intensity of the chemical ozone production in Northern and Southern Europe is about 30% and 60%, respectively, of that in Western Europe. In all regions loss by dry deposition is the most important sink to ozone.

The large differences in the ozone production intensity among the European regions is not surprising seen in the light of distribution of precursors sources. About 30% of the European emissions of NO_x, CO (and anthropogenic NMVOC) is emitted in Western Europe. Due to its short lifetime most of the NO_x emitted is chemically transformed in other nitrogen species within the region itself. (This is, of course, not entirely true. The chemistry applies to ambient NO_x concentrations, which are determined not only by emissions, but also by import from other regions.) It seems that in all regions production of NO_x by emissions and loss by chemistry are in balance within 15%, the remainder accounted for by dry deposition. Only in Western Europe is net export an important term in the budget of NO_x. About 15% of the NO_x emitted is transported out of the region.

Due to its much longer lifetime transport is an important term in the budget of CO, whereas chemical decay is less important than it is for NO_x. About 40% of the CO emitted in Europe is transported out of the European domain.

The current version of the LOTOS model does not describe the deposition of PAN, which is estimated to be about 0.2-0.3 cm s^{-1}. (This omission should be fixed in future versions.) Therefore the budget of PAN is a very simple one. The PAN produced by chemistry is almost in balance with the net export of PAN. It is remarkable that the intensity of the PAN production in Western Europe is even more pronounced than that of the ozone production. Covering 6% of the European area it produces about 40% of the total European PAN.

The ozone production in Europe is about twice as large as in the U.S. (Jacob *et al.*, 1993) (Table 7.6). The area of the American model domain is 14.10^6 km^2, somewhat smaller than the LOTOS model domain. However, the domain in the Jacob *et al.*, (1993) model contains a considerable amount of sea surface (about 4.10^6 km^2), much more than the sea surface in the LOTOS domain. Therefore the intensity of ozone production per unit land area in Europe is only slightly larger than in the U.S. Compared with the calculated ozone production rates in the 35°-65° NH (0-2 km) zonal belt it means that Europe contributes about one-third to the net chemical production of ozone in the lowest 2 km of the northern mid-latitudes.

Table 7.6 Budgets of ozone (oxidant), NO_x and CO; NO_x in NO_2 equations

	Europe	U.S. [1]	2D model [2]	2D model
	35.5-69N; 09W-58E; 0-2 km; July-Aug.	24-48N; 128W-68W; 0-2.6 km; June-Aug.	35-55N; 0-360; 0-2 km; June	25-85N; 0-360; 0-2 km; June
Area (10^6 km^2)	16.7	14	63	146
Ox (Tg $month^{-1}$)				
emissions	0.1	small	0.1	0.2
chemistry	21.3	9.2	45.1	83.3
dry depos.	-16.8	-7.5	-39.6	-76.1
wet depos.	- 0.0	-0.0	-	-
net trans.	- 4.2	-3.0 (?)	- 5.5	- 6.0
NOx (Gg $month^{-1}$)				
emissions	1742	1550	3140	5207
chemistry	-1526		-1730	-3315
dry depos.	- 235		- 640	-1108
wet depos.	- 0		- 80	- 135
net trans.	- 81	- 100	- 720	- 689
CO (Tg $month^{-1}$)				
emissions	7.8		25.2	45.7
chemistry	-4.0		- 4.8	-12.6
dry depos.	-0.0		- 0.0	- 0.0
wet depos.	-0.0		- 0.0	- 0.0
net trans.	-3.0		-21.6	-35.0

[1] From: Jacob *et al.*, 1993.

[2] Based on global 2D TNO-Isaksen model; NO_y without HNO_3 is used.

The ozone production (net) efficiency is usually defined as the molecules of ozone chemically produced per molecule NO_x oxidised (Liu *et al.*, 1987; Lin *et al.*, 1988). It turns out that the ozone production efficiency in relatively unpolluted and NO_x -poor areas is higher than in NO_x-rich areas such as Western Europe or the eastern U.S. (Table 7.7).

Table 7.7 Ozone production efficiency; the number of O_3 molecules produced per molecule of NO_x oxidised

Region	Ozone production efficiency
Europe North	17.0
Europe West	6.9
Europe South	14.8
Europe	13.4
U.S. East (Jacob *et al.*, 1993)	4.4
U.S. West (Jacob *et al.*, 1993)	12.4
U.S. (Jacob *et al.*, 1993)	6.3
2D model 35-55N	26.0
2D model 25-85N	24.1

The ozone production rate in Western Europe is much higher than in Northern or Southern Europe due to the much higher NO_x concentrations in Western Europe. The **ozone production efficiency** decreases when NO_x concentrations exceed 100 ppt. However, the **ozone production rate**, which is proportional to the product of ozone production efficiency and NO_x concentrations still increases with increasing NO_x concentrations at least to NO_x concentrations of approximately 4-5 ppb.

7.4 Modelled exceedances

The excess O_3 parameter was addressed in section 7.2.2 in the evaluation of measured data. From measurements it becomes clear if and how much excess ozone occurs during a year. Abatement strategies are directed to formulate reduction scenarios of the emissions of ozone precursors, in order to attain the UN-ECE guideline. Since the effectiveness of such reduction scenarios cannot be derived from the observations, models are used to obtain an idea of what is necessary.

However, models give only a rough description of the presumably most important processes in the atmosphere. The ability of models to reproduce the observations (assuming representative observations) is limited to within a band of uncertainty of about 20 ppb. The model intercomparison also showed that different models produce different results and that discrepancies between modelled ozone concentrations may easily be as large as 20 ppb. If, for instance, model 1 produces for one reason or another systematically higher ozone concentrations of 10 ppb than model 2, the excess ozone (based on the threshold level of 40 ppb) calculated with model 1 may be considerably higher than the excess ozone according to model 2. Especially when the growing-season averaged ozone in model 1 is just above 40 ppb, and in model 2 just below 40 ppb, enormous differences in excess ozone between the two models may arise. Theoretically it is possible for model 1 to calculate a certain amount of excess ozone for one year, while model 2 calculates no excess ozone.

From this finding it follows that using just one model to study the required emission reductions can be very deceptive. In the last example no emission reduction is necessary according to model 2, whereas, according to model 1, some reduction action does have to be implemented.

A better strategy would be to use the model results relatively. The intercomparison study but also many other studies have shown that most models are very consistent in terms of calculating the relative (in percentages) reduction of ozone concentrations due to changes in emissions. The relative change of the ozone concentrations as a result of, for instance, a 50% reduction of NO_x emissions is nearly the same in model 1 as in model 2. Two options are possible which both have pros and cons:

1. Assessing from the observations how much relative ozone reduction is required to meet the UN-ECE guideline. This is followed by the use of the model to analyse which emission reduction is the most effective to achieve the anticipated ozone reduction.
2. Constructing a model-oriented ozone-excess threshold level such that the excess ozone calculated with a particular model equals the excess ozone based on the measurements. The model can then be used to calculate the measures necessary to bring the calculated ozone concentrations below the model-oriented threshold level.

8 OZONE IN EUROPE IN RELATION TO THE GLOBAL ATMOSPHERE

Species emitted in Europe not only affect the chemistry in the European troposphere but also have an effect on the composition of the global atmosphere. The past several studies have addressed the question of the influence of European emissions on the global and European troposphere. Concentrations of ozone and oxidant at ground level in the Netherlands and background concentrations were calculated using a combination of the global TNO-Isaksen model and the MPA European trajectory model (Slooff *et al.*, 1987). Sensitivity runs with respect to emission changes were performed to assess the influence of European emission on ground-level ozone concentrations in the Netherlands.

The effect of halving and doubling the European NO_x emissions was studied by means of the two-dimensional TNO-Isaksen model (Roemer, 1991; Roemer and Van den Hout, 1988, 1992). Table 8.1 presents results obtained by the 2D model for the base run and the 50% reduction run.

The table shows that Europe contributes about 40% to the total NO_x emissions in the 35°-55° NH zonal belt. A 50% reduction means a reduction by about 20% averaged over this zonal belt, which is reflected in the change in NO_x concentrations at the lowest grid cell. In the summer the reduction in NO_x concentration is somewhat lower than 20% due to the effect of chemical reaction. Due to the reduction in NO_x concentrations less HO_2 is converted into OH and the concentrations of the OH radical decreases. As a result of this, the concentrations of species like CO and NMVOC increase slightly.

The effect on ozone is relatively small, with a reduction of 5% in the summer (June) and 2% in the winter (December). At higher altitudes the effect of a ground-level European NO_x emission reduction becomes smaller. This finding is in agreement with previous studies (Roemer and Van den Hout, 1989; de Leeuw *et al.*, 1990).

The global effects of an increase of emissions in Europe was studied with the global three-dimensional Moguntia model via the so-called *European Renaissance* (ER) scenario (The and Beck, 1995). This scenario was developed to study the global economic developments. According to this scenario the developments in Europe will show new impetus and the United States, initially lagging behind, gradually recovers after 2005. The scenario assumes an increase in anthropogenic CH_4 and NO_x emissions of 1.3% and 2.6% per year, respectively. We note that the specific global effects of emissions in Europe cannot be isolated from this study since increases in emissions elsewhere are modelled as well. However, the results give some indication of the impact of 'worst-case' increasing emissions in Europe.

The results indicate an increase in the tropospheric burden of CH_4 of 19.3% in 25 years. The increase in CH_4 emissions throughout the same period is slightly less: 18.6%. The fact that the concentrations are growing more rapidly than the emissions is caused by feedback between CH_4 and hydroxyl. The modelled increase in tropospheric ozone is largest in the middle and upper troposphere in the northern hemisphere, with a maximum up to 20% on average. About 30% of this increase can be attributed to the effect of CH_4.

Table 8.1 Effect of 50% European NO_x emission reduction at 50° NH; concentrations in ppb, OH in mol cm^{-3}, ozone production in Tg m^{-1};

Height	0.25 km	0.25 km	3.25 km	3.25 km
	Base run	-50% E_{nox}	Base run	-50% E_{nox}
June				
O_3	43.7	- 5 %	51.7	- 4 %
O_3 prod.	45.1	- 6 %	- 0.9	-23 %
NO_x	0.67	-16 %	0.04	- 5 %
NO_y	1.28	-13 %	0.36	- 6 %
PAN	0.59	- 8 %	0.34	- 6 %
OH	1.77E06	- 8 %	1.11E06	- 6 %
CO	148.	+ 2 %	96.	+ 2 %
December				
O_3	24.0	- 2 %	40.8	- 2 %
O_3 prod.	21.1	- 4 %	6.5	- 6 %
NO_x	1.66	-20 %	0.27	-16 %
NO_y	2.12	-18 %	0.62	-11 %
PAN	0.43	- 8 %	0.32	- 7 %
OH	0.27E06	- 8 %	0.16E06	- 6 %
CO	202.	+ 1 %	149.	+ 1 %

9 CONCLUSIONS

The current set of variables measured at the Dutch TOR site Kollumerwaard consists of O_3, NO, NO_2, CO, CO_2, CH_4, PAN, speciated NMVOCs, J(NO_2) and meteorological parameters. The location of the site, on the North Sea coast, and its package of measurements provide an important facility for the study of tropospheric issues, as posed in the TOR project proposal. The international TOR network enables high quality scientific work on the photo-oxidant problem in Europe. Furthermore, it is expected to be 'the condensation nucleus' for the monitoring of air pollution on a Pan-European scale during the next century and an important source of information for policy-oriented work e.g. the evaluation of abatement strategies.

The TOR database, hosted by RIVM, Bilthoven is a strategic source of information both for the TOR participants but also for workers on other aspects of air pollution. The TOR data set is available via the World Wide Web (http://torwww.rivm.nl:8000).

The Kollumerwaard data set indicates that the free tropospheric background value of O_3 is 25 - 29 ppb in winter and about 35 ppb in summer. The summertime internal European production of O_3 in air advected to the observatory is about 3 ppb. The continent acts as an O_3 sink in winter due to dry deposition and titration of O_3 with emissions of NO. The contribution of European NO_x emissions to the NO_x climatology at the site is substantial. The NMVOC measurements indicate that the site acts as a relatively clean site for long-lived components (e.g. ethane), but they reveal polluted 'fingerprints' from shorter lived components from local emissions of particularly traffic (e.g. acetylene, benzene).

Table 9.1 reveals the climatology of several components at the site.

For the 1980s a statistically significant downward trend in the annual average ozone and oxidant concentrations of about -1% per year are found at the Kollumerwaard / Kloosterburen stations. This change is possibly related to changes in emissions of ozone precursors. However, the decrease in emissions of NMVOC and CO and the small decline of NO_x emissions, as reported in emission inventories, can't be considered responsible for the downward trend observed. The Dutch Moerdijk data set (10 years of NMVOC data) indicates a downward trend of -30% in acetylene concentrations over the period 1981-1991. Other factors as possible changes in the circulation over Europe need to be addressed.

Table 9.1 Concentrations (in ppb) of O_3, NO_2, SO_2, PAN (1993 data), CO, CO_2, CH_4, ethane and acetylene, averaged yearly and for summer and winter, at Kollumerwaard (1994 data).

Component	Year	Winter (Dec, Jan, Feb)	Summer (Jun, Jul, Aug)
O_3	22	17	26
NO_2	8	11	3
SO_2	2	2	1
CO	260	280	230
CO_2	372×10^3	373×10^3	371×10^3
CH_4	1980	1990	1980
PAN	0.47	0.27	0.48
ethane	1.9	2.2	1.4
acetylene	0.8	1.3	0.4

The NMVOC pattern over Europe, as derived from all TOR data, shows a concentration maximum over the Netherlands, Belgium and the south of the United Kingdom. A second maximum during winter is found over the eastern part of Germany, the western part of Poland and the Czech Republic. This spatial pattern is in agreement with the pattern in emission inventories. However, the speciation of NMVOCs and their concentration ratios are not entirely consistent with what emission inventories and models suggest.

In summer the general European spatial pattern of the average diurnal maximum ozone concentration shows a gradient with lower values (30 - 40 ppb) in the northwestern part and higher concentrations (60 - 70 ppb) towards the southeastern part of the TOR network. In winter a decreasing gradient is exhibited from the northwest to the southeast. An estimate of the European internal production and destruction of ozone led to a summer mean internal production of 10 - 15 ppb in some areas in central Europe, while during winter an ozone sink was found.

The current UN-ECE critical level (40 ppb) for the prevention of vegetation damage has been exceeded regularly over the whole of Europe; the O_3 exposure limit of 5,300 ppb.h (product of the residual ozone concentration above a threshold (40 ppb) value and exposure duration in the daylight hours of the months May, June and July) was exceeded at nearly all monitoring sites. Concentrations above 10,000 ppb.h were calculated for several sites in central Europe.

Modelled simulations of the European boundary layer ozone budget indicate that during summer the net chemical production of O_3 is high. A net chemical production of ozone over the entire European area (Iceland excluded) and in the lowest 2 km of the troposphere of about 21 Tg ozone per month in the summer (July-August) was calculated. In central Europe, this led to an increase in the O_3 concentration of 10 ppb relative to the Atlantic background modelled. A comparison of this result to the estimate of 10-15 ppb derived from data-analysis shows that the agreement between the two methods is reasonable. Most of the ozone is lost by dry deposition (17 Tg per month). Net transport out of Europe accounts for about 4 Tg per month. During episodic conditions the loss of O_3 by dry deposition accounts for less than half of the O_3 produced chemically.

The intensity of the (net) chemical production of ozone (oxidant) is highest in Western Europe. Covering only 6% of the European area it is responsible for almost 13% of the net chemical production of ozone. Consequently, also the contribution of dry deposition and net transport out of the domain is disproportionally higher. If scaled per unit area the intensity of the chemical ozone production in Northern and Southern Europe is about 30% and 60%, respectively, of that in Western Europe. In all regions loss by dry deposition is the most important sink to ozone. In winter, the situation is reversed: the amount of O_3 lost by dry deposition exceeds the chemically produced O_3, and consequently, there is a net import of O_3 from elsewhere.

Emissions from Europe also contribute to O_3 formation elsewhere by a net transport of precursors. In summer the net transport of NO_x out of Europe is about 10% of the NO_x emitted; 5% in the form of NO_x and 5% as PAN. About 40% of emissions of longer lived species, like CO, is transported out of the European model domain.

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APPENDIX A

TOR / EMEP STATIONS

no.	Site name	degr. N	degr. E or W
2	Birkenes (N)	58 23 00	08 15 00
3	Utö Island (SF)	59 47 00	21 23 00
4	Areskutan (S)	63 26 00	13 06 00
5	Rörvik (S)	57 23 00	11 55 00
7	West-Beckham (GB)	52 40 00	01 20 00
8	Mace Head (IR)	53 19 34	-09 54 14
9	Kollumerwaard (NL)	53 20 02	06 16 38
10	Brennilis (F)	48 21 19	-03 52 12
11	Schauinsland (D)	47 54 00	07 48 00
14	Pic du Midi (F)	42 56 00	00 09 00
15	K-puszta (H)	46 58 00	19 33 00
16	Zagreb-RBI (CR)	45 48 43	15 58 52
17	Izaña (E)	28 17 55	-16 29 25
19	Aspvreten (S)	58 48 00	17 23 00
20	Tour du Donon (F)	48 30 05	07 08 29
21	Wank (D)	47 40 00	11 09 00
22	Zugspitze (D)	47 25 00	10 59 00
23	Ukkel (B)	50 47 55	04 21 29
24	Jülich (D)	50 54 41	06 24 35
25	OHP (F)	43 55 09	05 42 08
27	Zeppelinfjellet (N)	78 54 00	11 53 00
51	Puntijarka (CR)	45 48 44	15 58 53
211	Sion (CH)	46 13 00	07 20 00
212	Payerne (CH)	46 49 00	06 57 00
213	Tänikon (CH)	47 29 00	08 54 00
223	Schauinsland (D)	47 54 00	07 48 00
241	Ulborg (DK)	56 17 00	08 26 00
242	Frederiksborg (DK)	55 58 00	12 20 00
261	Birkenes (N)	58 23 00	08 15 00
264	Brestebakke (N)	59 00 00	11 32 00
265	Svanvik (N)	69 27 00	30 02 00
267	Nordmoen (N)	60 16 00	11 06 00
268	Kaarvatn (N)	62 47 00	08 53 00
269	Jeloya (N)	59 26 00	10 36 00

270 Jergul (N)	69 27 00	24 36 00
272 Osen (N)	61 15 00	11 47 00
273 Tustervatn (N)	65 50 00	13 55 00
274 Voss (N)	60 36 00	06 32 00
275 Valle (N)	59 03 00	07 34 00
291 Ahtari (SF)	62 33 00	24 13 00
292 Utö Island (SF)	59 47 00	21 23 00
293 Virolahti (SF)	60 31 00	27 41 00
294 Oulanka (SF)	66 19 00	29 25 00
301 Norra Kvill (S)	57 49 00	15 34 00
302 Rörvik (S)	57 23 00	11 55 00
303 Vavihill (S)	56 01 00	13 09 00
304 Vindeln (S)	64 15 00	19 46 00
305 Aspvreten (S)	58 48 00	17 23 00
311 Aston Hill (GB)	52 30 00	-03 20 00
312 Bottesford (GB)	52 56 00	-00 49 00
313 Bush (GB)	55 52 00	-03 12 00
314 Central London (GB)	51 29 00	-00 08 00
315 Eskdalemuir (GB)	55 19 00	-03 12 00
316 Great Dun Fell (GB)	54 41 00	-02 27 00
317 Glazebury (GB)	53 28 00	-02 28 00
318 Harwell (GB)	51 34 00	-01 19 00
319 High Muffles (GB)	54 20 00	-00 48 00
320 Ladybower (GB)	53 20 00	-01 45 00
321 Lullington Heath (GB)	50 47 00	00 11 00
322 Lough Navar (GB)	54 27 00	-07 54 00
323 Mace Head (GB)	53 19 34	-09 54 14
324 Sibton (GB)	52 18 00	01 28 00
325 Stevenage (GB)	51 53 02	-00 12 09
326 Strath Vaich (GB)	57 44 00	-04 47 00
327 Wharley Croft (GB)	54 37 00	-02 28 00
328 Yarner Wood (GB)	50 36 00	-03 42 00
343 Brennilis (GB)	48 21 19	-03 52 12
345 Kosetice (P)	49 35 00	15 05 00
346 Rucava (LIT)	56 13 00	21 13 00
351 Illmitz (A)	54 21 00	48 56 00
352 Koloman (A)	54 20 00	47 26 00

APPENDIX B

TECHNICAL DESCRIPTION OF THE KOLLUMERWAARD MEASUREMENT STATION

In Kollumerwaard ambient air measurements of several components are performed. Table B.1 shows an overview of the components measured at TOR site Kollumerwaard along with the method used, the time basis on which the measurements are performed and by which institute. In addition RIVM and KEMA performed measurements of several meteorological parameters.

Table B.1 Components measured at Kollumerwaard

component	measurement method	measurement frequency	institute
O_3	CRANOX system	continuously	RIVM
NO	CRANOX system	continuously	RIVM
NO_2	CRANOX system	continuously	RIVM
PAN	gaschromatograph (ECD)	1x/2 hours	TNO
NMVOC	gaschromatograph VOC-AIR	1x/15 minutes	TNO
$J(NO_2)$	$J(NO_2)$ Radiometer	1x/15 minutes	TNO
CO	gaschromatograph (FID)	1x/15 minutes	KEMA
CO_2	gaschromatograph (FID)	1x/15 minutes	KEMA
CH_4	gaschromatograph (FID)	1x/15 minutes	KEMA
wind speed	cup anemometer	1x/5 seconds	RIVM/KEMA
wind direction	weather vane	1x/5 seconds	RIVM/KEMA
aerosols	MVS-LVS	phys. properties 1x/ minute chem. composition 1x/ day	RIVM
wet deposition	Van Essen, wet only type ECN	1x/ day	RIVM
chemical composition		1x/ day	
air pressure	vacuum membrane	1x/5 seconds	KEMA
temperature	PT-100 sensor	1x/5 seconds	KEMA
rel. humidity	solid state sensor	1x/5 seconds	KEMA
global radiation	pyranometer	1x/5 seconds	KEMA

In the next sections the technical details of the performed measurements are given.

B.1 Sampling

Sampling for NO, NO_2 and O_3 is performed via an EPA certified Andersen, type 246B, sampling tube (47 mm i.d. flowrate 100 l/minute, residence time 1 s).

PAN, NMVOC, CH_4, CO and CO_2 are measured in the new measuring accommodation. Sampling takes place using a stainless steel sampling line. The main specifications of the sampling line are summarized below:

- Sampling inlet height: 8.6 m above ground level;
- Inside diameter: 47.8 mm;
- Material of the sampling line: Stainless steel 316;
- The inside surface has been electro-polished;
- The pipes are coupled with Swagelok connections; all connections are weldless;
- Flow: 12 l s^{-1} (turbulent flow: Reynolds number 22,000);
- Distance between inlet and sampling devices: 7.5 m;
- Sample velocity in the sampling line: 6.7 m s^{-1};
- Residence time: 1.1 second.

The samples for the measurement of the different components are taken from the continuous flow of ambient air through the sampling line.

B.2 Measurement specifications

B.2.1 Measurement of nitrogen monoxide, nitrogen dioxide and ozone

Method

For the measurement of oxides of nitrogen and ozone a CRANOX system is used. This system consists of:

- Two identical NO analyzers;
- A photolytic converter in series with one of the NO analyzers;
- An O_3 analyzer;
- A calibration unit;
- A clean air supply;
- An automatic air drying unit.

All components are placed in a temperature controlled housing. The vacuum pumps for the analyzers and a compressor for the clean air supply are placed separately. An external microprocessor controls the calibration unit and the individual instruments. Data acquisition and validation and calculation of the concentrations is also done by the microprocessor.

Equipment used

NO analyzer: NO is measured using a chemiluminescent reaction of NO with O_3 in a reaction chamber, the signal is integrated during a selected period. Zero measurement is performed by reaction of O_3 and interfering components in a pre-reaction chamber and after that measured in the

	reaction chamber. The difference between the two signals equals the NO concentration.
NO_2 analyzer	NO_2 is measured by photolytic conversion to NO, followed by NO analysis with an identical NO analyzer as described above. Photolytic dissociation of NO_2 to NO takes place at a wavelength of 320 - 420 nm (resulting in NO_c). NO and NO_c are measured simultaneously. The difference between the two equals the NO_2 concentration (after correction for the ozone concentration).
O_3-analysis:	O_3 is measured by the absorbance of UV light (254 nm) in the measuring cell. This is compared to reference measurements with ozone-free air (scrubber) in the same cell. The ozone concentration is calculated from the Lambert-Beer law.
Calibrator:	Microprocessor controlled mass-flow controllers with dilution ratio (practically) between 85 and 950 for diluting NO-calibration mixtures in cylinders (calibration of NO system). A built-in O_3 source is used to convert the NO partly (by gas phase titration) to NO_2 (calibration of NO_2 system). This source is also used for checking the O_3 analyzer. The required zero air is produced by the clean air system.
Clean air:	Air from a diaphragm compressor is filtered and fed to an ozonator and scrubbers. This clean air is then cooled to remove water vapour.
Drying unit:	The drying unit for the air for the ozonators of the NO analyzers consists of two columns, filled with silica gel. When one column is in use, the other column will be regenerated by heating and flushing.

Sampling

Air is sampled from a central air sampling system (47 mm i.d. flowrate 100 l/minute, residence time 1 s). The Cranox air sample is drawn from this system through a 6.35 x 4.35 mm FEP tubing (total length = 5 m) and an additional PFA inline filter (Galtek type 411-4) with a glassfiber filter element (Whatman GF/C). The total volume of the sample line and filter is about 125 ml. The sampled volume flow is about 6.5 l/minute, so the residence time is less than 1.2 s. The total residence time is less than 2.2 s.

Sampling frequency

The sampling frequency is continuous.

Main system performance

- Lower detectable limit:	< 0.05 ppb (30 s integration time)	
	< 0.015 ppb (600 s integration time)	
- Measuring range:	0.005 to 500 ppb (in 5 steps)	
- Precision:	< 0.5%	
- Interferences:	NH_3 < 1 % (NO_2 equivalent)	
	SO_2 < l.d.l	
	H_2O < 8 % / % H_2O (abs.)	
- Interferences of the NO_2 converter:	HNO_3 (similar concs as NO_2)	< 0.1% (NO_2)
	NO_3 "	< 1%
	N_2O_5 "	< 1%
	HO_2NO_2 "	< 1%
	$ClONO_2$ "	< 1%
	PAN "	< 1%
	HONO "	< 20%
- Analysis time:	At the observatory a 60 s integration time is used. Therefore every 122 s new measured and computed values are produced.	

B.2.2 Measurements of methane, carbon dioxide and carbon monoxide

Method

Concentration measurements of the trace gases CH_4, CO_2 and CO in ambient air are performed continuously at 15 minute intervals. Using the multi-component capabilities of gaschromatography (GC) as an analytical technique, three real time comparable time-series of concentrations are produced.

A Chrompack CP 9000 GC is operated with three columns in series, packed with HayeSep (1 and 2) and Molsieve (3) respectively. Following sample injection, backflush and heart-cut techniques are performed using two 10 port switching valves. After separation, components are led to a hydrogen-fed Ni catalyst (methanizer) where CO_2 and CO are converted to CH_4. Final detection is done by means of a flame ionisation detector (FID).

Separation of a composite peak (containing N_2, O_2, CO, CH_4, CO_2 and any available higher hydrocarbons) is achieved on the first HayeSep column. When the CO_2

peak has passed the splitting point between first and second HayeSep columns, the first 10-port valve is switched to backflush, thus leading any available Non Methane HydroCarbon (NMHC) to the FID (the backflush channel has its own detector). Further separation of composite peak and CO_2 is achieved on the second HayeSep column and carrier gas flow is directed on to the Molsieve column. The outlet of the Molsieve column is vented to ambient air to prevent oxygen from entering the methanizer and thus disturbing its performance. The second 10-port valve is switched before the CO_2 peak arrives, bypassing the Molsieve column where CO_2 would be permanently retained and led through the methanizer to the FID. CO and CH_4 enter the Molsieve column and are led through the methanizer to the FID. Total separation time is 14 minutes, but from a practical point of view the total run time is set to 15 minutes, thus providing four measurements each hour.

Equipment used

- Columns: Two columns each 1.5 metre 1/8 inch filled with HayeSep C 80-100 mesh and one 1.9 metre 1/8 inch filled with Molsieve 13 × 80-100 mesh. Operation isothermal 50°C.
- Detection: Flame ionisation detection on both frontflush and backflush channels. Detector temperature 200°C. The front flush channel for CO, CH_4 and CO_2 contains a methanizer (Ni-catalyst) operated at 375°C to convert both CO and CO_2 to CH_4 prior to detection.
- System gases:
  - Carrier: N_2 from bottles, Air Products quality 5.0
  - FID supply: H_2 produced by Packard Hydrogen generator
  - FID supply: Air, compressed ambient air from Chrompack Air generator.
- Valves: Two pressure actuated 10-port Valco valves (1/16 inch ports) for sample injection and column switching. Fixed sample loop 1 cm^3, all lines 1/16 inch stainless steel).

Sampling

From the 2-inch sample stack air is led through 1/4 inch SS tubing at a flow rate of 5 l min^{-1} using a critical orifice and a vacuum pump to a dual permapure dryer system. The dryers (PermaPure type MD-125-12S) have an outside diameter of 1/8 inch and are operated at flow rates of 50 ml min^{-1} for both sample and purge lines. Air flows are created by a applying pressure drop over stainless steel capillaries. To prevent capillaries from clogging, sample and purge flows are filtered through 2 μm SS filters (Nupro). The dew point is decreased to far less than -25°C depending on air moisture content. Dried air is drawn permanently at a flow rate of 10 ml min^{-1} through the internal piping (1/16 inch

SS) of the GC to the injection valve. Shortly before the final injection of 1 ml air the sample flow is cut off to equilibrate sample pressure to ambient pressure level.

Sampling frequency
The sampling frequency is once every 15 minutes.

Main system performance

- Lower detectable limit:	CO:	0.05	ppm
	CO_2:	5	ppm
	CH_4:	0.05	ppm
- Measuring range:	CO:	0.05 - 1.5	ppm
	CO_2:	5 - 800	ppm
	CH_4:	0.05 - 15	ppm
- Precision (std.dev.):	CO:	0.01	ppm
	CO_2:	1.8	ppm
	CH_4:	0.01	ppm
- Analysis time:	CO:	15	minutes
	CO_2:	15	minutes
	CH_4:	15	minutes
- Interferences:	none		

B.2.3 Measurement of non-methane hydrocarbons (C_2 - C_9)

Method
The non-methane hydrocarbon measurements are measured with a commercially available gaschromatograph VOC-AIR (Chrompack International, Middelburg, The Netherlands). The gaschromatograph contains an Al_2O_3 plot column and flame ionization detection (FID). Sampling takes place by cooled (-20°C) adsorption on Carbotrap adsorbent and subsequent temperature-programmed analysis of 30 - 40 hydrocarbons (C_2 – C_9 aliphatic, aromatic and halogenated hydrocarbons). Higher boiling compounds are backflushed.

The instrument was purchased in spring 1992. Before unattended operation at TOR station 9 (Kollumerwaard, Netherlands) the method has been tested and evaluated in the laboratory in Delft. Before the method became commercially available the method has been tested successfully during one year (1989-1990) by RIVM.

In principle, it is possible to measure halocarbons with the same equipment. By means of an inlet splitter-part of the sample can be analyzed on halocarbons on a cpsil-13 cb column with electron capture detection (ECD). Due to technical problems with the ECD and complications with the standard hydrocarbon measurements halocarbon measurements have not been performed yet.

Equipment used

- Gaschromatograph: The gaschromatograph is a Chrompack model CP 9000 gaschromatograph with auto-TCT for sample concentration.
- Carrier gas: Nitrogen.
- Injection: After sampling the sample is thermally desorbed and preconcentrated on a cold spot followed by injection via flash heating.
- Column: The column is a 25-m capillary 0.32 mm Al_2O_3/KCl plot column.
- Detection: Detection of the hydrocarbons takes place using a flame ionization detection (FID).

Sampling

Sampling takes place by trapping 550 ml sample at - 20°C during 54 minutes (flow about 10 ml/min) on a three-layered carbon trap; 1: Carbosieve;
2: Carbotrap;
3: Carbotrap C.

Sampling frequency

Once every two hours. The measurements started in 1993 on an hourly basis. In 1994 the measurements continued on a two hourly basis.

Main system performance

- Lower detectable limit: 0.01 - 0.1 μg m^{-3} (depending on the compound measured);
- Measuring range: 0.03 μg m^{-3} (depending on the compound measured) - mg m^{-3} level (estimated);
- Precision: 1 - 5 % (depending on the concentration level);
- Analysis time: 45 minutes;
- Interferences: none.

B.2.4 Measurement of peroxyacetylnitrate

Method

Peroxyacetylnitrate (PAN) is measured using a gaschromatographic method with electron capture detection (ECD). The GC is a Packard model 437 A gaschromatograph with pneumatically activated gas sampling rotating valve.

The method is the same as used in the STEP-EC PAN project of contract DG XII nr. EV4V-CT90-0222 with NILU (Norway) as project coordinator. In this EC-PAN project the gas chromatographic PAN method and the calibration procedures were tested and evaluated. The method was described in detail in Hollander (1991).

Equipment used

- Column:	The column has a length of 0.30 m and a diameter of ¼ inch. The column is made of an o.d. stainless steel tube packed with Chromosorb G-AW-DMCS, 80/100 mesh coated with diglycerol (0.15%) and QF-1 (5%). The column temperature is 36°C. Nitrogen make-up gas is used to diminish dead volume effects.
- Carrier gas:	Nitrogen from Air Products (5.0 quality) is used as a carrier gas. The carrier gas is moistened by leading it through a cartridge containing hydrated copper sulphate. Because the TOR station is temperature controlled (± 2°C) temperature does not effect the function of the cartridge.
- Detection:	Detection of PAN takes place using an Electron Capture Detector (ECD)> The ECD contains a ^{63}Ni source, of 10 mCi operated at 100°C.

Sampling

The sampling system consists of a 1.5-ml sample loop with a pneumatically operated valve. All connections to and from the valve are stainless steel. The sampling inlet line includes a fine (stainless steel) particle filter. The valve is maintained at a temperature of 35°C to prevent water condensation from the sample.

Because the ECD is very sensitive to minor amounts of oxygen, the sampling valve is shielded with a box, which is purged with nitrogen to minimize diffusion of oxygen from ambient air.

Sampling frequency

The sampling frequency is once every 15 minutes.

Main system performance

- Lower detectable limit:	0.02 ppb
- Measuring range:	0.02 - 20 ppb
- Precision:	About 10 % on the basis of the international intercalibration project of STEP/NILU/TNO a.o.
- Drift:	< 1 % for concentrations > 1 ppb < 7 % for concentrations 0.02 - 1 ppb.
- Analysis time:	5 minutes
- Interferences:	none

B.2.5 Measurement of $J(NO_2)$

Method

The $J(NO_2)$ instrument determines the rate of the in-situ NO_2-photolysis in the atmosphere via a continuous measurement of the actinic flux in the appropriate wavelength. It is constructed as a 180-degree system and is designed to be mounted together to a 360-degree radiometer. The basic design is adopted from the device described by Perner *et al.* (1987). It was thus modified that the dependence of the signal on the angle of the incending light could be minimized by using a set of quartz diffusers. It is insensitive to atmospheric parameters and does not consist of any movable parts. The $J(NO_2)$ Radiometer was developed by Meteoconsult, Dr. R. Schmitt, Glashütten, Germany and is used by many TOR participants. The instrument measures 5 metres above the roof of the cabin, which is about 8 metres above ground level.

Equipment used

- Filters:	Schott UG 11 (band-pass); Schott WG 305 (high-pass);
Spectral response:	300 nm - 390 nm;
Transmissivity:	see figure adopted from A.Kochs, KFA;
- Detector:	HAMAMATSU R840;
Material:	SbCs;
Spectral response:	185 - 650 nm.

Sampling

Each second the signal is recorded by the computer system. An average signal of each 12-min (720 readings) measurements is calculated and stored by the HP/Nelson computer system at Kollumerwaard. The data are stored in a computer file at the site, which is taken to Delft when the site is visited for regular maintenance of the instrumentation.

Sampling frequency

The sampling frequency equals 4 measurements per hour. Each 15 minutes measurements are started for a period of 12 minutes.

Main system performance

- Transmissivity: > 99 %;
- Field of view: 2 * 180 degrees;
- Angular dependence:
  - < 80° zenith distance < ± 4 % (w.resp. to averaged signal from - 80° + 80°);
  - > 80° zenith distance < - 10 % (w.resp. to averaged signal from - 80° + 80°);
- Sensitivity: about 1.5 * 10^{-6} per sec/mV;
- Linearity: better than 2 % according to characteristics of the detector.

B.3 Quality assurance and quality control

B.3.1 Nitrogen oxide, nitrogen dioxide and ozone

Calibration

Calibration takes place automatically twice per 44 hours. At the end of every calibration procedure new calibration factors are determined for both NO analyzers. This is done by determining the instrument response for zero-air (from the zero-air generator) as well as for a known amount of NO calibration gas. The latter is produced by dilution of NO-gas from a bottle of zero-air.

Furthermore, calibration tests are carried out to check the performance of the photolytic converter and the O_3 analyzer. A check on the NO_2 contents of the NO calibration gas in the cylinder is performed as well.

Data Processing

All measured data are saved in a specific file per day. This file may contain:

a) every single measurement; time interval depends on selected integration time, and/or;

b) average values over a selected period of time (theoretically from 1 min to up to 24 h), and/or;

c) gliding average value over a selected period of time (theoretically from 1 min to up to 24 h).

Data acquisition is also possible at the laboratory in "remote control" mode.

B.3.2 Carbon monoxide, carbon dioxide and methane

Calibration

Calibration is integrated in a control routine of the long-term stability of the chromatographic system. Every three hours one of four standard gas mixtures, each containing CO, CH_4, and CO_2, is measured. The concentrations of the three components in the four standard mixtures cover a concentration range according to expected ambient concentration levels. This control routine produces daily two results for each of the four existing concentration levels per component. These results yield the response function for each component using first-order regression. Calculated slopes and intercepts are used to produce concentration values for ambient measurements for the respective day. Absolute concentration levels of the four different gas mixtures are verified twice per year using a comparison method with certified reference materials according to ISO 6143.

This calibration scheme is shown below:

- Every 3 hours:	Injection of standard gas mixture (CO, CH_4, and CO_2) to establish long-term stability and daily response functions.
- Daily:	Control of system operation by viewing status files in PC using modem communication from home lab (manual).
- Monthly:	Control and registration of system parameters (e.g.sample flows, vacuum pump performance, H_2 generator status, gas supplies for N_2 and air, detector base line levels, GC temperatures).
- Semi annually:	Validation of concentration levels of control and calibration gas mixtures using NIST reference materials (manual). Check of performance of Perma Pure Dryer system using Karl Fischer technique to determine absolute moisture content of incoming and outgoing air.
- Occasionally:	Participation in Round Robin tests for gas mixtures.

In addition all non-regular phenomena or specific events regarding performance of equipment, meteorological situation, visits of personnel are recorded in log-books.

Data Processing

Analog FID signals are processed using a two-channel Nelson intelligent interface (RS 232 version) and a commercial Nelson software package on a HP Vectra computer.

Concentrations are calculated by the Nelson software using peak height and regression function of daily performed calibrations. Validated and checked concentration values are corrected to standard ambient conditions p = 1013.25 mbar and T = 25°C according to WMO recommendations using locally measured meteorological information.

Dedicated customized software is linked to Nelson after each run, performing several functions:

- data control on retention times, overrange peaks and ratio of peak area for last and previous run;
- data reduction and storage (on hard disk) after acceptance of testing criteria;
- steering of injection of standard gas mixture at 3-h intervals;
- creating control files for remote check of system performance by modem communication;
- resetting the general system alarm.

Data are copied to floppy disk during station visits necessary for calibration and taken to home lab.

B.3.3 Non-methane hydrocarbons (C_2 - C_9)

Calibration

Three types of calibration are distinguished: daily, quarterly and yearly calibrations. The time span for quarterly and yearly calibrations is not very strict but depends on how the measurements proceed. The different types of calibration are discussed below.

- Daily:	A home-made 18 component reference mixture (2 - 5 ppb level) is used to check the quality of the chromatogram. In a later stage these measurements are used for peak identification in the chromatograms measured. These measurements are performed once every 23 hours to avoid any systematical deviations because of lack of data at a given time of day.
- Quarterly:	Calibration with n-butane/benzene mixture (NIST standard - 10 ppb level).
- Yearly:	If possible participation in international intercomparison programmes like EU/ISPRA, IGAC/NCAR or TOR is aimed at.

Data processing

The detection and integration of peaks is performed by Nelson integration software

(Nelson Xtra Chrom II) on a Hewlett Packard HP 9000/310 series computer. Conversion of peak areas to concentrations takes place via response factors per atom C based on an n-butane/benzene standard (NIST - 10 ppb level).

Identification of the peaks takes place on basis of retention time and comparison with a standard mixture of 18 compounds. The concentrations for the different compounds are collected as area tables.

The area tables are recorded on disk after integration on Nelson integration software. Monthly, the area tables are converted to concentrations using the daily calibration measurements for peak identification and the quarterly standard measurements for the absolute level of the hydrocarbons.

Daily, the performance of the VOC-AIR monitor is checked via a modem connection. In the case of any malfunctions it is possible to stop and restart the measurements by means of the modem connection. The data are backed up on a local tape streamer.

Quarterly, the data are checked for outliers and apparent faults. The data are stored in our own database and after conversion to the ISO format also sent to the central TOR database at RIVM.

B.3.4 Peroxyacetylnitrate

Calibration

Three types of calibration are distinguished: daily, quarterly and yearly. The time span for quarterly and yearly calibrations is not very strict but depends on how the measurements proceed. The different types of calibration are discussed below.

- Daily:	The response of the gaschromatograph is checked for drift with n-propylnitrate (about 1 ppb) from a calibration gas cylinder. These measurements are performed once every 23 hours to avoid any systematical deviations because of lack of data at any given time of day.
- Quarterly:	The system is calibrated with a freshly prepared gasphase PAN sample out of stock solution of PAN in octane certified by FTIR measurement.
- Yearly:	In the past years TNO-MW participated in a number of intercalibration programmes against reference standards of PAN, all within the framework of an EC sponsored project called PAN-STEP, organized by NILU.

Data processing

Quantification takes place by integration of the peak area of the PAN peak in the chromatogram by Nelson integration software (Nelson Xtra Chrom II) on a Hewlett Packard HP 9000/310 series computer. The response of the system is checked daily with the measurement of n-propylnitrate from a calibration gas cylinder. The data are transferred weekly through a modem connection to the laboratory and are also backed up on a local floppy disk. The data are checked quarterly for outliers and apparent faults and are then stored and converted to the ISO format and sent to the central TOR database at RIVM.

Because the PAN monitor shows some change in sensitivity over longer periods of time all measurements are corrected. All corrections are made on the basis of the daily n-propylnitrate measurements. The procedure that is followed by making the corrections consists of the following points:

- A trend in the change of sensitivity of the monitor is calculated from the daily propylnitrate measurements (this change might be an increase or a decrease in sensitivity). This is done with a typical time span of a few weeks.
- From the change in sensitivity over several weeks a daily change is calculated.
- This is used to calculate the response factor for PAN each day, which is then used to correct the measured PAN data.

In Figure B.1 a typical change in sensitivity is shown.

B.3.5 J(NO_2)

Calibration

The primary calibration of the instrument is performed by Forschungszentrum Jülich (KfA) ICH2. Every year the instrumentation is recalibrated by Meteoconsult in Germany.

Yearly calibrations (one week) by Meteoconsult and yearly calibration of master-radiometers of Meteoconsult with the KFA Jülich IGC2 absolute method, the primary calibration.

Data Processing

The calibration of the instrument is performed in such a way that the measured data need no further processing. The data are put into a computer file at the site directly. This file is taken to the laboratory in Delft every six months. The data are then converted to the ISO format and sent to the central TOR database at RIVM.

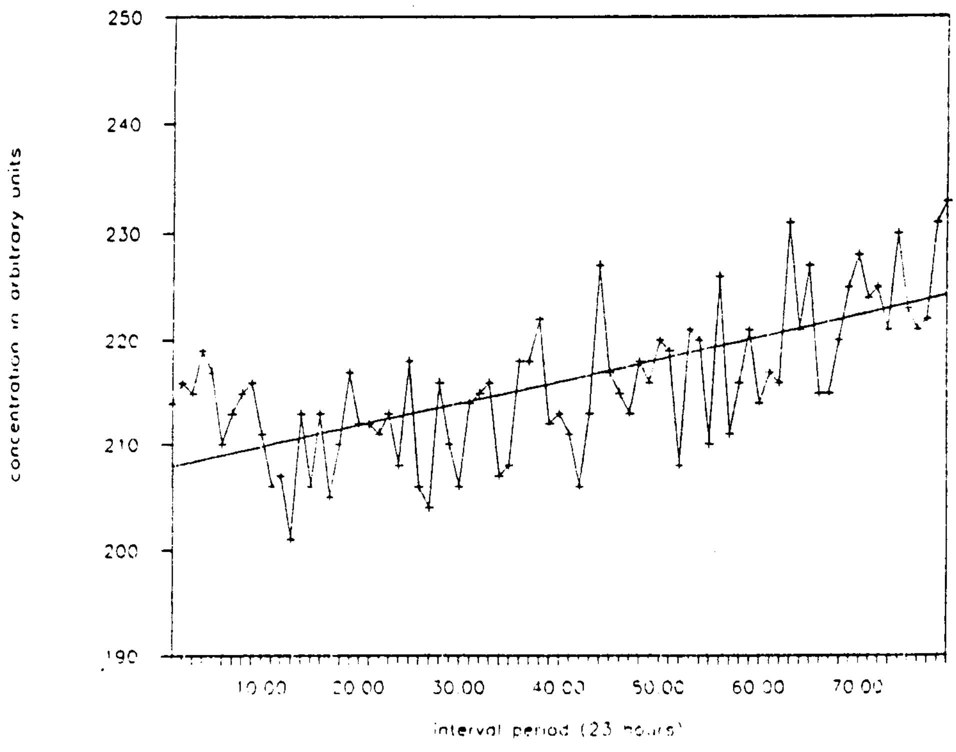

Figure B.1 Typical change of sensitivity of the PAN monitor.

B.4 Round Robin tests, procedures, experiments and results

B.4.1 Nitrogen oxide, nitrogen dioxide and ozone

A TOR O_3-intercalibration experiment took place in March 1993 at KFA, Jülich. RIVM participated with a standard LML network monitor. The result of this experiment, expressed as a correlation to the Standard Reference Photometer (SRP11) at ITM Air Pollution Laboratory, Studsvik, Sweden, was: RIVM = 0.983 * SRP11 + 0.3 ppb.

A NO-intercalibration experiment took place in January 1995 at KFA, Jülich, Germany. RIVM participated with a reference mixture, to be used to calibrate the NO cylinder at the Kollumerwaard observatory. The difference between both analyses was 0.1 ppm at a level of 30 ppm (0.3%).

B.4.2 Carbon monoxide, carbon dioxide and methane

KEMA participated in three intercomparison programmes for methane, one of these programmes was a combined programme for methane and carbon monoxide:

- The TOR Interlaboratory Comparison Experiment for methane and carbon monoxide, was organized by Jürgen Hahn, in April 1992. The results of this intercomparison programme were reported in a final report in March 1994 (Hahn, 1994). There were only a few participants in this intercalibration programme, nevertheless the results for methane showed that the relative deviations of the participants from the respective IFU reference values were found to range from + 0.66 to + 2.31 %. The results for carbon monoxide showed that the relative deviations of the participants from the respective IFU reference values were found to range from - 2.21 to + 2.38 %.
- A methane laboratory intercomparison programme in 1992 in cooperation with ECN, TNO and KEMA. This programme was performed within the framework of the Dutch National Research Programme on Global Air Pollution and Climate Change.
- A methane laboratory intercomparison programme in 1993 in cooperation with ECN, TNO, LUW and KEMA. This programme was performed within the framework of the Dutch National Research Programme on Global Air Pollution and Climate Change. From this exercise it could be concluded that interlaboratory variation of ambient methane (2.0 ppmv) is better than 2 % (R.S.D.). The within-laboratory variation varied from between 0.1 - 0.9 % (R.S.D.).

There was no participation in any carbon dioxide intercomparison programme.

B.4.3 Non-methane hydrocarbons (C_2 - C_9)

The quality of the hydrocarbon measurements has been tested by participation in several intercomparison programmes. In the period from October 1991 till December 1993 TNO has participated in three international intercomparison programmes concerning the analysis of volatile organic components.

The programmes that TNO participated in are:

- TOR intercomparison programme	1992;
- IGAC intercomparison programme	1991, 1992, 1993;
- EC-ISPRA intercomparison programme	1993.

All intercomparisons and the hydrocarbon measurements of ambient air (except for the first round of the IGAC programme) were referenced against a certified gravimetric NIST standard containing about 10 ppb of n-butane and benzene in nitrogen. This standard was acquired through the TOR programme in april 1992. Generally, the per ppbC sensitivity derived from the concentration of n-butane in the NIST standard was used to quantify the concentrations of all compounds in the gas mixtures analyzed. The results for the EC intercomparison were referenced against the concentration of propene in the gravimetric standard mixture supplied. The propene concentration in the mixture was given.

A cross-check was made between home-made laboratory standards based on the permeation and diffusion tubes and the NIST standard used as a reference. The results of this cross-check are shown in table B.2.

Before the different intercomparison programmes are discussed, it should be noted that some of the results in the first two intercomparison programmes were obtained with another GC system than that is used for the measurements on site. This is because the equipment that is used on site was not received at the moment these intercomparison programmes started.

Table B.2 Results of the analysis of the certified n-butane benzene mixture

number CLM-003805	n-butane ppb	sd ppb	n	benzene ppb	sd ppb	n
certified by NIST 27 Feb, 1992	10.27	n.a.		10.20	n.a.	
results TNO May 15, 1992	10.20	0.07	4	10.85	0.19	4

n.a. = not applicable

The system that was used to analyze these samples consisted of:

- Varian model 3400 gaschromatograph;
- 25 m 0.53 mm Al_2O_3 plot column with FID detection;
- Temperature programme: initial 30°C, 10°C per min up to 200°C;
- 200 ml air sample was led over a cooled pre-column to trap the hydrocarbons. The hydrocarbons were analyzed by heating the pre-column followed by cryofocusing on a cold spot at the beginning of the column.

The different intercomparison programmes are discussed separately in the following subsections, though it should be noted that several links exist between the different programmes mentioned above because of participation of institutes in more than one programme. Specifically, NCAR mentions the cross-check of NIST standards with those from NPL and IFU mentions their results within the IGAC programme.

TOR intercomparison programme for hydrocarbon measurements

The TOR programme, was coordinated by J.Hahn, FhG-IFU, Garmisch-Partenkirchen (Hahn, 1994). The intercomparison consisted of two rounds (May and October 1992) in which almost identical (from the same batch) compressed ambient air mixtures were offered for the analysis of the major C_2 - C_7 components at concentration levels ranging from well below 1 ppb up to a few ppb.

The analyses for TOR rounds 1 and 2 were carried out with a laboratory system based on a Varian 3400 gaschromatograph[8]. The second TOR round was then carried out parallel to the first one on the equipment used for the measurements on site which had become available (October 1992).

Results of the reference gas mixtures

A reference gas mixture with pressurized compressed ambient air was received for analysis. The Reference Gas Mixture prepared by Hahn consisted of 24 hydrocarbons and was contained in a Spectra-K gas cylinder (9-l volume) with cylinder no. 83212 SG. A BOC pressure regulator with special adapter CGA 350 was delivered too.

For most of the 19 compounds considered in this intercomparison programme the relative deviations of the various laboratories were in the range of - 35 to + 35 % of the respective reference values. Our results were well within this range. However, some significant differences were observed in comparing the results from the two rounds. For example: n-hexane shows a - 20 % deviation in the first round and a + 20 % deviation in the second; other examples of such divergence can also be found. From the results it appears that in our case particularly unsaturated compounds presented most difficulties in quantification.

In the second round there was a typical distinction between the lighter hydrocarbons with negative deviations from the reference values and the heavier ones with positive deviations.

IGAC intercomparison programme for NMVOC

International Global Atmospheric Chemistry (IGAC) programme, within the framework of the International Hydrocarbon Intercomparison Experiment, coordinated by E.C.Apel, NCAR, Boulder, Colorado. This intercomparison experiment consisted of three parts:

- N-butane/benzene mixture; October 1991

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[8] The results in the first two intercomparison programmes were obtained with a different GC system than the one that is used for the measurements on site later on. This is because the equipment used on site was not yet available when these intercomparison programmes started.

- 16-component reference mixture;	July 1992
- 62-component **non-certified** mixture.	December 1993

After each round the results were evaluated; when the results of a laboratory were within "satisfactory limits" the laboratory was invited for the next round.

The analyses for IGAC rounds 1 and 2 were carried out with a laboratory system based on a Varian 3400 gaschromatograph.

In the first round two-component mixtures containing n-butane and benzene at about 10 ppb level each were distributed. These mixtures were prepared by transfer of aliquots from a NIST gravimetric standard to stainless-steel sample canisters.

In the second round 16-component mixtures of C_2 - C_9 hydrocarbons at concentration levels between about 10 and 100 ppb were distributed. These mixtures were gravimetrically prepared by NIST and supplied in Scott Accu-life treated aluminum cylinders.

In the third round mixtures containing 62 major C_2 - C_{11} components at concentrations between about 1 and 30 ppb in stainless steel canisters were distributed. The mixtures that were distributed in the third round were not gravimetric standards, unlike the first two experiments.

The results of the different rounds of this intercomparison programme are discussed below.

Results of the n-butane/benzene mixture

In January 1992 a stainless steel canister containing n-butane and benzene prepared by NIST was received. The two compounds were quantified against reference gas streams generated in our own gas standards laboratory. N-butane was generated via diffusion tube and benzene via a permeation tube. The reference gas streams were quantified according to weight losses of the permeation/diffusion tubes.

The results of the analyses of the two-component mixture are shown in Table B.3. The results were accepted by NCAR as sufficiently reliable for participation in the second round of this ring test.

Only the results for n-butane were reported quantitatively from the first phase because of problems with benzene storage in the canisters. The average % deviation between the reported values from 37 participants and the NIST value was - 5 %, with a standard deviation of 13 %. We reported 9.5 ppb differing - 15 % from the NIST value of 11.2 ppb.

For both n-butane and benzene our results were qualitatively reported to be "within satisfactory limits". From the value of n-butane in the NIST standard and our chromatographic data we derived a value for benzene in the NIST standard of 10.2 ppb, while our reported value was 11.3 ppb (+ 10 % deviation).

Table B.3 Results of the analysis of the n-butane benzene mixture

number 21428C	n-butane ppb	sd ppb	n	benzene ppb	sd ppb	n
NIST February 1991	11.2	n.a.		10.2	n.a.	
results TNO november 1991	9.5	0.1	2	11.3	0.1	2

n.a. = not applicable

The results show the rather wide tolerance used for data to be within satisfactory limits (at least ± 15 %). Taking into account the reproducibility of the analyses, differences between standards of the size given above should be avoidable. In a cross-check of our laboratory standard with the NIST standard acquired through the TOR programme we obtained a much better agreement between n-butane and benzene concentrations, see Table B.2 (within 1 % for n-butane and within 6 % for benzene). The results in the first phase of the IGAC programme certainly suffered from some temporal technical problems with the permeation and diffusion system, due to an internal removal. This impaired the stability of the gas mixtures produced, as could in retrospect be deduced from the apparent large difference in sensitivity per ppbC of the FID for the two compounds. In later stages the FID responded with only minor differences in sensitivity per ppbC for these compounds.

Results of the 16-component reference gas mixture

A certified mixture containing 16 compounds was analyzed in the second phase. Twelve out of 28 participants identified all 16 of the compounds correctly. We did not attempt to identify compounds with retention times longer than that of toluene and misidentified the co-eluting n-hexane and isoprene as n-hexane only. Problems with stability were reported for O-pinene (anticipated) and, in some canisters, for acetylene (anticipated in retrospect). The average % deviation between reported and NIST values was for all compounds (excluding O-pinene and acetylene) below 20 % (in most cases negative) with standard deviations ranging from 10 to 60 %. The average % deviation taken over all compounds per participant averaged - 6 % with a standard deviation of 15 %. Our results showed an average deviation of - 4 %. For individual compounds deviations were between - 14 and + 4 %. The results of this intercalibration round are shown in Table B.4.

The results of this intercalibration round were also qualified as "within satisfactory limits". So TNO-MW was invited to participate in the third intercalibration round.

Results of the 62-component gas mixture

Only preliminary results were reported for the third phase. From about 50 compounds in the mixture eluting before toluene we correctly identified 34 compounds, could not identify 10 compounds en missed 6 compounds, which probably co-eluted with others. The % deviation from the reference values for the identified compounds was less than 5% for 60 % of the compounds and less than 20% for 80 % of the compounds (cumulative). Large differences were observed in cases where we were not absolutely sure of the identification. To what extent co-elution of compounds has interfered with the quantification has yet to be investigated.

Table B.4 Results of the analysis of the 16 component mixture

component	concentration NIST (ppb)	concentration TNO (ppb)	% difference relative to NIST
ethylene	45.86	42.50	- 7.33
acethylene	40.85	18.60	- 54.47
ethane	131.00	136.30	4.05
propylene	13.10	11.20	- 14.50
propane	55.74	54.90	- 1.51
i-butane	19.02	18.20	- 4.31
n-butane	28.26	27.60	- 2.34
i-pentane	48.80	48.70	- 0.20
n-pentane	22.82	22.10	- 1.83
isoprene	101.50	103.08	1.56
n-hexane	10.02	-	-
benzene	19.43	18.60	- 4.37
toluene	41.47	38.80	- 6.44
o-xylene	5.02	-	-
ó-pinene	49.51	-	-
1,2,4-trimethylbenzene	10.07	-	-

ISPRA intercomparison programme for NMVOC

The ISPRA intercomparison programme was coordinated by E. de Saeger, Working Group NMVOC-measurement techniques, Commission of the European Communities (DG XI), Joint Research Centre, ISPRA, Varese. Participation of TNO only concerns the second round of this intercomparison, which was organized in December 1993.

The second round consisted of two samples:

- A 26-component mixture, gravimetrically prepared by NPL (UK), containing C_2 - C_9 hydrocarbons at 10 to 100 ppb levels;
- An authentic urban air sample with hydrocarbon concentrations up to 10 ppb.

At the moment of writing this report no results have been disclosed by the coordinator. Still it can be mentioned that relative standard deviations over five chromatographic runs for hydrocarbons up to C_7 in the gravimetric standard mixture with relatively high concentrations were within 2 %. Some components with higher boiling points than toluene showed larger RSD because of the occurrence of double peaks, which made quantification less reliable.

The lower concentrations in the urban air mixture (although partially compensated for by taking larger samples) resulted in somewhat higher RSD over the five chromatographic runs. The RSD were, with four exceptions where values up to 25 % were noted, generally between 1 and 5 %. Compounds with more than seven carbon atoms were not quantified, again because of the occurrence of double peaks in the chromatograms.

General conclusions from the intercalibration programmes

In drawing general conclusions from the results of these intercomparison programmes it should be taken into account that:

- The exercises span a period of more than two years in which new analytical instrumentation has been introduced and in which experience and knowledge has grown;
- Concentration levels differed considerably in the various intercomparisons.

With the restraint mentioned, the following general conclusions can be drawn from the intercomparison programmes:

- Participation in the intercomparison rounds has contributed considerably to the identification of systematic errors in the analytical method. These errors are mainly of instrumental origin. Specifically, losses in the sampling system and contamination from the sampling system have to be mentioned.
- Quantification appears to be accurate at concentration levels of 10 ppb and higher (about 1 %). At levels of 1 ppb results are significantly less reliable (about 5 %). This is not only shown by deviations from reference values, but also in larger RSD between multiple chromatographic runs of the same gas mixture.
- The use of a single (per ppbC) calibration factor for all components in the range C_2 - C_7 is presently not limiting accuracy in the quantification of these compounds.
- The analyses of real ambient air mixtures requires some improvement in the identification of chromatographic peaks.

B.4.4 Peroxyacetylnitrate

The method described is the same method as used in the STEP-EC PAN project of contract DG XII nr. EV4V-CT90-0222 (Hollander, 1991). The gaschromatographic PAN method and the calibration procedures have been tested in this EC-PAN project and will be reported separately. The intercalibration rounds for PAN proved the validity of our FTIR measurements. The FTIR measurements now serve as our primary standard.

B.4.5 J(NO_2)

The quality of the measurements is assured by the yearly calibrations. All instruments of this kind used by the different contributors for TOR are (inter)calibrated yearly by Meteoconsult.

B.5 Ambient air measurements

B.5.1 Nitrogen oxide, nitrogen dioxide and ozone

Measurements of oxides of nitrogen and ozone started in 1989 when the Kollumerwaard observatory was opened. In fact, these observations are a continuation from the measurement made at Kloosterburen during the 1980s. Until mid-1994 the instrument used for NO_x was a Philips PW 9762 chemiluminescence monitor. This instrument uses a ferrosulphate NO_2 converter which also tends to convert a major fraction of the NO_y components. For this reason we use the more specific Cranox instrument for TOR purposes now (see section B.2.1). Since summer 1994 both monitors have been operated in a parallel mode at the observatory.

Ozone is measured by two instruments as well. Firstly, the LML standard Thermo Environmental Instruments 49W monitor (since 1989), and secondly, the Environics S300 instrument included in the Cranox system (since mid-1994).

B.5.2 Carbon monoxide, carbon dioxide and methane

Since July 1991 ambient air measurements have been performed for CO_2, CH_4 and CO. Except for some minor disturbances the instrumentation performed very well during the whole period. Every six months, reports are published concerning the measurements of the greenhouse gases as well as the meteorological measurements (KEMA, 1993a; 1993b;

1993c; 1994a; 1994b; 1994c; 1995a; 1995b). These reports give a complete picture of the performed measurements, disturbances, calibrations and results.

The Dutch Oil Company (NAM) started seismological research and drilling activities in order to quantify the amount of natural gas in the Wadden Sea, nearby the measuring site, at the beginning of 1993. As a result of these activities several drilling rigs have been set up nearby the measuring site in different directions. Most of the time no drilling activities are performed but, on occasion, it is possible that the hydrocarbon (and methane) measurements are biased because of these activities.

B.5.3 Non-methane hydrocarbons (C_2 - C_9)

The instrumentation was received in October 1992. An extended set of laboratory tests with calibration gases was performed. These tests showed good results and the instrumentation was prepared for unattended use at the measuring site. The instrumentation was moved to the site in June 1993. For the first two months the results were unreliable for several reasons:

- Fluctuating sensitivity of the detector because of a fluctuating oxygen content in the accommodation caused by the liquid nitrogen supply;
- Contamination of the sampling lines after the removal to the new accommodation;
- Deviations from the measuring scheme caused by software problems;
- Results for higher hydrocarbons were less reliable.

Except for the problems with the higher hydrocarbons all problems could be solved, and from September till October 1993 measurements were performed on site, with reliable results for the C_2 - C_5/C_6 hydrocarbon measurements. In November 1993 the instrumentation was taken back to the laboratory in Delft to improve the measurements of the higher hydrocarbons and the data communication software. In addition, this provided an opening to take part in two more intercomparison programmes (IGAC and ISPRA). These intercomparison programmes became of great importance because of the problems with the quantification of higher hydrocarbons.

The problems with the higher hydrocarbons were caused by the drying system of the instrumentation which caused shifts in retention time, especially for higher hydrocarbons. The instrumentation was taken back to the site to continue the measurements of ambient air in may 1994. At first, high blanks were found, which became lower when the measurements proceeded. From July 1994 on, the instrumentation was in working order and showed good results.

B.5.4 Peroxyacetylnitrate

The PAN monitor was tested for several months at our lab in Delft before it was transferred to the measuring site in June 1991. The monitor, including automatic calibration, has been in operation at Kollumerwaard from July 1991 on. Apart from some drop-outs due to malfunctions, the removal to the new measuring accommodation or periodic maintenance of the system measurements have been performed continuously. Because of the removal to the new accommodation and the start-up problems that occurred data in the period form 15 June till 5 September 1993 are not reliable and have not been reported to the TOR database. An extensive overview of the data is presented in separate reports (Baas and Bosman, 1995; Baas and Van Ditshuizen, 1995; Roemer *et al.*, 1996; Roemer and Esser, 1996; Roemer, 1996).

B.5.5 J(NO_2)

Due to several malfunctions in the instrumentation, all repaired by Meteoconsult the instrumentation was not installed at the measuring site before June 1994. In June 1994 the measurements at the site started after the instrumentation had been recalibrated by Meteoconsult in the spring of 1994. At the moment few data are available and the available data have not been evaluated yet.

B.6 Description of additional LML measurements

Wind direction (KNMI-Tdm 3a TBv 4603/2070a)
Principle of operation: Gonio metre angle detection
Measuring range: 0-360°
Sensitivity: 0.28 m s^{-1}
Measuring height: 10 m above ground level

Wind speed (Thies 4.3300)
Principle of operation: Contactless counting of pulses originating from a revolving disc with slits
Maximum measuring range: 35 m s^{-1}
Sensitivity: 0.2 m s^{-1}
Non-linearity: none
Measuring height: 10 m above ground level

Medium Volume Sampler (MVS) RIVM method
Principle of operation: air filtration by a Whatman nr. 42 filter. Element analysis by atom absorption spectrometry and X-ray fluorescence
Sampling flow: 6.9 l min^{-1}
Sampling height: 3.6 m above ground level
Analysed elements: Ca, Pb, Zn, As, Cd

Low Volume Sampler (LVS) RIVM method
Sampling flow: 1.4 l min^{-1}
Sampling height: 3.6 m above ground level
Analysed elements: NH_4+, Cl^-, NO_3^-, SO_4^{2-}

Wet deposition (van Essen, wet only type ECN)
Principle of operation: wet only, light protected
Hysteresis of lid closing mechanism: 2.5 min
Sampling height: 1.5 m above ground level
Sampling cycle: fortnightly
Sampling orifice: 400 cm^2
Analysed elements: pH, H, NH_4, Na, Mg, Ca, K, Zn, F, Cl, SO_4, NO_3, Cu, Cd, Fe, Mn, Ni, Pb, V

Specifications are in accordance with the 'Ontwerp Norm NEN 6585 Regenwatermonsterneming van de natte depositie' (Design standard NEN 6585 Rainwater sample taken of wet deposition).

Sulphur dioxide (Thermo Environmental Instruments Inc. Model 43W, version 2)

Principle of operation:	gas phase fluorescence
Measuring range:	0 - 750 ppb (0 - 2000 \g m^{-3})
Lower detection limit:	1 ppb
Precision (80 % full scale):	1 %
Temperature influence on:	
- zero	< 0.05 ppb °C^{-1}
- sensitivity:	< 0.1 % °C^{-1}
Zero drift:	< 1 ppb day^{-1} and < 15 ppb year^{-1}
Sensitivity drift:	< 2 % week^{-1} or < 5 % year^{-1}
Nonlinearity:	< 0.5% of measured value or less than 0.5 ppb
Response time (99 %):	6 min or less
Sampling flow:	< 0.5 l min^{-1}

Selectivity:

- moisture less than 3 % change in the SO_2 signal following a change in the relative humidity from 0 % to 80 % at 20 °C;
- aromatic hydrocarbons total contribution of aromatic hydrocarbons from motorized traffic to the SO_2 signal is less than 5 ppb at a CO-level of 15 ppm;
- nitric oxide contribution to the SO_2 signal is less than 0.5 % of the ambient NO concentration;
- carbon disulphide contribution to the SO_2 signal is less than 5 % of the CS_2 concentration.

Calibration:

- zero once a day by removing the pollutant from the sampling flow by means of impregnated and activated carbon, type Norit RB; pellet size 1 mm;
- span once in seven days by means of a pressure bottle containing the pollutant in a concentration certified by the "Nederlands Meetinstituut" (Netherlands Measuring Institute).

The monitoring and calibration unit are in procedural accordance with the requirements of the 'Besluit luchtkwaliteit zwaveldioxide en zwevende deeltjes', Staatsblad (1986) nr. 78 and the additional 'Meetbesluit zwaveldioxide en zwevende deeltjes (zwarte rook)' of 13 February 1986.

References appendix B

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APPENDIX C

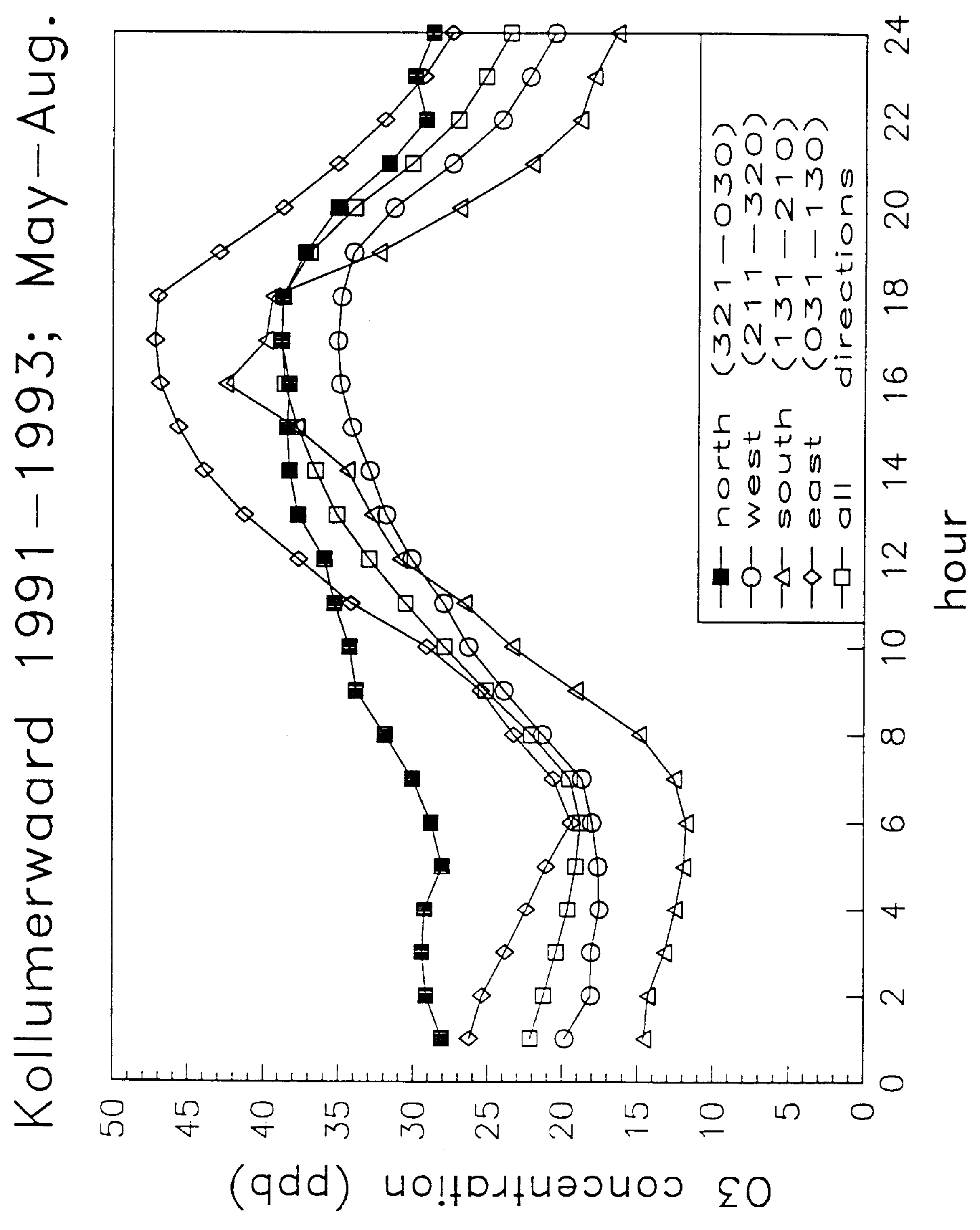

Figure C.1a The averaged diurnal cycle in the O_3 concentration during the summer months for the complete data set and each of four wind sectors (1991-1993 data).

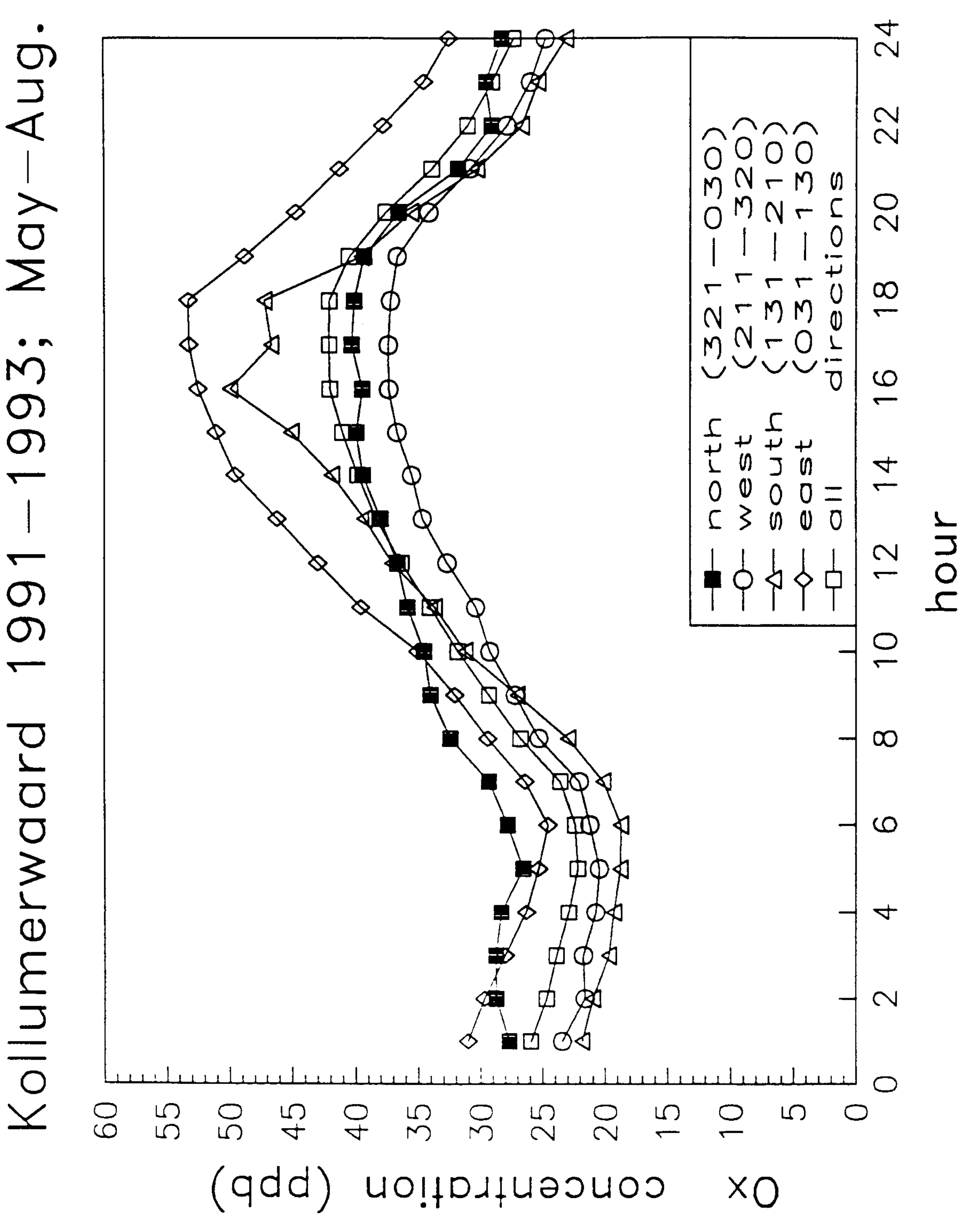

Figure C.1b The averaged diurnal cycle in the O_x concentration during the summer months for the complete data set and each of four wind sectors (1991-1993 data).

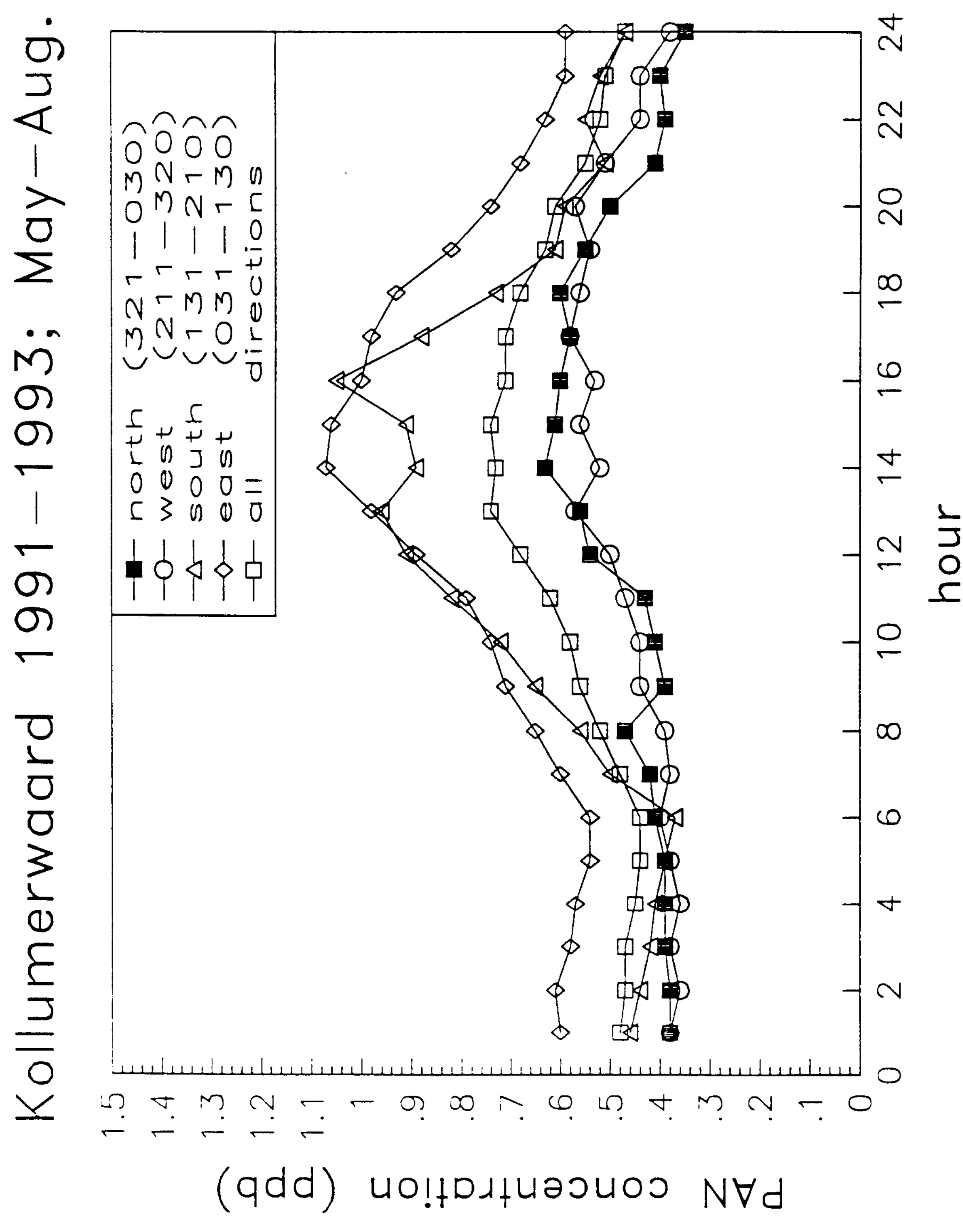

Figure C.1c The averaged diurnal cycle in the PAN concentration during the summer months for the complete data set and each of four wind sectors (1991-1993 data).

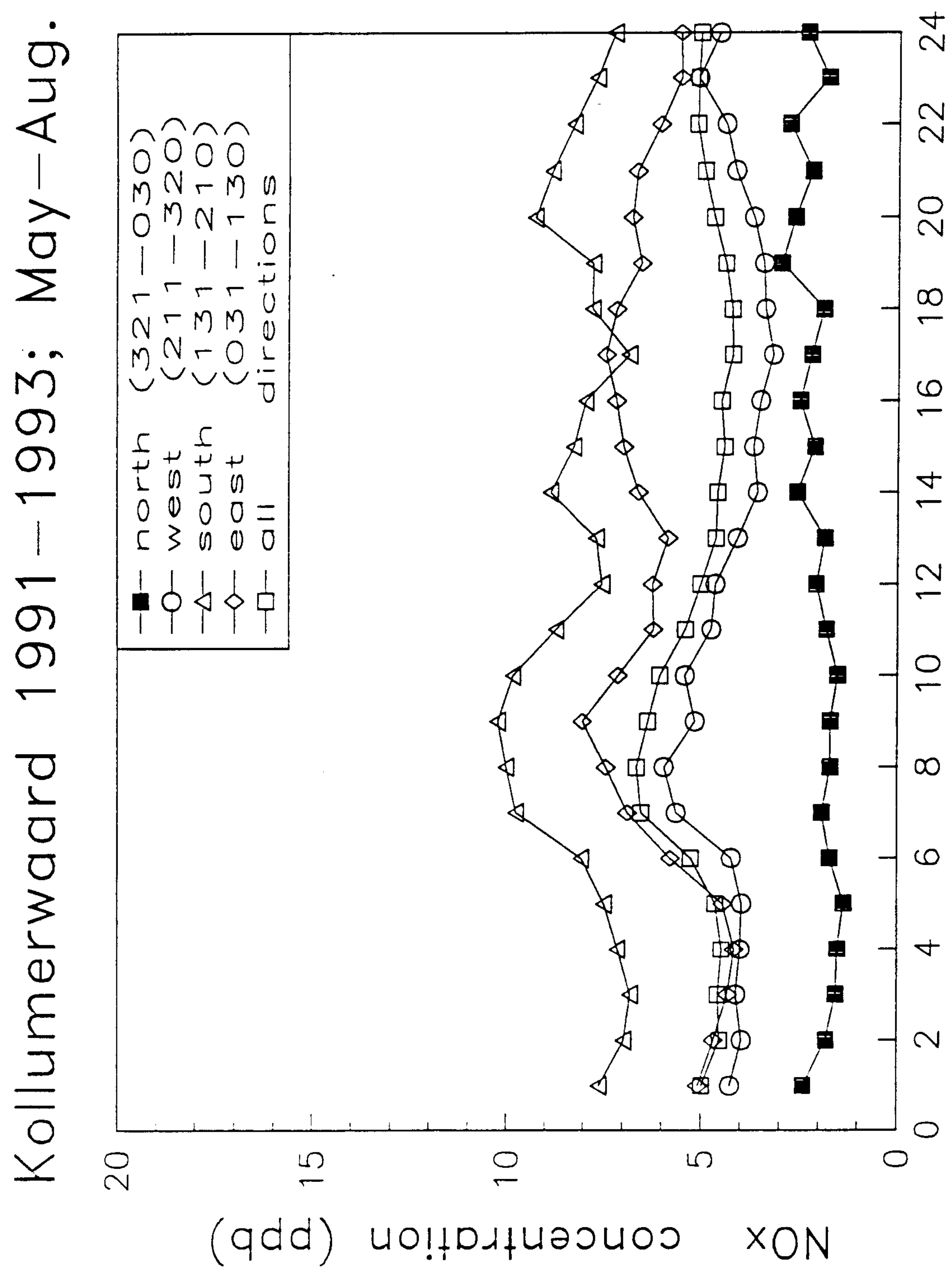

Figure C.2a The averaged diurnal cycle in the NO_x concentration during the summer months for the complete data set and each of four wind sectors (1991-1993 data).

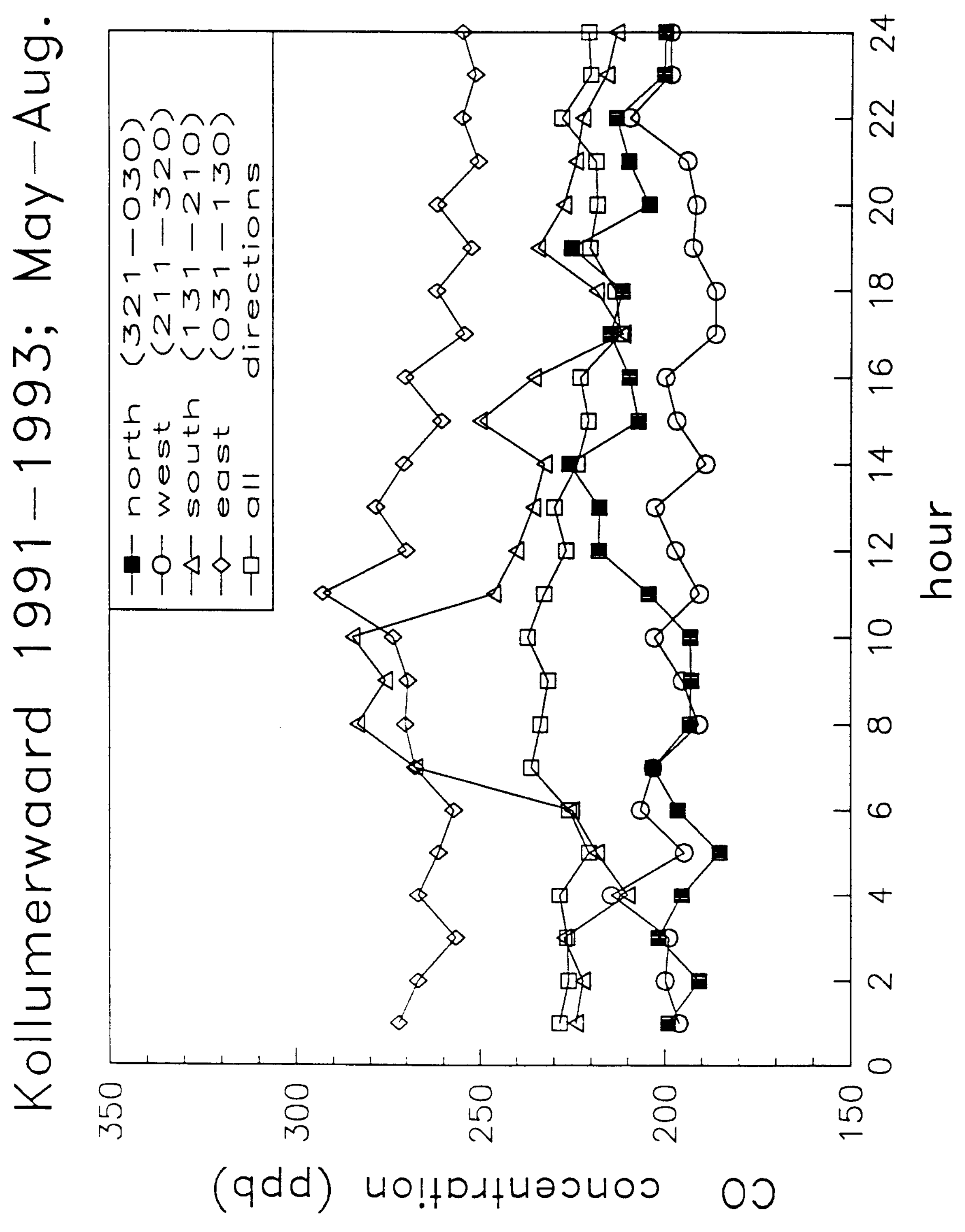

Figure C.2b The averaged diurnal cycle in the CO concentration during the summer months for the complete data set and each of four wind sectors (1991-1993 data).

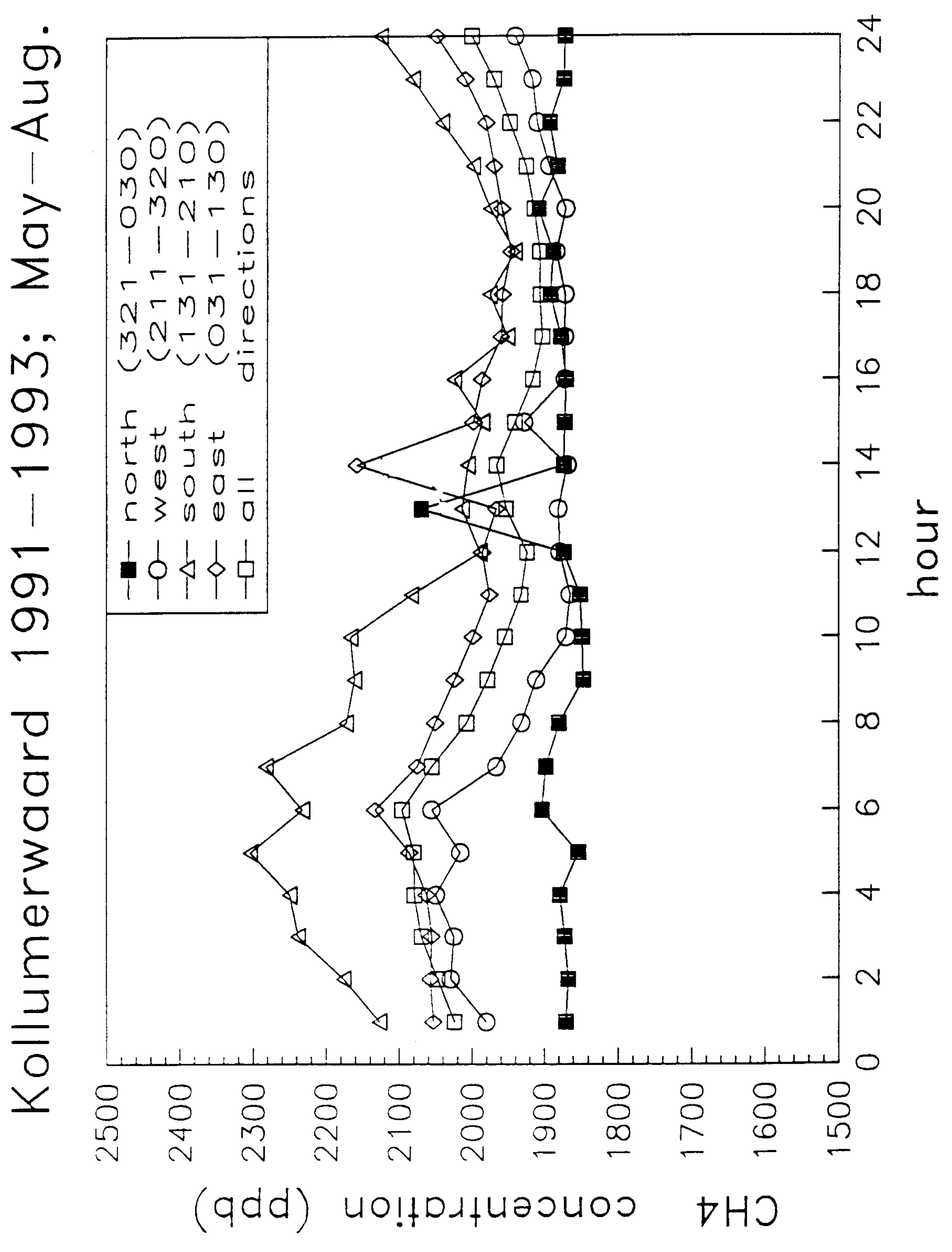

Figure C.2c The averaged diurnal cycle in the CH_4 concentration during the summer months for the complete data set and each of four wind sectors (1991-1993 data).

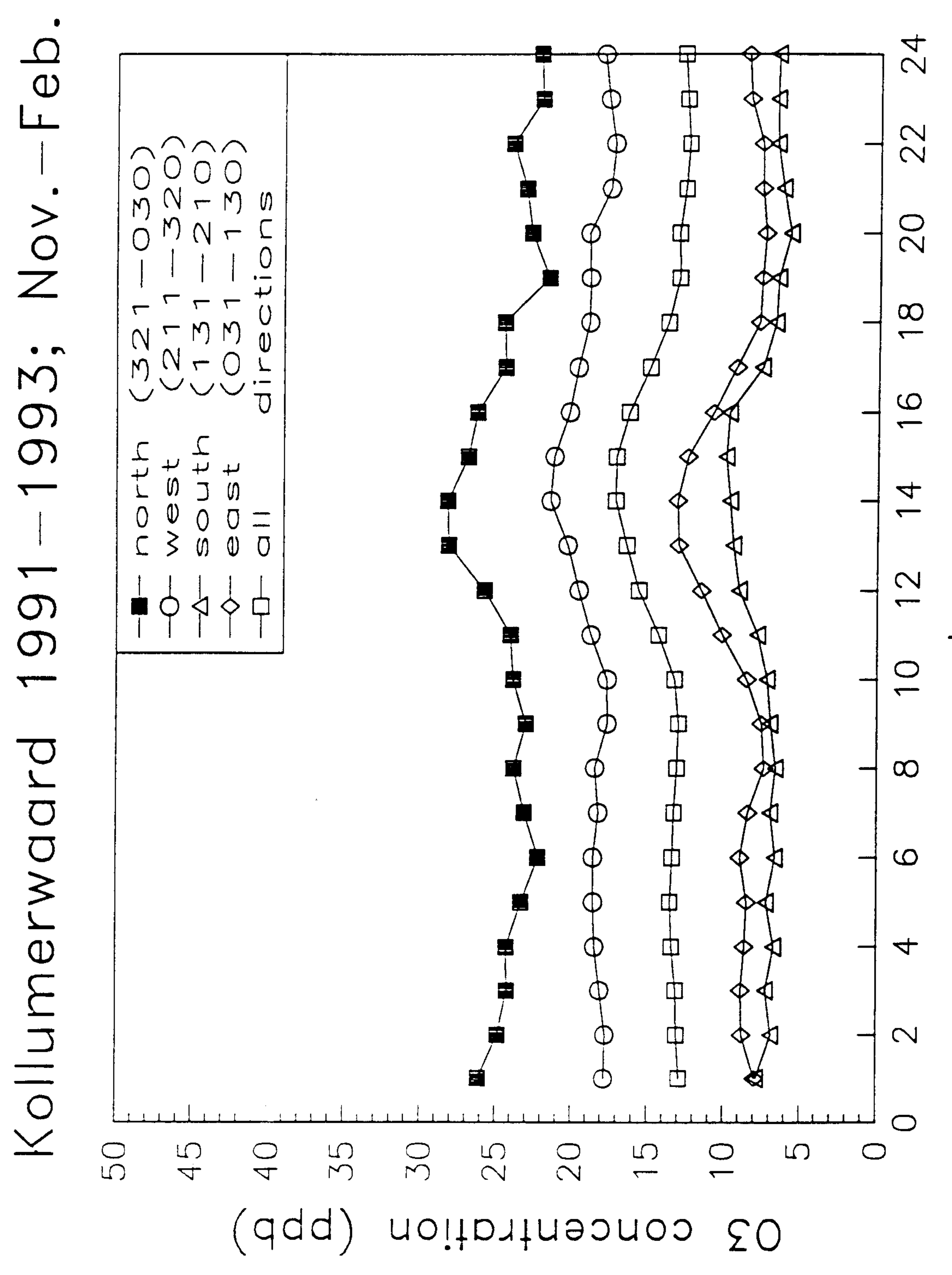

Figure C.3a The averaged diurnal cycle in the O_3 concentration during the winter months for the complete data set and each of four wind sectors (1991-1993 data).

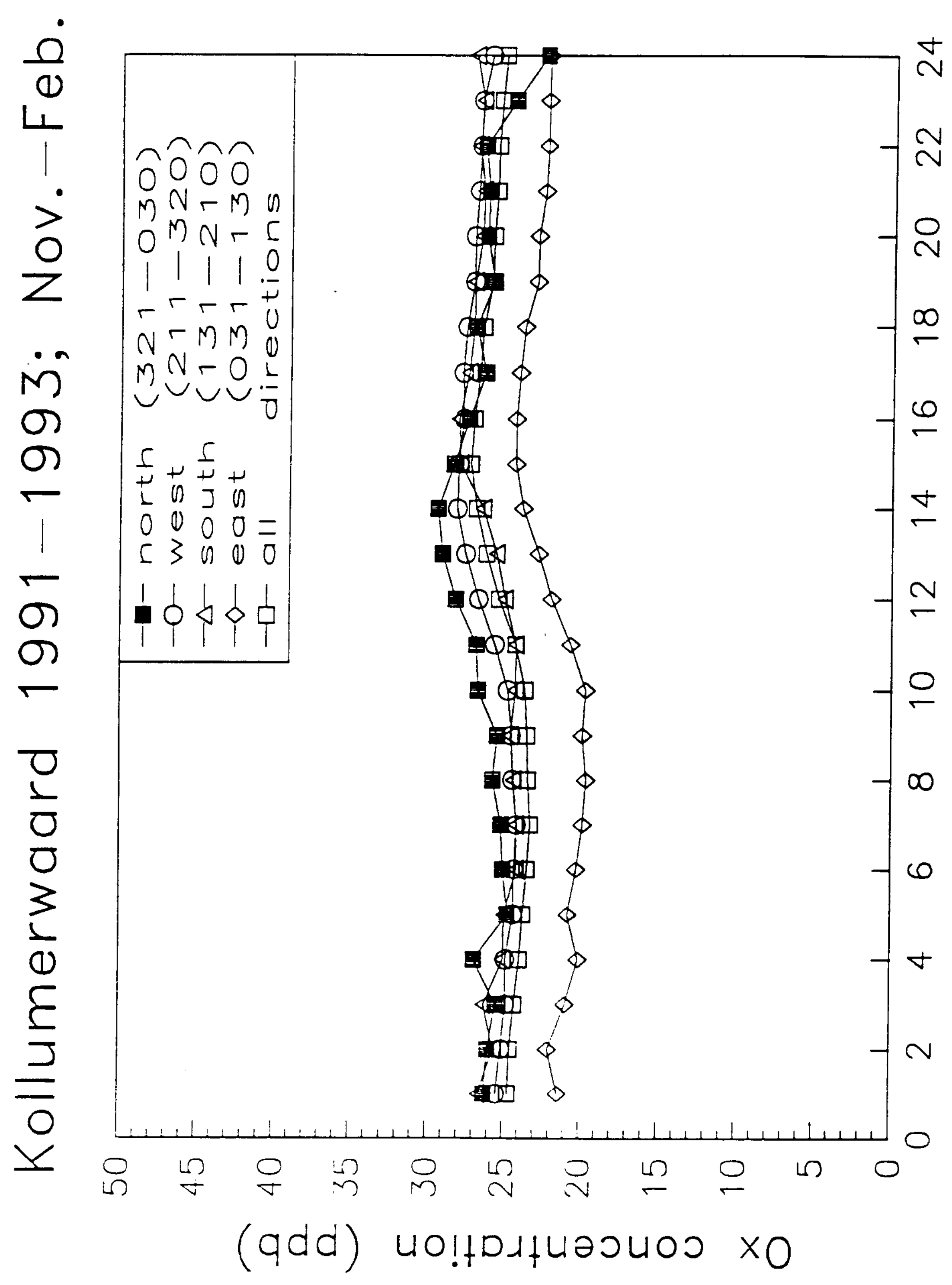

Figure C.3b The averaged diurnal cycle in the O_x concentration during the winter months for the complete data set and each of four wind sectors (1991-1993 data).

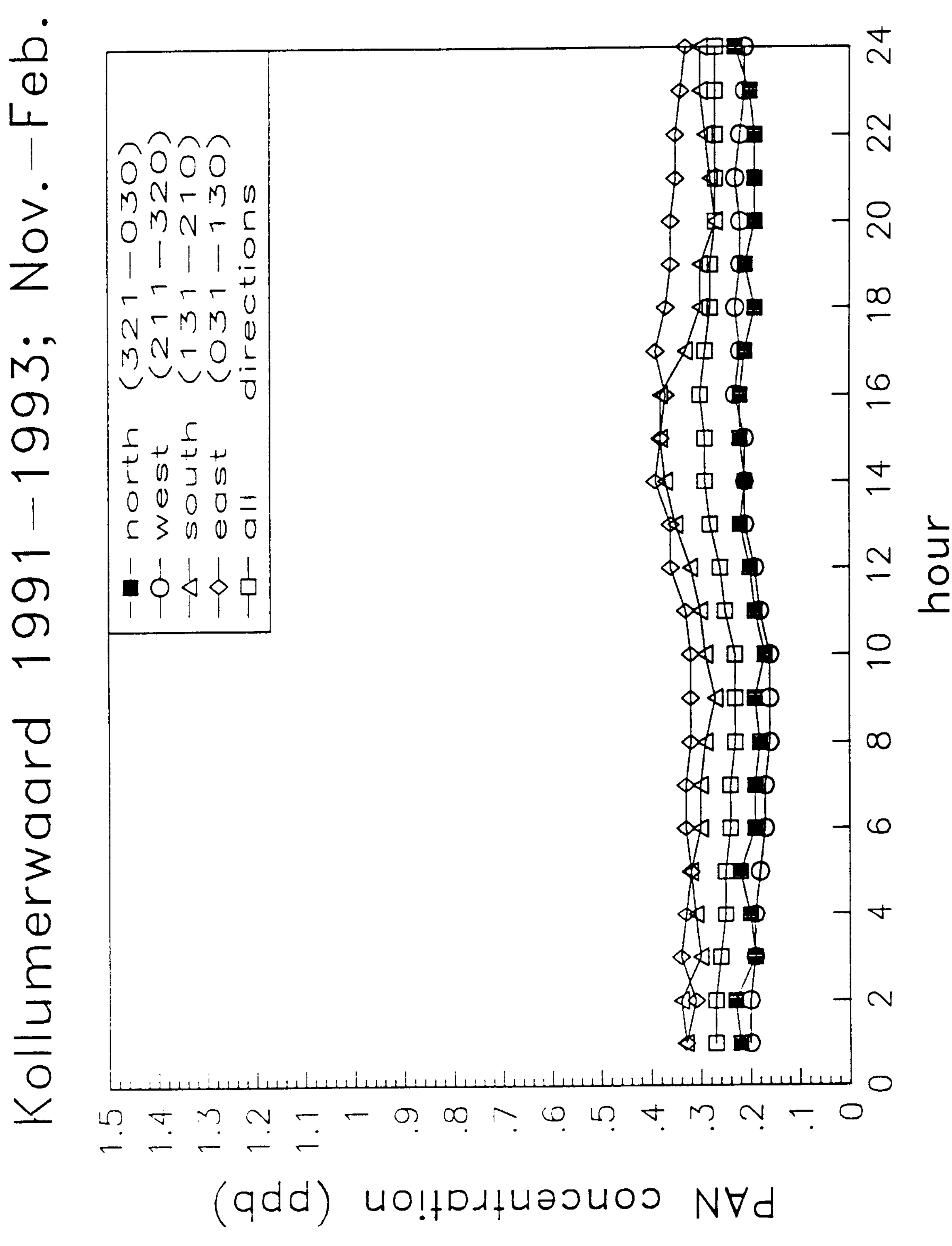

Figure C.3c The averaged diurnal cycle in the PAN concentration during the winter months for the complete data set and each of four wind sectors (1991-1993 data).

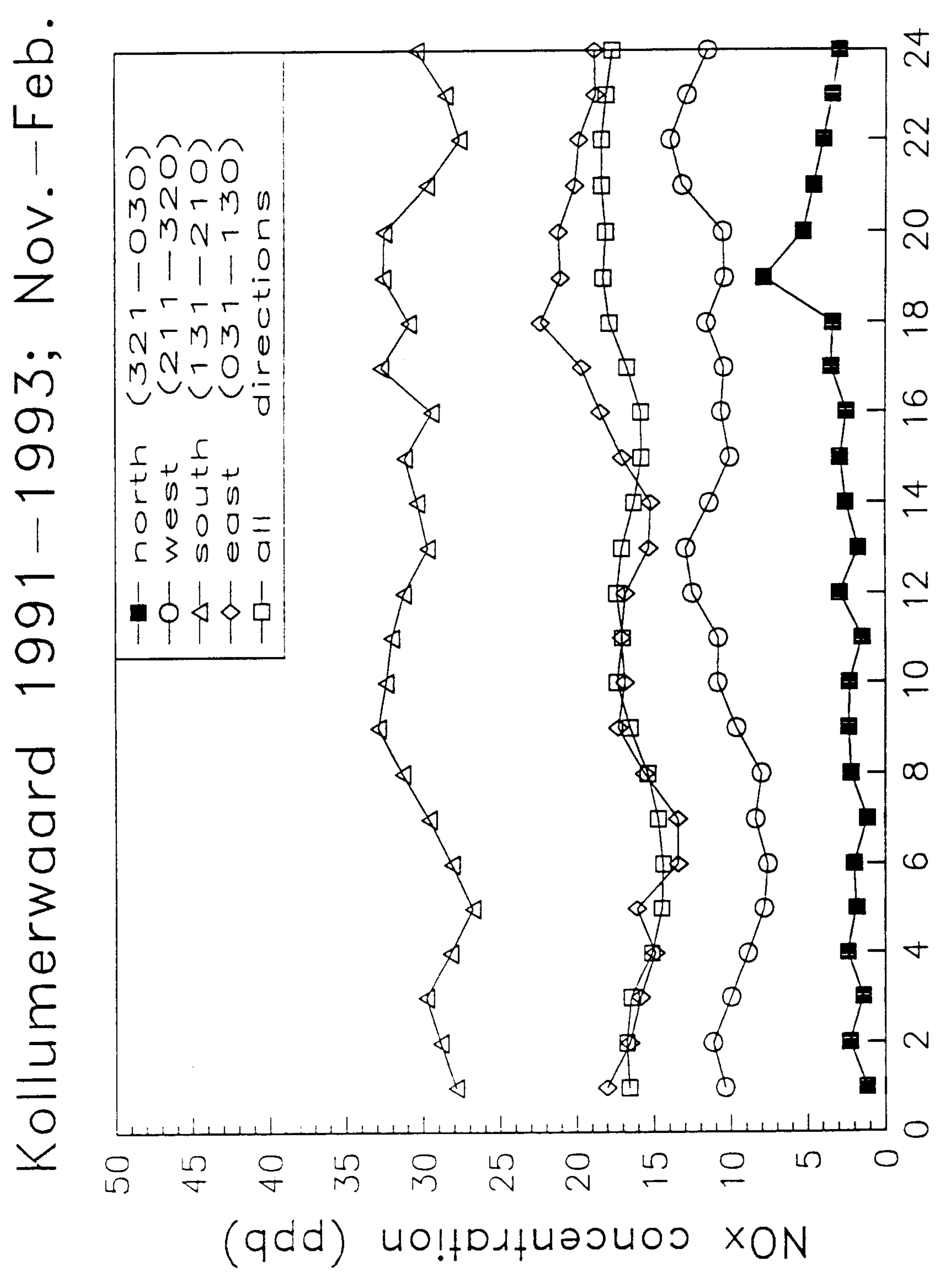

Figure C.4a The averaged diurnal cycle in the NO_x concentration during the winter months for the complete data set and each of four wind sectors (1991-1993 data).

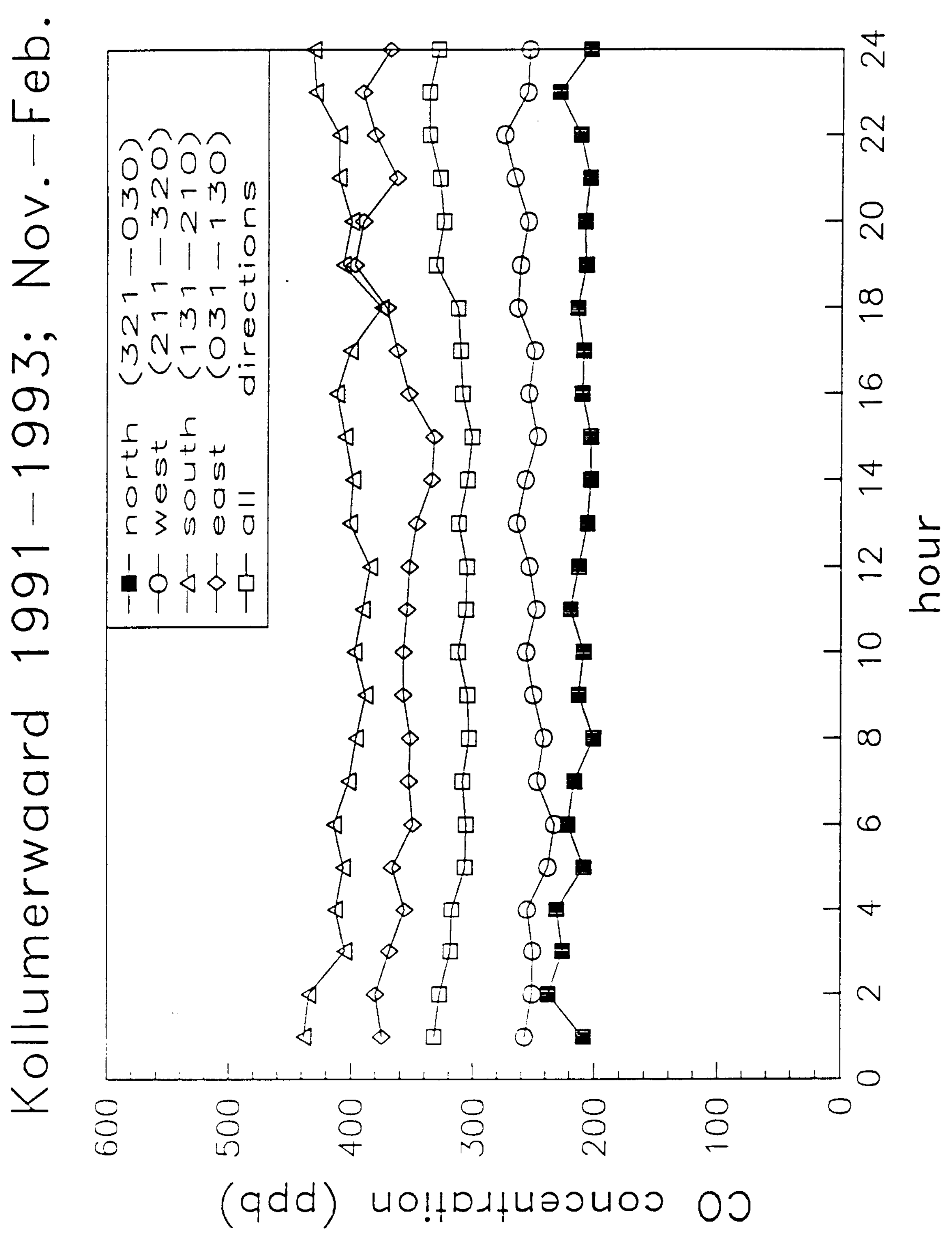

Figure C.4b The averaged diurnal cycle in the CO concentration during the winter months for the complete data set and each of four wind sectors (1991-1993 data).

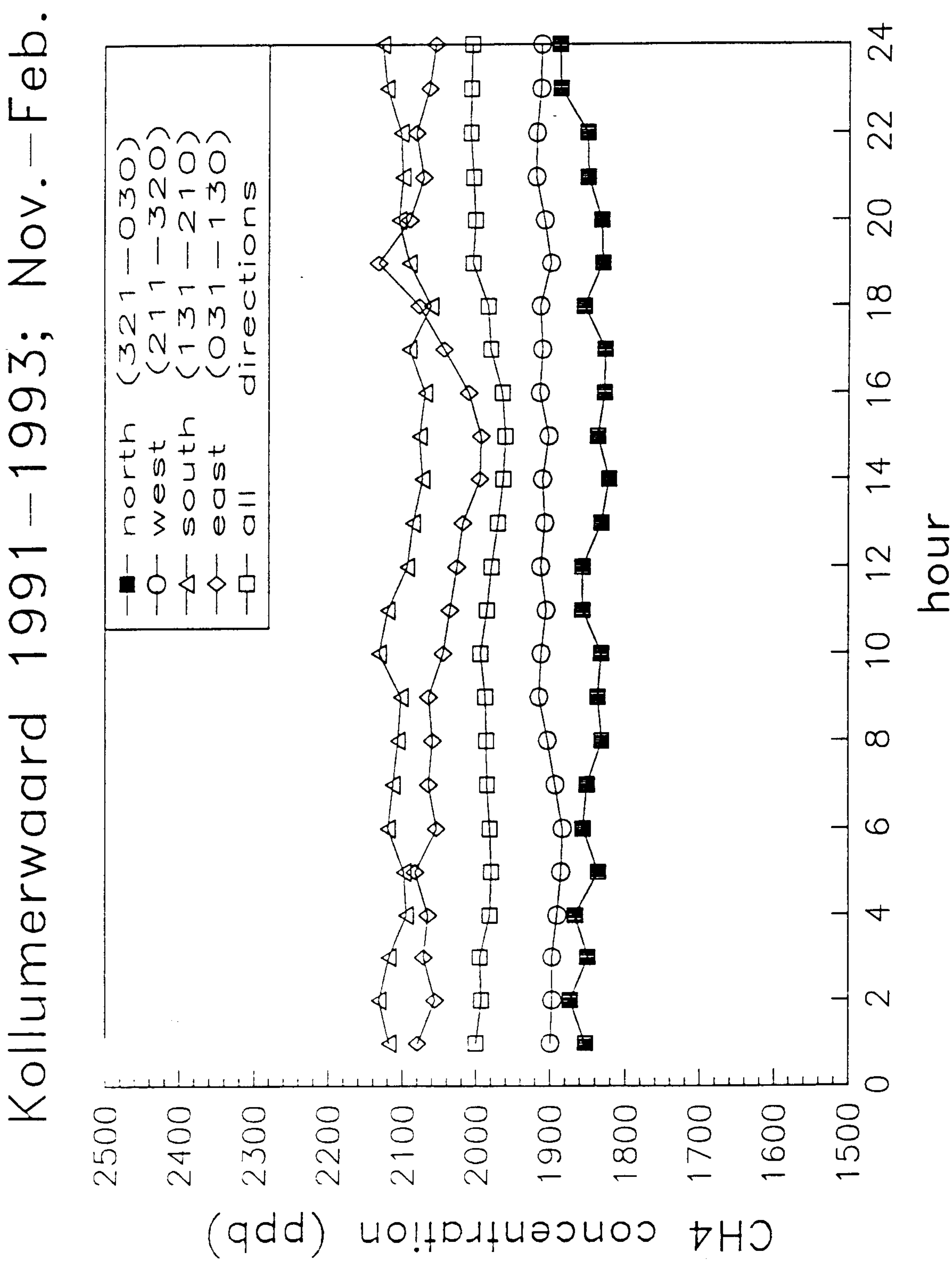

Figure C.4c The averaged diurnal cycle in the CH_4 concentration during the winter months for the complete data set and each of four wind sectors (1991-1993 data).

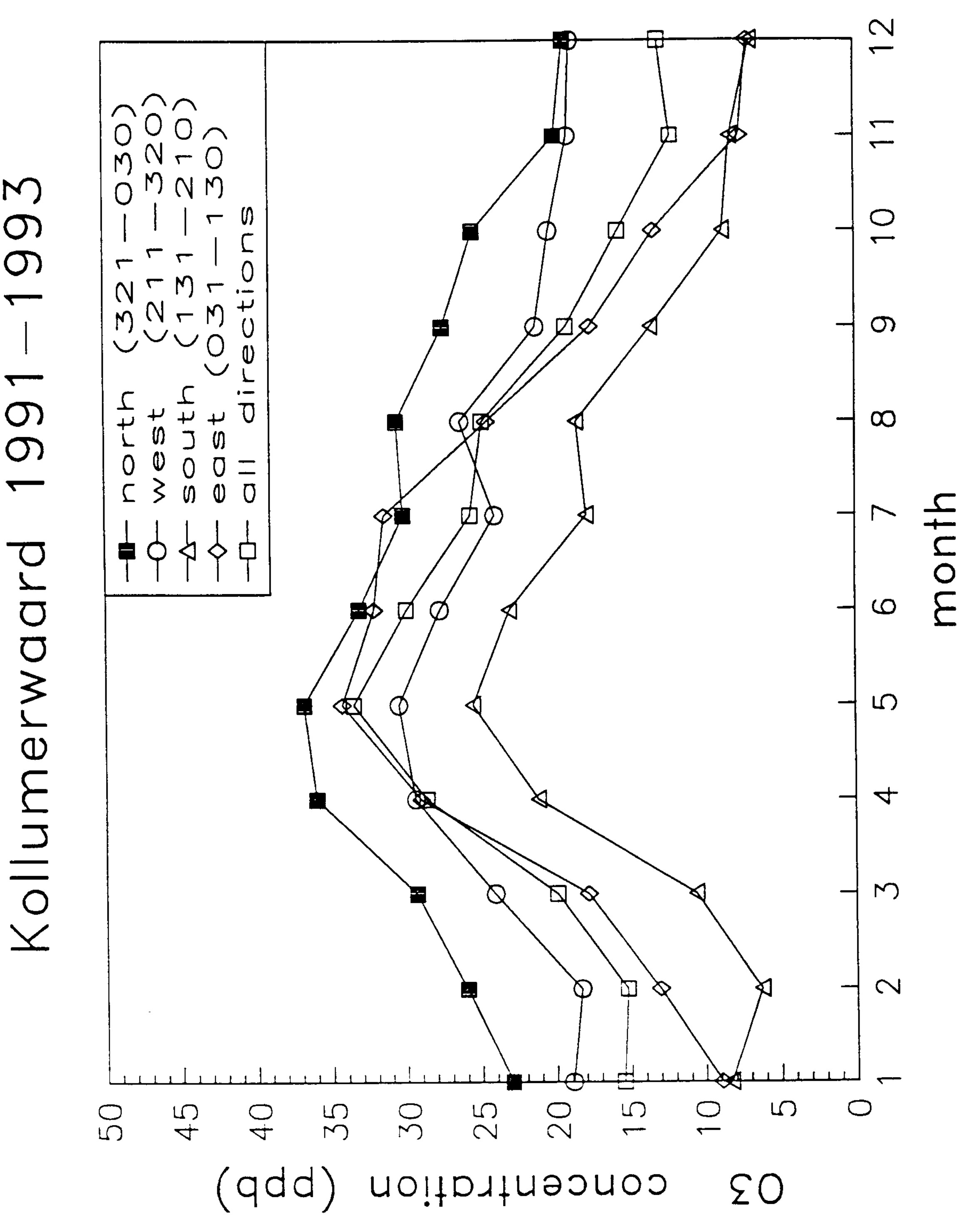

Figure C.5a The averaged seasonal cycle in the O_3 concentration for each of the four wind sectors (1991-1993 data).

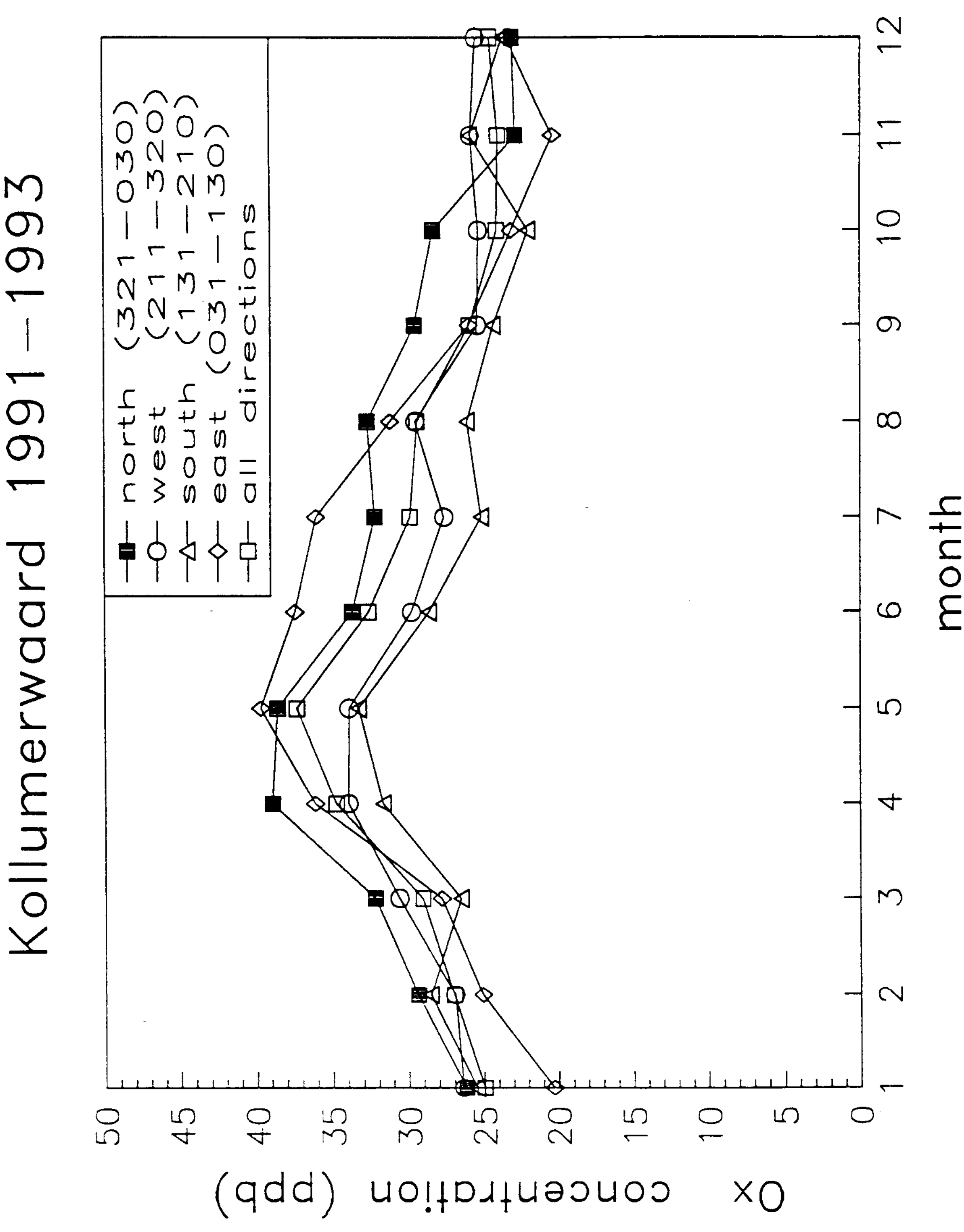

Figure C.5b The averaged seasonal cycle in the O_x concentration for each of the four wind sectors (1991-1993 data).

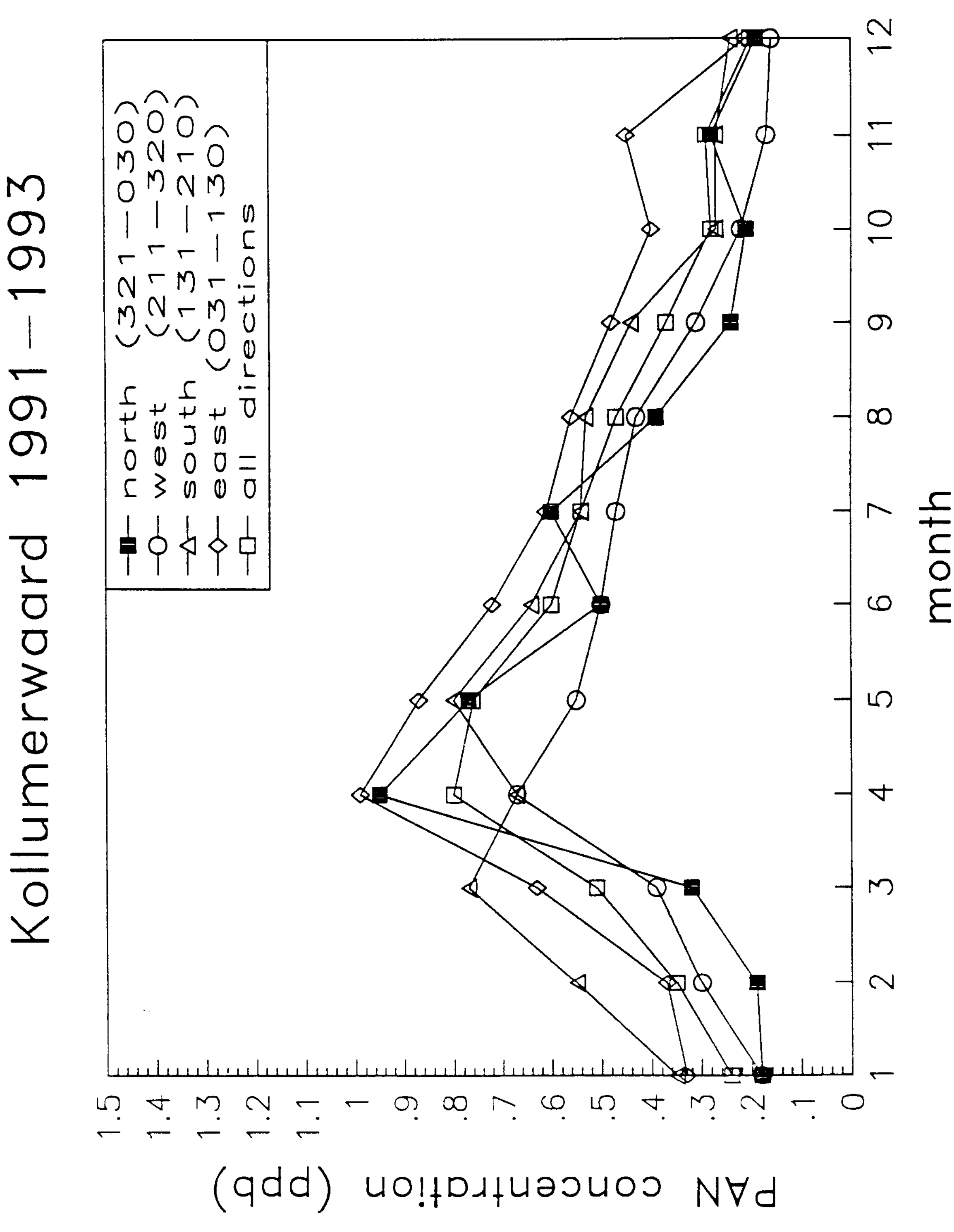

Figure C.5c The averaged seasonal cycle in the PAN concentration for each of the four wind sectors (1991-1993 data).

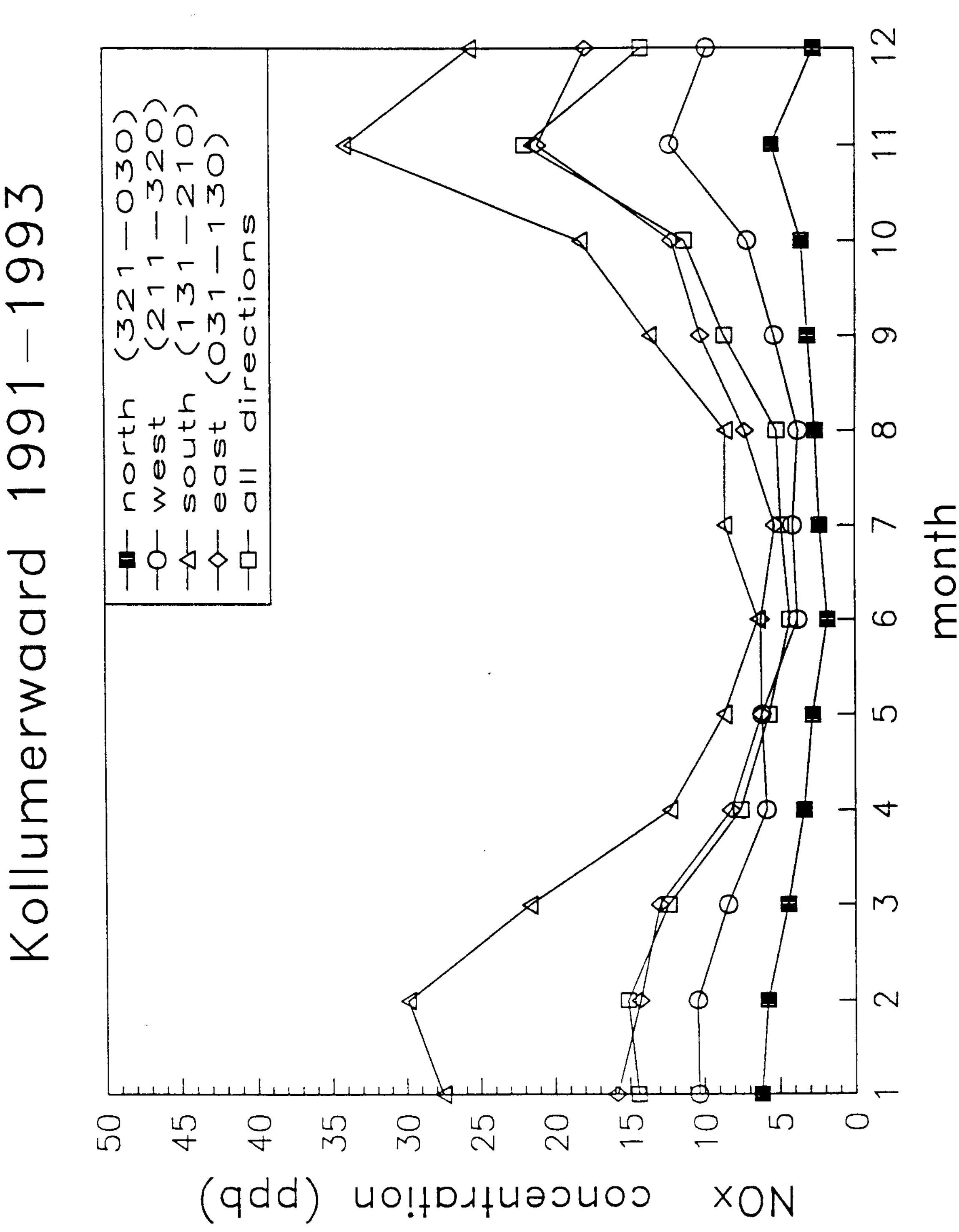

Figure C.6a The averaged seasonal cycle in the NO_x concentration for each of the four wind sectors (1991-1993 data).

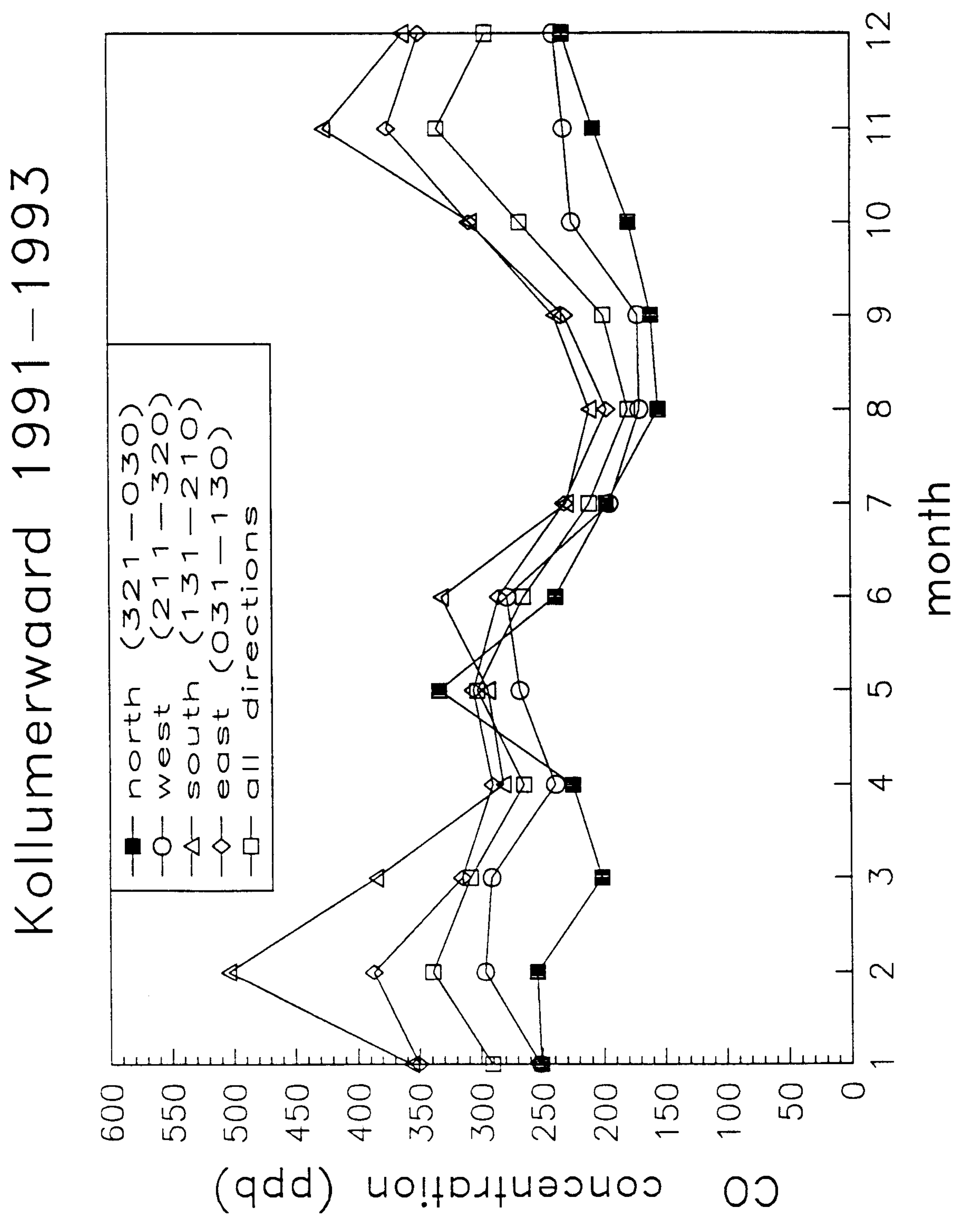

Figure C.6b The averaged seasonal cycle in the CO concentration for each of the four wind sectors (1991-1993 data).

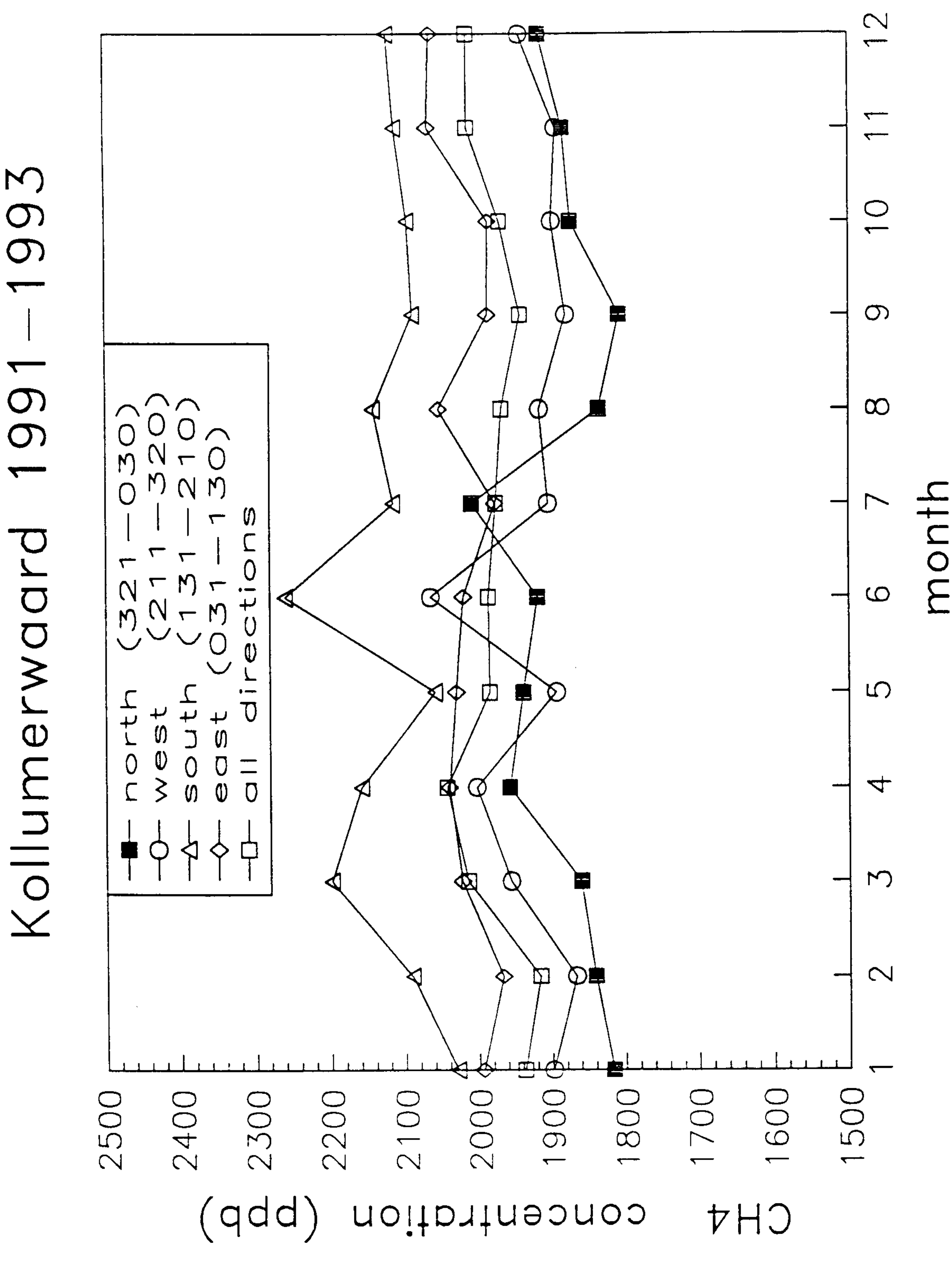

Figure C.6c The averaged seasonal cycle in the CH_4 concentration for each of the four wind sectors (1991-1993 data).

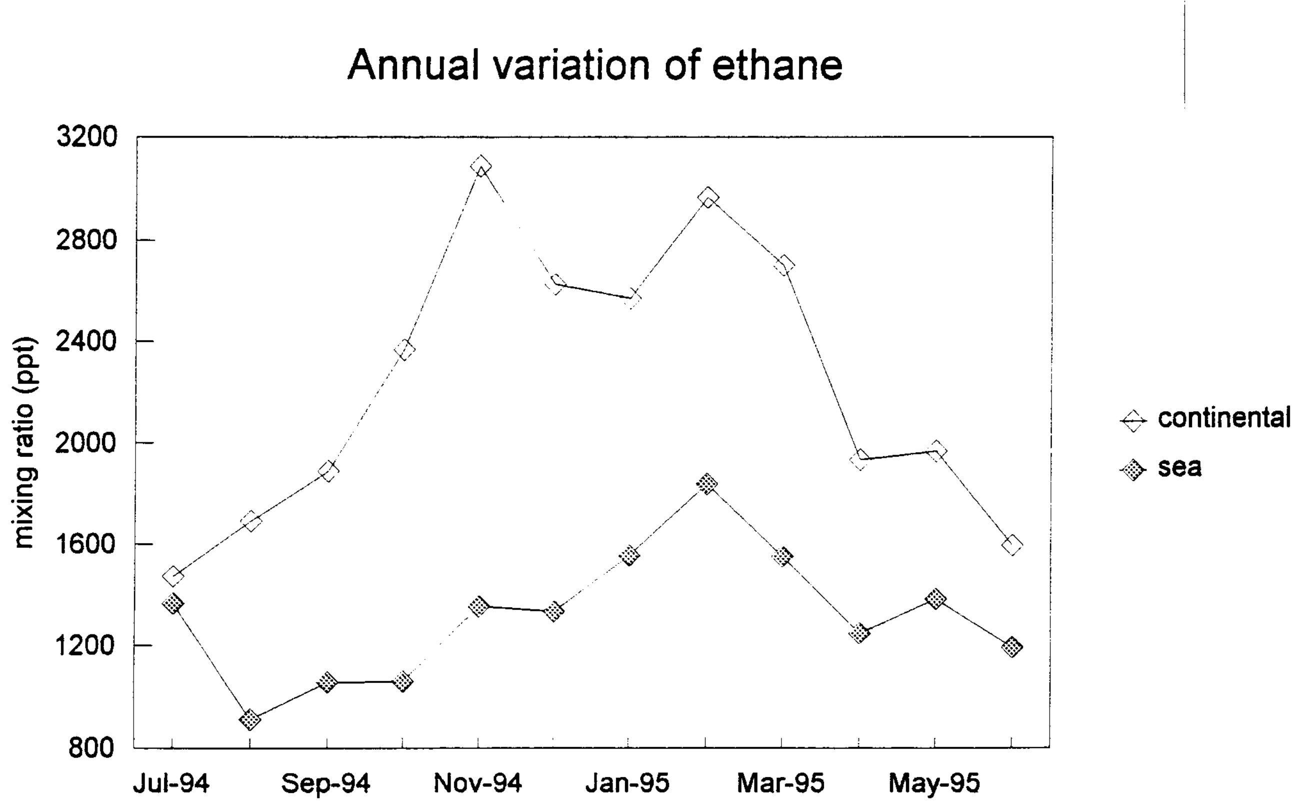

Figure C.7a Annual variation of ethane for continental and sea sector.

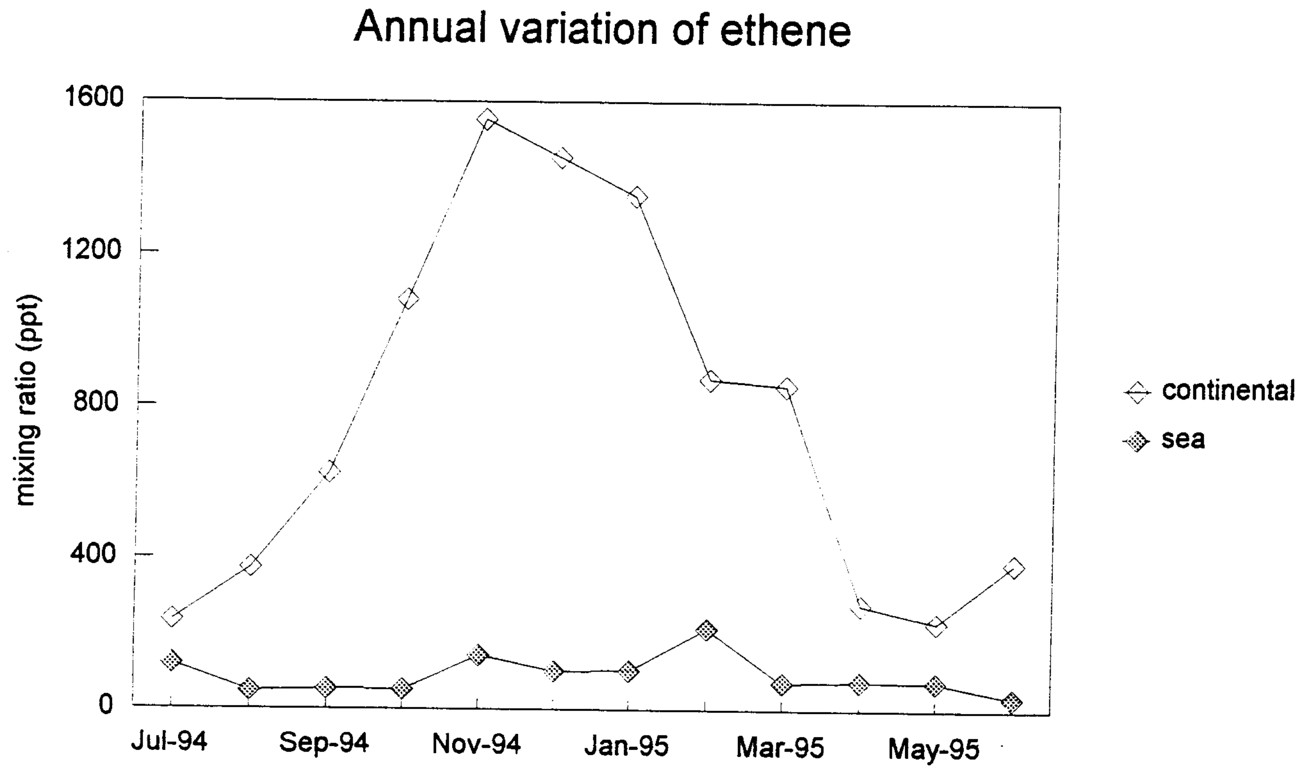

Figure C.7b Annual variation of ethene for continental and sea sector.

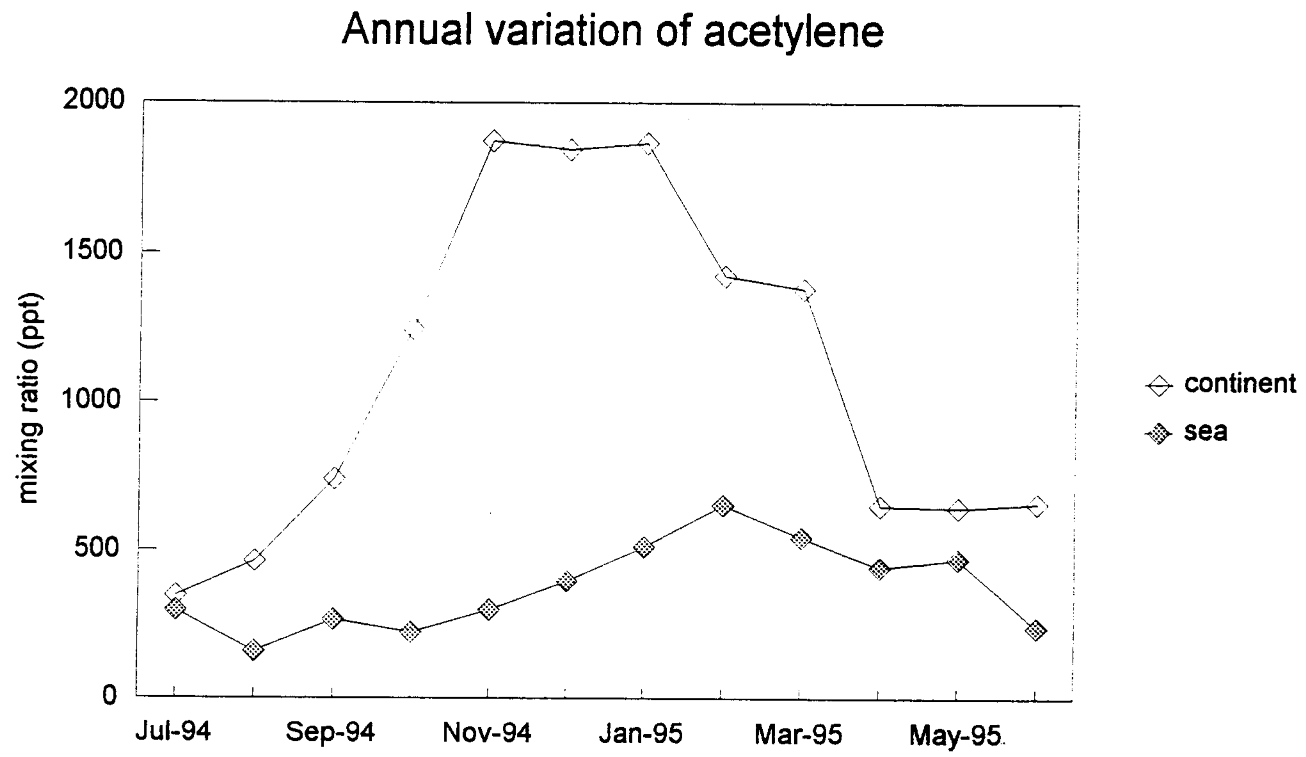

Figure C.7c Annual variation of acetylene for continental and sea sector.

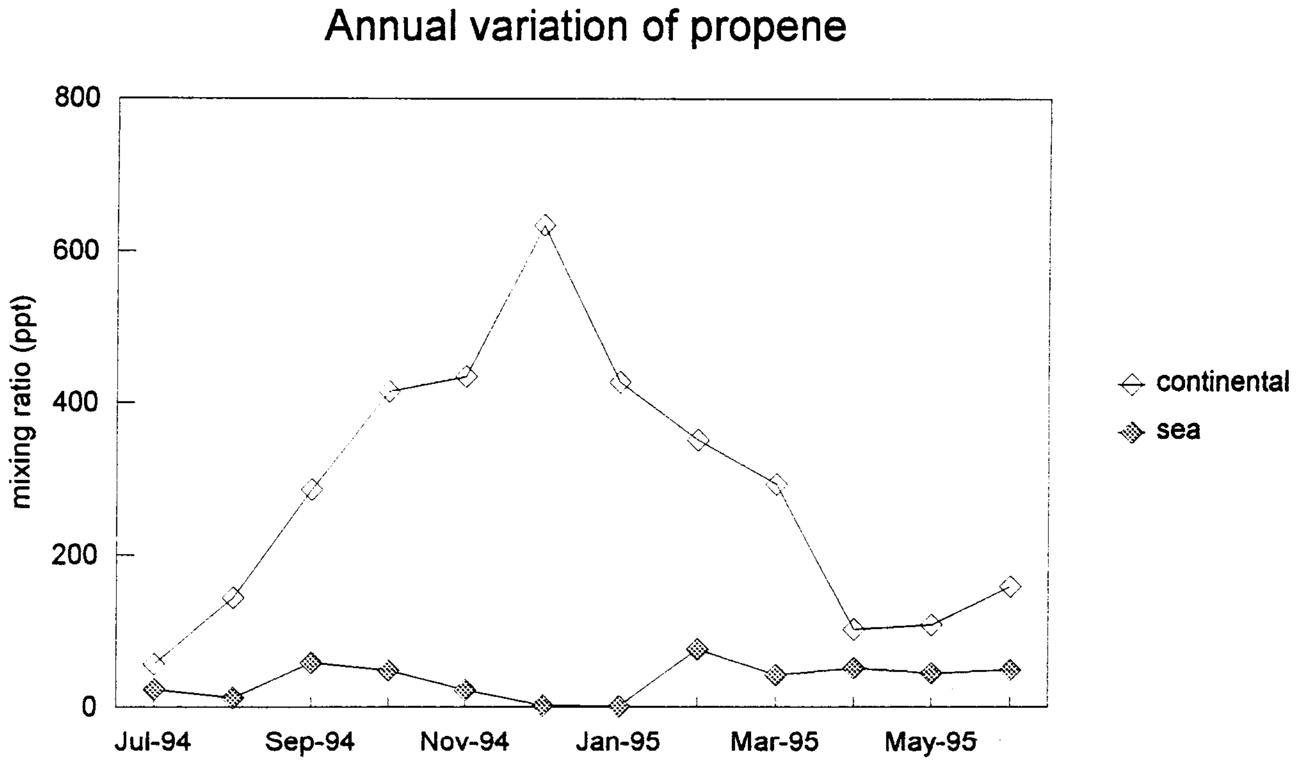

Figure C.7d Annual variation of propene for continental and sea sector.

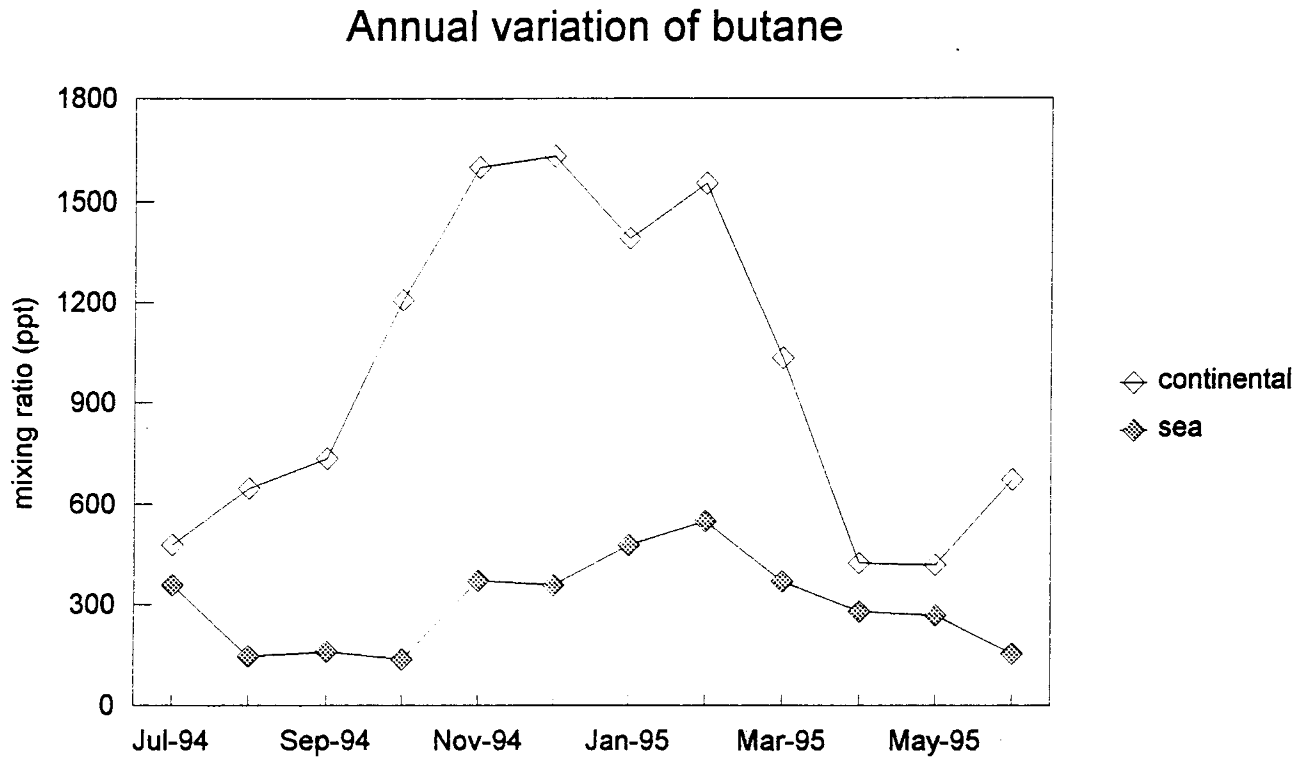

Figure C.7e Annual variation of butane for continental and sea sector.

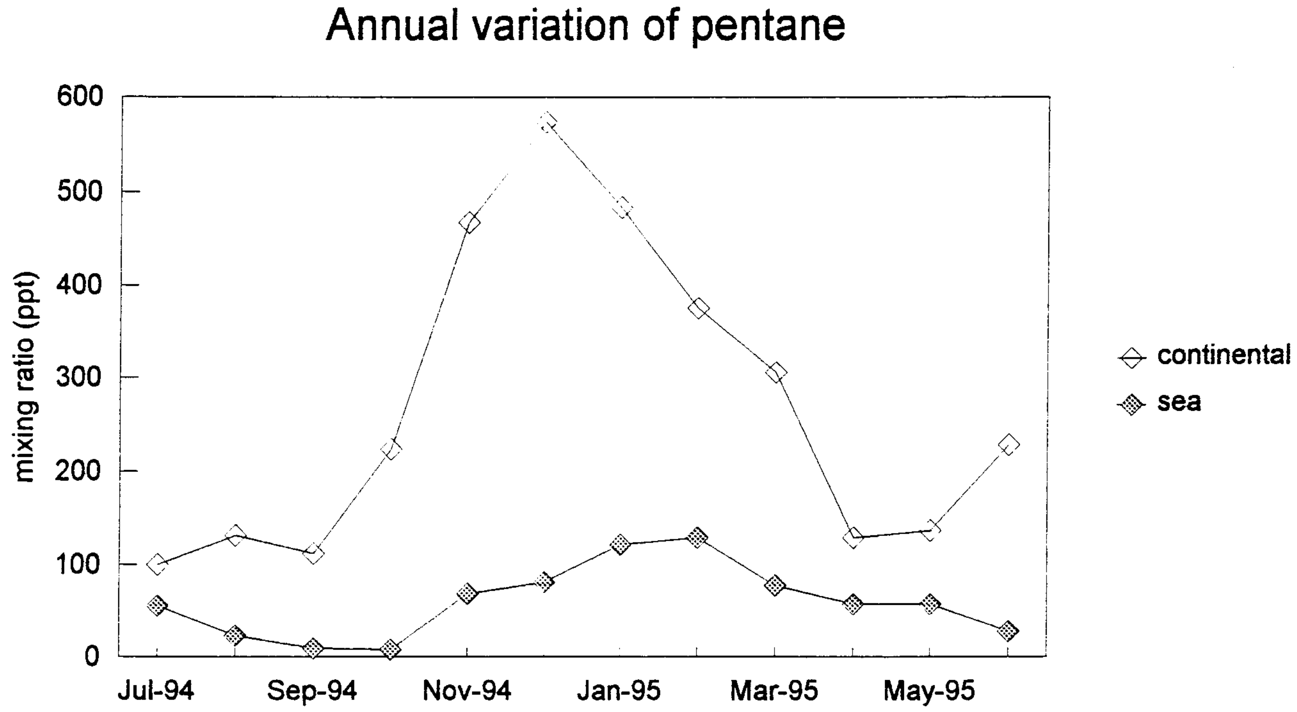

Figure C.7f Annual variation of pentane for continental and sea sector.

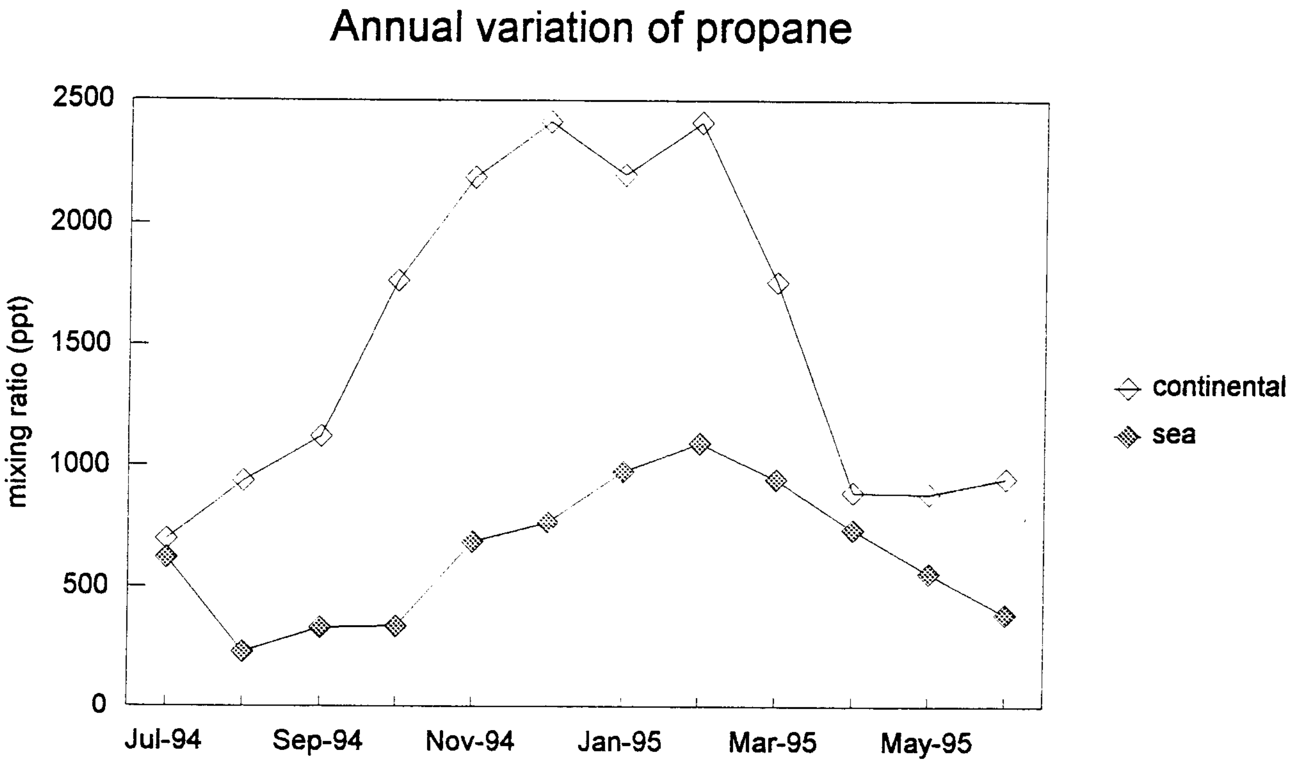

Figure C.7g Annual variation of propane for continental and sea sector.

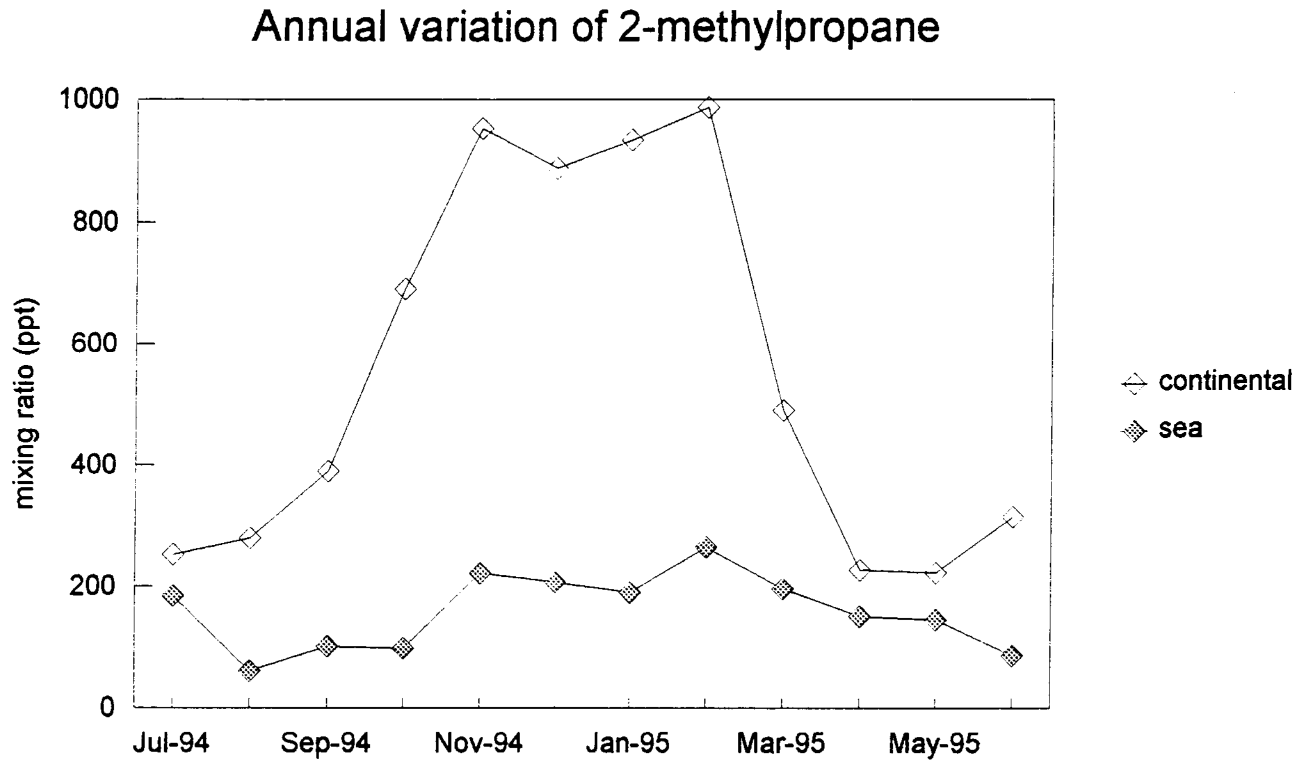

Figure C.7h Annual variation of 2-methylpropane for continental and sea sector.

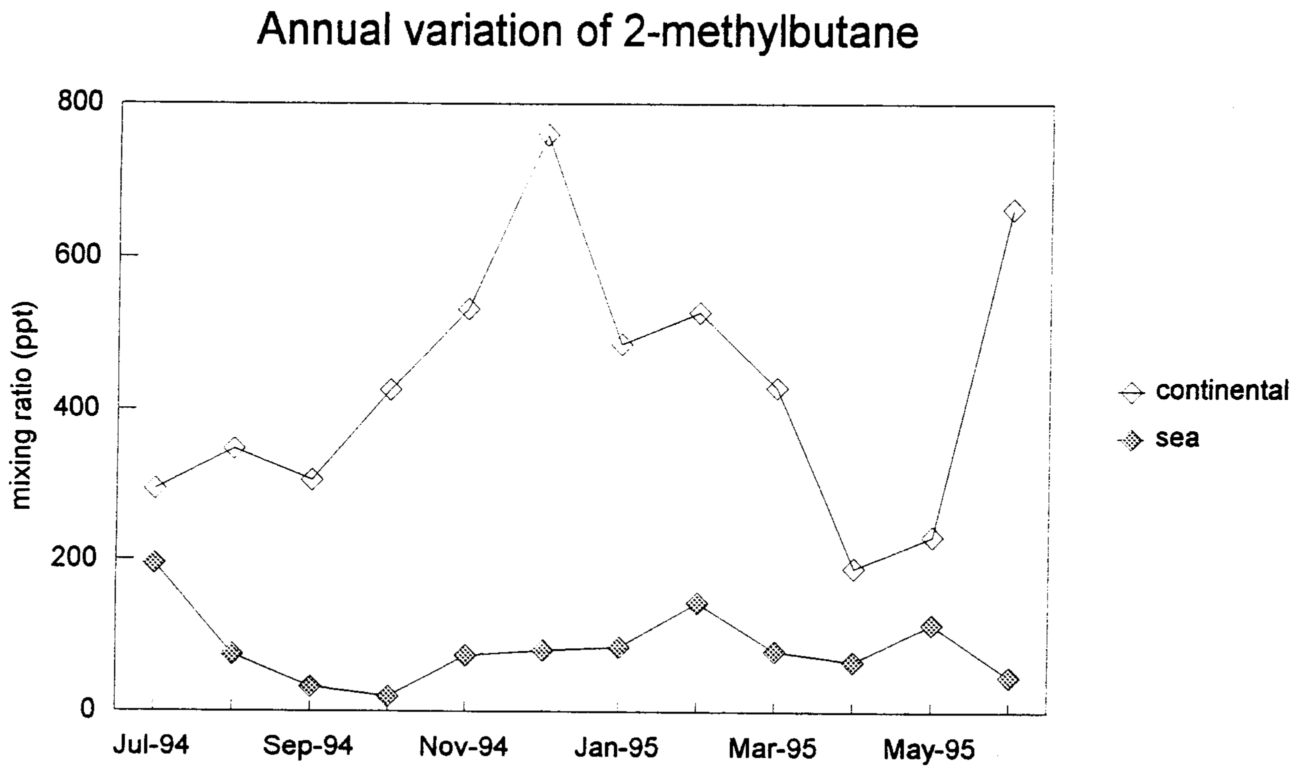

Figure C.7i Annual variation of 2-methylbutane for continental and sea sector.

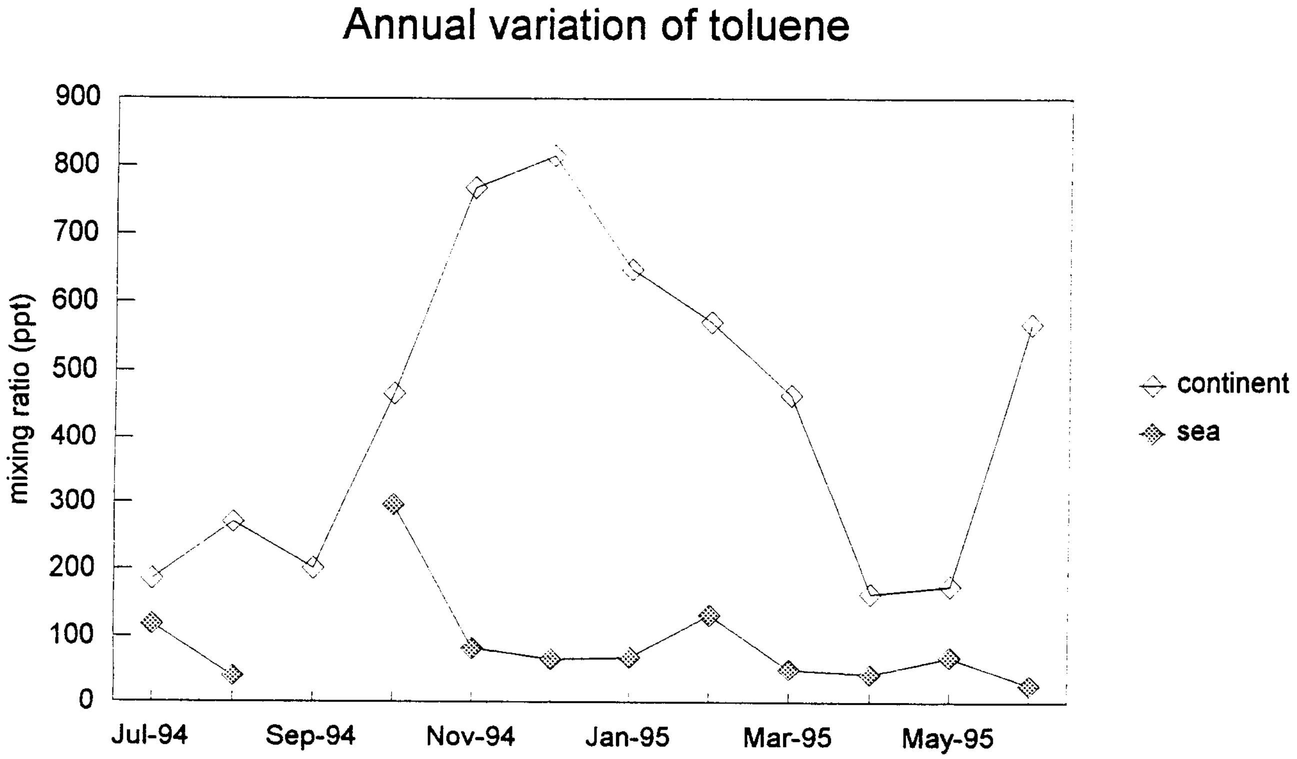

Figure C.7j Annual variation of toluene for continental and sea sector.

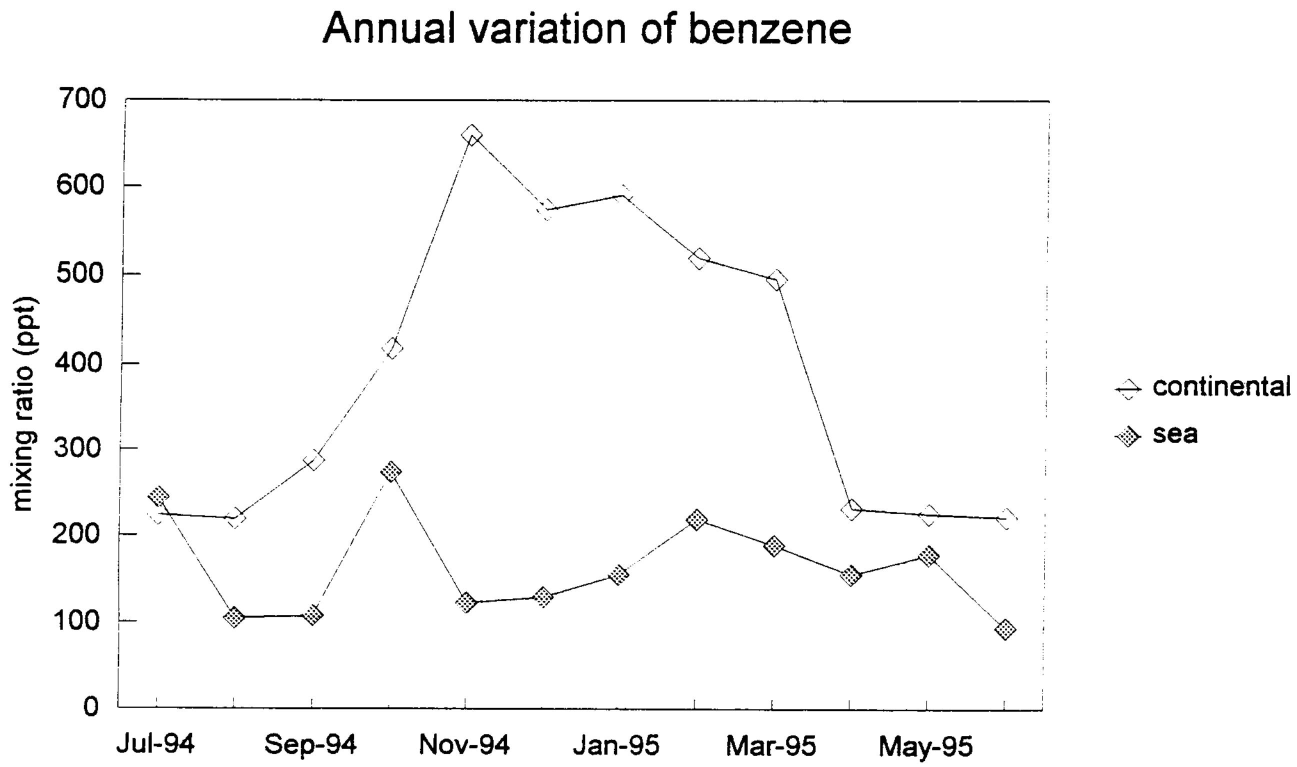

Figure C.7k Annual variation of benzene for continental and sea sector.

APPENDIX D

D.1 Statistical analysis of O_3 data

$$N(\text{month}) = C + \beta_T \, . \, t \qquad [D1]$$

where:		
	$N =$	concentration;
	month=	January, ..., December;
	$\beta_T =$	linear trend coefficient;
	$t =$	number of months from the beginning of the record;
	$C =$	constant representing a seasonal term (mean concentration in a given month over the whole period of time).

Since we solve this equation for each of 12 months we get for every month:

$$N = \mu(i) + \beta_T \, . \, t \qquad [D2]$$

Here we use the whole dataset and monthly means as calculated above:

$$\beta_T = [N - \mu(i)] \;\; t^{-1} \qquad [D3]$$

$$N - \mu(i) = \beta_T \, . \, t + \text{residual} \qquad [D4]$$

The linear trend β_T [ppb year^{-1}] = (β_T / <μ(i)>) . 100% [% year^{-1}].

The error in β_T is not better than ≈ (residual / <N>) . 100% when you draw a line through the data $N = C + \beta_T \, . \, t$; where C = constant.

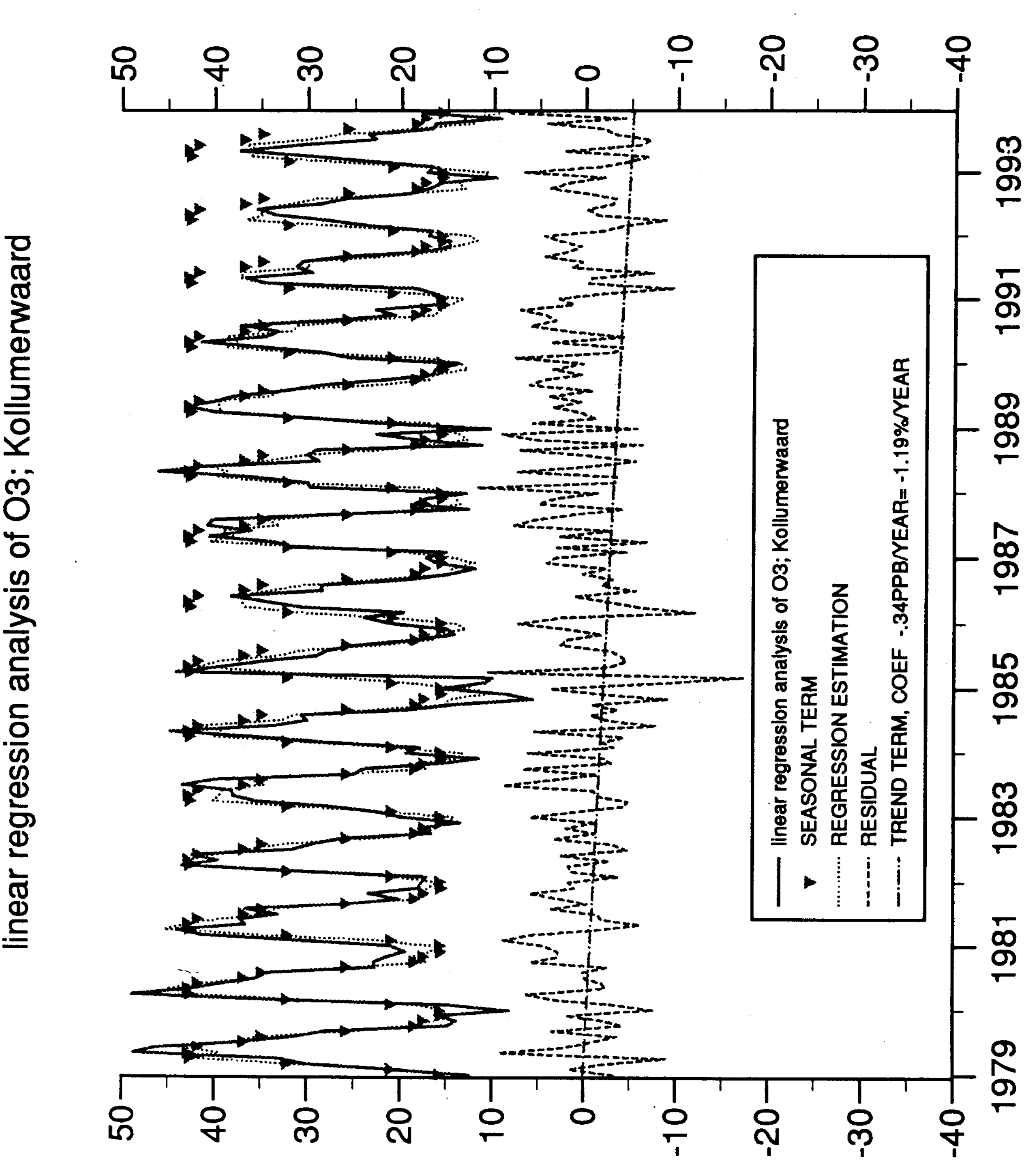

Figure D6.1a The trend in the ozone concentration at the Kollumerwaard station (whole dataset).

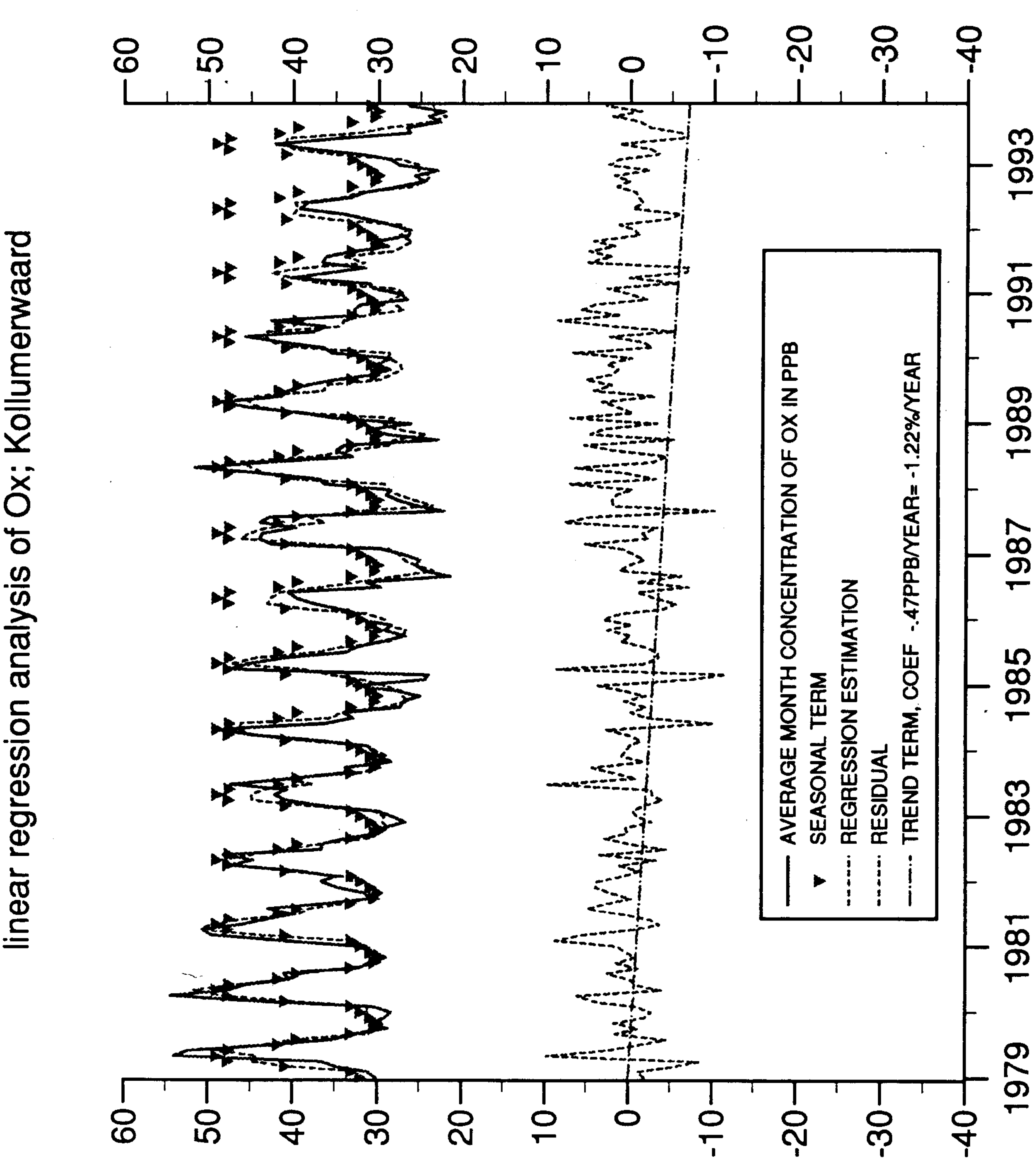

Figure D6.1b The trend in the oxidant concentration at the Kollumerwaard station (whole dataset).

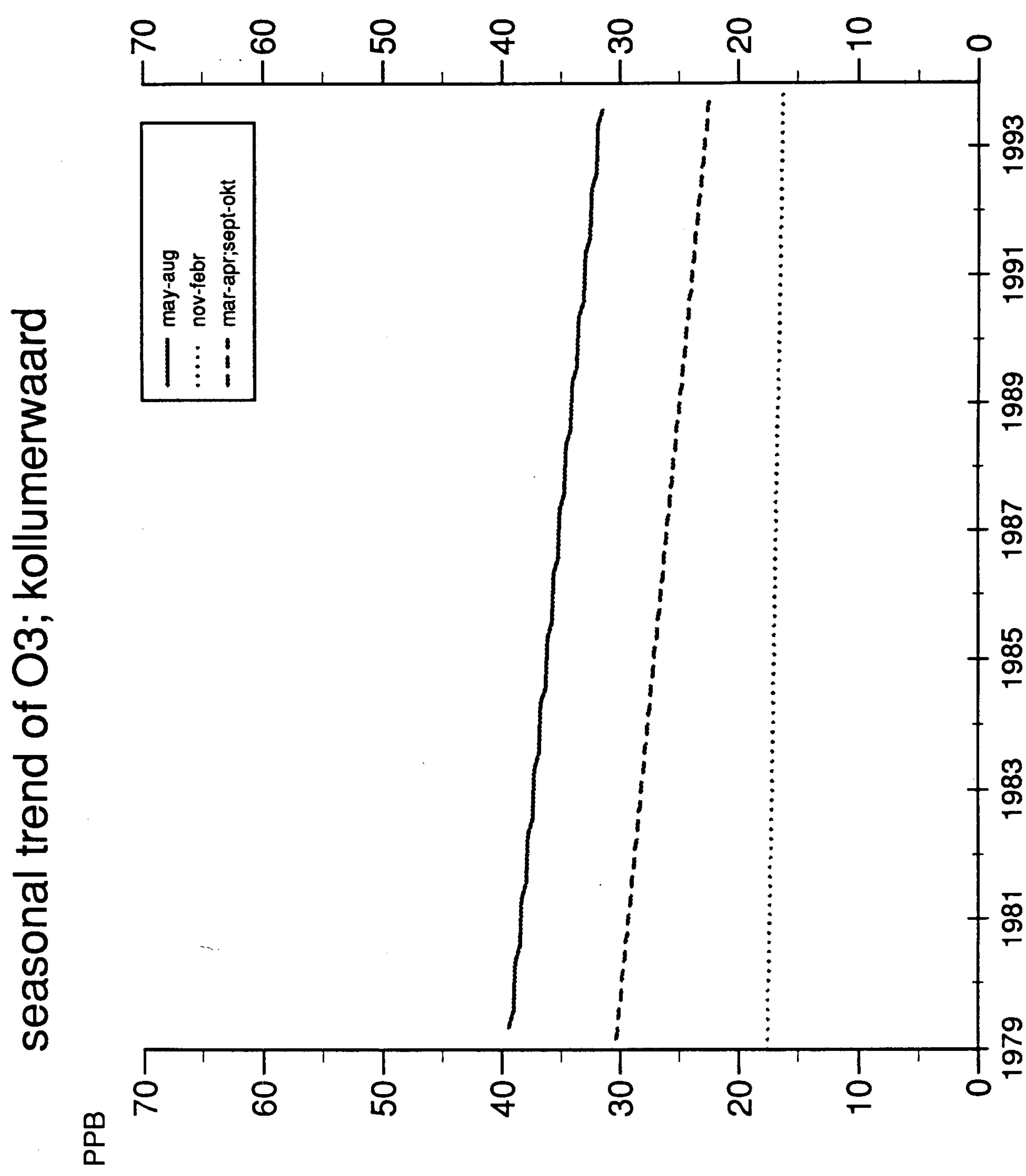

Figure D6.2a The trend in the ozone concentration at the Kollumerwaard station durin summer (May - August), winter (November - February) and the transition period (March - April; September - October).

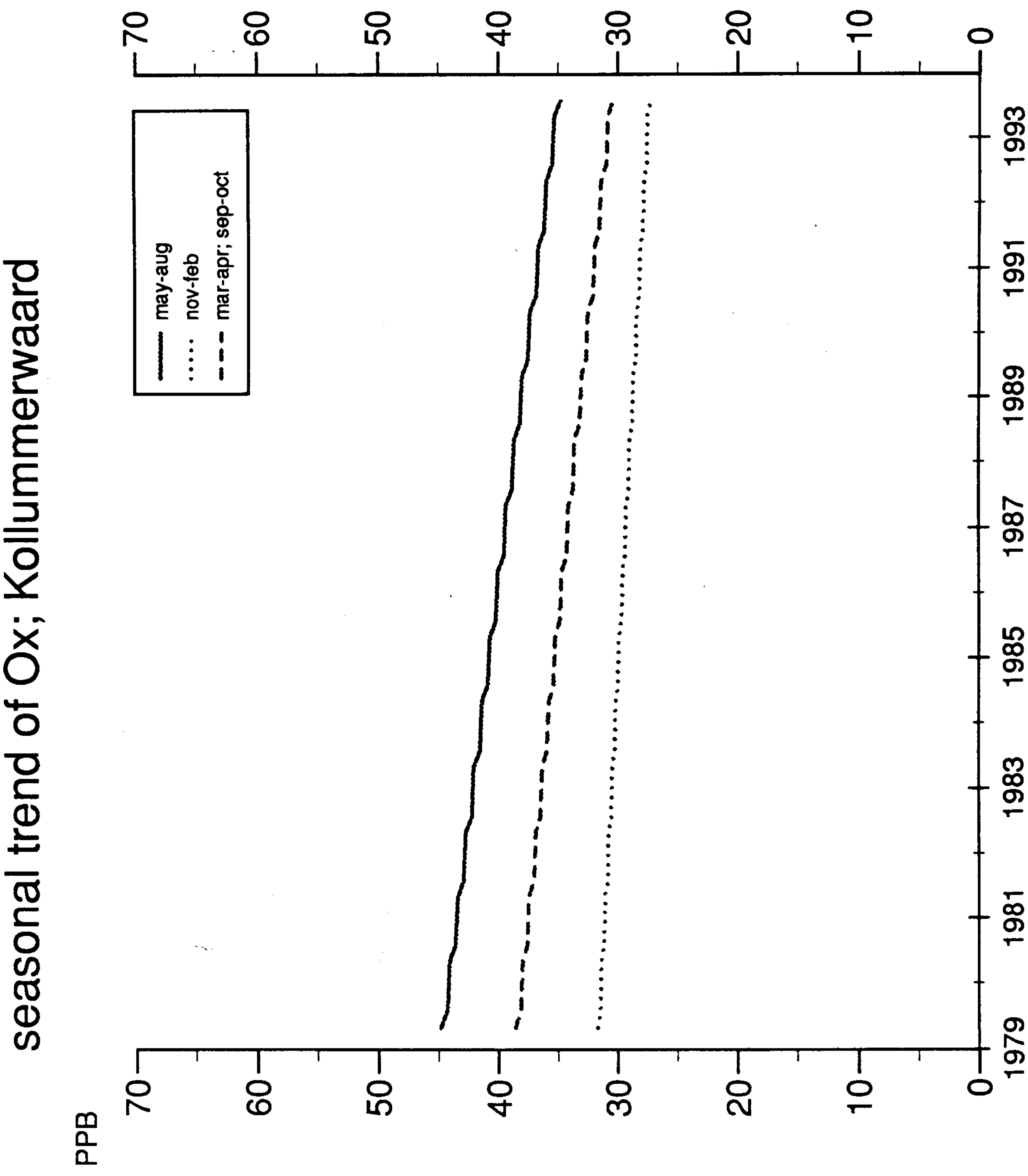

Figure D6.2b The trend in the oxidant concentration at the Kollumerwaard station durin summer (May - August), winter (November - February) and the transition period (March - April; September - October).

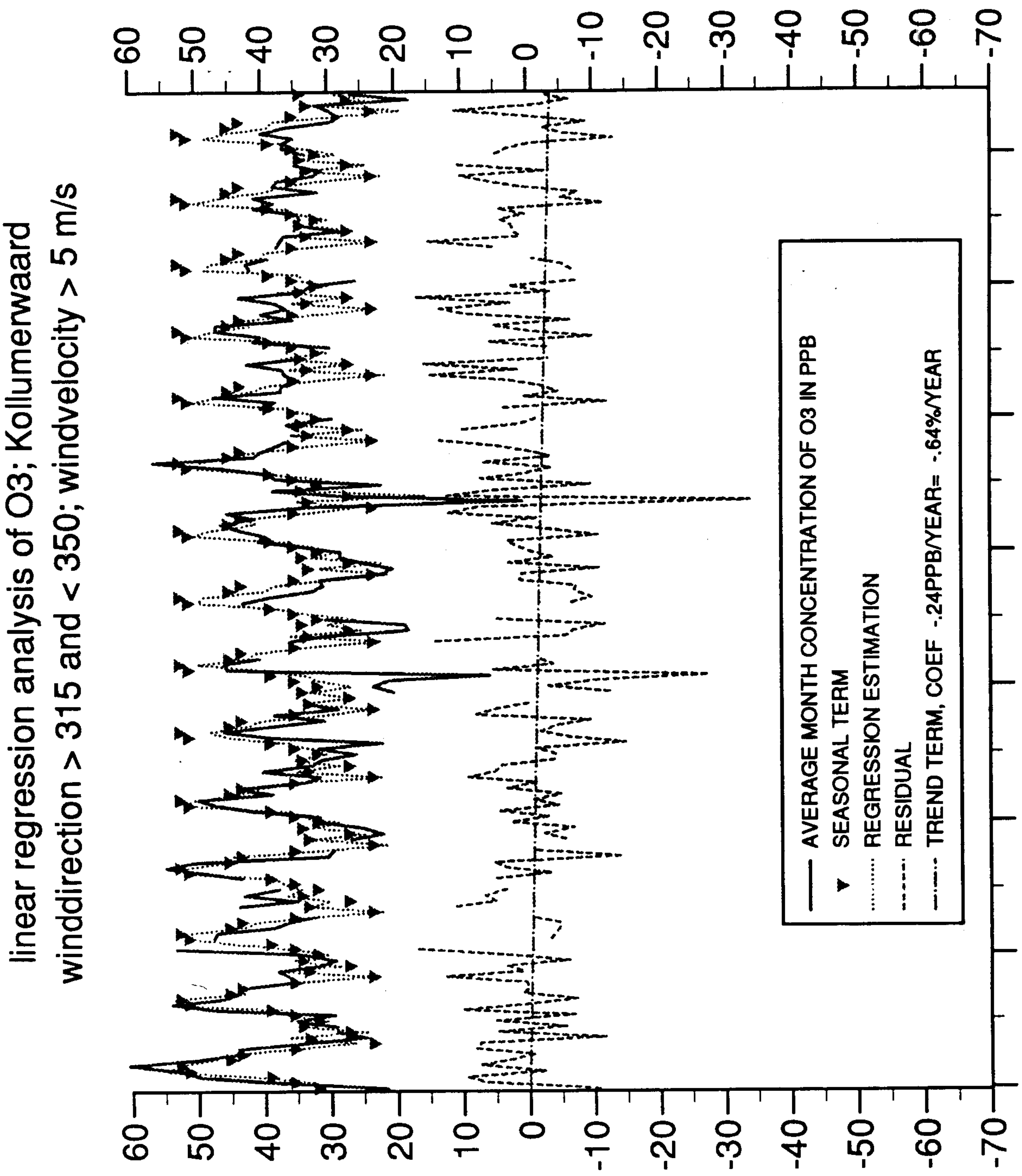

Figure D6.3a The trend in the ozone concentration at the Kollumerwaard station; clean sector data (Wind direction between 315° and 350° and wind speed > 5 m s^{-1}).

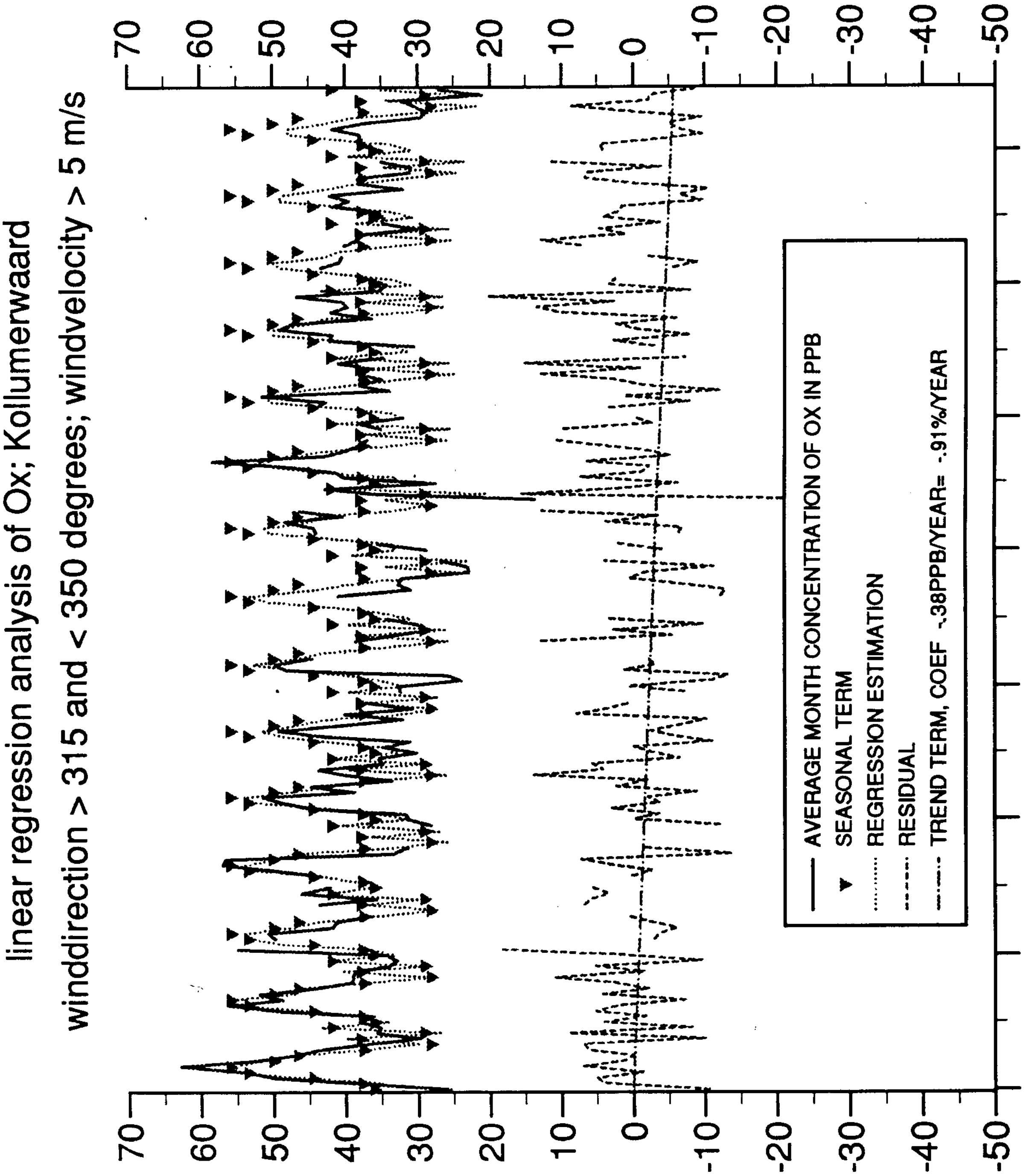

Figure D6.3b The trend in the oxidant concentration at the Kollumerwaard station; clean sector data (Wind direction between 315° and 350° and wind speed > 5 m s^{-1}).

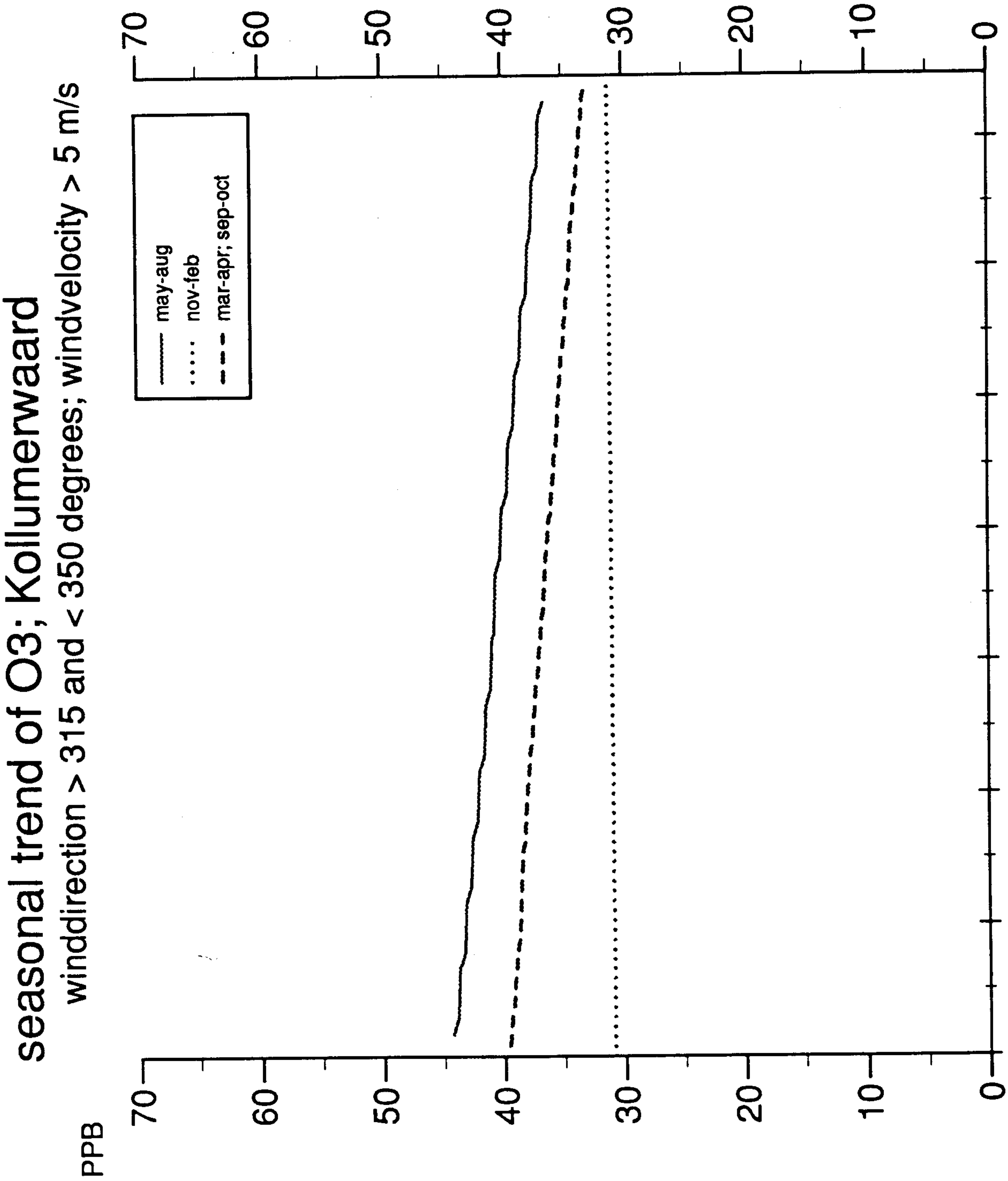

Figure D6.4a The trend in the ozone concentration at the Kollumerwaard station; clean sector data per season (Wind direction between 315° and 350° and wind speed > 5 m s^{-1}; in summer (May - August), winter (November - February) and the transition period (March - April; September - October).

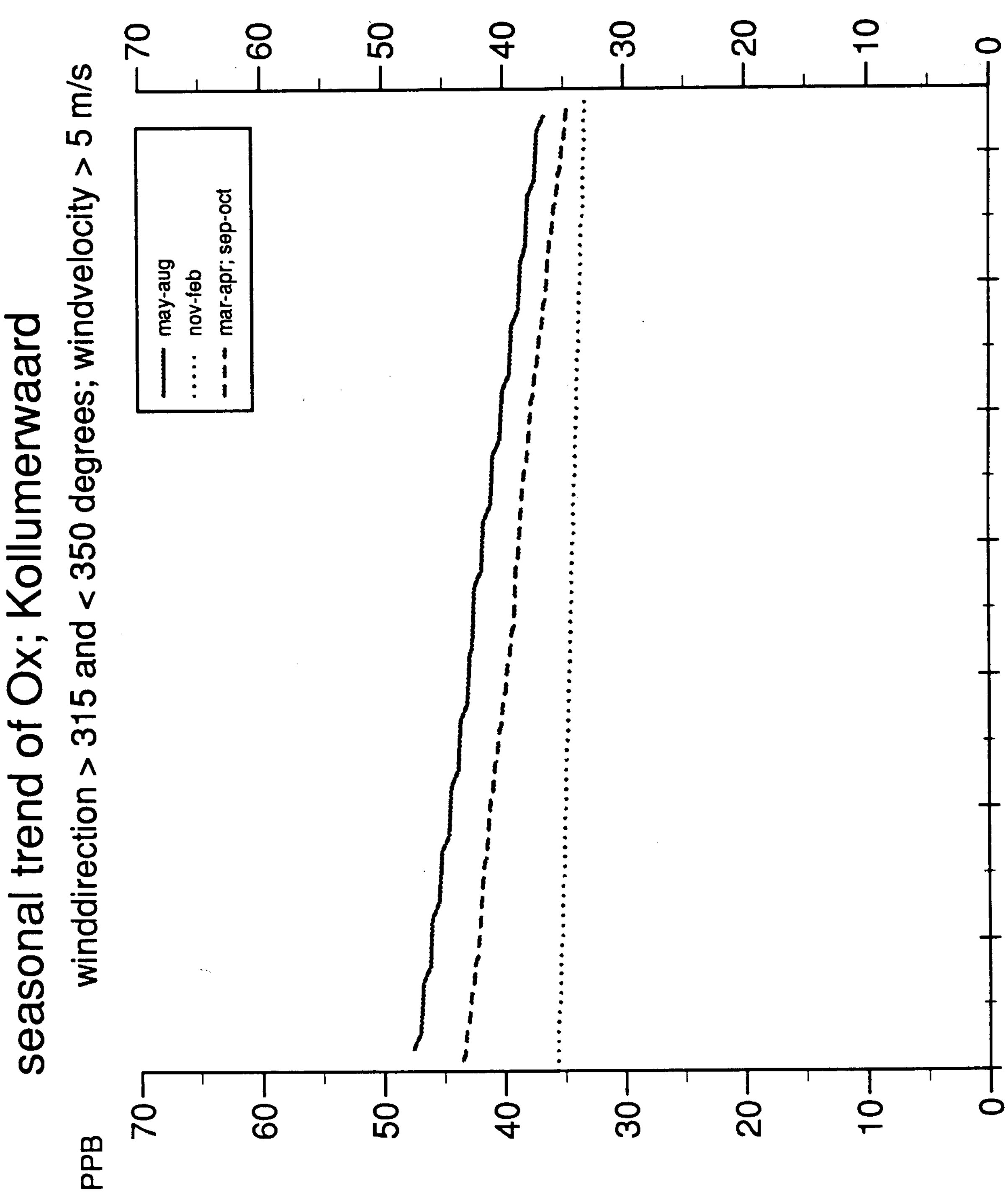

Figure D6.4b The trend in the oxidant concentration at the Kollumerwaard station; clean sector data per season (Wind direction between 315° and 350° and wind speed > 5 m s^{-1}; in summer (May - August), winter (November - February) and the transition period (March - April; September - October).

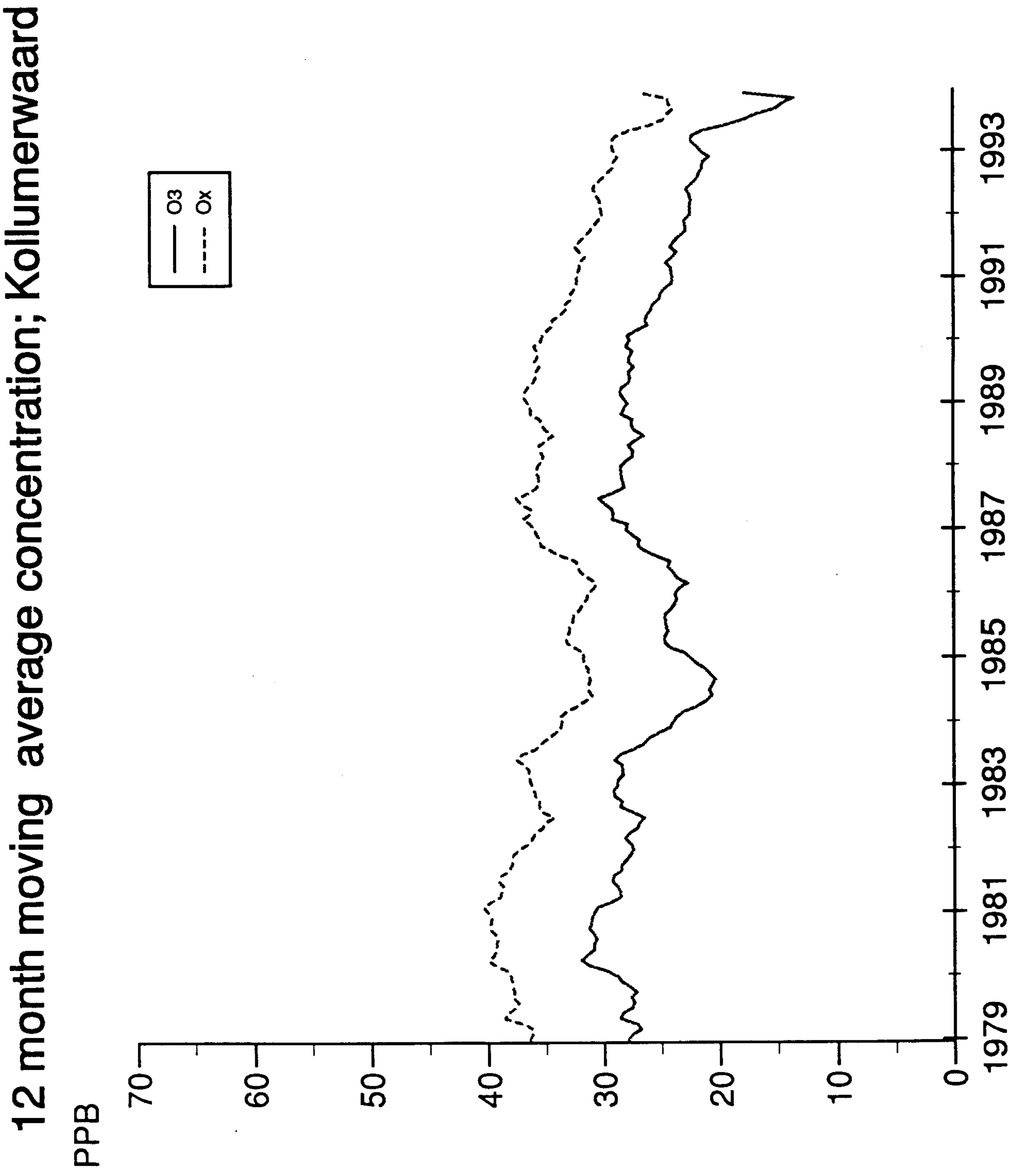

Figure D6.5 The trend in the ozone and oxidant concentration at Kollumerwaard as a 12 months moving average.

APPENDIX E

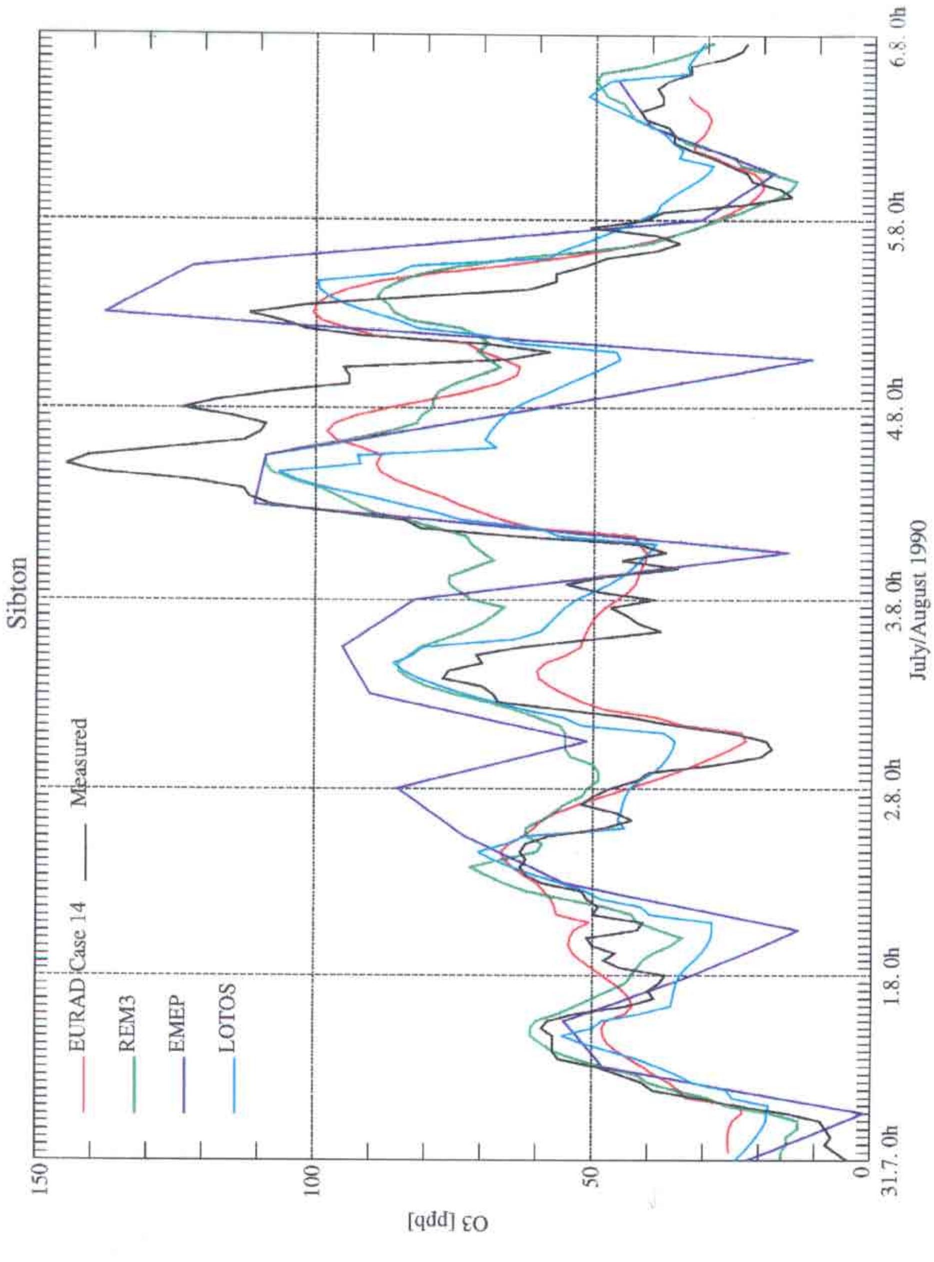

Figure E7.2 Calculated and measured O_3 concentrations at Sibton (UK). Calculated values are generated by the EURAD, REM3, EMEP and LOTOS models.

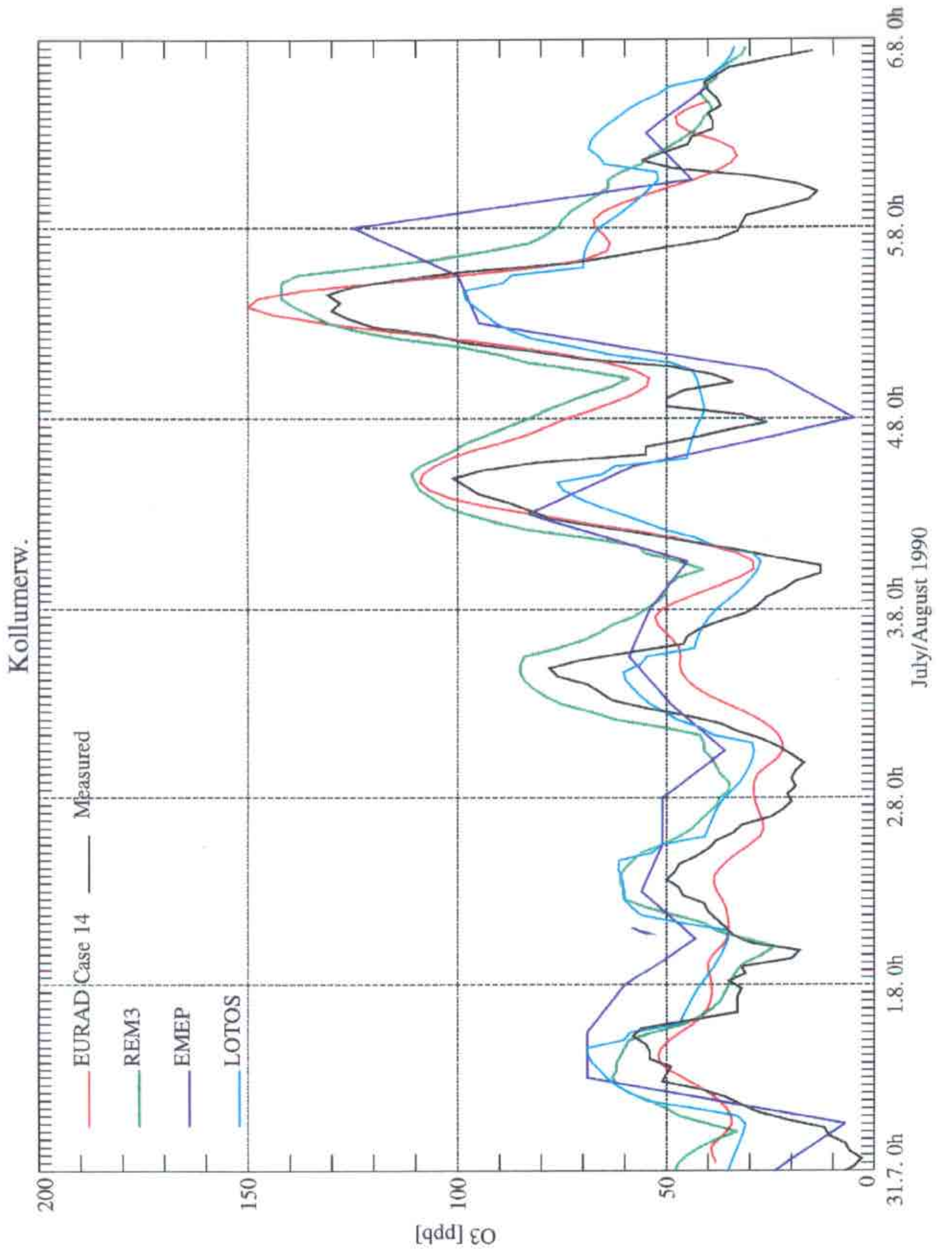

Figure E7.3 Calculated and measured O_3 concentrations at Kollumerwaard (NL). Calculated values are generated by the EURAD, REM3, EMEP and LOTOS models.

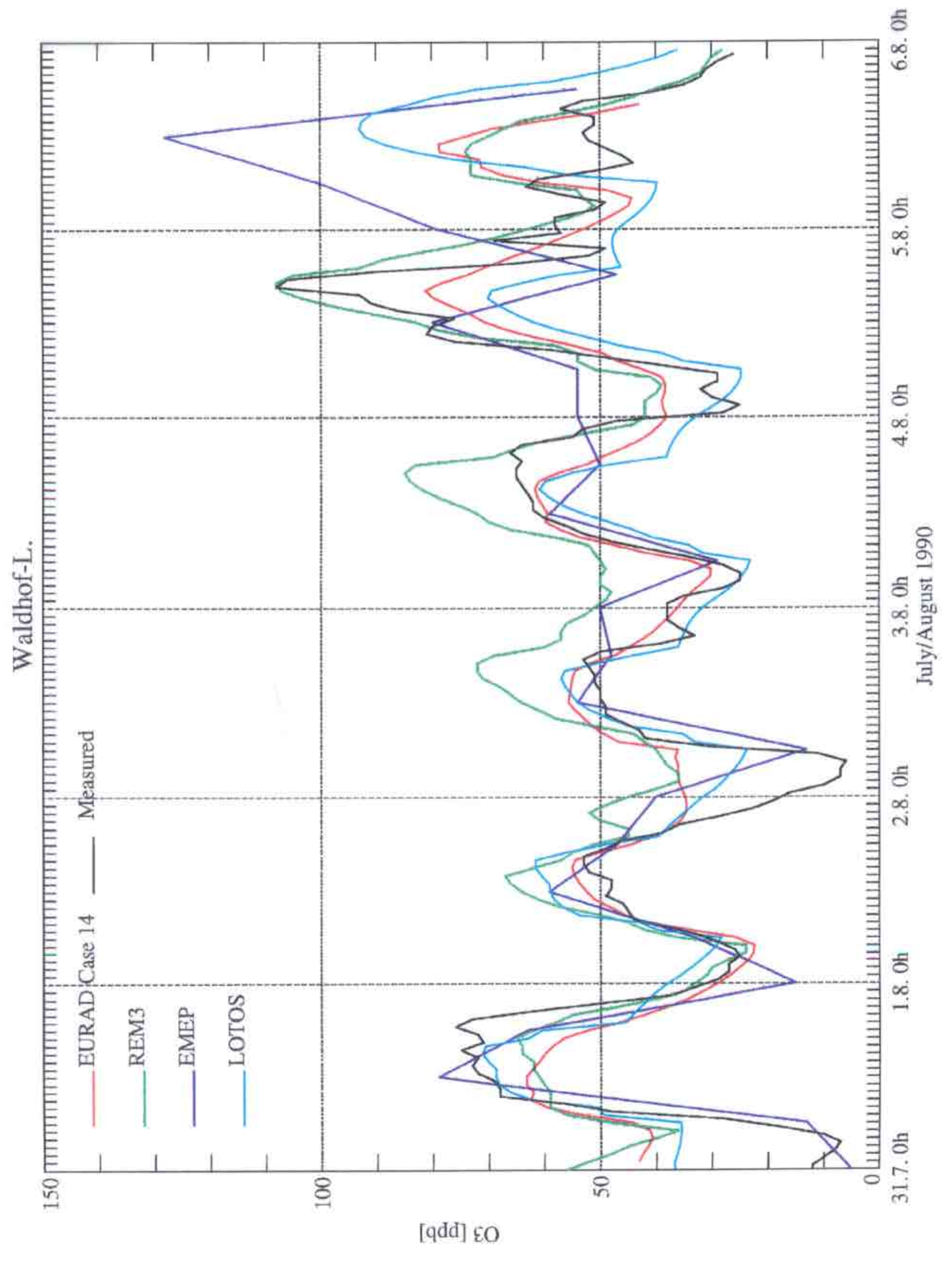

Figure E7.4 Calculated and measured O_3 concentrations at Waldhof-Langenbrügge (D). Calculated values are generated by the EURAD, REM3, EMEP and LOTOS models.

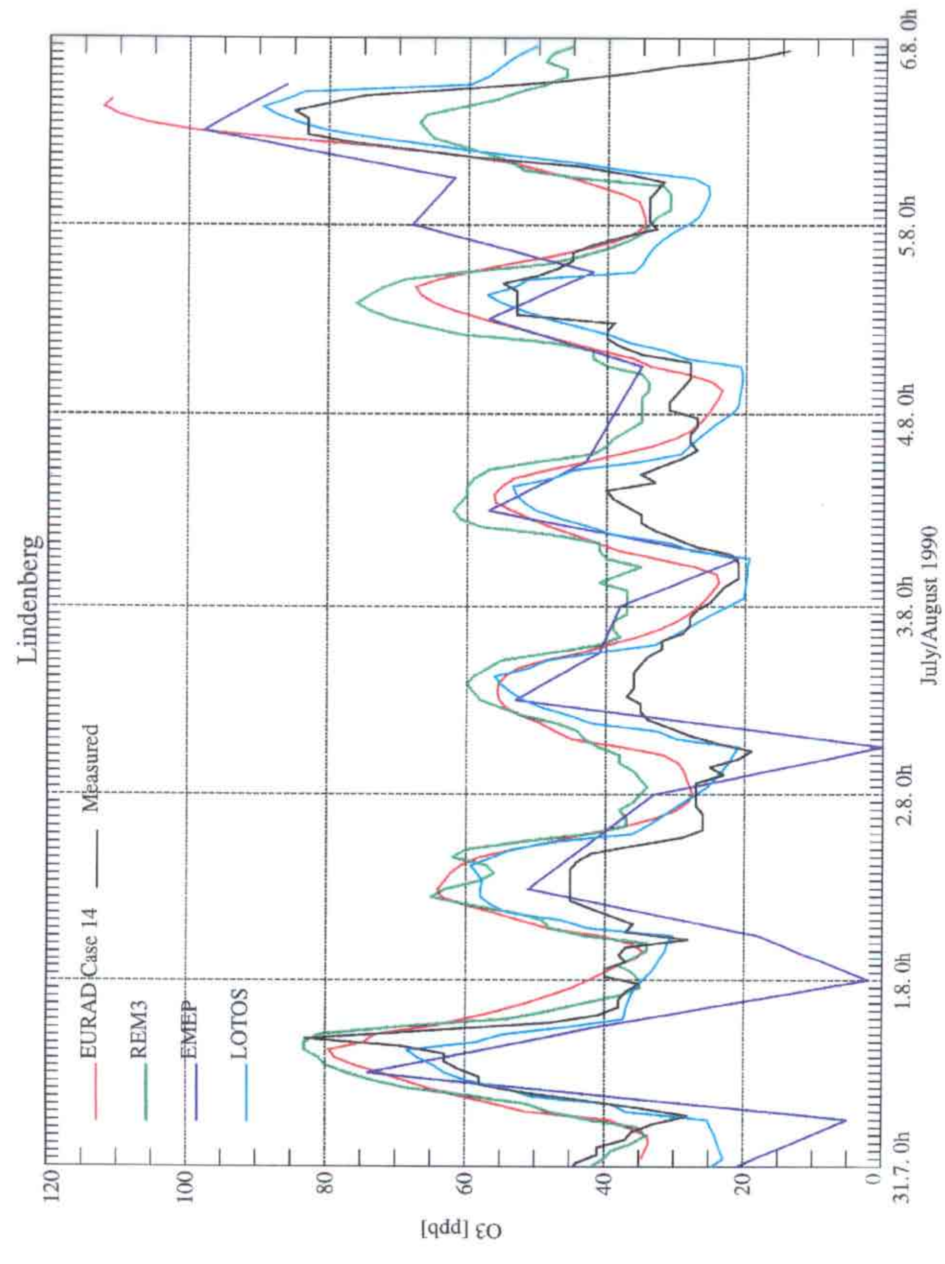

Figure E7.5 Calculated and measured O_3 concentrations at Lindenberg (D). Calculated values are generated by the EURAD, REM3, EMEP and LOTOS models.