Working Paper

Statistical Analysis of Tropospheric Ozone Concentration

Anu Kettunen, Wolfgang Schöpp,
Zbigniew Klimont

WP-94-88
August 1994

IIASA International Institute for Applied Systems Analysis □ A-2361 Laxenburg □ Austria
Telephone: +43 2236 71521 □ Telex: 079 137 iiasa a □ Telefax: +43 2236 71313

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Foreword

The problem of locally and regionally increased concentrations of tropospheric ozone is currently subject of scientific research carried out by IIASA's Transboundary Air Pollution Project. Work aims at the development of an integrated approach to assess strategies to reduce environmental damage caused by tropospheric ozone in cost-effective ways. However, on this way many important questions come up, which are still unresolved. One of these problems is related to the relevant temporal exposure pattern actually determining environmental damage for human health, agricultural crops, forests, etc. Obviously, strategies to reduce short-term peak ozone during episodes might be different from strategies aiming at reducing long-term exposure.

As an initial step in order to get a first insight into the current situation the work carried out by Any Kettunen analyzed the temporal exposure patterns of ozone for 50 European monitoring stations. This work was performed as part of IIASA's Young Scientist's Summer Programme in 1993.

Acknowledgements

This work was carried out at the International Institute for Applied Systems Analysis (IIASA) during the summer of 1993. I was a student in the Young Scientists' Summer Program (YSSP) working with the Transboundary Air Pollution research project. The leader of the group, Dr. Markus Amann, showed continuous interest in the work, which I greatly appreciate. Dr. Amann created a free and enjoyable working atmosphere among the project members that helped a lot in the work. The Vice Dean of Young Scientists' Summer Program, Ger Klaassen gave encouraging comments throughout the summer. The project secretary, Margaret Gottsleben, was always ready to help with practical questions.

Finally, I thank my husband Mika for supporting and encouraging me to accept the opportunity to work at IIASA and to accomplish this work.

Anu Kettunen
YSSP student 1993

First and foremost, we thank Anu Kettunen for her work during summer of 1993 which resulted in this paper as well as created solid basis for further work, in Transboundary Air Pollution project, on related issues. We are pleased to acknowledge the co-operation of Anu and we believe it was beneficial for both sides.

We would like to express our gratitude also to the Norwegian Institute for Air Research in Lillestrom and the Austrian Environmental Agency, Vienna, for providing the underlying data bases.

The critical review of this work by our colleagues from Transboundary Air Pollution project at IIASA is gratefully acknowledged.

Wolfgang Schöpp,
Zbigniew Klimont
Transboundary Air Pollution

Contents

Abstract

This paper analyzes ozone monitoring data obtained from 50 European stations operated by the Co-operative Programme for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe (EMEP) and two stations maintained by the Austrian Environmental Agency. Data used in the analyses covered the summer period of the year 1990.

The analysis explores first time series of ozone concentration and establishes simple statistical parameters such as maximum, average, daily variation and exceedance indices. It is shown that different indices rank high at different locations in Europe, stressing the importance of well-based information when establishing relationships to environmental impacts. Different characteristic exposure patterns are identified for Northern Europe, Central Europe and the UK.

The analysis shows that at some stations also night time ozone concentration has a remarkable effect on cummulated excess ozone. Thus, caution should be exerted when excluding the nighttime values until more detailed data on the biological effects of nighttime high concentrations are obtained.

Statistical Analysis of Tropospheric Ozone Concentration

Anu Kettunen,[*] *Wolfgang Schöpp,*[**]
Zbigniew Klimont[**]

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[*] Systems Analysis Laboratory, Helsinki University of Technology, FIN-02150 Espoo, Finland
Tel: +358 0 451 3054
Fax: +358 0 451 3096
E-mail: akettune@leka.hut.fi
[**] International Institute for Applied Systems Analysis, A-2361 Laxenburg, Austria
Tel: +43 2236 715210
Fax: +43 2236 71313
E-mail: schoepp@iiasa.ac.at; klimont@iiasa.ac.at

1 Introduction to the Ozone Problem

1.1 Ozone in Stratosphere and Troposphere

Ozone (O_3) is a chemical compound consisting of three oxygen atoms. Ozone concentration in the earth's atmosphere reaches its maximum in the stratosphere where a mixing ratio of over 10,000 parts per billion (ppb = 1 ozone molecule per 10^9 molecules of air) is typically found. The stratospheric ozone layer is important for protecting life on earth, because it absorbs a great proportion of ultraviolet radiation from the sun. Due to human activity, the stratospheric ozone concentration is decreasing, which is believed to cause an increase in human skin cancers [18].

Although most of the atmospheric ozone is found in the stratosphere, the troposphere contains about 10–15 % of the total ozone in the atmosphere [8]. Nowadays, tropospheric ozone concentrations range typically within a few tens ppb. In the past a trend of increasing tropospheric ozone concentration has been observed. About 100 years ago, the surface ozone concentration near Paris averaged about 10 ppb [28] and today, even the lowest European average ozone concentrations range between 20 and 45 ppb [11]. During the 1980s, an average increase of 1% per year in European tropospheric ozone concentration was measured [26] [27].

1.2 The Importance of Ozone Data Analysis

Exposure to high tropospheric ozone concentrations cause harm to plants and animals. The biological effects of high ozone concentration depend, however, on the exposure time as well as on the concentration itself. It has been shown that short-term exposures can cause visible plant leaf injury, while long-term exposures are likely to result in reduced yield [3]. There exists, however, still scientific discussion about the relation of temporal exposure patterns to environmental damage. Some researchers emphasize the importance of short-term exposure to plants (see [19, p.37] for a summary of these studies). Others are questioning the "biological significance" of single peak values in the light of the vegetation's recovering ability [3]. As far as humans are concerned, the short-term high concentration exposures affect the respiratory system [16]. The effects of chronic exposure to humans have not been extensively studied.

Critical threshold levels for ozone concentrations have been suggested for short-term (from 1 to 8 hours) and long-term (e.g., growing period) exposures. Various short-term limits have been proposed and used [1, 2, 3, 19]. Similarly, also different proposals on critical long-term levels exist. As will be shown in the following analysis, the temporal characteristics of local ozone exposure show significant variations over Europe, not all of the suggested limit values are usually exceeded at individual sites at the same time. For example, at some rural places the one-hour mean is almost never exceeded, whereas the long-term average can be very high. For urban areas the situation may be reversed [3].

It should be noted that the average ozone concentration does not correlate with injuries to plants, as the same mean can result from different exposure patterns [3]. Cumulative indices have been proposed by Lefohn and Benedict [14] and used by Lee [12, 13] and Lefohn [15] to describe potential damage from ozone exposure. Looking at agricultural crops, indices emphasizing peak concentrations or accumulated exceedances of a threshold fit better to observed yield data than indices based on average concentrations [12, 15]. In addition, exposure patterns with episodic peaks seem to be more harmful to plants than exposures without episodic peaks [10, 17].

In view of the uncertainties around the proper exposure index for describing environmental threats imposed by increased ozone concentrations this paper carries out various statistical analyses on available European monitoring data to identify basic characteristics of ozone exposures in Europe.

2 Description of Ozone Data

For this analysis two data on ozone monitoring data were obtained. A European data set compiled by the Chemical Coordinating Center of EMEP at the Norwegian Institute for Air Research (NILU) provides measurement results from 50 stations, mainly located in the North-west of Europe. This data set enables initial analysis of the regional characteristics of ozone exposure in Europe. The second data set contains ozone monitoring results together with meteorological information from two Austrian stations and was used to explore the relationship between ozone concentration and meteorological conditions.

2.1 Austrian Stations

Data from two Austrian measurement stations were provided by the Austrian Environmental Agency. The station with the code AS01 is situated in Illmitz close to the Hungarian border. Station AS02 is located in St. Koloman in the central regions of the Alps. The geographical location of Austrian stations can be seen in Figure 1. The period of measurements covered three years, beginning in 1990. In addition to ozone concentration (O_3), temperature (T), radiation (R), wind speed (W_s) and wind direction (W_d) were measured at both stations. Furthermore, St. Koloman reports also concentrations of nitrogen oxides (NO and NO_2). The sample interval was 30 minutes.

For this analysis only the measurements during the vegetation period were considered, because the ozone concentrations are greater and their effects on plants and animals in the growing season are more important. The actual growing period varies from country to country. For these two sites the summer period has been defined from April 1 to September 30.

Since the original data files provide data on ozone, NO, and NO_2 concentrations in parts per billion (ppb), no conversion was necessary. Temperature is in Celsius degrees, radiation in $\frac{mV}{s}$ (1 mV corresponds to 61 $\frac{W}{m^2}$), wind speed in $\frac{m}{s}$, and wind direction in degrees, zero meaning calm, 90 east, 180 south, 270 west and 360 north. Wind speed in the direction east-west or north-south was calculated from absolute wind speed and direction with sin and cos transformations;

$$\begin{aligned} W_x &= W_s sin(W_d) \\ W_y &= W_s cos(W_d) \end{aligned}$$

Thus, winds blowing from east and north are positive and southern and western winds are negative. Since a value of zero in wind direction means calm weather, corresponding wind speed should also be zero (see Appendix I).

The original data files received from the Austrian authorities were in a raw format, requesting some basic consistency and plausibility checks. Non-available (missing) values were marked with an asterisk. Concentration values, radiation and wind speed should always be non-negative. Although, in principle, temperature can be negative, during the summer period temperatures far below zero are highly unlikely. For the further statistical analysis suspicious values have been treated equal to missing values (see Appendix I).

2.2 International Stations

Data from 50 international EMEP measurement stations were obtained from Chemical Coordinating Center (CCC-EMEP) installed at the Norwegian Institute for Air Research (NILU). The codes and names for the stations, as well as the geographical coordinates, are shown in Table 1. The locations of the stations on the map are shown in Figure 1.

From Table 1 and Figure 1 it can be seen that the stations are not situated uniformly all over Europe. Data for southern and eastern stations are missing, except for the Portuguese station. Northern and western European stations are well represented. For these 50 stations,

Figure 1: The geographical location of ozone measurement stations. Stations PO04 and NO42 are not shown on the map.

Code	Name	Country	Longitude	Latitude
AS01	Illmitz	Austria	16.80	47.77
AS02	St. Koloman	Austria	13.25	47.50
BE01	Offagne	Belgium	5.20	49.88
BE31	Berendrecht	Belgium	4.34	51.35
BE32	Eupen	Belgium	6.00	50.63
BE33	Moerkerne	Belgium	3.36	51.26
BE34	St. Denijs	Belgium	3.37	50.75
CH02	Payerne	Switzerland	6.95	46.82
CH31	Sion	Switzerland	7.33	46.22
CH32	Taenikon	Switzerland	8.90	47.48
DK31	Ulborg	Denmark	8.43	56.28
DK32	Fredriksborg	Denmark	12.33	55.97
IT04	Ispra	Italy	8.63	45.80
NL02	Witteveen	The Netherlands	6.67	52.82
NL08	Bilthoven	The Netherlands	5.20	52.12
NL31	Kollumerwaard	The Netherlands	6.20	53.30
NO01	Birkenes	Norway	8.25	58.38
NO30	Jergul	Norway	24.60	69.45
NO39	Kaarvatn	Norway	8.88	62.78
NO41	Osen	Norway	11.78	61.25
NO42	Zeppelinfjellet	Norway	11.88	78.90
NO43	Prestebakke	Norway	10.60	59.00
NO44	Nordmoen	Norway	11.10	60.27
NO45	Jeloya	Norway	10.60	59.43
NO47	Svanvik	Norway	30.03	69.45
NO48	Voss	Norway	6.53	60.60
NO49	Valle	Norway	7.57	59.05
NO50	Tustervatn	Norway	13.92	65.83
PO04	Monte Velho	Portugal	-8.80	38.08
SE02	Rorvik	Sweden	11.93	57.42
SE11	Vavihill	Sweden	13.15	56.02
SE32	Norra Kvill	Sweden	15.57	57.82
SE35	Vindeln	Sweden	19.77	64.25
SF04	Ähtäri	Finland	24.22	62.53
SF09	Utö	Finland	21.38	59.78
UK02	Eskdalemuir	United Kingdom	-3.20	55.32
UK06	Lough Navar	United Kingdom	-7.90	54.45
UK13	Yarner Wood	United Kingdom	-3.70	50.60
UK14	High Muffles	United Kingdom	-0.80	54.33
UK15	Strath Vaich	United Kingdom	-4.78	57.73
UK31	Aston Hill	United Kingdom	-3.33	52.50
UK32	Bottesford	United Kingdom	-0.82	52.93
UK33	Bush	United Kingdom	-3.20	55.87
UK34	Glazebury	United Kingdom	-2.47	53.47
UK35	Great Dun Fell	United Kingdom	-2.45	54.68
UK36	Harwell	United Kingdom	-1.32	51.57
UK37	Ladybower	United Kingdom	-1.75	53.33
UK38	Lullington Heath	United Kingdom	0.18	50.78
UK39	Sibton	United Kingdom	1.47	52.30
UK40	Stevenage	United Kingdom	-0.20	51.88
UK41	Wharley Croft	United Kingdom	-2.47	54.62
UK42	Central London	United Kingdom	-0.13	51.48

Table 1: The code, name and geographical locations of the stations.

only ozone concentration measurements were available. The sample interval was one hour. The measurement period covered the year 1990, but only the summer period from the beginning of April until the end of September was used in this analysis. The ozone concentrations were measured with different methods at different stations. Belgian, Swiss, Dutch, Norwegian and United Kingdom ozone concentrations were measured by UV absorption. UV photometry was used at the Danish and Finnish stations, UV spectroscopy at the Italian station and chemiluminescence at the Swedish stations. For the Portuguese station it was only indicated that a method based on UV radiation was used. A discussion of the different measurement methods can be found in [19]. The unit used in original data files was either ppb (United Kingdom stations) or $\frac{\mu g}{m^3}$. The conversion from $\frac{\mu g}{m^3}$ to parts per billion was obtained as follows (for details see [23, p.7]): Given the ozone mass concentration m_o (in μg per m^3) the molecular ozone concentration cm_o is written

$$cm_o = 10^{-6} \times \frac{m_o}{M_o}$$

where $M_o = 3 \times 16 = 48\frac{g}{mol}$ is the molecular mass of ozone. The ozone concentration in parts per billion is expressed using molar concentration of ozone

$$c_o = 10^9 \times \frac{cm_o}{c}$$

where $c = \frac{p}{RT}$ is air moles at temperature T and pressure p where R is the gas constant (R= $8.314 \cdot 10^{-2}$ mbar m^3 K^{-1} mole^{-1}). Substituting cm_o and c to the expression of c_o the formula

$$c_o = 10^3 \times \frac{RT}{pM_o} m_o$$

is obtained.

At normal atmospheric pressure (1000 mbar) and temperature (273 K), the coefficient $10^3 \times \frac{RT}{pM_o}$ is approximately 0.5, which was considered as sufficiently accurate for the analyses in this paper.

3 Data Analysis

3.1 Missing Data

In an ideal situation all the measurements would be available. In practice, however, some values are missing, due to technical problems and human errors. In data analysries the missing values have to be dealt with. For this study missing (non-available) measurements have been skipped and only the valid data have been used.

The amount of non-available measurements clearly affects the quality of data analyses. The more measurements that can be used in calculating an estimate of a statistical parameter, the better the estimate will approximate the true value, if the estimators of statistical parameters are consistent, as they generally are. In an extreme case, where there are only non-available measurements, naturally, no estimates can be calculated. The share of available valid measurements for different stations is presented in Table 2. Some measurement stations have very few, or no missing values, as, for example, the Italian station IT04 or the Norwegian stations NO41, NO43 and NO44; UK02¿95while others, e.g., the Belgian stations BE01 and BE32 and the Austrian station AS02 (for summer 1990), have very many missing values.

In addition to the amount of non-available measurements, their distribution in time is also important, since the available measurements might not correctly represent the real distribution of the whole data. Any calculated statistics could be tampered with, e.g., changes of the ratio of available daytime to nighttime ozone measurements. If more daytime values are missing, the remaining ozone concentrations would be lower, on average, than if more nighttime measurements are missing. Fortunately, missing values occurred in ozone data files as often during daytime as during nighttime. The monthly proportion of daytime available measurements to all measurements, which is 50 % in the ideal case, varied between 45 % and 55 % when all the measurement stations were considered.

Ozone concentrations show considerable diurnal variation. As a result, days with no missing values give far more reliable estimates for daily parameter values than days with many missing values. An analysis using only days with no missing values would be one reasonable possibility. In practice, however, excluding all days with some missing data would have lead to a considerable loss of information, since only a small proportion of days would have been left for some stations. There were seven stations (AS01-92, AS02-91, BE01, BE31, BE32, BE33, DK31) with less than 30 days without missing values and 14 stations (AS01-92, AS02-90, AS02-91, BE01, BE31, BE32, BE33, BE34, DK31, SF09, UK06, UK14, UK34, UK38) having less than 120 days. Therefore, all the available data was used, i.e., when missing values occurred, only these data points (hourly measurements) were disregarded and not the entire days. An exception to this rule was the calculation of the index describing the daily variation (see Chapter 3.3.3), where the diurnal variation was considered critical and only days without missing values were included in the calculation.

What should be noticed, in addition to the issue of missing values, is the question of measurement errors. In general, random errors are averaged out when a large amount of data is used in calculating the estimates of the statistical parameters. However, systematic errors remain in the estimates. In principle, different ozone concentration levels are reported if the calibration of ozone measurement differs from one station to another. On the basis of the analyses that were carried out it is not possible to deduce whether there are systematic differences in the measurements when different measurement stations are compared.

3.2 Time Series of Ozone Measurements

It is worthwhile to look at the plots of all the measurement data for individual stations. These plots give the basic characteristics of the stations. In Figure 2 the measured ozone concentrations are shown for three different stations. On average, the Portuguese station PO04 (Fig. 2.a) has a lower ozone concentration level than the Finnish SF04 (Fig. 2.b) or the British UK31 (Fig.

Station	Summer	April	May	June	July	August	September
AS01-90	99%	100%	100%	99%	100%	100%	93%
AS01-91	95%	86%	100%	97%	91%	100%	97%
AS01-92	94%	93%	95%	95%	98%	93%	91%
AS02-90	47%	0 %	0 %	6 %	98%	83%	95%
AS02-91	94%	78%	98%	98%	98%	98%	96%
AS02-92	95%	89%	97%	100%	98%	100%	86%
BE01	33%	24%	59%	0 %	47%	21%	43%
BE31	80%	47%	69%	93%	90%	93%	86%
BE32	54%	12%	0 %	31%	88%	97%	95%
BE33	82%	75%	95%	68%	86%	78%	88%
BE34	90%	83%	92%	91%	94%	83%	97%
CH02	86%	100%	83%	70%	63%	100%	100%
CH31	97%	100%	100%	100%	84%	100%	100%
CH32	99%	100%	100%	100%	97%	100%	100%
DK31	67%	0 %	42%	91%	92%	85%	89%
DK32	87%	79%	97%	73%	99%	98%	75%
IT04	100%	100%	100%	100%	100%	100%	100%
NL02	96%	86%	100%	91%	98%	100%	98%
NL08	95%	100%	89%	94%	86%	100%	100%
NL31	90%	73%	81%	89%	100%	98%	100%
NO01	98%	100%	99%	100%	100%	100%	93%
NO30	97%	95%	94%	99%	95%	99%	99%
NO39	85%	77%	66%	68%	99%	99%	100%
NO41	100%	100%	100%	99%	100%	100%	100%
NO42	95%	100%	98%	100%	100%	99%	70%
NO43	99%	100%	99%	100%	99%	99%	99%
NO44	100%	100%	100%	99%	100%	100%	100%
NO45	99%	100%	99%	100%	100%	98%	99%
NO47	100%	100%	100%	100%	100%	100%	99%
NO48	87%	66%	100%	100%	100%	100%	58%
NO49	83%	77%	60%	100%	79%	80%	100%
NO50	82%	100%	100%	100%	15%	76%	100%
PO04	82%	97%	96%	92%	87%	24%	100%
SE02	96%	99%	89%	97%	100%	92%	100%
SE11	97%	89%	100%	98%	99%	100%	98%
SE32	97%	95%	95%	97%	99%	99%	99%
SE35	100%	100%	100%	100%	100%	100%	99%
SF04	97%	96%	96%	97%	98%	99%	99%
SF09	75%	97%	89%	77%	17%	74%	97%
UK02	99%	95%	100%	100%	98%	100%	100%
UK06	95%	93%	100%	97%	88%	96%	97%
UK13	91%	98%	92%	100%	98%	62%	100%
UK14	95%	96%	100%	97%	86%	99%	93%
UK15	97%	97%	100%	99%	94%	95%	95%
UK31	98%	97%	100%	97%	98%	100%	99%
UK32	98%	96%	100%	100%	99%	92%	100%
UK33	98%	97%	97%	100%	99%	100%	95%
UK34	79%	82%	99%	91%	56%	91%	53%
UK35	96%	91%	100%	92%	100%	100%	92%
UK36	97%	90%	90%	100%	100%	100%	100%
UK37	98%	97%	100%	99%	100%	99%	93%
UK38	93%	82%	100%	85%	97%	96%	100%
UK39	98%	91%	99%	100%	99%	99%	99%
UK40	89%	99%	51%	94%	90%	99%	99%
UK41	96%	97%	97%	98%	100%	88%	97%
UK42	72%	100%	97%	100%	76%	62%	0%

Table 2: Proportion of non-missing measurements in percent.

2.c) stations. Figure 2 can support the statement that the variation in the ozone concentration is larger for station UK31 than for stations SF04 and PO04. However, it is very difficult to base more detailed analysis on plotted ozone concentrations and, in general, statistical parameters can give more exact information than simple data plots.

3.3 Simple Statistics

3.3.1 Maximum value

The maximum ozone concentration is important information, in particular when environmental effects are concerned. The maximum, however, is sensitive to the outlayers in the data. A better indicator of the maximum value might be the high percentile value. The maxima for the whole summer period and the monthly maxima for the measurement stations are shown in Table 3. If there were no appropriate measurements from which the maximum could be derived, the maximum was marked as non-available (NA).

In this data set the highest monthly maximum values occurred most frequently in July and August and the lowest in April and September.

The distribution of the summer maximum values for different stations is shown in Figure 3 in the form of a histogram. Based on this histogram a classification of the stations into three groups was made. The station was considered to have a high (H) maximum if the summer maximum exceeded 130 ppb, medium (M) if it was between 85 and 130 ppb and low (L) for a maximum below 85 ppb. The limits for the classes were obtained by dividing the range covered by the maximum values into three equal length intervals. The biological significance of high peak values was not taken into account.

Based on analysis of the data for the summer of 1990, three Belgian stations (BE31, BE33, BE34), six British stations (UK13, UK32, UK36, UK38, UK39, UK40), the Dutch station NL31, and the Austrian station AS01 belong to the group with high maximum values. Belgium and the Netherlands have high population density, and this generally results in high anthropogenic emissions of ozone precursors. The British stations classified into the high maxima group are situated in southern England, where the population density is higher than in the northern parts of the country. In southern England the continental ozone precursor sources might have an effect on maximum values as well. The group with low maxima includes Nordic stations (7 Norwegian, 1 Swedish and 2 Finnish stations), the Portuguese PO04 and the British station UK15. These stations are situated in the regions where population density is low and anthropogenic sources are therefore rare.

3.3.2 Average value

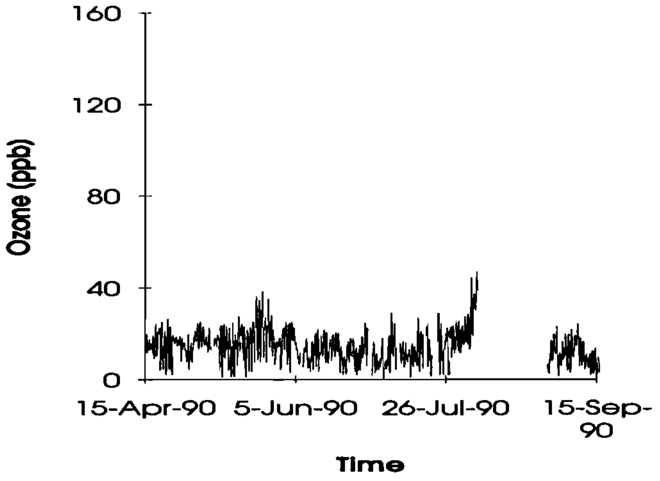
The estimate of average is less sensitive to outlayers than the maximum. The average measured ozone concentrations for the whole summer period and individual months at the measurement stations are shown in Table 4. If there were no appropriate measurements on which the estimate of the average could be based, the average was marked as non-available (NA).

At most of the stations the monthly average values were higher throughout April to August than in September. This might be an important feature when considering potential impacts on living matter. However, it is difficult to draw any specific conclusions about biological effects, since no data concerning damages to plants or animals were used in this analysis. The histogram of the summer average values is shown in Figure 4.

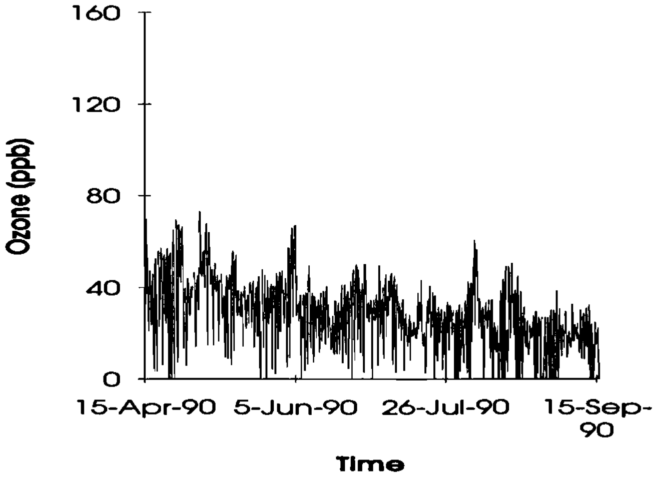
The stations were classified into three groups according to the whole summer average values. A station was assigned to the high average group (H) if the average was exceeding 35 ppb, to the medium (M) if it was between 20 and 35 ppb and to the low (L) for average values below 20 ppb.

Stations CH02, SE11, SE32, SF09, UK13, UK31, UK38, AS01 (summer periods of 1990 and 1992) and AS02 (summer periods of 1990, 1991 and 1992) were classified into high average group.

a) PO04



b) SF04



c) UK31

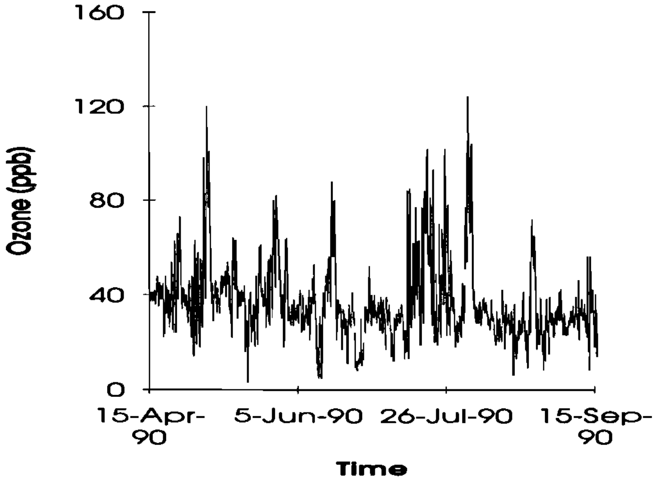


Figure 2: Ozone concentration plots for three different stations a) PO04 b)SF04 and c)UK31.

Station	Classification	Summer	April	May	June	July	August	September
AS01-90	H	139	70	91	85	139	103	88
AS01-91	M	109	63	62	76	109	81	85
AS01-92	M	102	79	102	82	95	96	70
AS02-90	M	101	NA	NA	68	101	91	65
AS02-91	M	101	89	69	88	91	101	79
AS02-92	M	105	69	84	74	87	105	58
BE01	M	90	49	65	NA	90	85	63
BE31	H	148	11	80	10	118	148	50
BE32	M	102	54	NA	63	92	102	60
BE33	H	255	255	99	82	134	148	68
BE34	H	144	88	91	99	142	144	57
CH02	M	96	73	77	80	96	96	70
CH31	M	85	59	73	77	85	80	60
CH32	M	104	54	82	88	94	104	67
DK31	M	111	NA	61	75	64	111	47
DK32	M	93	74	81	74	86	93	49
IT04	M	128	81	93	11	119	128	93
NL02	M	117	74	114	87	102	117	88
NL08	M	119	73	112	11	105	109	95
NL31	H	141	67	90	10	105	141	51
NO01	L	84	66	84	62	54	72	43
NO30	L	73	73	56	61	49	48	40
NO39	L	65	58	65	47	47	59	35
NO41	L	78	68	78	57	55	74	40
NO42	L	58	58	48	38	43	43	45
NO43	M	94	57	78	53	63	94	38
NO44	M	90	77	90	54	63	78	37
NO45	M	97	67	82	68	71	97	44
NO47	L	63	52	63	43	55	45	38
NO48	M	101	73	101	58	50	64	36
NO49	M	85	55	85	62	55	76	40
NO50	L	69	65	69	45	34	60	41
PO04	L	47	35	39	25	29	47	26
SE02	M	112	71	87	73	78	112	45
SE11	M	101	70	84	10	61	88	59
SE32	M	122	74	88	74	77	122	46
SE35	L	65	65	65	55	49	56	34
SF04	L	73	70	73	67	50	61	39
SF09	L	73	69	67	73	51	69	46
UK02	M	106	66	87	73	106	96	44
UK06	M	94	60	75	52	94	41	42
UK13	H	147	93	119	77	127	147	68
UK14	M	111	75	93	77	96	111	48
UK15	L	80	60	80	56	78	52	51
UK31	M	124	73	120	88	102	124	56
UK32	H	138	55	78	74	122	138	46
UK33	M	100	67	74	71	80	100	41
UK34	M	96	67	71	57	92	96	37
UK35	M	114	69	87	77	99	114	49
UK36	H	132	86	109	71	132	113	49
UK37	M	120	68	120	77	106	118	94
UK38	H	161	85	117	85	152	161	68
UK39	H	145	70	115	74	97	145	54
UK40	H	136	73	101	88	124	136	35
UK41	M	102	66	81	71	102	99	44
UK42	M	88	59	88	67	88	83	NA
Average		106	70	84	73	87	97	54

Table 3: Maximum values and the classification of stations based on whole summer maxima.

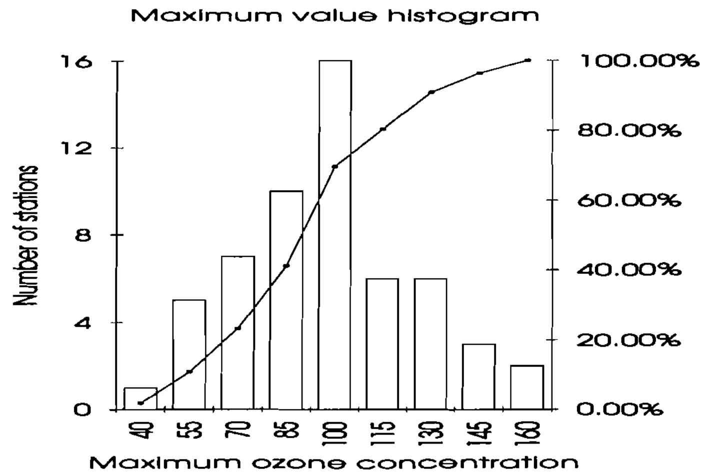


Figure 3: Histogram indicating the distribution of maximum values among the stations.

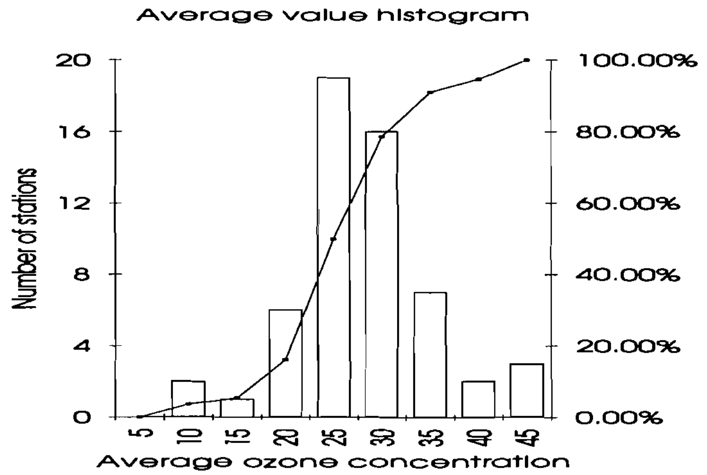


Figure 4: Histogram indicating the distribution of average values among the stations.

Station	Classification	Summer	April	May	June	July	August	September
AS01-90	H	40.28	37.79	43.03	41.65	45.16	44.95	27.91
AS01-91	M	34.78	33.33	34.61	36.94	39.25	36.28	28.19
AS01-92	H	41.99	38.12	43.09	42.30	45.99	48.32	33.29
AS02-90	H	48.62	NA	NA	48.11	55.5	53.81	36.67
AS02-91	H	46.03	48.19	44.82	44.14	48.82	50.51	39.81
AS02-92	H	46.31	44.24	49.92	45.66	48.45	51.30	36.43
BE01	M	30.58	21.43	28.85	NA	41.68	28.05	26.83
BE31	M	21.85	4.81	28.02	24.80	25.96	27.55	12.15
BE32	M	25.58	29.28	NA	23.67	24.34	31.72	20.42
BE33	M	26.91	26.41	29.40	24.50	30.12	30.89	19.54
BE34	M	29.73	30.86	33.99	29.18	35.20	33.84	16.04
CH02	H	35.52	31.12	38.76	33.57	51.42	39.44	24.01
CH31	M	24.83	24.16	28.79	22.57	33.29	25.82	15.30
CH32	M	33.39	25.51	36.61	35.50	38.54	39.05	24.82
DK31	M	28.65	NA	36.81	30.48	25.80	30.56	24.00
DK32	M	24.69	32.05	27.36	25.73	22.41	22.90	17.95
IT04	M	31.21	29.62	31.69	30.72	38.11	35.63	21.12
NL02	M	33.43	32.64	47.52	38.74	32.11	27.24	22.24
NL08	M	27.85	27.26	39.05	37.78	28.70	18.99	17.29
NL31	M	34.52	34.80	41.43	34.51	33.23	37.07	27.30
NO01	M	29.08	35.28	35.31	29.31	26.56	25.72	21.77
NO30	M	30.31	42.62	32.73	31.84	25.95	23.43	26.05
NO39	M	22.01	32.28	23.84	23.56	20.31	17.82	17.77
NO41	M	28.96	36.37	34.47	31.51	26.28	24.03	21.15
NO42	M	28.31	29.48	20.90	30.75	29.22	28.32	32.45
NO43	M	29.94	31.82	34.35	33.87	28.42	29.70	21.37
NO44	M	26.24	30.36	33.59	29.72	24.53	22.80	16.32
NO45	M	34.82	36.72	39.68	38.01	31.54	35.11	27.71
NO47	M	26.55	32.30	36.34	24.32	25.87	20.50	19.82
NO48	M	32.27	41.50	40.99	35.46	27.97	24.98	21.49
NO49	M	27.98	37.01	38.92	29.26	26.57	22.28	18.75
NO50	M	32.58	42.84	36.08	29.21	23.52	26.68	28.13
PO04	L	13.87	14.17	16.94	13.08	12.62	21.17	10.56
SE02	M	31.41	39.09	33.39	33.96	28.44	30.85	23.07
SE11	H	35.12	38.52	44.28	40.27	29.56	32.85	25.44
SE32	H	38.07	43.65	42.84	42.72	31.93	38.89	28.87
SE35	M	26.38	31.48	31.84	29.89	25.45	20.90	18.73
SF04	M	27.63	36.45	35.96	30.12	24.49	21.19	18.10
SF09	H	37.02	43.39	38.71	38.56	36.96	34.63	29.80
UK02	M	28.58	34.50	36.22	29.78	27.93	21.84	21.52
UK06	M	25.75	33.45	32.24	25.30	25.22	18.76	19.60
UK13	H	37.37	41.88	46.15	31.14	38.97	37.09	29.38
UK14	M	30.71	35.08	38.15	29.05	31.37	26.74	23.47
UK15	M	33.63	39.79	39.62	35.58	29.84	26.65	29.88
UK31	H	36.74	39.41	44.37	32.58	38.81	33.95	31.01
UK32	M	20.16	19.66	21.01	16.96	25.23	22.82	15.18
UK33	M	27.41	34.76	30.58	28.52	25.87	22.36	22.51
UK34	M	21.72	25.28	24.20	19.97	25.30	18.62	16.07
UK35	M	34.51	39.99	42.10	33.87	34.42	28.46	28.07
UK36	M	28.95	30.88	36.29	24.43	30.79	29.55	22.44
UK37	M	30.02	33.61	36.71	27.51	31.91	27.14	22.62
UK38	H	37.43	39.13	43.34	30.53	39.23	40.95	30.47
UK39	M	30.88	32.96	35.67	27.17	31.59	34.68	23.07
UK40	L	18.48	22.31	23.55	14.90	22.94	18.89	10.70
UK41	M	28.71	34.25	34.76	27.45	29.34	25.17	20.86
UK42	L	13.27	13.37	15.38	11.60	13.97	11.58	NA
Average		30.53	32.91	35.10	30.77	31.30	29.66	23.37
Var		48.43	66.23	56.37	59.09	72.41	80.90	39.97

Table 4: Average ozone concentrations and the classification of the stations based on the whole summer average.

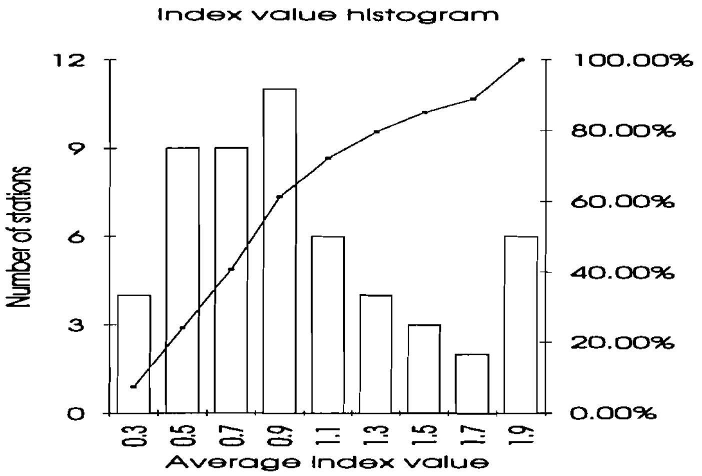


Figure 5: Histogram indicating the distribution of the average variation index values v among the stations.

These stations, except the Swiss station CH02, are not situated in areas with comparably high population density. It was somehow surprising that two Swedish and one Finnish station had very high average ozone concentrations.

The low average group consisted of the Portuguese PO04 and the British stations UK40, UK42. The geographical location of the station PO04 near the Atlantic Ocean and in low population density area could explain the low average. The low average concentrations measured at the British stations could be caused by strong local emission sources with possibly destructing effect on ozone in Central London and not far away from London (Stevenage).

3.3.3 Daily Variation Index

To describe the diurnal variation of ozone an index was suggested by G. Dollard [5]. This variation index was calculated as follows

$$\text{DailyIndex} = \frac{\text{DailyMaximum} - \text{DailyMinimum}}{\text{DailyAverage}}$$

As mentioned before this index was not calculated for days that have one or more non-available (missing) measurements.

The variation index v for a given period was calculated as the average of the daily indices during this period. One possible explanation for differences in this indices is the vicinity of local emission sources. An index value below 0.7 should indicate that the ozone concentrations were measured in the countryside with no intense traffic or large point sources near the station. In this paper such remote rural sites are marked with RR. Rural sites (R) should have the average index value between 0.7 and 1.7, and urban sites (U) superior to 1.7 [5].

The variation index v for the whole summer period and monthly indices are shown in Table 5. If there were no days without missing values, the index value could not be calculated and thus was marked as non-available (NA). The histogram of summer period index values is also presented graphically in Figure 5.

In Table 5 a classification based on the summer period variation index values v is presented. Monthly index values are shown as well. According to this analysis for most stations it does not make any difference whether the whole summer period or a certain month is chosen as the basis for classification.

To study the relation between the classification according to the calculated index v and the classification based on geographical analysis, only the whole summer index values were

Station	Summer	April	May	June	July	August	September	Classification
AS01-90	1.0	0.9	1.1	1.0	1.0	1.1	1.0	R(6+1)
AS01-91	1.0	0.9	0.8	1.0	1.1	1.1	1.3	R(6+1)
AS01-92	NA	NA	NA	NA	NA	NA	NA	NA
AS02-90	0.5	NA	NA	0.4	0.5	0.5	0.6	RR(4+1)
AS02-91	0.5	0.3	0.6	0.3	0.7	NA	0.5	RR(4+1),R(1)
AS02-92	0.5	0.4	0.4	0.5	0.6	0.5	0.6	RR(6+1)
BE01	1.1	1.2	1.0	NA	1.3	NA	1.1	R(4+1)
BE31	1.8	NA	NA	1.6	NA	3.0	2.3	U(2+1),R(1)
BE32	1.3	NA	NA	NA	NA	1.3	NA	R(1+1)
BE33	2.0	NA	NA	NA	NA	2.0	2.1	U(2+1)
BE34	1.6	1.7	1.4	0.9	1.6	1.5	2.0	R(5+1),U(1)
CH02	1.5	1.4	1.5	1.3	1.4	1.5	1.8	R(5+1),U(1)
CH31	2.1	1.7	1.8	2.1	1.9	2.2	2.8	U(6+1)
CH32	1.3	1.0	1.3	1.0	1.3	1.4	1.6	R(6+1)
DK31	NA	NA	NA	NA	NA	NA	NA	NA
DK32	1.4	1.2	1.5	1.5	1.3	1.5	1.5	R(6+1)
IT04	2.1	1.6	2.0	1.9	2.1	2.2	2.8	U(5+1),R(1)
NL02	1.6	1.1	1.3	1.5	1.6	2.0	2.1	R(4+1),U(2)
NL08	2.1	1.7	1.7	1.7	1.9	2.4	2.8	U(5+1),R(1)
NL31	1.1	0.9	1.0	1.1	0.9	1.4	1.1	R(6+1)
NO01	1.0	0.7	0.9	1.1	0.9	1.1	1.1	RR(5+1),R(1)
NO30	0.6	0.4	0.6	0.7	0.6	0.8	0.8	R(4+1),RR(2)
NO39	1.3	0.5	1.5	1.2	1.3	1.6	1.3	R(5+1),RR(1)
NO41	1.0	0.6	0.9	0.9	1.0	1.4	1.1	R(5+1),RR(1)
NO42	0.5	1.0	1.1	0.2	0.2	0.2	0.2	RR(4+1),R(2)
NO43	0.8	0.6	0.8	0.7	0.8	0.9	0.9	R(5+1),RR(1)
NO44	1.4	1.2	1.2	1.2	1.3	1.6	1.8	R(5+1),U(1)
NO45	0.7	0.6	0.7	0.7	0.7	0.7	0.6	RR(3+1),R(3)
NO47	0.8	0.6	0.5	0.8	0.6	0.9	1.3	R(3+1),RR(3)
NO48	0.7	0.4	0.5	0.6	0.6	0.8	0.9	RR(4+1),R(2)
NO49	1.1	0.5	0.9	1.3	1.1	1.4	1.4	R(5+1),RR(1)
NO50	0.5	0.2	0.4	0.5	0.8	0.7	0.4	RR(4+1),R(2)
PO04	1.1	1.0	1.0	1.0	1.2	0.8	1.2	R(6+1)
SE02	1.0	0.7	1.2	0.9	0.9	1.1	1.1	R(5+1),RR(1)
SE11	0.8	0.6	0.7	0.8	0.8	0.9	0.8	R(4+1),RR(2)
SE32	0.7	0.5	0.6	0.7	0.8	1.0	0.5	R(2+1),RR(4)
SE35	1.0	0.8	0.8	0.9	1.0	1.6	1.1	R(6+1)
SF04	1.1	0.9	0.9	1.1	1.1	1.6	1.4	R(6+1)
SF09	0.5	0.4	0.5	0.5	0.5	0.5	0.5	RR(6+1)
UK02	0.9	0.7	0.9	0.8	0.9	0.9	1.0	R(5+1),RR(1)
UK06	1.2	1.3	1.2	0.8	1.2	1.1	1.6	R(6+1)
UK13	0.7	0.5	0.8	0.8	0.7	0.8	0.9	R(4+1),RR(2)
UK14	0.8	0.6	0.7	0.8	1.0	1.0	0.9	R(5+1),RR(1)
UK15	0.5	0.4	0.5	0.5	0.6	0.5	0.5	RR(6+1)
UK31	0.6	0.5	0.7	0.6	1.0	0.6	0.5	RR(5+1),R(1)
UK32	1.8	1.7	1.8	1.8	1.6	2.0	1.8	U(5+1),R(1)
UK33	0.9	0.6	1.2	0.8	1.2	0.9	0.9	R(5+1),RR(1)
UK34	1.6	1.4	1.7	1.5	1.6	1.8	NA	R(3+1),U(2)
UK35	0.5	0.3	0.5	0.5	0.7	0.6	0.4	RR(6+1)
UK36	1.2	0.8	1.4	1.0	1.3	1.3	1.3	R(6+1)
UK37	0.9	0.6	0.8	0.9	0.9	1.0	1.1	R(5+1),RR(1)
UK38	0.9	0.8	0.8	0.9	0.9	1.4	1.0	R(6+1)
UK39	1.1	0.9	1.0	1.1	1.1	1.3	1.2	R(6+1)
UK40	1.9	1.7	2.2	1.7	1.7	2.1	2.2	U(3+1),R(3)
UK41	0.8	0.6	0.7	0.8	0.9	0.8	0.9	R(5+1),RR(1)
UK42	2.0	1.9	2.0	1.9	2.0	2.5	NA	U(5+1)
Average	1.10	0.87	1.04	1.00	1.07	1.27	1.23	
Var	0.23	0.20	0.21	0.19	0.18	0.35	0.41	

Table 5: Variation index values v for different stations.

used. In Table 6, the classification according to the calculated variation index v for the whole summer period and the classification based on geographical analysis g is presented. For the geographical analysis monitoring sites were checked against large cities (as potential sources of VOC emissions) and of industrial sources of VOC emissions in a circle of 50 kilometres around the stations. This analysis made use of the database program PC-GLOBE (where cities bigger than 100,000 inhabitants are included) and of conventional maps. Figure 6 shows the large European cities included in the PC-GLOBE database and the locations of the ozone measurement stations.

In Table 6 the cities identified in the vicinity of the stations are listed and the distance from the station is provided. To distinguish between larger and smaller cities, small cities are indicated by the symbol s after the distance.

Large point sources were identified from the CORINAIR'85 database, where data on emissions of air pollutants for countries of the European Community (EC) are stored. Unfortunately, no data for large point sources were available for Austria, Switzerland, Norway, Sweden, and Finland. In addition, the data for some countries are very rough; for example, in some cases the type of the source was not indicated. To be able to fully analyze the local effects of large point sources, the type of the source, the stack height, operating regime, the VOC species emitted, and the prevailing wind directions should be known. The stack height was included in the database. If the stack height exceeded 100 meters, the large point source was considered to be a power plant and its contribution to VOC emissions is locally negligible. If the sum of the VOC emissions from the remaining large point sources within 50 kilometres range from a measurement station was greater than 3000 tons per year, the large point sources were considered to have a probable influence on the measured ozone concentrations. This is indicated by a '+' in Table 6. The symbol '-' does not necessarily mean that no local point source influence is present, but shows that, based on the data available, an influence does not seem likely. In Figures 7.a–7.c, the large point sources and ozone measurement stations are shown on the maps of Belgium, Italy and United Kingdom.

Deciding about limits for the classification based on geographical analysis is not easy. In this analysis, a station was chosen to be remote rural (RR) if no big cities (more than 100,000 inhabitants) and no large point sources were found within 50 kilometers and no small cities (less than 100,000 inhabitants) were identified within 15 kilometers from the station. If there were no big cities found within the 15 kilometers zone, the station was classified as rural (R). Stations located closer than 15 kilometers from a big city were classified as urban (U). The large point sources of VOC emission were taken into account by ranking a station as rural instead of remote rural and urban instead of rural.

A comparison of the classifications according to the the whole summer index v and the results of the geographical analysis g gave matching results in 26 cases out of 54 studied. In 15 cases, where the classifications differed, the whole summer index values v were close to the limit for two classes, and monthly indices suggested, at least for some months, similar classifications as in the geographical analysis.

In 13 cases out of 54 studied, however, the classification based on geographical analysis and the calculated variation indices gave different results. Further analysis will be necessary for a satisfactory explanation of this phenomenon.

3.4 Ozone Concentration Histograms

To analyze the distribution of different ozone concentration levels in the data, histogram plots were studied. The range for one histogram class was chosen to be 5 ppb and 33 classes were defined. The range of 5 ppb was considered large enough to satisfactorially smooth the data, but small enough to maintain the differences between different ozone level distribution patterns among the stations. The upper limit of 160 ppb was chosen, based on the maximum ozone concentrations which rarely exceeded this value. A smaller upper limit might have been chosen, but a smaller limit would have led to loss of information about the distribution of high ozone

Station	Classification according to v	Geographical classification g	Cities within 50 km (distance in km:s, s indicating small city)	Probable influence from large point sources of VOCs
AS01-90	R	R	Wien(50),Eisenstadt(15,s)	NA
AS01-91	R	R	Wien(50),Eisenstadt(15,s)	NA
AS01-92	NA	R	Wien(50),Eisenstadt(15,s)	NA
AS02-90	RR	R	Salzburg(30)	NA
AS02-91	RR/R	R	Salzburg(30)	NA
AS02-92	RR	R	Salzburg(30)	NA
BE01	R	RR	–	–
BE31	U/R	U	Antwerpen(10)	+
BE32	R	U	Eupen(0,s)	+
BE33	U	U	Brugge(10),Ghent(10)	+
BE34	R/U	U	Ghent(10)	–
CH02	R/U	R	Bern(40)	NA
CH31	U	R	Sion(0,s)	NA
CH32	R	R	Zürich(20)	NA
DK31	NA	RR	–	–
DK32	R	R	Copenhagen(30)	–
IT04	U/R	U	Milano(30)	+
NL02	R/U	RR	–	–
NL08	U/R	U	Utrecht(5)	–
NL31	R	R	Groningen(20)	–
NO01	RR/R	RR	–	NA
NO30	R/RR	RR	–	NA
NO39	R/RR	RR	–	NA
NO41	R/RR	RR	–	NA
NO42	RR/R	RR	–	NA
NO43	R/RR	RR	–	NA
NO44	R/U	RR	–	NA
NO45	RR/R	R	Oslo(50)	NA
NO47	R/RR	RR	–	NA
NO48	RR/R	R	Bergen(50)	NA
NO49	R/RR	RR	–	NA
NO50	RR/R	RR	–	NA
PO04	R	R	–	+
SE02	R/RR	U	Göteborg(0)	NA
SE11	R/RR	R	Helsingborg(40),Malmö(40)	NA
SE32	R/RR	RR	–	NA
SE35	R	RR		NA
SF04	R	RR	–	NA
SF09	RR	RR	–	NA
UK02	R/RR	RR	–	–
UK06	R	RR	–	–
UK13	R/RR	R	Torquaz(10,s)	–
UK14	R/RR	R	Middlebrough(20,s),York(25,s)	+
UK15	RR	RR	–	–
UK31	RR/R	RR	–	–
UK32	U/R	U	Nottingham(15)	–
UK33	R/RR	U	Edinburg(15)	+
UK34	R/U	U	Manchester(0)	+
UK35	RR	RR	–	–
UK36	R	R	Oxford(15,s)	–
UK37	R/RR	R	Manchester(20)	–
UK38	R	R	Brighton(15,s)	–
UK39	R	RR	–	–
UK40	U/R	R	London(25)	–
UK41	R/RR	RR	–	–
UK42	U	U	London(0)	+

Table 6: Classification in groups according to variation index v of ozone concentration and geographical classification g.

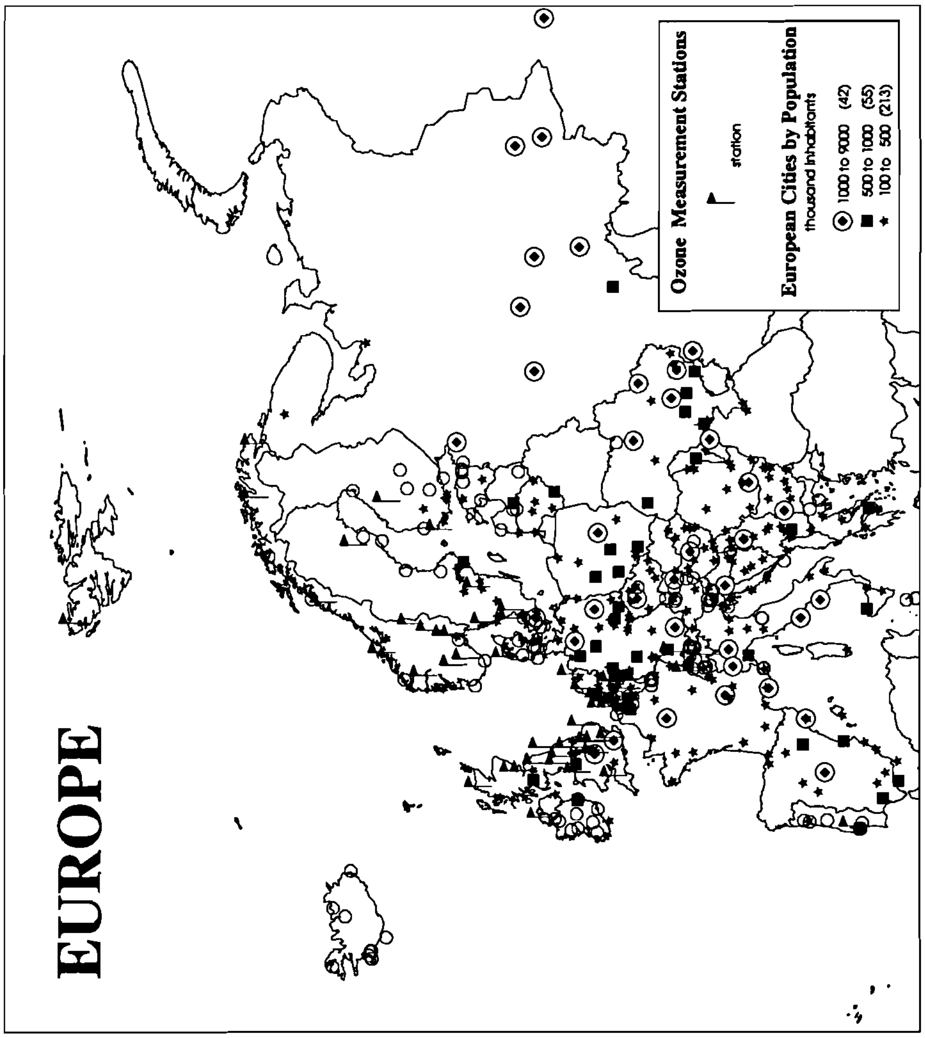


Figure 6: The ozone measurement stations and large European cities.

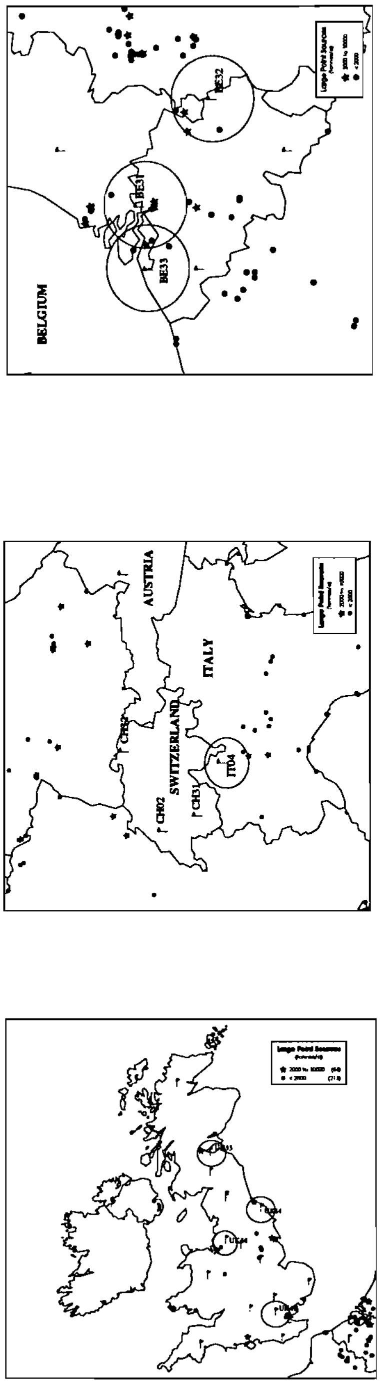


Figure 7: Large point sources in the neighbourhood of ozone measurement stations a) Belgium b) Italy and c) United Kingdom.

Figure 8: Geographical distribution of the stations classified according to the variation index v.

GI	GII	GIII	GIV	GV	GVI	GVII
NO01	AS01-90	AS02-90	BE31	DK32	BE01	PO04
NO30	AS01-91	AS02-91	CH31	NO39	BE33	
NO41	AS01-92	AS02-92	IT04	NO44	BE34	
NO42	UK02	CH32	NL08	NO49	BE32	
NO43	UK13	DK31	UK32	SE02	CH02	
NO45	UK14	NL31	UK34	SE35	NL02	
NO47	UK31	UK39	UK40	SF04		
NO48	UK33		UK42	UK06		
NO50	UK35					
SE11	UK36					
SE32	UK37					
SF09	UK38					
UK15	UK41					

Table 7: Classification in 7 groups, according to histograms of ozone concentration.

concentrations. In this study, differences in the upper range of the histograms were given emphasis because the high concentrations play important role in damage to plants and animals.

In order to classify the stations, histogram plots were analyzed visually, applying criteria defined on the basis of the histogram patterns. Based on this approach, seven classes were identified (see Table 7 for classification).

Typical representative of group I (GI) histogram is shown in Figure 9a. Stations included in this group were characterized by a bell-shaped histogram with few observations of low (from zero to ten ppb) and high (exceeding 60 ppb) ozone concentrations. The measured ozone concentration did not exceed 80 ppb even once for most of the stations in this group, and the majority of measured ozone concentrations were between 20 and 35 ppb. Group I consisted of Nordic stations, i.e., 9 Norwegian, 2 Swedish, 2 Finnish and 1 British. The stations belonging to group I (Fig. 10) are geographically clustered far North in areas with low population density.

The histograms of the stations classified to group II (GII) resembled those in group I (Fig. 9.b) but differed when the high ozone concentrations were considered. Ozone concentrations superior to 80 ppb were quite common for stations in group II. Ten stations situated in United Kingdom were classified to this group. The Austrian station St. Koloman was classified to this group based on the data for the summer periods of 1990, 1991 and 1992, which indicates that this kind of classification is not too sensitive to annual changes in weather patterns. The geographical distribution of the group II members (Fig. 10 and Table 6) shows that group II stations are not situated in urban areas with high population density, but tend to be rural environments.

Considering the similarity of the histograms of groups I and II at low concentration, it should be noted that if there were less emphasis on high concentrations or the number of groups were to be reduced, groups I and II might be combined.

A typical histogram representing group III (GIII) is shown in Figure 9c. This histogram does not show a clear bell-shape, when compared with groups I and II, but is flatter throughout the ozone range, with a greater number of observations of low ozone concentrations. The high ozone level pattern is intermediate to those of group I and II. Only 5 stations were classified to group III and, thus, it would be possible to reduce the number of groups by combining group III with either group I or group II.

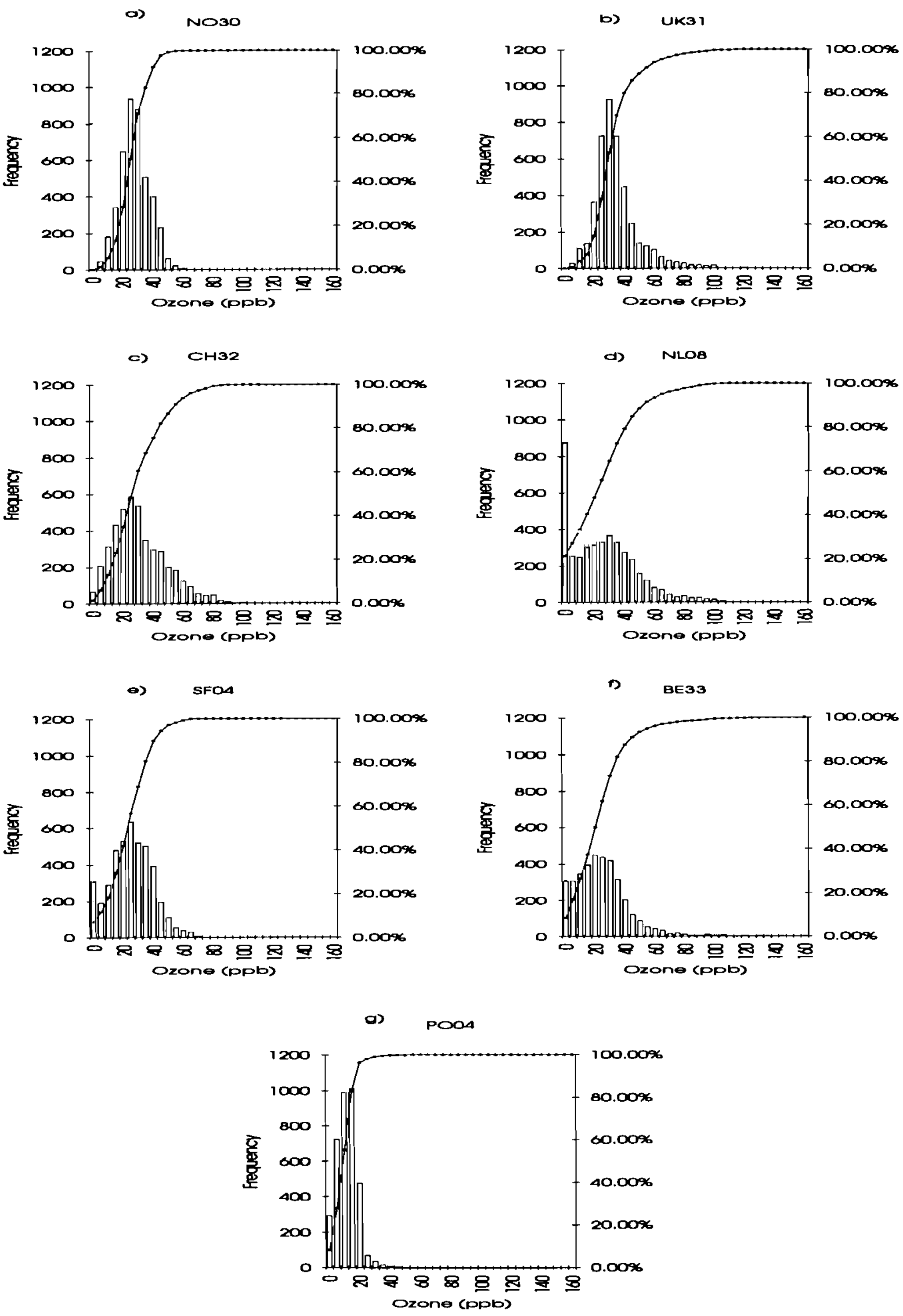


Figure 9: Typical histogram patterns in different groups a) GI b) GII c) GIII d) GIV e) GV f) GVI and g) GVII.

The most obvious feature of a typical group IV (GIV) histogram was the domination of low ozone concentrations (zero to five ppb) over other ranges (Fig. 9d). At the same time, very high ozone concentrations were measured at the stations included in this group. Group IV included four central European stations and four British stations.

In group V (GV) histograms (Fig. 9.e), the dominating range was around 30 ppb, but the zero to five ppb range was important as well. Stations belonging in group V had histograms with two maxima. This group is represented by stations in Norway (3), Sweden (2), Denmark (1), Finland (1), Northern Ireland (1). Thus, the geographical distribution of group V is weighted towards northern rural areas. With a suitable choice of group limits and range classes, groups IV and V could probably be combined, if the reduction of the number of groups was considered important.

A typical histogram in group VI (GVI) is shown in Figure 9f. Group VI histograms are very flat in shape and the measurements are almost uniformly distributed from zero to 50 ppb. Group VI stations are situated in Benelux countries and in Switzerland, i.e., in relatively high populated regions.

Group VII (GVII) consisted of a single station, namely the Portuguese. At the Portuguese station, the measured ozone concentration never exceeded 50 ppb. The histogram pattern is different from all the other histogram patterns and, thus, the classification in a class of its own seems to be the only acceptable solution.

3.5 The Excess Ozone

Accumulated exposure indices have been proposed for establishing exposure limits for agricultural crops and forests [12, 15]. In this analysis the so-called 'excess ozone' $e_{p,x}$ was calculated as follows:

$$e_{p,x} = \sum_{t \in p} \sum_{i=x}^{\infty} (o_{i,t} - x)$$

x being the threshold value, p the period for which the index is calculated, and $o_{i,t}$ the ozone measurements on level i during time instant t. Only measurements that exceed the threshold are taken into account. The summation over time t can cover different periods p. In this analysis, two thresholds, x=50 ppb and x=75 ppb, were studied.

Different periods of a day can be studied in calculating the excess ozone. It is possible to use 24 hours data or concentrate on certain periods, for example, on daytime ozone concentrations. In this analysis the significance of the nighttime ozone concentrations was studied in more detail. Nighttime was defined as the hours from 19.00 (7 p.m.) to 7.00 (7 a.m.) and daytime the remaining hours from 7.00 (7 a.m.) to 19.00 (7 p.m.). These limits for day and night were based on the thickness of the atmospheric inversion layer, which varies daily (see Figure 11).

Let $e_{d,x}$ be the daytime exceedance sum, $e_{n,x}$ the nighttime exceedance and $e_{w,x}$ the whole day exceedance so $e_{w,x} = e_{d,x} + e_{n,x}$. First assume that no values are missing. Then, if there were no ozone concentrations exceeding threshold during nighttime, $e_{d,x}$ and $e_{w,x}$ would be equal and $e_{n,x}$ would be zero. At the same time, if high ozone concentrations were as probable during nighttime as during daytime, $e_{d,x}$ and $e_{n,x}$ would be equal and the ratios $e_{d,x}/e_{w,x}$ and $e_{n,x}/e_{w,x}$ would be 0.5. The fact that missing values occur in a time series makes this kind of thinking more complicated, but the principle remains. Fortunately, the missing values did not greatly affect the proportion of daytime and nighttime values and, thus, the ratios $e_{n,x}/e_{w,x}$ are comparable between different stations.

To analyze the contribution of nighttime ozone concentration to the exceedance sum, the ratios $e_{n,50}/e_{w,50}$ and $e_{n,75}/e_{w,75}$ were calculated for all stations. If both $e_{n,x}$ and $e_{w,x}$ were zero, the ratio was defined to be zero as well. The contribution of nighttime ozone concentrations was considered negligible if the ratio was below 10%. Ratios from 10% to 30% are not very significant, but when the ratio exceeds 30%, the significance should at least be discussed.

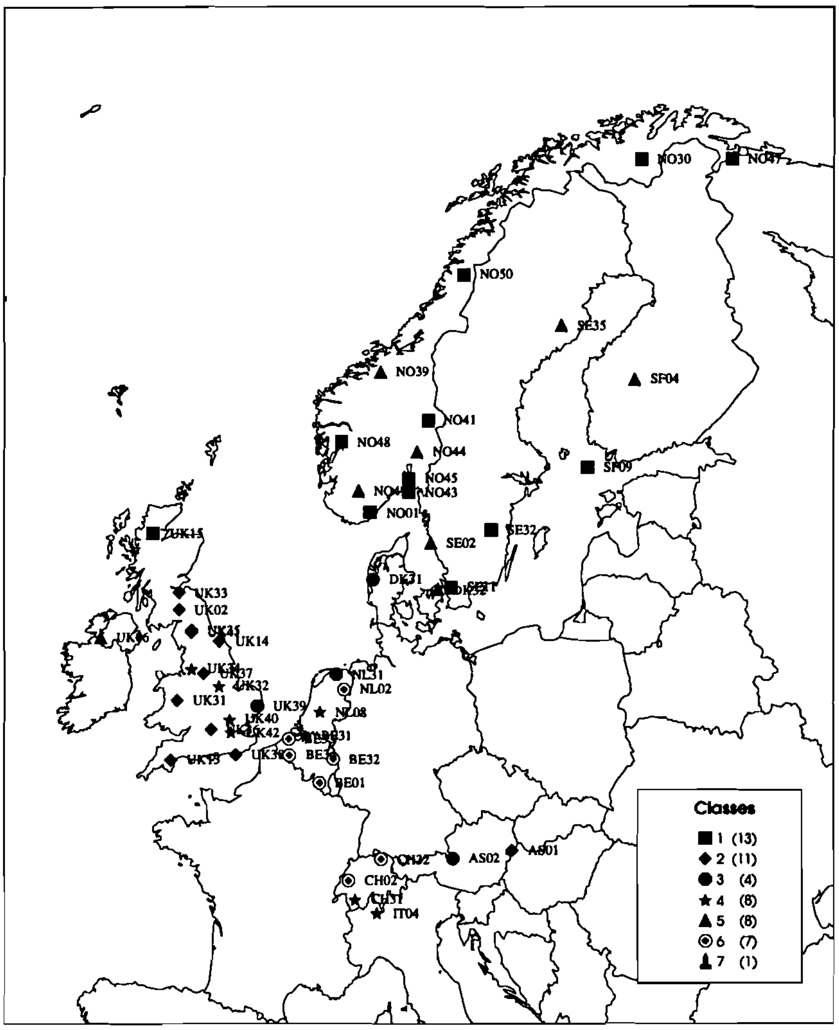


Figure 10: Geographical distribution of different histogram groups.

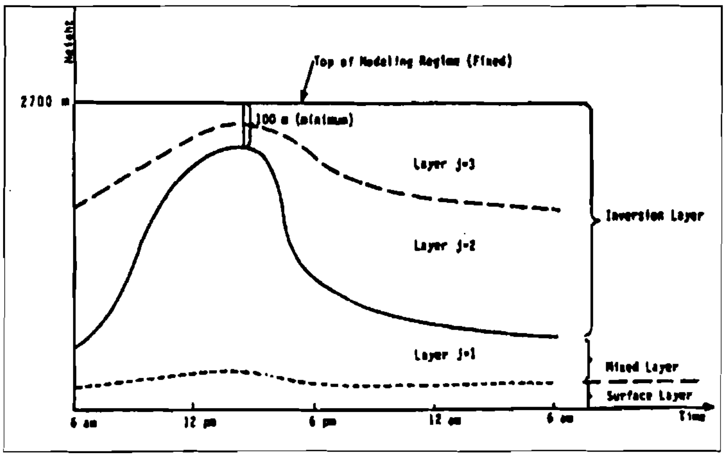


Figure 11: The thickness of the inversion layer in the function of daytime.

With a threshold of 50 ppb, the ratio for the summer period remained below 10% for 16 cases out of 56 (see Table 8). For 27 stations, the ratio was between 10 and 30% and for 9 stations (AS02-91, AS02-92, NO30, NO48, UK14, UK31, UK33, UK35, and UK38) the ratio exceeded 30% but was less than 50%. Ratios exceeding 50% were found in 4 stations (NO39, NO50, SF09, AS02-90). In addition, one or more monthly ratios exceeding 30% were found for 13 stations (BE01, BE32, DK31, NO43, NO45, SE02, SE32, SE35, SF04, UK02, UK06, UK13, UK41) and one or more monthly ratios exceeding even 50% for 4 stations (NO01, NO41, NO47, UK15) among the stations for which the summer period ratio remained below 30%. Very high nighttime contributions were found for stations NO01 in July (93%), NO41 in July (91%), NO47 in April (100%), NO50 in August (90%), and UK15 in September (100%). As the monthly indices are considered, it is worth noticing that in September the nighttime contribution very often remained zero due to the fact that $e_{w,50}$ was zero.

With 75 ppb selected as the threshold level the summer period ratio remained below 10% for 34 cases out of 56 (Table 9). This ratio was between 10 and 30% for 14 stations and for 6 stations (AS02-91, BE01, NO45, SE02, UK33, UK35) exceeded 30% but was less than 50%. Ratios exceeding 50% were found in 2 cases (AS02-90, NO43). In addition, one or more monthly ratios exceeding 30% were found for 5 stations (AS02-92, UK14, UK31, UK38, UK39) and one or more monthly ratios exceeding even 50% for 2 stations (CH31, UK02) among the stations for which the summer period ratio remained below 30%. Very high nighttime contributions were found for stations AS02-91 in September (92%), NO43 during whole summer (95%), NO43 in August (100%), and CH31 in June (100%).

In most cases, when both the summer period ratios and the monthly ratios were zero, it was due to the fact that $e_{w,75}$ was zero (see Table 9).

Based on the contribution of nighttime ozone presented in Tables 8 and 9, caution should be taken in excluding the nighttime ozone measurements, especially when no detailed knowledge on the effects of high nighttime ozone concentrations on vegetation is available.

To be able to make full use of the data, both exceedances $e_{w,x}$ and $e_{d,x}$ were calculated in this analysis. When comparing the exceedance for different stations, the sum itself is not a very good measure since the proportion of non-available values affects the magnitude of the sum. For comparison between stations, normalized exceedance indices $\epsilon_{p,x}$ were used.

$$\epsilon_{p,x} = \frac{1}{n_p} e_{p,x}$$

Station	Summer	April	May	June	July	August	September
AS01-90	9%	7%	7%	7%	13%	7%	0%
AS01-91	8%	4%	6%	6%	13%	3%	1%
AS01-92	9%	4%	11%	8%	12%	9%	1%
AS02-90	50%	0%	0%	43%	51%	49%	43%
AS02-91	49%	42%	50%	48%	48%	52%	52%
AS02-92	47%	47%	47%	47%	47%	45%	85%
BE01	23%	0%	5%	0%	30%	1%	0%
BE31	3%	0%	0%	1%	2%	4%	0%
BE32	10%	0%	0%	31%	3%	12%	0%
BE33	3%	0%	4%	0%	2%	4%	0%
BE34	9%	7%	3%	2%	12%	12%	0%
CH02	13%	9%	7%	17%	16%	13%	7%
CH31	12%	5%	21%	17%	12%	5%	0%
CH32	6%	0%	1%	5%	7%	6%	8%
DK31	10%	0%	37%	5%	0%	9%	0%
DK32	14%	9%	1%	22%	0%	25%	0%
IT04	5%	12%	9%	6%	6%	3%	0%
NL02	9%	0%	12%	8%	11%	4%	0%
NL08	8%	13%	9%	9%	11%	0%	0%
NL31	10%	18%	8%	20%	5%	9%	0%
NO01	9%	3%	12%	16%	93%	1%	0%
NO30	43%	44%	82%	0%	0%	0%	0%
NO39	59%	84%	0%	0%	0%	62%	0%
NO41	17%	23%	2%	0%	91%	47%	0%
NO42	18%	18%	0%	0%	0%	0%	0%
NO43	29%	2%	25%	3%	6%	43%	0%
NO44	11%	20%	5%	0%	0%	18%	0%
NO45	29%	23%	27%	45%	14%	36%	0%
NO47	28%	100%	27%	0%	9%	0%	0%
NO48	42%	67%	33%	6%	0%	56%	0%
NO49	15%	11%	17%	22%	0%	0%	0%
NO50	56%	49%	62%	0%	0%	90%	0%
PO04	0%	0%	0%	0%	0%	0%	0%
SE02	15%	6%	8%	3%	10%	33%	0%
SE11	22%	13%	27%	14%	15%	23%	0%
SE32	23%	35%	17%	12%	22%	22%	0%
SE35	9%	7%	11%	30%	0%	0%	0%
SF04	15%	4%	21%	30%	0%	33%	0%
SF09	50%	39%	55%	63%	79%	44%	0%
UK02	18%	6%	19%	17%	32%	9%	0%
UK06	11%	42%	9%	0%	10%	0%	0%
UK13	28%	27%	28%	9%	28%	35%	0%
UK14	31%	35%	34%	38%	26%	30%	0%
UK15	21%	4%	27%	0%	19%	0%	100%
UK31	35%	14%	41%	43%	25%	44%	18%
UK32	15%	0%	0%	18%	15%	17%	0%
UK33	30%	23%	38%	1%	33%	34%	0%
UK34	2%	0%	4%	0%	0%	3%	0%
UK35	43%	42%	44%	46%	43%	42%	0%
UK36	11%	5%	6%	19%	12%	15%	0%
UK37	18%	2%	11%	11%	24%	26%	4%
UK38	31%	30%	26%	30%	33%	34%	14%
UK39	19%	9%	15%	0%	17%	25%	0%
UK40	5%	5%	0%	0%	8%	5%	0%
UK41	23%	18%	21%	4%	17%	33%	0%
UK42	0%	0%	0%	0%	0%	0%	0%

Table 8: Contribution of night hours ($e_{n,50}/e_{w,50}$) to exceedance of 50 ppb ozone concentration.

Station	Summer	April	May	June	July	August	September
AS01-90	1%	0%	0%	0%	2%	0%	0%
AS01-91	1%	0%	0%	0%	1%	0%	0%
AS01-92	1%	0%	4%	0%	0%	0%	0%
AS02-90	51%	0%	0%	0%	50%	55%	0%
AS02-91	46%	0%	0%	53%	53%	31%	92%
AS02-92	18%	0%	35%	0%	32%	4%	0%
BE01	36%	0%	0%	0%	41%	0%	0%
BE31	1%	0%	0%	0%	0%	1%	0%
BE32	0%	0%	0%	0%	0%	0%	0%
BE33	1%	0%	0%	0%	0%	2%	0%
BE34	6%	0%	0%	0%	8%	5%	0%
CH02	3%	0%	0%	0%	4%	2%	0%
CH31	12%	0%	0%	100%	12%	0%	0%
CH32	0%	0%	0%	0%	0%	0%	0%
DK31	0%	0%	0%	0%	0%	0%	0%
DK32	2%	0%	0%	0%	0%	3%	0%
IT04	1%	9%	0%	3%	1%	0%	0%
NL02	5%	0%	6%	3%	2%	5%	0%
NL08	3%	0%	3%	4%	3%	0%	0%
NL31	3%	0%	0%	2%	0%	4%	0%
NO01	0%	0%	0%	0%	0%	0%	0%
NO30	0%	0%	0%	0%	0%	0%	0%
NO39	0%	0%	0%	0%	0%	0%	0%
NO41	0%	0%	0%	0%	0%	0%	0%
NO42	0%	0%	0%	0%	0%	0%	0%
NO43	95%	0%	0%	0%	0%	100%	0%
NO44	0%	0%	0%	0%	0%	0%	0%
NO45	35%	0%	0%	0%	0%	44%	0%
NO47	0%	0%	0%	0%	0%	0%	0%
NO48	16%	0%	16%	0%	0%	0%	0%
NO49	0%	0%	0%	0%	0%	0%	0%
NO50	0%	0%	0%	0%	0%	0%	0%
PO04	0%	0%	0%	0%	0%	0%	0%
SE02	40%	0%	0%	0%	0%	48%	0%
SE11	2%	0%	4%	0%	0%	0%	0%
SE32	12%	0%	0%	0%	0%	13%	0%
SE35	0%	0%	0%	0%	0%	0%	0%
SF04	0%	0%	0%	0%	0%	0%	0%
SF09	0%	0%	0%	0%	0%	0%	0%
UK02	16%	0%	10%	0%	58%	5%	0%
UK06	0%	0%	0%	0%	0%	0%	0%
UK13	20%	6%	14%	0%	23%	22%	0%
UK14	20%	0%	37%	0%	6%	21%	0%
UK15	16%	0%	23%	0%	0%	0%	0%
UK31	28%	0%	31%	39%	15%	35%	0%
UK32	11%	0%	0%	0%	10%	12%	0%
UK33	36%	0%	0%	0%	0%	37%	0%
UK34	0%	0%	0%	0%	0%	0%	0%
UK35	41%	0%	68%	75%	44%	34%	0%
UK36	5%	0%	0%	0%	3%	9%	0%
UK37	12%	0%	0%	0%	16%	14%	0%
UK38	28%	0%	10%	18%	36%	29%	0%
UK39	27%	0%	0%	0%	0%	36%	0%
UK40	2%	0%	0%	0%	2%	2%	0%
UK41	12%	0%	0%	0%	0%	18%	0%
UK42	0%	0%	0%	0%	0%	0%	0%

Table 9: Contribution of night hours ($e_{n,75}/e_{w,75}$) to exceedance of 75 ppb ozone concentration.

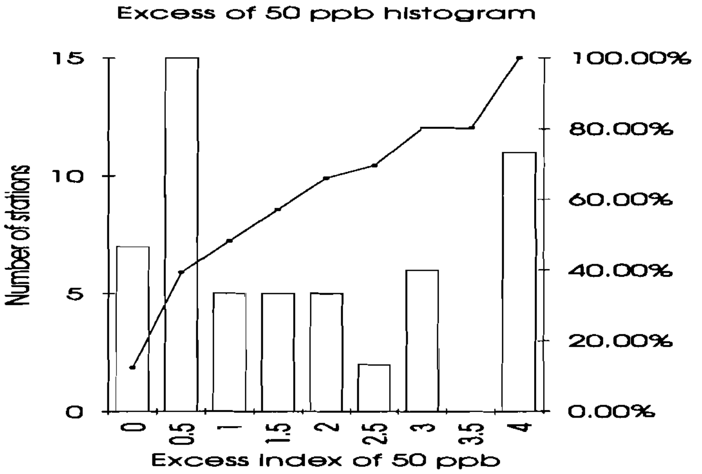


Figure 12: Histogram indicating the distribution of excess ozone index $\epsilon_{w,50}$ with a threshold of 50 ppb.

where n_p is the number of non-missing ozone measurements during period p.

In Tables 10 and 11, the normalized summer period and monthly exceedance indices $\epsilon_{w,50}$ and $\epsilon_{d,50}$ are shown. The stations were classified according to the summer period exceedance index into three categories. When $\epsilon_{p,50}$ was less than 1.5, the station was classified into the low excess category (L). Stations with the index value between 1.5 and 3.0 were placed in the medium category (M), and those with an index exceeding 3.0 into a high excess category (H). These limits are not based on biological significance of the exceedance index, since information on the relation of biological damage to exceedance index values $\epsilon_{p,x}$ was not available at the time of this study. Thus, the limits for the classes were based on the division of the range covered by the index values to three intervals having the same length.

Considering the whole day indices $\epsilon_{w,50}$, the monthly indices are lowest, on average, in September and April and highest during midsummer. Based on the whole day exceedance index $\epsilon_{w,50}$, there were 35 stations classified to low, 13 to medium and 8 to the high exceedance category (Table 10). The distribution of the classification based on $\epsilon_{w,50}$ is shown in Figure 12. The stations included in the class H were AS01-90, AS02-90, AS01-92, AS02-92, CH02, IT04, NL02, and UK38. In addition, 11 stations (AS01-90, AS02-90, AS01-92, AS02-92, BE34, CH02, IT04, NL02, NL08, UK13, UK38) had very high (over 5.0) monthly exceedance indices. Most stations that were classified as high were Central European stations situated in industrialized regions with high population density.

The exceedance index $\epsilon_{w,50}$ is strongly affected by the interannual meteorologic variability, as can be derived from a comparison of indices calculated for Austrian stations for different summers. The summer period index varied between 1.18 and 3.71 for AS01 and between 2.84 and 6.21 for AS02. For example, the exceedance indices calculated for May at station AS01 were 3.80, 0.25 and 3.85 for 1990, 1991, and 1992, respectively.

The monthly daytime indices $\epsilon_{d,50}$ (Table 11) were low in September and April and high during midsummer. Based on the summer period daytime exceedance, 26 stations were classified as low (L), 13 as medium (M) and 17 as high (H). The distribution of the classification based on $\epsilon_{d,50}$ is shown in Figure 13. The classification differs, depending on whether $\epsilon_{w,50}$ or $\epsilon_{d,50}$ is used. In 9 cases, the classification was low based on $\epsilon_{w,50}$ and medium based on $\epsilon_{d,50}$, and in 9 cases medium based on $\epsilon_{w,50}$ and high based on $\epsilon_{d,50}$. All the changes resulted in an upward shift in classification. It might be reasonable to adjust the limits of the classes to 3.0 and 6.0 for the day time exceedance index (stations with $\epsilon_{d,50} < 3.0$ as low, stations with $3.0 < \epsilon_{d,50} < 6.0$ as medium and stations with $\epsilon_{d,50} > 6.0$ as high). Limits for the classification in this paper are

Station	Classification	Summer	April	May	June	July	August	September
AS01-90	H	3.41	1.03	3.80	3.28	6.03	5.74	0.19
AS01-91	L	1.18	0.53	0.25	1.07	3.07	1.51	0.67
AS01-92	H	3.71	1.25	3.85	2.55	5.89	7.22	1.16
AS02-90	H	6.21	0.00	0.00	3.82	10.43	7.91	0.34
AS02-91	M	2.84	3.00	1.75	1.84	4.33	4.45	1.60
AS02-92	H	3.22	1.91	4.91	1.82	4.45	5.44	0.09
BE01	M	1.51	0.00	0.30	0.00	4.73	1.87	0.22
BE31	M	1.80	0.00	1.03	1.39	2.59	4.52	0.00
BE32	L	1.07	0.07	0.00	0.20	0.85	2.57	0.09
BE33	M	1.67	0.86	1.13	0.46	2.87	4.49	0.10
BE34	M	2.77	1.88	1.99	1.61	4.98	6.34	0.03
CH02	H	3.27	0.89	3.09	1.74	10.60	4.91	0.36
CH31	L	1.28	0.23	0.91	0.77	4.21	1.91	0.04
CH32	M	2.32	0.01	1.94	2.12	4.92	4.51	0.32
DK31	L	0.36	0.00	0.18	0.24	0.05	1.26	0.00
DK32	L	0.49	0.76	0.62	0.40	0.15	0.91	0.00
IT04	H	4.11	1.42	3.65	3.04	8.50	6.39	1.46
NL02	H	3.29	0.55	8.18	4.41	3.04	2.12	0.96
NL08	M	2.53	0.41	5.36	5.87	2.22	1.06	0.71
NL31	M	1.76	0.52	2.90	1.45	1.27	4.21	0.00
NO01	L	0.43	0.47	1.57	0.11	0.01	0.40	0.00
NO30	L	0.09	0.55	0.02	0.02	0.00	0.00	0.00
NO39	L	0.02	0.09	0.04	0.00	0.00	0.03	0.00
NO41	L	0.36	0.77	0.99	0.05	0.01	0.36	0.00
NO42	L	0.02	0.10	0.00	0.00	0.00	0.00	0.00
NO43	L	0.36	0.14	0.95	0.02	0.17	0.88	0.00
NO44	L	0.42	0.67	1.22	0.03	0.07	0.50	0.00
NO45	L	0.70	0.50	1.78	0.40	0.44	1.03	0.00
NO47	L	0.05	0.00	0.28	0.00	0.01	0.00	0.00
NO48	L	0.83	1.38	2.82	0.17	0.00	0.43	0.00
NO49	L	0.47	0.08	2.99	0.21	0.05	0.23	0.00
NO50	L	0.28	0.88	0.37	0.00	0.00	0.15	0.00
PO04	L	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SE02	L	0.64	0.91	1.14	0.26	0.42	1.17	0.00
SE11	L	1.20	0.80	3.34	1.55	0.17	1.24	0.02
SE32	M	1.96	2.95	2.33	1.78	0.77	3.93	0.00
SE35	L	0.12	0.36	0.32	0.02	0.00	0.03	0.00
SF04	L	0.41	1.19	0.77	0.43	0.00	0.09	0.00
SF09	L	0.64	1.29	0.52	1.20	0.02	0.39	0.00
UK02	L	0.73	0.42	1.54	0.46	0.91	0.98	0.00
UK06	L	0.41	0.11	1.41	0.01	0.90	0.00	0.00
UK13	M	2.83	2.05	5.07	0.85	4.20	5.64	0.27
UK14	L	1.10	0.85	1.78	0.40	2.02	1.51	0.00
UK15	L	0.37	0.30	1.21	0.09	0.55	0.00	0.00
UK31	M	2.30	0.83	4.13	1.12	4.24	3.23	0.05
UK32	L	0.84	0.03	0.41	0.22	1.93	2.48	0.00
UK33	L	0.50	0.29	0.64	0.33	0.67	1.02	0.00
UK34	L	0.58	0.09	0.74	0.09	1.90	0.82	0.00
UK35	M	1.53	1.28	2.39	0.74	2.40	2.11	0.00
UK36	M	1.61	0.50	2.99	0.45	2.66	2.97	0.00
UK37	L	1.21	0.40	2.06	0.49	2.29	1.77	0.07
UK38	H	3.27	2.18	3.42	1.21	4.52	7.15	0.64
UK39	L	1.43	0.58	1.32	0.35	2.03	4.09	0.01
UK40	L	1.16	0.27	2.21	0.23	2.42	2.31	0.00
UK41	L	0.80	0.42	0.88	0.27	1.48	1.76	0.00
UK42	L	0.31	0.02	0.47	0.12	0.49	0.58	0.00
Average		1.41	0.70	1.79	0.92	2.20	2.30	0.17
Var		1.67	0.51	2.77	1.51	6.63	5.04	0.13

Table 10: Normalized exceedence index of 50 ppb ozone concentration $\epsilon_{w,50}$.

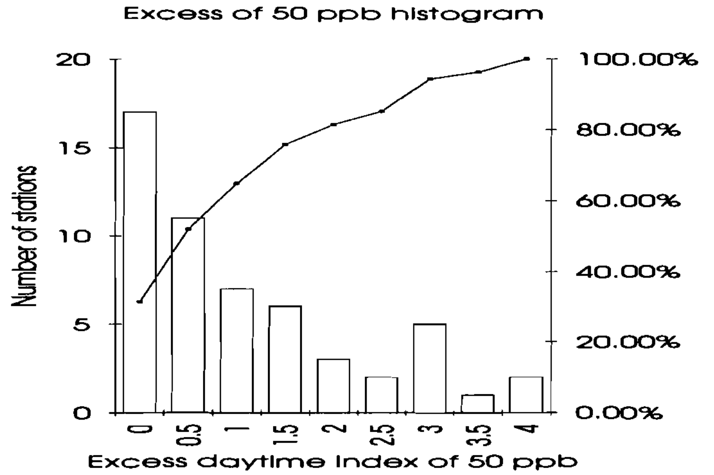


Figure 13: Histogram indicating the distribution of daytime excess ozone index $\epsilon_{d,50}$ with a threshold of 50 ppb.

quite arbitrary in any case, because it has not been possible to correlate the exceedance indices with biological effects. The stations belonging to class H (high) were AS01-90, AS02-90, AS01-92, AS02-92, BE31, BE33, BE34, CH02, CH32, IT04, NL02, NL08, NL31, SE32, UK13, UK31, and UK38. High (superior to 5.0) monthly exceedance indices were found at 22 stations. If the limits were 3.0 and 6.0, only 4 cases (AS01-90, AS02-90, AS01-92, IT04) would be classified as high.

Normalized summer period and monthly exceedance indices $\epsilon_{w,75}$ and $\epsilon_{d,75}$ are shown in Tables 12 and 13, respectively. The classification to three groups was carried out on the basis of the summer period exceedance indices. The low exceedance category (L) included stations having $\epsilon_{p,75}$, i.e., less than 0.3. The medium category (M) included stations with an exceedance index between 0.3 and 0.6 and the high category (H) with an index exceeding 0.6. Again, the classes were chosen so that the interval covered by $\epsilon_{w,75}$ was divided to three equal-length intervals. The distribution of $\epsilon_{w,75}$ among the stations is shown as a histogram in Figure 14.

The monthly indices $\epsilon_{w,75}$ tend to be the lowest in spring and in autumn, while at the end of summer (July and August) the indices are high. Analyzing the exceedance index $\epsilon_{w,75}$ (Table 12); there were 40 stations classified as low, 9 as medium and 7 as high. The distribution of the classification based on $\epsilon_{w,75}$ is shown in Figure 14. The stations AS02-90, BE34, IT04, UK13, and UK38 were classified as high. In addition, 16 stations (AS01-90, AS02-90, BE31, BE33, BE34, CH02, IT04, NL02, NL08, NL31, SE32, UK13, UK31, UK38, UK39, UK40) had very high (over 0.8) monthly exceedance indices. The two British stations, two Central European stations and the Italian station are located in industrialized and highly populated regions.

The exceedance index $\epsilon_{w,75}$ is affected by yearly changing conditions, as seen in comparison of indices calculated for Austrian stations for different summers. Based on the summer period of 1990, station AS01 was classified as medium and AS02 as high, while for the summers of 1991 and 1992, the classification of both stations was low.

For most of the stations the monthly daytime indices $\epsilon_{d,75}$ (Table 13) were the lowest in September and April and the highest during midsummer. Based on the whole summer daytime exceedance, 35 stations were classified as low (L), 6 as medium (M) and 15 as high (H). The classification based on $\epsilon_{d,75}$ is shown in Figure 15. The classification of 10 stations changed from medium to high and for 5 stations from low to medium, when the daytime index was taken as the basis for classification. As in the case of threshold of 50 ppb, the limits might be adjusted to 0.6 and 1.2 since n_w is also, in this case, about two times as big as n_d. The stations belonging to class H (high) were AS01-90, AS02-90, BE31, BE33, BE34, CH02, IT04, NL02, NL08, NL31,

Station	Classification	Summer	April	May	June	July	August	September
AS01-90	H	6.23	1.91	7.07	6.02	10.50	10.66	0.38
AS01-91	M	2.17	1.01	0.47	2.00	5.38	2.94	1.30
AS01-92	H	6.48	2.28	6.51	4.50	10.12	12.66	2.25
AS02-90	H	6.18	0.00	0.00	4.60	10.19	7.98	0.38
AS02-91	M	2.86	3.43	1.71	1.88	4.45	4.21	1.51
AS02-92	H	3.42	1.99	5.13	1.92	4.68	6.03	0.03
BE01	M	2.34	0.00	0.62	0.00	6.73	3.56	0.43
BE31	H	3.49	0.00	1.99	2.76	5.02	8.48	0.00
BE32	M	1.89	0.13	0.00	0.26	1.62	4.50	0.18
BE33	H	3.33	1.74	2.19	0.96	5.76	8.89	0.22
BE34	H	5.08	3.65	3.94	3.23	8.72	10.89	0.06
CH02	H	5.64	1.61	5.70	2.87	17.50	8.58	0.66
CH31	M	2.27	0.45	1.42	1.29	7.39	3.64	0.08
CH32	H	4.37	0.03	3.82	4.02	9.13	8.52	0.60
DK31	L	0.63	0.00	0.22	0.44	0.10	2.23	0.00
DK32	L	0.84	1.39	1.24	0.62	0.30	1.37	0.00
IT04	H	7.77	2.52	6.68	5.75	16.00	12.39	2.92
NL02	H	5.99	1.11	14.35	8.15	5.46	4.06	1.92
NL08	H	4.65	0.71	9.79	10.71	3.98	2.13	1.42
NL31	H	3.16	0.84	5.37	2.32	2.41	7.67	0.00
NO01	L	0.79	0.91	2.77	0.18	0.00	0.80	0.00
NO30	L	0.11	0.61	0.01	0.04	0.00	0.00	0.00
NO39	L	0.02	0.03	0.09	0.00	0.00	0.02	0.00
NO41	L	0.60	1.17	1.95	0.09	0.00	0.38	0.00
NO42	L	0.03	0.17	0.00	0.00	0.00	0.00	0.00
NO43	L	0.51	0.27	1.41	0.05	0.32	1.00	0.00
NO44	L	0.74	1.07	2.33	0.05	0.14	0.82	0.00
NO45	L	0.99	0.77	2.58	0.44	0.76	1.31	0.00
NO47	L	0.07	0.00	0.40	0.00	0.01	0.00	0.00
NO48	L	0.97	0.91	3.75	0.32	0.00	0.37	0.00
NO49	L	0.79	0.15	4.94	0.33	0.09	0.46	0.00
NO50	L	0.24	0.90	0.28	0.00	0.00	0.03	0.00
PO04	L	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SE02	L	1.09	1.73	2.08	0.50	0.75	1.61	0.00
SE11	M	1.89	1.39	4.84	2.65	0.29	1.92	0.04
SE32	H	3.02	3.81	3.81	3.16	1.20	6.20	0.00
SE35	L	0.22	0.66	0.56	0.03	0.00	0.07	0.00
SF04	L	0.71	2.32	1.26	0.62	0.00	0.12	0.00
SF09	L	0.66	1.60	0.47	0.92	0.01	0.45	0.00
UK02	L	1.19	0.79	2.49	0.77	1.25	1.78	0.00
UK06	L	0.74	0.12	2.54	0.02	1.68	0.00	0.00
UK13	H	4.03	2.97	7.21	1.54	5.91	7.14	0.53
UK14	M	1.52	1.12	2.36	0.49	2.92	2.11	0.00
UK15	L	0.58	0.56	1.77	0.18	0.91	0.01	0.00
UK31	H	3.01	1.43	4.90	1.32	6.52	3.60	0.09
UK32	M	1.44	0.07	0.82	0.36	3.28	4.18	0.00
UK33	L	0.70	0.44	0.80	0.65	0.89	1.35	0.00
UK34	L	1.08	0.17	1.40	0.17	3.57	1.44	0.00
UK35	M	1.74	1.48	2.65	0.78	2.75	2.46	0.00
UK36	M	2.90	0.95	6.20	0.73	4.67	5.06	0.00
UK37	M	1.98	0.78	3.67	0.88	3.47	2.64	0.13
UK38	H	4.52	3.04	5.06	1.55	6.24	9.88	1.09
UK39	M	2.30	1.03	2.25	0.69	3.42	6.13	0.02
UK40	M	2.22	0.52	4.43	0.47	4.45	4.39	0.00
UK41	L	1.23	0.69	1.38	0.51	2.45	2.36	0.00
UK42	L	0.62	0.04	0.95	0.24	1.01	1.17	0.00
Average		2.22	1.06	2.90	1.52	3.47	3.62	0.29
Var		3.87	0.99	7.66	4.63	16.06	12.90	0.39

Table 11: Normalised exceedance of 50 ppb ozone concentration during daytime $\epsilon_{d,50}$.

Station	Classification	Summer	April	May	June	July	August	September
AS01-90	M	0.35	0.00	0.17	0.12	1.10	0.65	0.01
AS01-91	L	0.05	0.00	0.00	0.00	0.25	0.01	0.04
AS01-92	L	0.22	0.01	0.29	0.03	0.44	0.52	0.00
AS02-90	H	0.61	0.00	0.00	0.00	1.44	0.36	0.00
AS02-91	L	0.08	0.01	0.00	0.09	0.19	0.16	0.02
AS02-92	L	0.08	0.00	0.09	0.00	0.11	0.24	0.00
BE01	L	0.14	0.00	0.00	0.00	0.50	0.16	0.00
BE31	M	0.56	0.00	0.02	0.38	0.76	1.72	0.00
BE32	L	0.15	0.00	0.00	0.00	0.05	0.46	0.00
BE33	M	0.54	0.33	0.12	0.02	0.97	1.77	0.00
BE34	H	0.70	0.13	0.08	0.29	1.55	2.23	0.00
CH02	M	0.33	0.00	0.01	0.02	1.59	0.63	0.00
CH31	L	0.03	0.00	0.00	0.00	0.18	0.01	0.00
CH32	L	0.21	0.00	0.04	0.10	0.58	0.53	0.00
DK31	L	0.05	0.00	0.00	0.00	0.00	0.23	0.00
DK32	L	0.03	0.00	0.01	0.00	0.01	0.13	0.00
IT04	H	0.79	0.02	0.20	0.45	2.45	1.45	0.10
NL02	M	0.52	0.00	1.56	0.35	0.52	0.48	0.08
NL08	M	0.53	0.00	0.99	1.35	0.52	0.32	0.09
NL31	M	0.39	0.00	0.20	0.20	0.30	1.49	0.00
NO01	L	0.02	0.00	0.10	0.00	0.00	0.00	0.00
NO30	L	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NO39	L	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NO41	L	0.00	0.00	0.01	0.00	0.00	0.00	0.00
NO42	L	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NO43	L	0.01	0.00	0.00	0.00	0.00	0.06	0.00
NO44	L	0.02	0.00	0.09	0.00	0.00	0.01	0.00
NO45	L	0.02	0.00	0.03	0.00	0.00	0.11	0.00
NO47	L	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NO48	L	0.06	0.00	0.31	0.00	0.00	0.00	0.00
NO49	L	0.02	0.00	0.15	0.00	0.00	0.00	0.00
NO50	L	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PO04	L	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SE02	L	0.06	0.00	0.04	0.00	0.01	0.31	0.00
SE11	L	0.07	0.00	0.16	0.15	0.00	0.08	0.00
SE32	L	0.15	0.00	0.08	0.00	0.00	0.82	0.00
SE35	L	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SF04	L	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SF09	L	0.00	0.00	0.00	0.00	0.00	0.00	0.00
UK02	L	0.09	0.00	0.13	0.00	0.09	0.32	0.00
UK06	L	0.02	0.00	0.00	0.00	0.12	0.00	0.00
UK13	H	0.62	0.15	0.96	0.00	1.08	2.06	0.00
UK14	L	0.14	0.00	0.15	0.00	0.25	0.43	0.00
UK15	L	0.00	0.00	0.02	0.00	0.01	0.00	0.00
UK31	M	0.45	0.00	0.82	0.09	0.72	1.00	0.00
UK32	L	0.25	0.00	0.01	0.00	0.50	1.01	0.00
UK33	L	0.05	0.00	0.00	0.00	0.01	0.28	0.00
UK34	L	0.06	0.00	0.00	0.00	0.18	0.21	0.00
UK35	L	0.19	0.00	0.10	0.01	0.35	0.63	0.00
UK36	M	0.34	0.02	0.67	0.00	0.56	0.78	0.00
UK37	L	0.23	0.00	0.27	0.01	0.49	0.55	0.03
UK38	H	0.86	0.05	0.53	0.08	1.41	2.85	0.00
UK39	M	0.33	0.00	0.16	0.00	0.30	1.44	0.00
UK40	M	0.38	0.00	0.53	0.02	0.96	0.82	0.00
UK41	L	0.10	0.00	0.01	0.00	0.18	0.41	0.00
UK42	L	0.04	0.00	0.08	0.00	0.08	0.06	0.00
Average		0.20	0.01	0.16	0.07	0.37	0.50	0.01
Var		0.05	0.00	0.09	0.04	0.28	0.43	0.00

Table 12: Normalized exceedance of 75 ppb ozone concentration $\epsilon_{w,75}$.

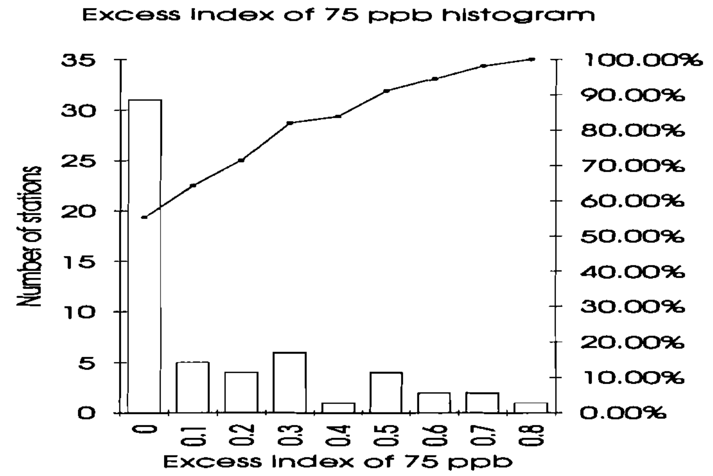


Figure 14: Histogram indicating the distribution of the excess ozone index $\epsilon_{w,75}$ with a threshold of 75 ppb.

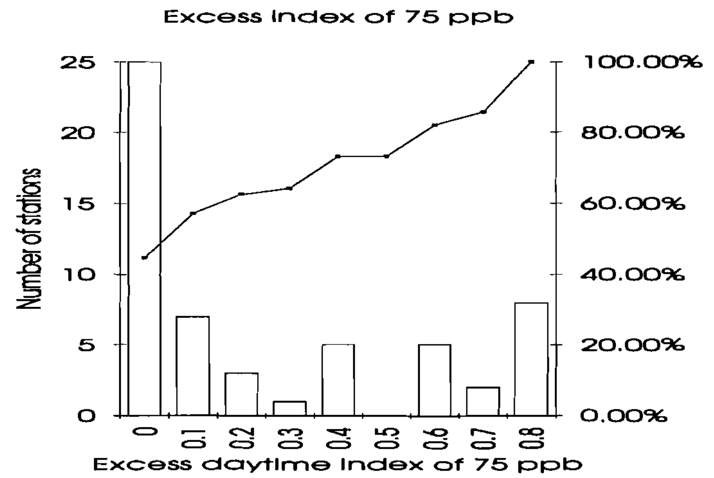


Figure 15: Histogram indicating the distribution of daytime excess ozone index $\epsilon_{d,75}$ with a threshold of 75 ppb.

UK13, UK31, UK36, UK38 and UK40. High (higher than 0.8) monthly exceedance indices were found at 25 stations. If the limits were 0.6 and 1.2, respectively, only 3 stations (BE34, IT04, UK38) would be classified as high. The exceedance index $\epsilon_{d,75}$ seems to be affected by yearly changing conditions, as seen in comparison of indices calculated for Austrian stations for different summers. The station AS01 was classified to high, based on the summer of 1990, as low based on the summer of 1991 and as medium, based on summer of 1992, and the classifications of AS02 were high, low and low, respectively.

Station	Classification	Summer	April	May	June	July	August	September
AS01-90	H	0.69	0.00	0.33	0.23	2.14	1.30	0.02
AS01-91	L	0.10	0.00	0.00	0.00	0.51	0.01	0.09
AS01-92	M	0.42	0.02	0.53	0.06	0.86	1.01	0.00
AS02-90	H	0.60	0.00	0.00	0.00	1.46	0.32	0.00
AS02-91	L	0.09	0.02	0.00	0.09	0.18	0.22	0.00
AS02-92	L	0.13	0.00	0.12	0.00	0.15	0.46	0.00
BE01	L	0.18	0.00	0.00	0.00	0.59	0.31	0.00
BE31	H	1.11	0.00	0.03	0.75	1.50	3.35	0.00
BE32	M	0.31	0.00	0.00	0.00	0.10	0.92	0.00
BE33	H	1.09	0.67	0.23	0.05	1.99	3.59	0.00
BE34	H	1.35	0.27	0.16	0.59	2.86	4.12	0.00
CH02	H	0.63	0.00	0.02	0.04	3.01	1.24	0.00
CH31	L	0.05	0.00	0.00	0.00	0.32	0.03	0.00
CH32	M	0.42	0.00	0.07	0.20	1.15	1.06	0.00
DK31	L	0.10	0.00	0.00	0.00	0.00	0.45	0.00
DK32	L	0.06	0.00	0.03	0.00	0.03	0.25	0.00
IT04	H	1.56	0.03	0.39	0.88	4.83	2.88	0.21
NL02	H	1.00	0.00	2.93	0.68	1.03	0.91	0.15
NL08	H	1.03	0.00	1.93	2.61	1.02	0.64	0.18
NL31	H	0.76	0.00	0.39	0.40	0.61	2.85	0.00
NO01	L	0.03	0.00	0.19	0.00	0.00	0.00	0.00
NO30	L	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NO39	L	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NO41	L	0.00	0.00	0.02	0.00	0.00	0.00	0.00
NO42	L	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NO43	L	0.00	0.00	0.01	0.00	0.00	0.00	0.00
NO44	L	0.03	0.00	0.17	0.00	0.00	0.01	0.00
NO45	L	0.03	0.00	0.05	0.00	0.00	0.12	0.00
NO47	L	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NO48	L	0.10	0.00	0.53	0.00	0.00	0.00	0.00
NO49	L	0.04	0.00	0.30	0.00	0.00	0.00	0.00
NO50	L	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PO04	L	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SE02	L	0.07	0.00	0.08	0.00	0.03	0.33	0.00
SE11	L	0.13	0.00	0.31	0.29	0.00	0.16	0.00
SE32	L	0.27	0.00	0.16	0.00	0.01	1.43	0.00
SE35	L	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SF04	L	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SF09	L	0.00	0.00	0.00	0.00	0.00	0.00	0.00
UK02	L	0.16	0.00	0.24	0.00	0.08	0.60	0.00
UK06	L	0.04	0.00	0.00	0.00	0.25	0.00	0.00
UK13	H	0.99	0.28	1.63	0.01	1.61	3.14	0.00
UK14	L	0.23	0.00	0.19	0.01	0.46	0.68	0.00
UK15	L	0.01	0.00	0.03	0.00	0.02	0.00	0.00
UK31	H	0.65	0.00	1.12	0.11	1.27	1.32	0.00
UK32	M	0.44	0.00	0.01	0.00	0.89	1.81	0.00
UK33	L	0.06	0.00	0.00	0.00	0.02	0.35	0.00
UK34	L	0.12	0.00	0.00	0.00	0.34	0.38	0.00
UK35	L	0.22	0.00	0.06	0.00	0.39	0.83	0.00
UK36	H	0.66	0.04	1.48	0.00	1.08	1.41	0.00
UK37	M	0.41	0.00	0.54	0.01	0.82	0.95	0.06
UK38	H	1.23	0.09	0.95	0.13	1.84	4.22	0.00
UK39	M	0.47	0.00	0.32	0.00	0.60	1.84	0.00
UK40	H	0.74	0.00	1.07	0.04	1.88	—1.61	0.00
UK41	L	0.17	0.00	0.02	0.00	0.36	0.68	0.00
UK42	L	0.08	0.00	0.15	0.00	0.16	0.12	0.00
Average		0.34	0.03	0.30	0.13	0.65	0.86	0.01
Var		0.17	0.01	0.31	0.15	0.91	1.29	0.00

Table 13: Normalized exceedance of 75 ppb ozone concentration during daytime $\epsilon_{d,75}$.

4 Concluding Remarks

Ozone concentration plots can be helpful in getting an idea of the quality and nature of the data. However, data analysis cannot be based on data plots because statistical analyses are needed. The maximum value gives information on peak exposures, especially if it is calculated as an average of n highest values. The average is probably related to long term exposure. The variation index indicates the variation of the daily ozone concentration pattern. The exceedance indices have been suggested as proxies for physical damage caused to plants and animals. As shown in this analysis the behaviour of these various indices do not show a homogeneous trend over the European monitoring stations. At most places some of the indices are high, whereas others are relatively low. Therefore, effect oriented research has not only to determine the magnitudes of ozone exposures related to a certain degree of damage, but perhaps even more importantly, should identify the relevant temporal exposure patterns leading to environmental damage.

On the basis of the statistical analyses that were carried out, some kind of a geographical clustering of the stations seems possible. In general, the Nordic stations were characterized by relatively low maximum values, intermediate average value and very low cummulative exceedance index values.

Ozone exposure at stations in Central Europe, i.e., in Austria, Belgium, Netherlands, Italy and Switzerland, is characterized by medium to high maximum values, relatively high average and compared to Nordic stations much higher exceedance values.

The British stations had lower maximum ozone values than the Central European, but higher than the Nordic stations. The average tended to be lower than at the Central European stations. The typical British stations had relatively high exceedance index values.

The relationship between different statistical parameters was studied by using spatial and temporal correlation. It was found that the daily variation index v and the exceedance indices reflect different properties of the data. Similarly, the classification of the stations based on the variation index and exceedance indices differed significantly. In 43 cases out of 56, the classification was the same when daily variation index and geographical analysis were used. This indicates that geographical information might be helpful in modelling diurnal variation of ozone concentration.

As knowledge of the biological significance of the different exposure patterns becomes more complete, new parameters may be discovered that reflect better the physical damage caused to plants and animals. A properly weighted sum of parameters might act as a complete index giving a basis on which a station could be easily characterized and clustered to the appropriate group.

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Appendix I: Odd Data Values

First of all, it was observed that none of the 50 EMEP stations, nor the Austrian stations, had negative or otherwise odd ozone concentration measurements.

The Illmitz Station (AS01)

All of the radiation measurements made in the summer of 1992 (2406) were below zero. These measurements were made mainly during nighttime and the magnitude was always inferior to 0.02. Thus, it was concluded that they resulted in an inaccurate zero calibration of radiation measurement and were replaced by zero.

Six negative temperature measurements were detected. Their magnitude was quite small and they occurred in early spring (April 22, 1991) during nighttime. It was assumed that they were correct and therefore they were not replaced.

One negative value (September 17,1990 at 11:00 o'clock) was detected in the wind direction time series during summer periods and was marked as a missing value. In addition, zero values were detected between 11:30 o'clock on September 17 and 24:00 o'clock on September 30th. Zero values and negative values continued in October, November and December, 1990 and also during January and February, 1991. Zero wind direction is in principle possible, indicating calm weather, but zero wind speed should correspond to zero wind direction. As the wind speed had both negative and positive values between September 19-30, the whole period from noon on September 17 until the end of September 1990 was reset to be missing. Another periods, where wind direction was zero, had the corresponding wind speed of zero.

The St. Koloman Station (AS02)

All of the radiation measurements made in the summer of 1992 (664) were below zero. The measurements were made mainly during nighttime and their magnitude was always inferior to 0.03. Thus, it was concluded that they resulted in an inaccurate zero calibration of radiation measurement and were replaced by zero.

Negative temperature was detected 441 times. Their magnitude was quite small and had occurred in early spring (April 17-25, 1991, May 3-5, 1991, May 16-18, 1991 and April 17-19, 1992) during nighttime. Except for a period having negative values between August 29-31, 1990, negative values on June 28, 1990 and on August 7, 1992. The periods with temperatures below zero in June and August were considered unlikely and these values were marked as missing.

No negative values were detected in the wind direction and wind speed time series during summer periods. In addition, when wind direction indicated calm weather, the wind speed was zero. On May 10, 1992, however, the wind speed was 40580 m/s and wind direction 19000 degrees. These values were marked as missing values.

The measurements of NO_2 concentration were never negative, but concentrations of NO had negative values (17) in April and July 1992 and these values were considered missing.