INSTITUTE OF TERRESTRIAL ECOLOGY
(NATURAL ENVIRONMENT RESEARCH COUNCIL)

ITE PROJECT T07057c1

DOE CONTRACT PECD7/10/119

Final Report to the
Department of the Environment
May 1990

MONITORING OF NITROGEN OXIDES AND OZONE IN SCOTLAND, AND ANALYSIS OF PAST UK DATA

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May 1990

CONTENTS

EXECUTIVE SUMMARY

1) Surface ozone data have been recorded at Bush Estate and Eskdalemuir since 1986. Data capture averages 95% over the 4 year period (page 8).

2) NO, NO_2, NO_x, SO_2, wind speed, wind direction and solar radiation data have been monitored at the Bush Estate site since 1987. Data capture for these parameters exceeds 89% in 1988 and 1989 (page 8).

3) The calendar year mean O_3 value for 1989 at the Bush Estate site is 27 ppbV. The value for Eskdalemuir is 28 ppbV. The values have increased by approximately 8% and 20% respectively since 1986 (page 10).

4) The extreme hourly O_3 concentrations recorded at the Bush Estate and Eskdalemuir sites over the period 1986 to 1989 are 103 ppbV at the Bush site in 1989 and 104 ppbV at the Eskdalemuir site in 1986. An extreme value of 90 ppbV was recorded at the Eskdalemuir site in 1989 (page 10).

5) The largest number of hours when ozone concentrations exceeded 60 ppbV were recorded at both sites during 1989. 68 hours > 60 ppbV were recorded at Bush Estate in that year, 111 hours > 60 ppbV were monitored at Eskdalemuir (page 10)

6) During each of the 3 major episodes which occurred in 1989, the meteorological parameters and pollutant concentrations were similar and typical of those which are normally present in the formation of photochemical ozone at the Bush Estate site (page 11)

7) The largest values for monthly mean and monthly maximum windspeeds at the Bush Estate site were recorded over the period January to March in both 1988 and 1989. Extreme values of 12 m/s and 14 m/s were monitored in January 1988 and January 1989 respectively (page 11).

8) From January to March, in particular, there is a strong correlation between O_3 concentrations and windspeed values at the Bush Estate site. When windspeeds average 4 to 5 m/s, ozone concentrations range from 30 to 35 ppb and are typical of concentrations found in free tropospheric air. When windspeeds fall to < 2 m/s, ozone concentrations decrease to only a few ppbV (page 12).

9) The large variations in windspeed values over the winter months at the Bush Estate site result in significant changes in vertical mixing processes and hence in O_3 depletion by the dry deposition process. These factors are well illustrated in the analysis of ozone frequency distributions for calendar year and summer and winter daytime and nighttime periods at the site (page 12).

10) Calendar year mean NO concentrations at the Bush Estate site average 1 ppbV. Those for NO_2 average 6 ppb. Their ratio of 1:6 reflects the rural nature of the site (page 13).

11) In 1988 the extreme value for NO was 62 ppb. In 1989 the extreme value was 142 ppb. The extreme values for NO_2 were very similar in both years at 43 ppbV and 45 ppbV respectively (page 13).

12) On a few occasions low O_3 concentrations at the Bush site are a result of the reaction $NO + O_3 \rightarrow NO_2 + O_2$, but overall dry deposition accounts for most of the O_3 depletion at the site (page 13).

13) Cumulative frequency distributions for NO_2 data which were recorded by a Scintrex (NO_2) analyser and Monitor Labs (NO_x) instrument are very similar down to the 1 ppbV concentration. Log-linearity is no longer observed by the Monitor Labs instrument below this concentration but the Scintrex analyser continues to exhibit log-linearity down to pptV levels. Approximately 10% of NO_2 data recorded at the Bush site lie below the 1 ppbV concentration, indicating the need for high sensitivity monitoring equipment (page 13).

14) The median and standard deviation calculated from the NO_2 cumulative frequency distribution at Bush Estate are 4.0 and 2.6. The large standard deviation indicates the prevalence of substantial periods when NO_2 concentrations are low (2 to 3 ppbV) (page 14).

15) Lower standard deviations are exhibited by UK suburban and urban sites. The range of values for different site environments indicates that differentiation of site type may be feasible using these statistical methods (page 14).

16) A comparison of NO_2 values recorded by the Monitor Labs (NO_x) analyser and the Scintrex (NO_2) instrument, during ozone episodes, is consistent with the presence of PAN at the Bush Estate site. When the 0_3 concentration exceeds 60 ppbV, the $\Delta N0_2$ values increase to > 2 ppbV. In these instances the 0_3:ΔNO_2 ratio is between 50:1 and 30:1 (page 14).

17) Calendar year SO_2 mean concentrations at the Bush Estate site average 2.8 ppbV. The SO_2 cumulative frequency plot is log-linear over the entire range of values indicating the primary nature of the pollutant. The median is 1.3 and the standard geometric deviation is 3.1 (page 15).

18) The SO_2:NO_2:0_3 calendar year mean ratio at the Bush Estate site is 1:2.5:9. The annual average concentrations of the three gases in combination do not exceed the WHO guidelines for phytotoxic effects. (page 15).

OBJECTIVES

The objectives of the report are to:

1) Illustrate that continuous monitoring of surface 0_3, NO_x and SO_2 over several years duration is required to determine their behavioural patterns in a rural environment.

2) Emphasize that simultaneous recordings of meteorological measurements are required in a full analysis of the gaseous pollutant data if climatic effects are to be determined: A detailed understanding of windspeed, data, especially in the north of the UK, for example, is essential in a statistical analysis of ozone data.

3) Show that 0_3 and NO_x data at a rural site exhibit entirely different properties from those at suburban and urban sites across the UK.

4) Show that simultaneous measurements of NO_x using analysers with varying sensitivity, over the short term, emphasise the need for the use of very high sensitivity instruments at rural sites.

5) Emphasize that there is a need in rural areas for specific measurements of nitrogen compounds such as PAN, especially during ozone episodes.

6) Show that further monitoring of combinations of pollutant gases such as 0_3, NO_x and SO_2 are necessary to determine their future impacts in crops and vegetation. Such measurements will also be useful in deposition studies.

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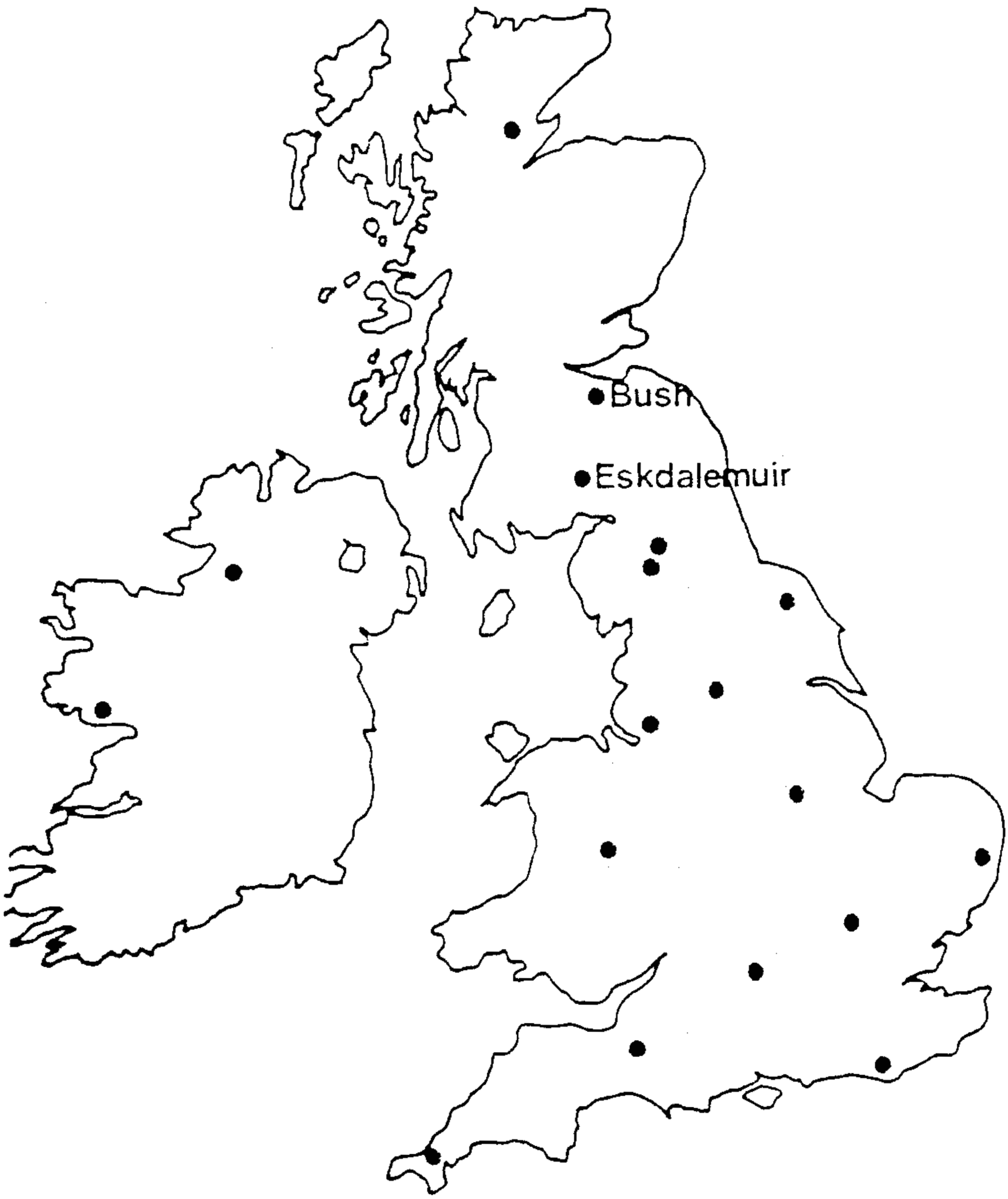
INTRODUCTION

Surface ozone data have been recorded at the Institute of Terrestrial Ecology's Bush Estate and Eskdalemuir sites since 1986. These two sites, whose locations are shown in Figure 1, form part of the UK national ozone network of 17 sites. The reasons for monitoring surface ozone concentrations across the UK and the reasons for choosing Bush Estate and Eskdalemuir as two of the UK network sites are described in detail elsewhere.[1] The results obtained during 1986 and 1987 at the two sites and indeed from the whole of the UK network have been summarized previously.[2,3]

The 1988 and 1989 ozone data for Bush Estate and Eskdalemuir are discussed here together with various other pollutant and meteorological data which have been recorded at the Bush Estate site over the same period. Details of all the data summarized in this report are listed in Table 1.



DoE OZONE MONITORING NETWORK

FIGURE 1.

Table 1. Data Monitored at Bush Estate and Eskdalemuir from 1988 to 1989

BUSH ESTATE (165m asl, 12 km south of Edinburgh, surrounded by arable farmland)

Pollutant/ Meteorological Parameter	**Analyser Type**	**Calendar Year** *Data Capture (%)*		**Calendar Year** *Mean Value (ppb)*		**Calendar Year** *Maximum (ppb)*	
		1988	**1989**	**1988**	**1989**	**1988**	**1989**
O_3	Monitor Labs (UV absorption)	97	99	27	27	89	103
SO_2	Monitor Labs (fluorescent)	86	65	2	3.5	50	71
	Teco (fluorescent)	-	80	-	3	-	46
NO	Monitor Labs (chemiluminescent)	94	80	1	2	62	142
	Analysis Automation (chemiluminescent)	47	35	-	-	-	-
NO_2	Monitor Labs (NO_x-NO) (chemiluminescent)	94	80	6	6	43	45
	Analysis Automation (NO_x-NO) (chemiluminescent)	47	35	-	-	-	-
	Scintrex (NO_2) (chemiluminescent)	88	68	6	6	43	40
	Diffusion Tubes			6	6		
Windspeed	Vector Instruments Anemometer	98	100	2.5m/s	3m/s	20m/s	14m/s
Wind Direction	Vector Instruments Wind vane	98	100				
Solar Radiation	Kipp Solarimeter	98	100				
Rainfall	Tipping Bucket	100	98				

ESKDALEMUIR (259 m asl, remote site in Dumfriesshire, rough/grazing land and pasture)

O_3	Monitor Labs (UV Absorption)	96	93	26	28	75	90

MONITORING METHODS, CALIBRATION TECHNIQUES AND DATA STORAGE

Ambient NO_x, O_3 and SO_2 concentrations are monitored at approximately 3 metres above ground level and meteorological data are recorded at approximately 5 metres above ground level.

At the Bush Estate site, zero and span drift checks are carried out on the Analysis Automation and Monitor Labs ozone analysers at weekly intervals. They are calibrated every month by ITE staff, using an ozone generator. Warren Spring Laboratory calibrate the Monitor Labs (network) instrument at six monthly intervals using their primary ozone standard. At the same time, they normally calibrate ITE's ozone generator with this standard.

The Warren Spring Laboratory's primary calibration is also carried out every six months at the Eskdalemuir site and calibration of the instrument by ITE staff is performed at monthly intervals; sooner if daily communication with the analyser via modem indicates instrument malfunction. Since the summer of 1989, WSL have also monitored Eskdalemuir ozone data via modem.

The SO_2, NO_x and NO_2 analysers are all checked daily for span and zero drift. They are calibrated at monthly intervals using permeation tubes and standard gas cylinders. In addition, the NO_x instruments are calibrated using the Gas Phase Titration technique.

The ambient pollutant concentrations and the various meteorological parameters are sampled at 5 second intervals. Their 15 minute averages are logged by a Campbell Scientific data logger which is downloaded regularly to an IBM computer. When the data have been carefully edited, both the 15 minute averaged data and the hourly averaged concentrations, calculated from these, are stored on a VAX mainframe. At present, the 15 minute averaged values are being transferred to an 'Oracle' database on the mainframe. The hourly mean concentrations are also processed to Lotus-1-2-3 spreadsheets.

O_3 MONITORING AT BUSH ESTATE AND ESKDALEMUIR: MEAN VALUES

The significant temporal and spatial patterns exhibited by surface ozone measurements over diurnal, monthly and seasonal periods of the year are well understood.(1) The data recorded at Bush Estate and Eskdalemuir in 1988 and 1989, show no exception to such behaviour.

Figures 2 and 3 show the daily mean ozone concentrations for Bush and Eskdalemuir in 1988 and 1989. The range of values (10-50ppb) exhibited by both sites throughout each year are very similar with largest daily mean concentrations occurring between April and September.

The daily mean values for both sites from January to March 1989 are noticeably larger however than those daily mean values for the same period in 1988. Further monthly variations from year to year are more easily observable in the plot of monthly mean values for the two sites which covers their entire monitoring period; from 1986-1989. These data are illustrated in Figures 4(a) and (b). Not only are the January to March monthly mean values larger 1989 than in 1988 for the Bush site but there is an average increase of 30% in ozone concentrations over the 3 monthly period from 1986 to 1989.

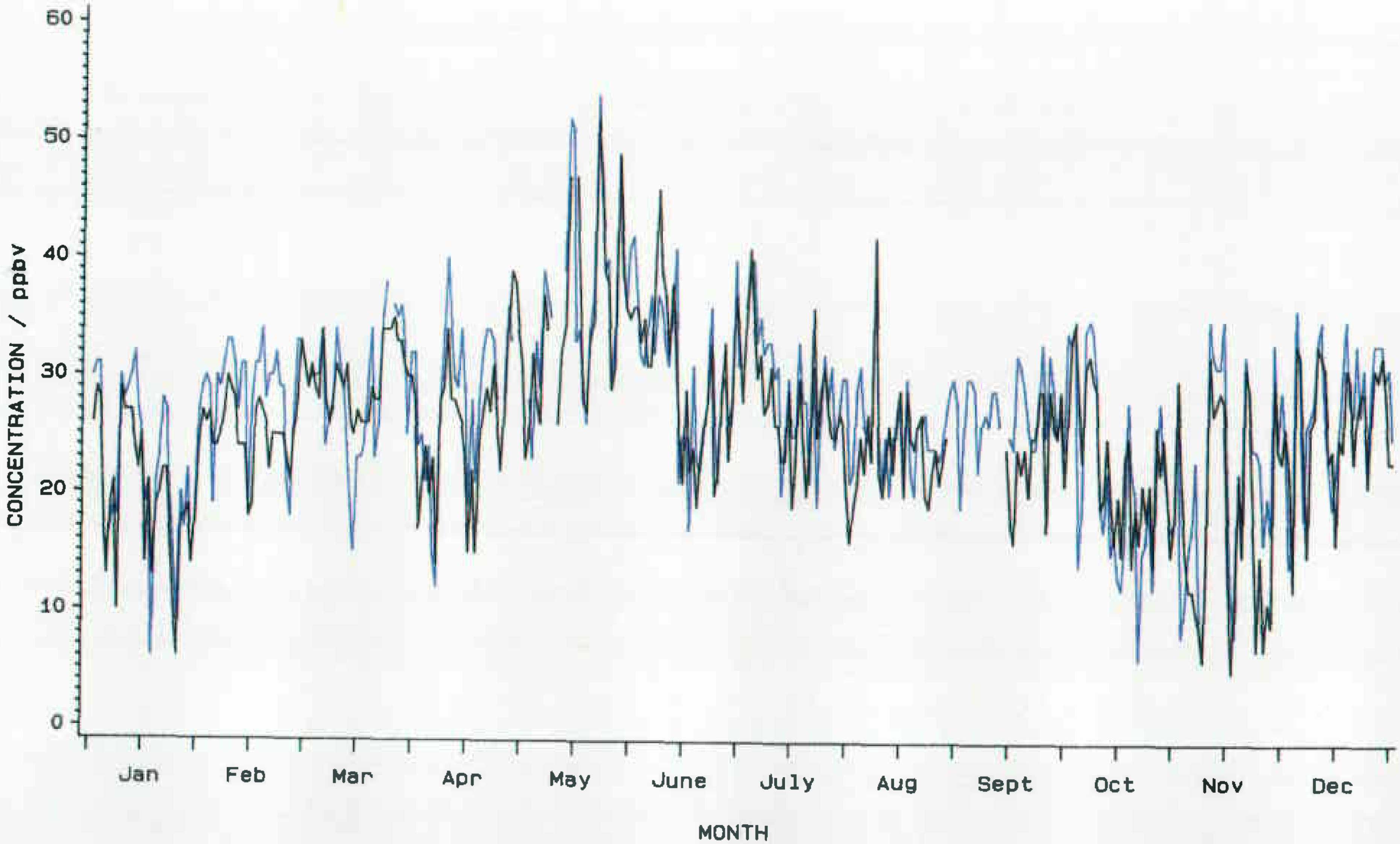
Operational failure over some of this period at the Eskdalemuir site prevents an accurate determination of ozone variations there. An approximate increase of 20% is observable in the available Eskdalemuir data plotted in Figure 4(b).

Monthly mean ozone concentrations at the Eskdalemuir site also show an overall increase of about 20% from April to December over the four year period which is not as clearly defineable in the Bush Estate data set. Bush Estate monthly mean ozone concentrations do exhibit a 15% increase from June to September over the four year period.

Year to year variations are also borne out by the calendar year and summertime mean values, listed in Table 2 and in the averaged diurnal data for the four year period which are plotted in Figures 5 and 6.

FIGURE 2.

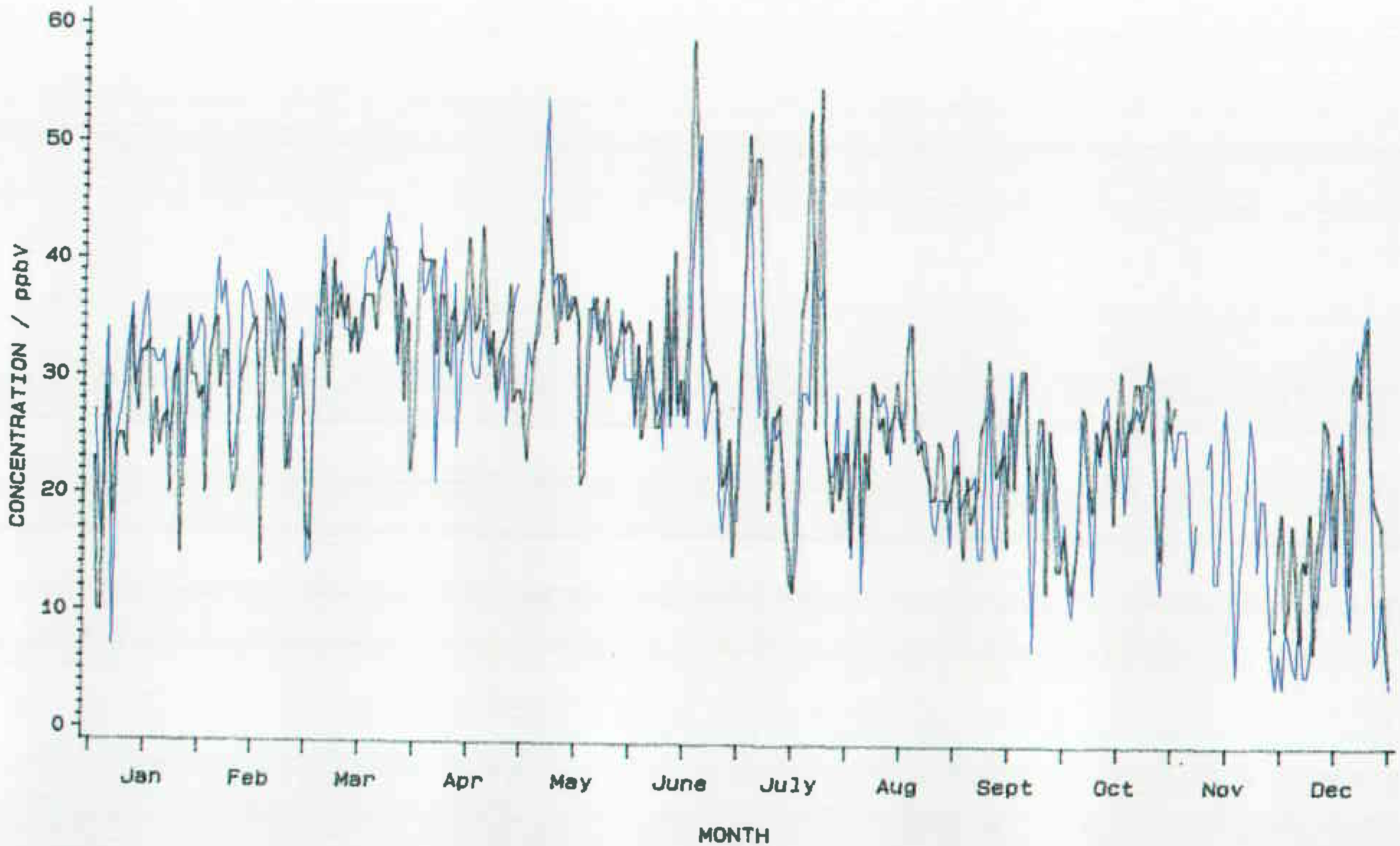
DAILY MEAN O3 VALUES FOR BUSH AND ESKDALEMUIR 1988



ESKDALEMUIR=BLACK, BUSH=BLUE

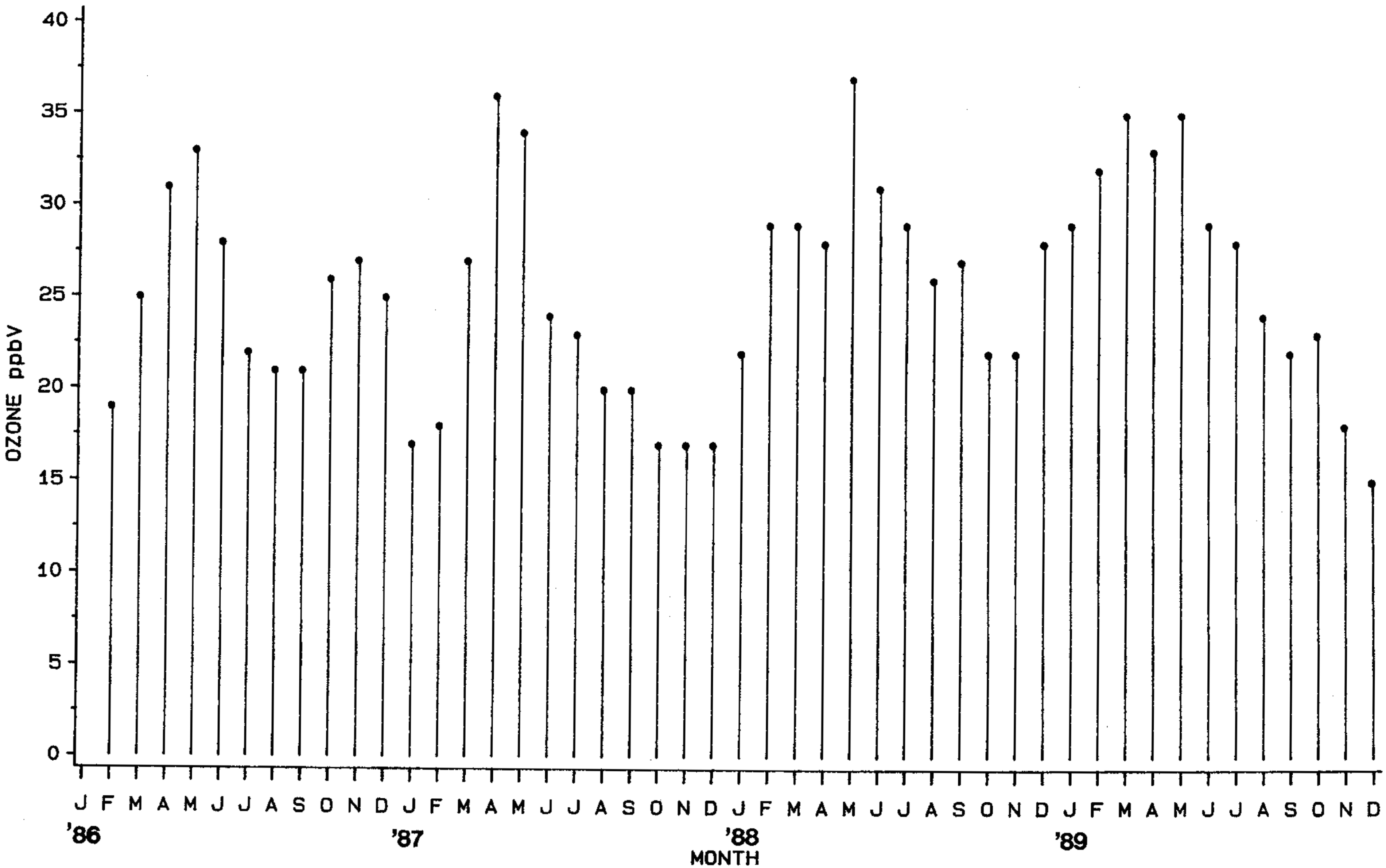
FIGURE 3.

DAILY MEAN O3 VALUES FOR BUSH AND ESKDALEMUIR 1989



ESKDALEMUIR=BLACK, BUSH=BLUE

MONTHLY AVERAGED OZONE VALUES AT BUSH FROM 1986 TO 1989



MONTHLY AVERAGED OZONE VALUES AT ESKDALEMUIR FROM 1986 TO 1989

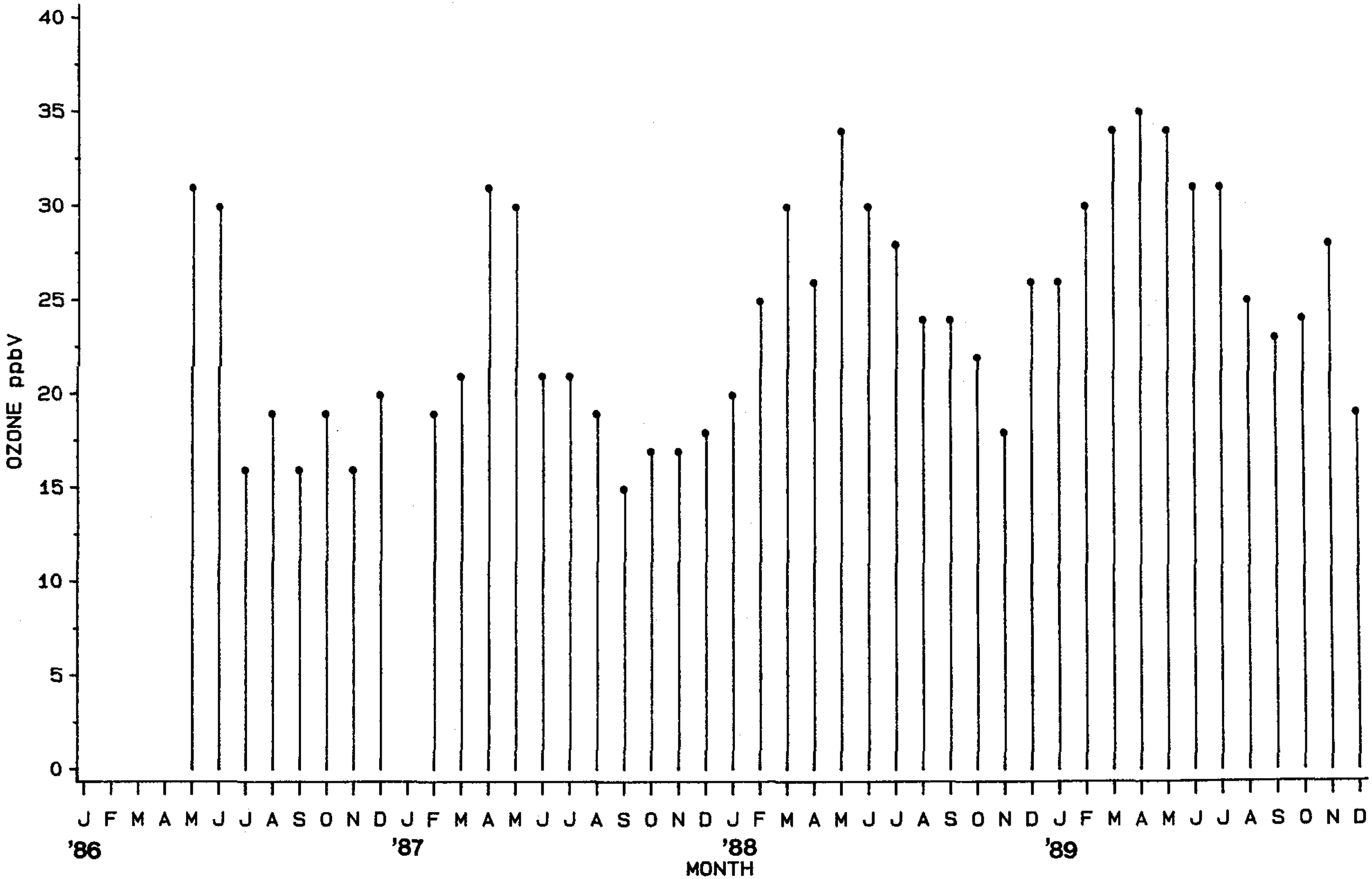
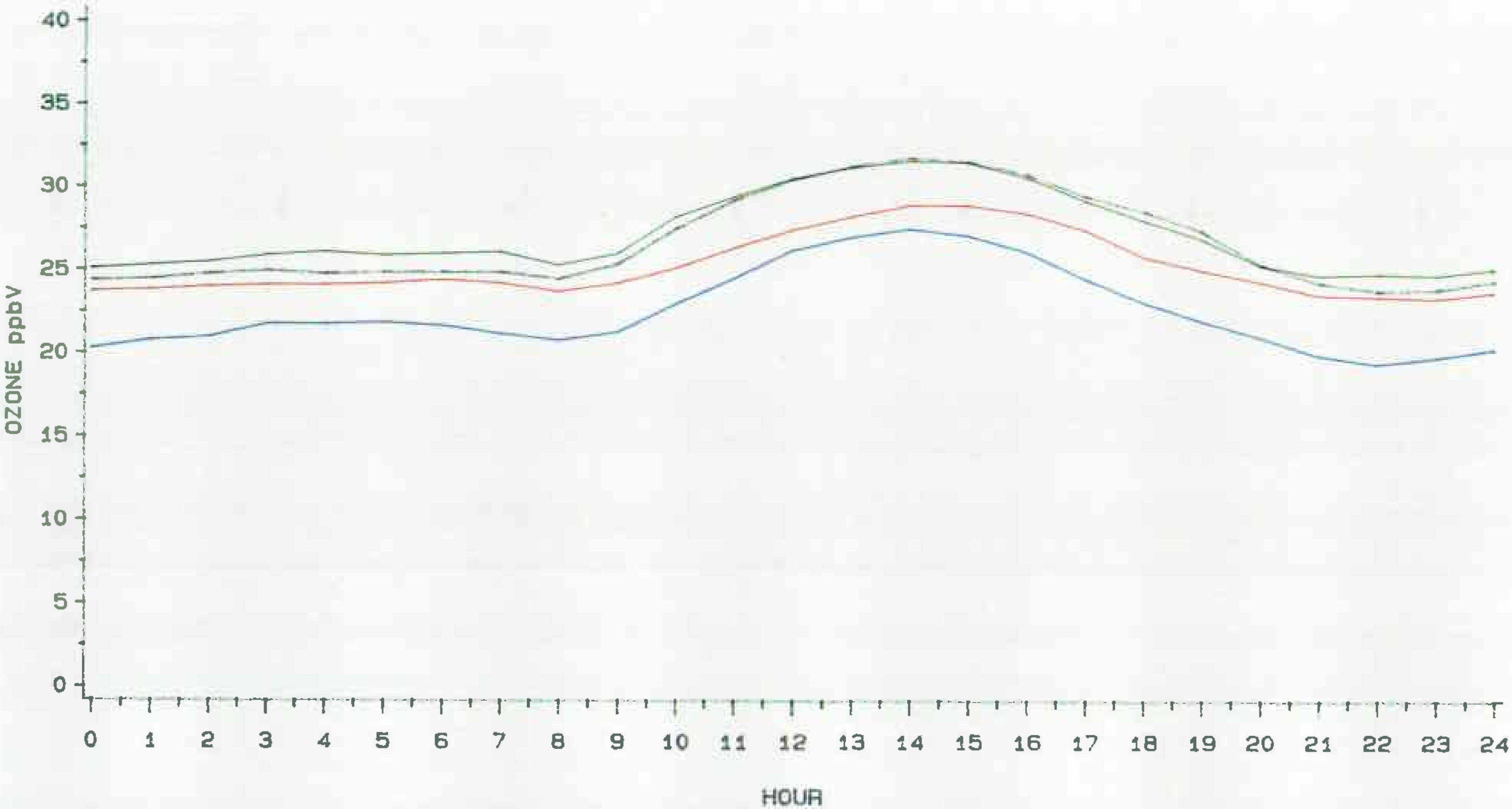


FIGURE 5.

AVERAGED DIURNAL OZONE VALUES AT BUSH FROM 1986 TO 1989



RED=1986
BLUE=1987
GREEN=1988
BLACK=1989

FIGURE 6.

AVERAGED DIURNAL OZONE VALUES AT ESKDALEMUIR FROM 1986 TO 1989

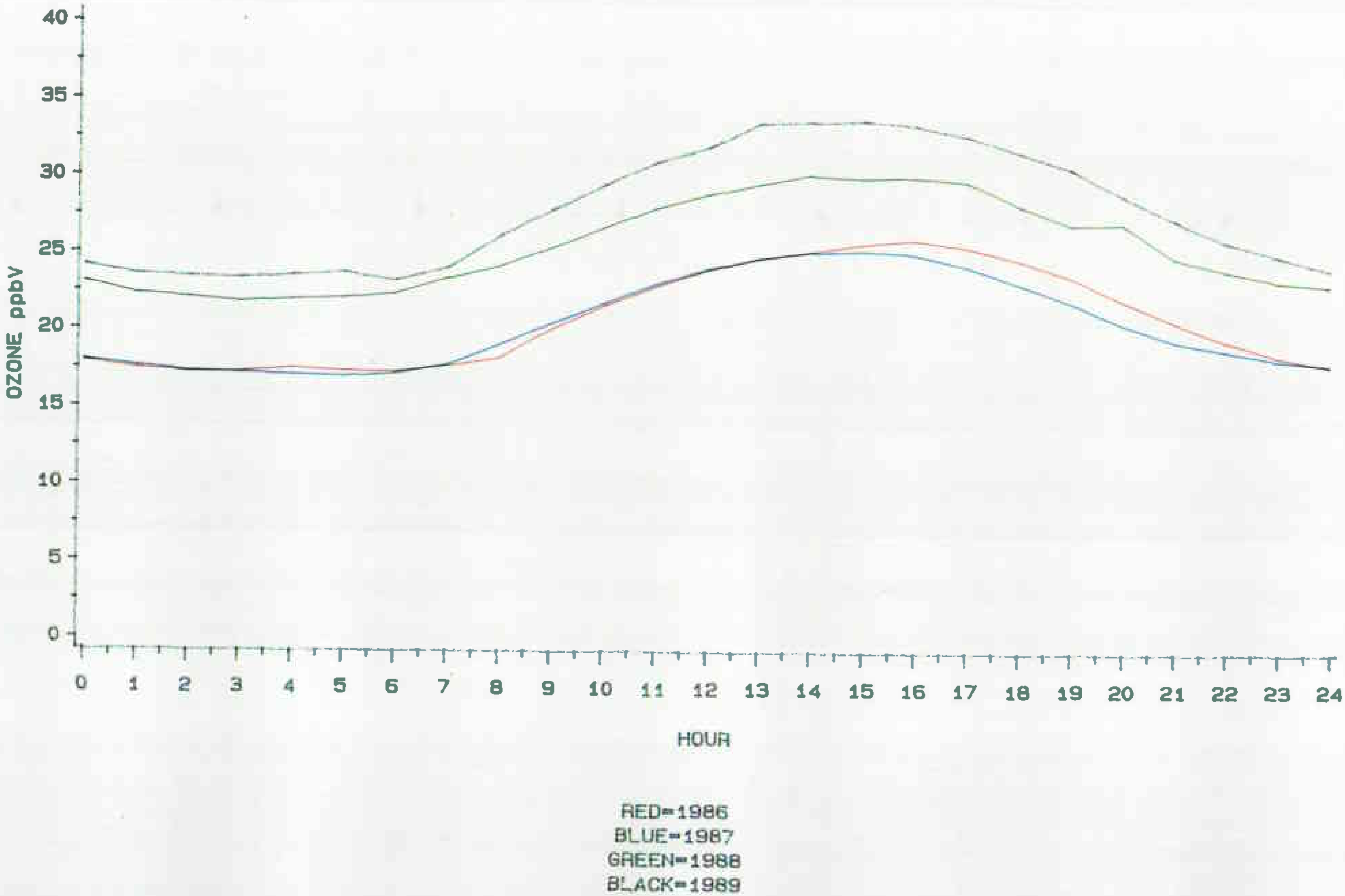


Table 2. Calendar Year and Summertime Mean O_3 Values for Bush and Eskdalemuir from 1986-1989.

	Bush		Eskdalemuir	
	Calendar Year mean	Summertime mean	Calendar Year mean	Summertime mean
1986	25	26	22	24
1987	23	26	21	23
1988	27	30	26	28
1989	27	28	28	30

03 MONITORING AT BUSH ESTATE AND ESKDALEMUIR: MAXIMUM VALUES

The maximum hourly ozone concentration recorded at the Bush Estate site during calendar year 1988 was 89 ppb. In 1989, the maximum hourly value recorded was 103 ppb. At Eskdalemuir, the maximum hourly ozone values recorded during calendar years 1988 and 1989 were 75 ppb and 90 ppb respectively. These extreme values are easily observable in Figures 7 and 8 which show the daily maximum ozone concentrations for both sites in 1988 and 1989. Similar to the daily mean ozone concentrations, the maximum daily values at Bush and Eskdalemuir follow much the same pattern in each of the years. During 1988 however, the Bush Estate site records slightly larger daily maximum ozone values than the Eskdalemuir site.

From January to May 1989, the maximum daily values at both sites are 5 ppb higher than over the same period in 1988: In 1989 the values range from 35-50 ppb over the 5 month period. In 1988 they range from 30-45 ppb. The opposite trend is apparent in the data sets from August to December 1988 and 1989. In the 1989 period, the values at both sites are approximately 5 ppb lower than those over the same period in 1988: Values range from 25-35 ppb in 1989 and 25-40 ppb in 1988 at both sites.

During 1988, there were a number of individual days at both sites when ozone episodes occurred. These occurrences are clearly visible, particularly during May, in Figure 7.

Only 1 hourly averaged ozone concentration exceeded 80 ppb at the Bush Estate site during the entire summer (1 April - 30 September) of 1988. At Eskdalemuir 0 hourly averaged ozone concentrations exceeded 80 ppb during the summertime period. The number of hours exceeding 60 ppb, as an hourly averaged concentration, were 36 and 33 at the Bush and Eskdalemuir sites respectively.

The episoidal situation was significantly different during the summer of 1989. Several episodes were recorded during June and July when hourly averaged ozone concentrations remained above 60 ppb for several hours on consecutive days at both sites. These occasions are well illustrated in Figure 8. Eskdalemuir recorded 111 hours when the hourly averaged concentration exceeded 60 ppb and Bush Estate recorded 68 hours above the same value. These time over limits are a factor of 3 and 2 greater than the time over limits for 60 ppb which were monitored at the Eskdalemuir and Bush Estate sites in 1988.

Table 3 lists the number of hours in which the averaged hourly ozone concentration exceeds 60 ppb, 80 ppb, 100 ppb and 120 ppb at the Bush and Eskdalemuir sites over their entire monitoring period; from 1986 to 1989. The data indicate that the largest number of time over limits, over the four year period, occur in 1989.

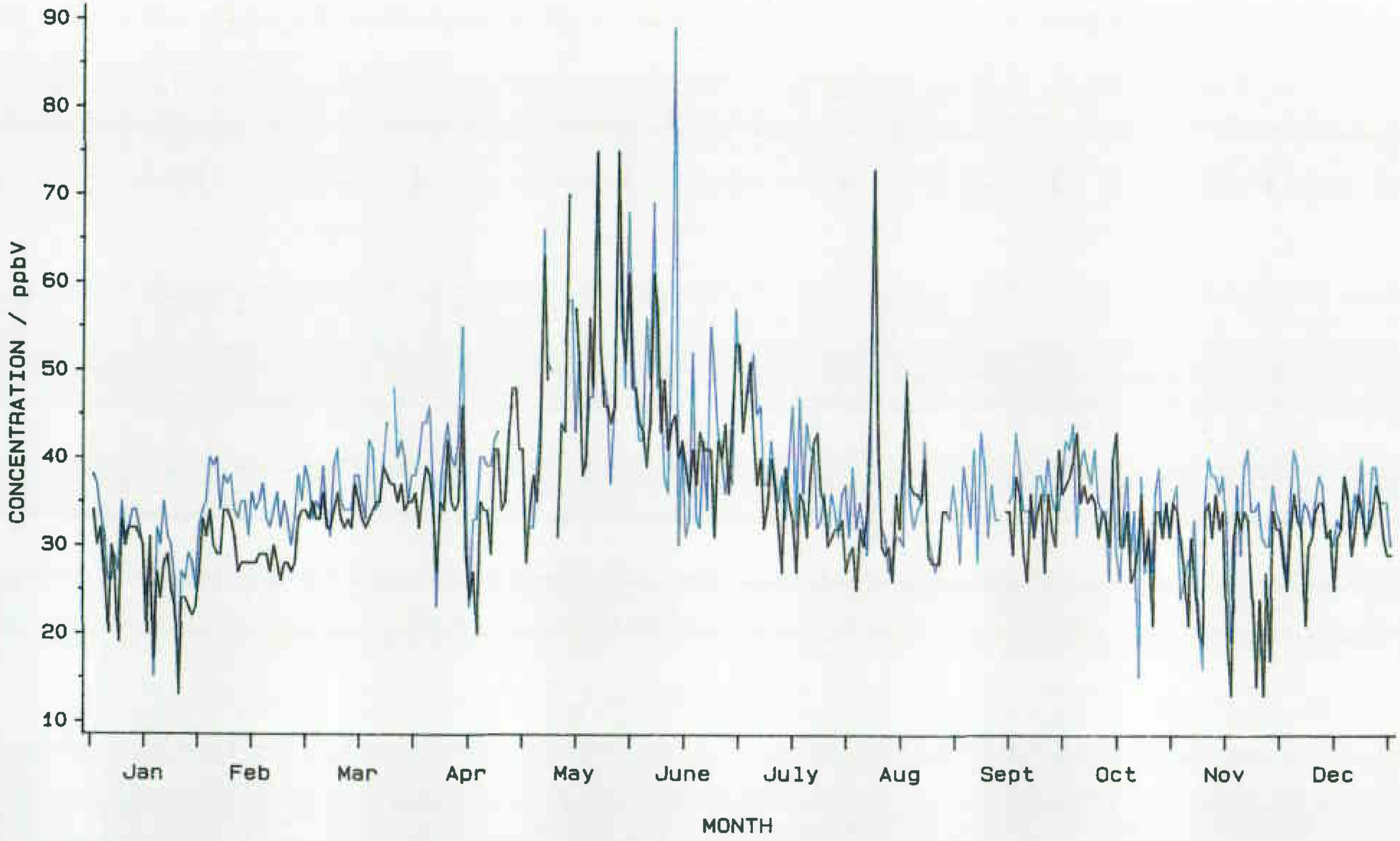
Table 3. Number of hours when hourly averaged ozone concentrations exceed 60 ppb, 80 ppb, 100 ppb and 120 ppb from 1986 to 1989 at the Bush and Eskdalemuir sites.

	BUSH				Calendar Year	ESKDALEMUIR				Calendar Year
	>60	>80	>100	>120	maximum	>60	>80	>100	>120	maximum
1986	12	0	0	0	73	32	8	2	0	104
1987	55	15	0	0	96*	52	4	0	0	84
1988	36	1	0	0	89	33	0	0	0	75
1989	68	14	3	0	103	111	23	0	0	90

*These data refer to the network, Monitor Labs ozone analyser. In April 1987, an analysis automation analyser operating close by recorded a maximum hourly value of 101 ppb at the same time as the 96 ppb value was recorded. Both analysers had received a

FIGURE 7.

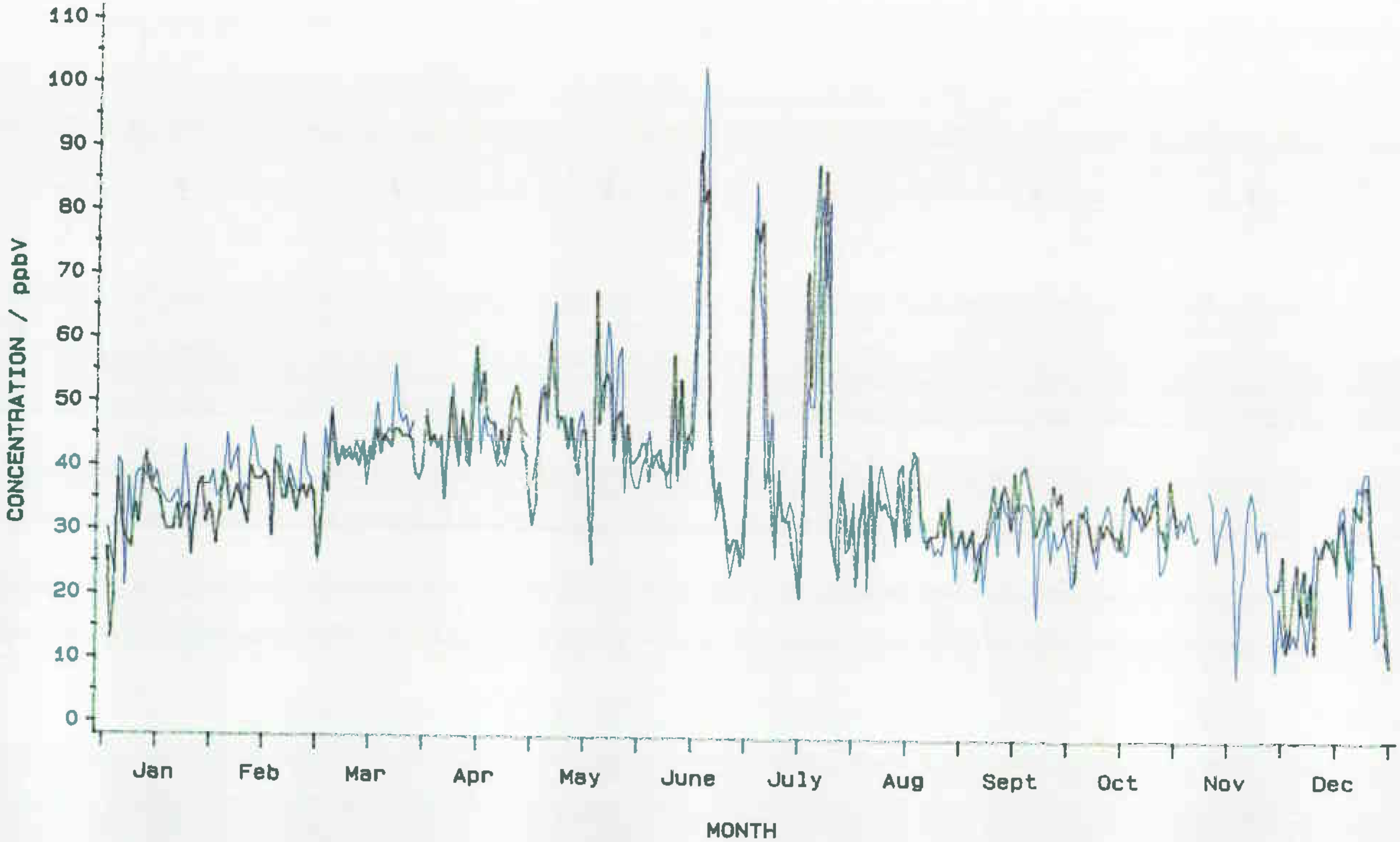
DAILY MAXIMUM O3 VALUES FOR BUSH AND ESKDALEMUIR 1988



ESKDALEMUIR=BLACK, BUSH=BLUE

FIGURE 8.

DAILY MAXIMUM O3 VALUES FOR BUSH AND ESKDALEMUIR 1989



ESKDALEMUIR=BLACK, BUSH=BLUE

WSL primary calibration two weeks previously.

OZONE EPISODES RECORDED DURING 1989

Three major ozone episodes were recorded at the Bush Estate and Eskdalemuir sites during the summer of 1989. These occurred from the 18-20 June, from the 3-6 July and from the 19-25 July. Figures 9 to 11 illustrate the hourly averaged ozone concentrations which were recorded at both sites during each episode. There is considerably more variation in the ozone concentrations recorded at the two sites from 19-25 July than during the two other episoidal periods when very similar patterns in ozone concentrations were recorded.

Table 4 lists the mean and maximum hourly averaged concentrations for 0_3, NO_x and SO_2 which were calculated for the duration of each episode. Also tabulated are wind direction, wind speed, solar radiation values and time over limits for ozone. The SO_2 and NO_x means and maxima for the 19-25 July are larger than those for the other two episodes but the meteorological variables for all three episodes are very similar. Hourly averaged values for the various parameters which are tabulated in Table 4 are plotted in Figures 12 to 15 for the episode which occurred from 3-6 July.

The low windspeed and high solar radiation values, together with the strong diurnal cycling in ozone concentrations and the south/south easterly wind direction, noted in the above episodes, are typical of the meteorological conditions which occur in summertime anticyclonic conditions and which are normally prevalent in the formation of photochemical ozone at the Bush Estate site.

OZONE CONCENTRATIONS AND WINDSPEED VALUES AT THE BUSH ESTATE SITE

Figures 16 and 17 show the daily mean and daily maximum windspeed values which were recorded at the Bush Estate site during 1988 and 1989. Both sets of values are larger in 1989 than in 1988 but the same seasonal pattern in windspeed values is observed in both years. The largest mean and maximum values are recorded from January to March in each year. The lowest mean values are recorded from April to December and the lowest maximum values from April to August. Both the year to year variations and the seasonal similarities in windspeed are clearly noticeable in Table 5 which lists the monthly mean and monthly maximum hourly averaged values for both years.

Table 5. Monthly mean and monthly maximum hourly averaged windspeed values for Bush Estate in 1988 and 1989.

	Windspeed m/s			
	mean		maximum	
	1988	1989	1988	1989
January	3	5	12	14
February	4	5	11	13
March	3	4	8	11
April	2	2	9	7
May	2	2	6	8
June	2	2	5	5
July	3	2	9	6
August	3	3	7	7
September	3	2	10	8
October	2	2	10	8
November	2	1	8	7
December	4	1	10	9

Figure 18 shows a smoothed plot of daily mean ozone and daily mean windspeed values for 1989. From January to March, on a daily basis, the ozone:windspeed ratio averages 6:1. For the rest of the year, the ratio is a factor of 2 to 3 larger at approximately 15:1. These results may be explained by consideration of the seasonal variation both in ozone and in meteorological parameters.

During the winter months (October to March) most ozone recorded at the surface is a result of the vertical transport of naturally occurring stratospheric ozone. Some will also result from reactions of hydrocarbons, nitrogen oxides and free radicals in tropospheric air. Only a very small percentage will be formed photochemically within the boundary layer itself; restricted principally by low solar radiation values which are normally prevalent in winter.

FIGURE 9.

HOURLY AVERAGED OZONE VALUES FOR BUSH & ESKADALEMUIR FROM 18-21 JUNE 1989

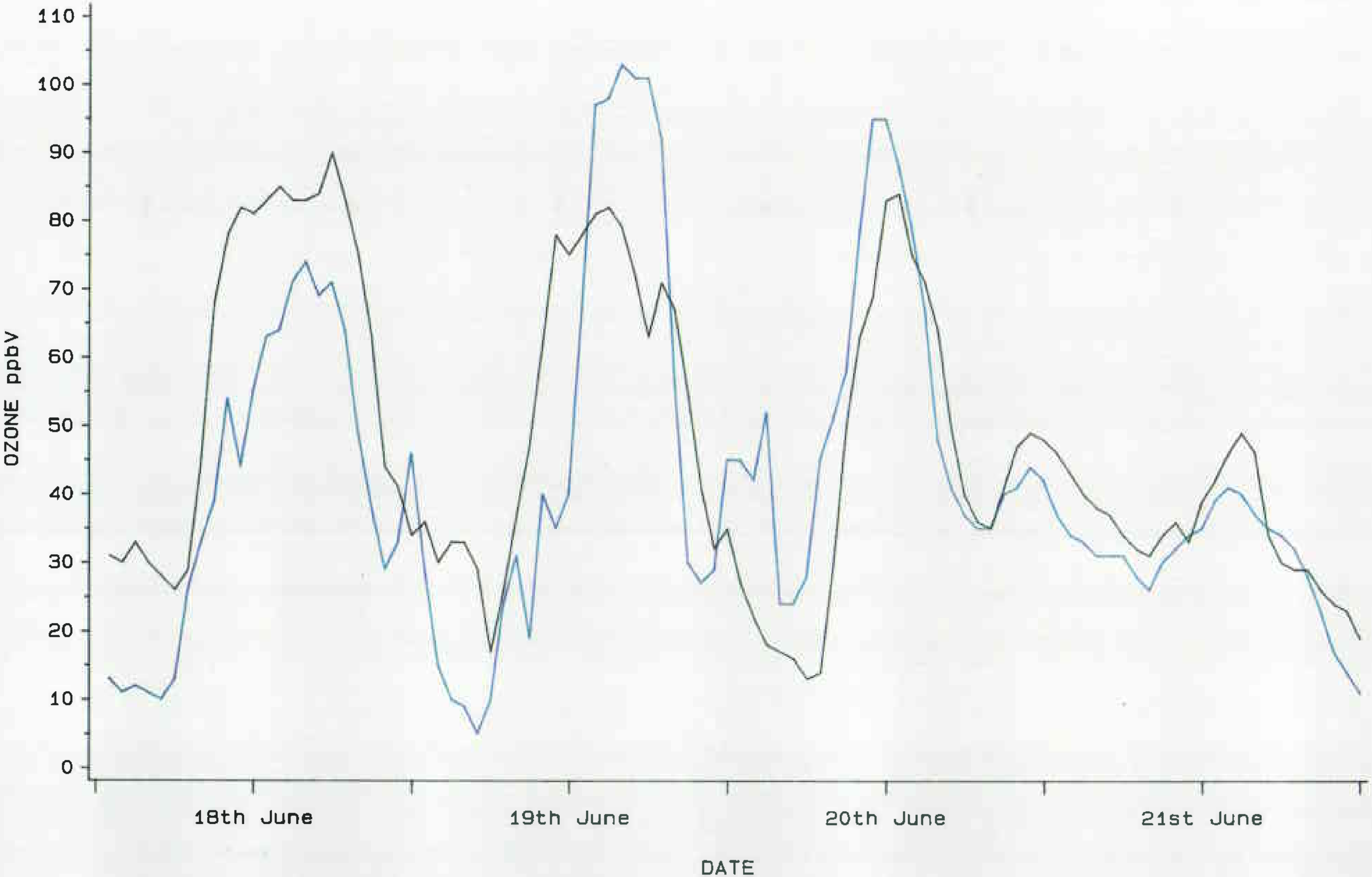


FIGURE 10.

HOURLY AVERAGED OZONE VALUES FOR BUSH & ESKADALEMUIR FROM 3–6 JULY 1989

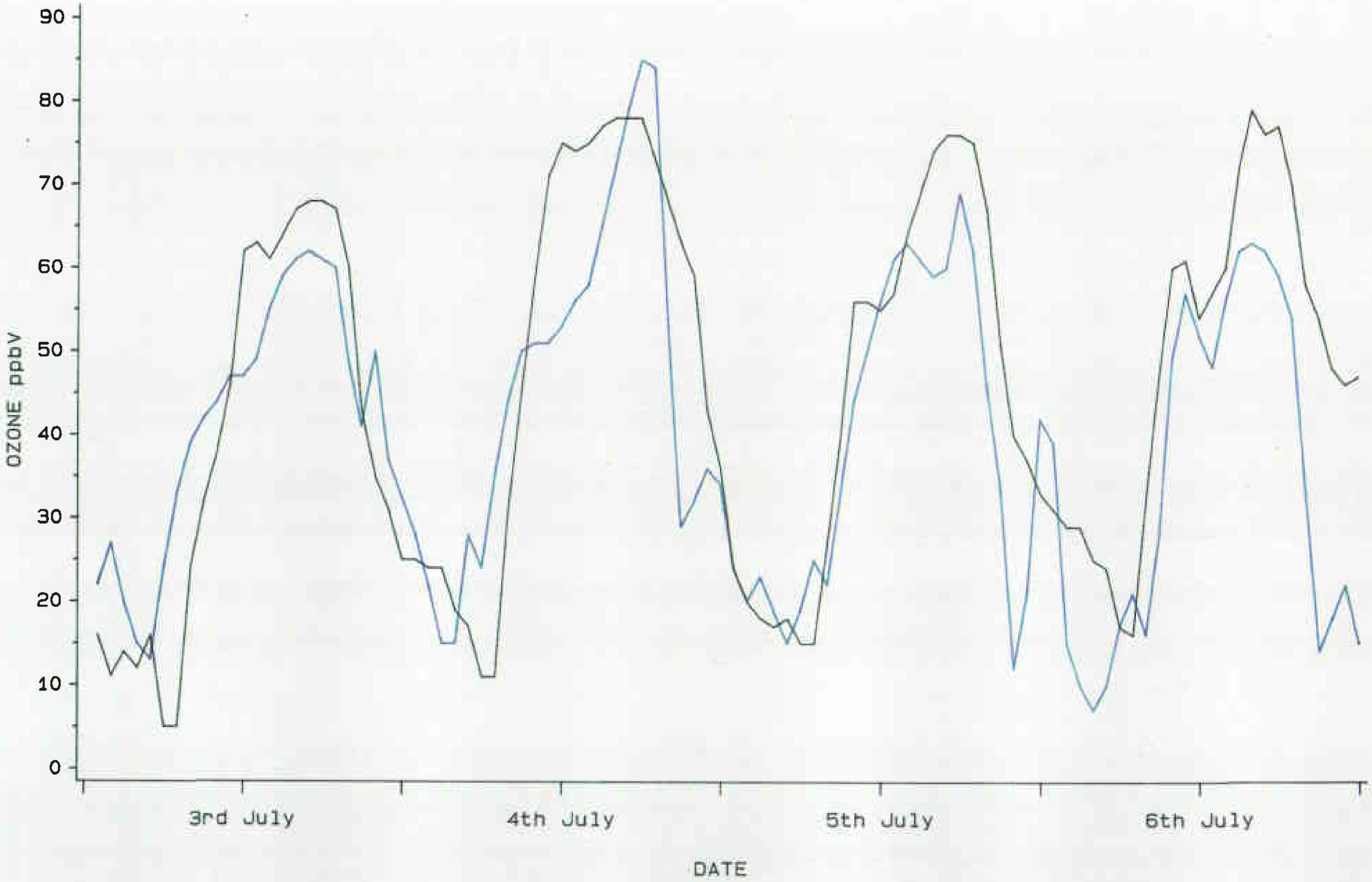


FIGURE 11.

HOURLY AVERAGED OZONE VALUES FOR BUSH & ESKADALEMUIR FROM 19–25 JULY 1989

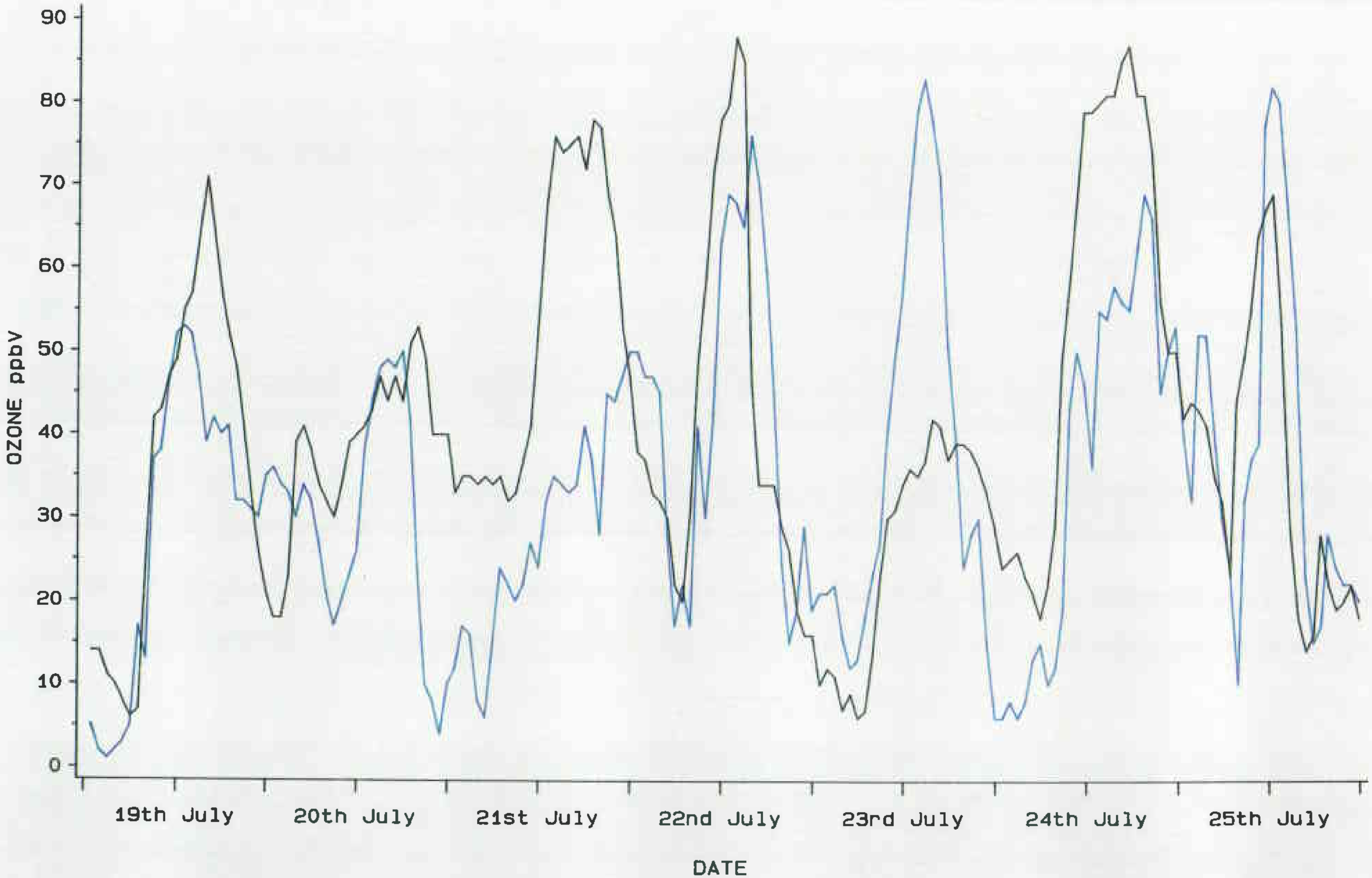


Table 4. Mean and maximum O_3, NO, NO_2, SO_2, windspeed, wind direction and solar radiation values calculated for the duration of each episode. Time over limits for O_3 are also listed.

DURATION OF EPISODE	MEAN O_3 BU	MEAN O_3 ESK	MAX O_3 BU	MAX O_3 ESK	MEAN NO	MAX NO	MEAN NO_2	MAX NO_2	MEAN SO_2	MAX SO_2	MEAN WS	MAX WS	WIND DIRECTION	SOLAR RADIATION MAX	NO. OF HOURS >60,>80,>100,120 ppb ON EACH DAY OF EPISODE AND MAX O_3 VALUE (TIME OF DAY) BUSH	DAY	ESK
18-29 June	45	51	103	90	1.2	14.7	11(ML) 7(SC)	35(ML) 23(SC)	4.8	28	1	3.2	south/south east veering to S West on 20th	~800w M^{-2}	(7,0,0,0)84(16)	18	(13,9,0,0)90(18)
															(7,6,3,0)103(16)	19	(11,2,0,0)92(15)
															(6,3,0,0)95(11)	20	(7,2,0,0)84(13)
															(20,9,3,0)		(31,13,00)
3-6 July	40	46	85	79	1.0	14.8	9(ML) 9(SC)	34(ML) 34(SL)	4.0	20	0.9	3.0	southerly	~800w m^{-2}	(4,0,0,0)62(17)	3	(9,0,0,0)68(17,18)
															(5,2,0,0)85(18)	4	(11,0,0,0)78(16,18)
															(6,0,0,0)69(18)	5	(7,0,0,0)76(17,18)
															(3,0,0,0)63(16)	6	(8,0,0,0)79(16)
															(18,2,0,0)		(35,0,0,0)
19-25 July	34	40	83	88	1.5	26.4	13(ML) 12(SL)	38(ML) 35(SL)	5.9	41.7	0.6	3.4	south/south east	~800w m^{-2}	-	19	(3,0,0,0)71(16)
															-	20	-
															-	21	(10,0,0,0)78(19)
															(7,0,0,0)86(16)	22	(5,3,0,0)99(14)
															(5,1,0,0)83(13)	23	-
															(3,0,0,0)69(20)	24	(11,7,0,0)87(18)
															(4,2,0,0)82(13)	25	(3,0,0,0)69(13)
															(19,3,0,0)		(32,1,0,0,0)

ML = Monitor Labs; SC = Scintrex; BU = Bush Estate; ESK = Eskdalemuir

FIGURE 12.

HOURLY AVERAGED O3, SO2, NO & NO2 VALUES FOR BUSH FROM 3-6 JULY 1989

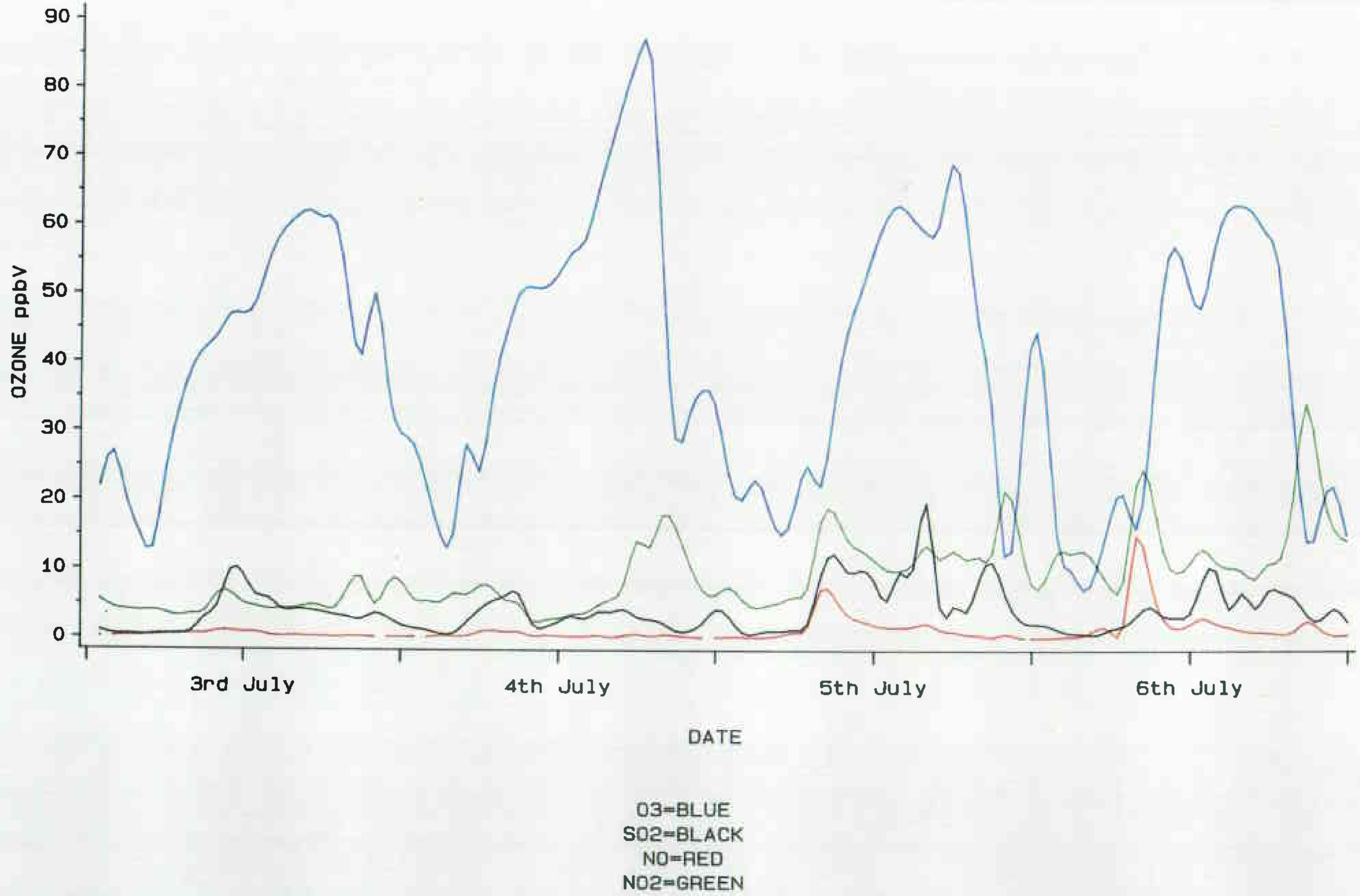


FIGURE 13.

HOURLY AVERAGED WINDSPEED VALUES FOR BUSH FROM 3–6 JULY 1989

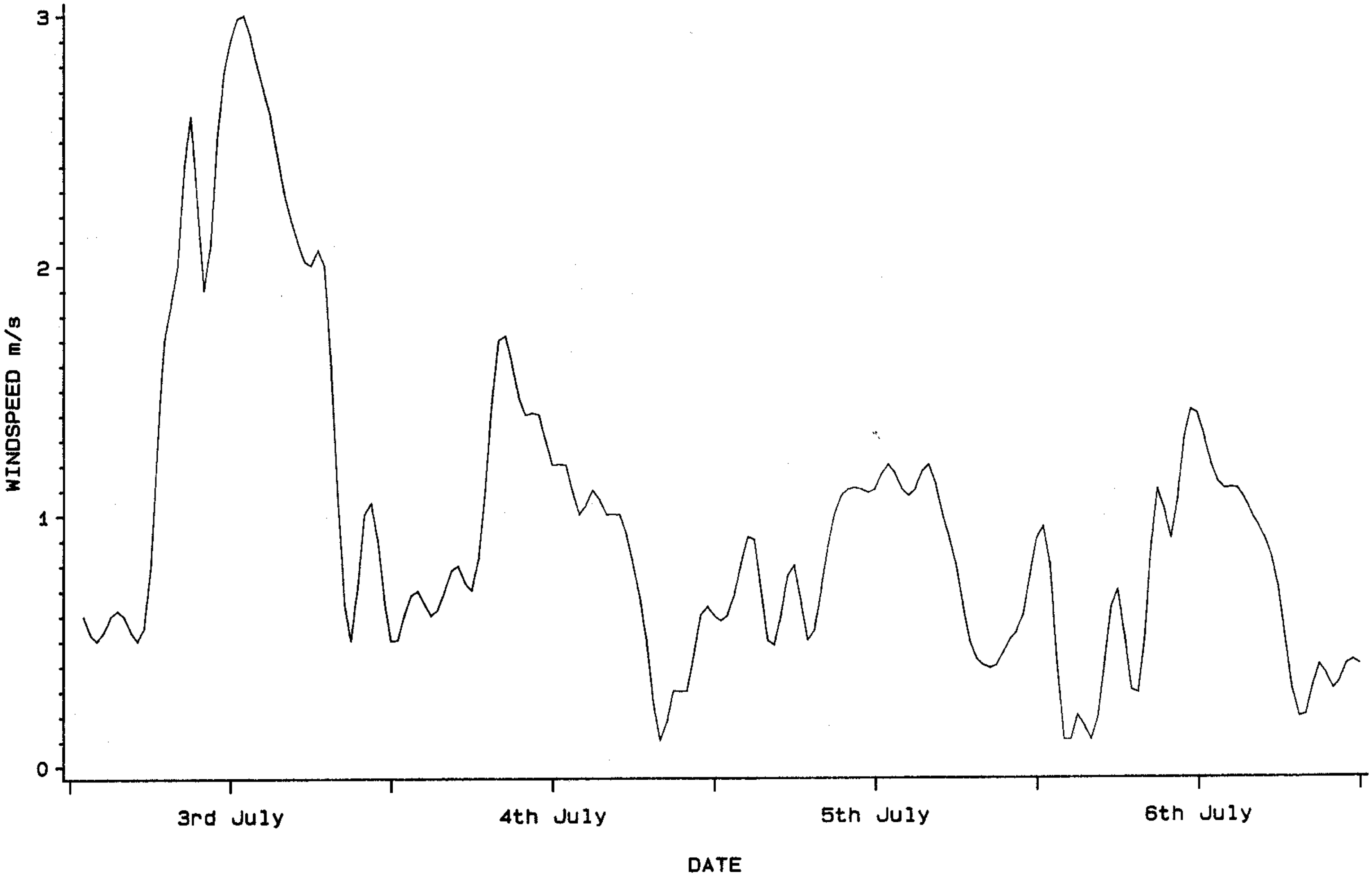


FIGURE 14.

HOURLY AVERAGED WIND DIRECTION VALUES FOR BUSH FROM 3-6 JULY 1989

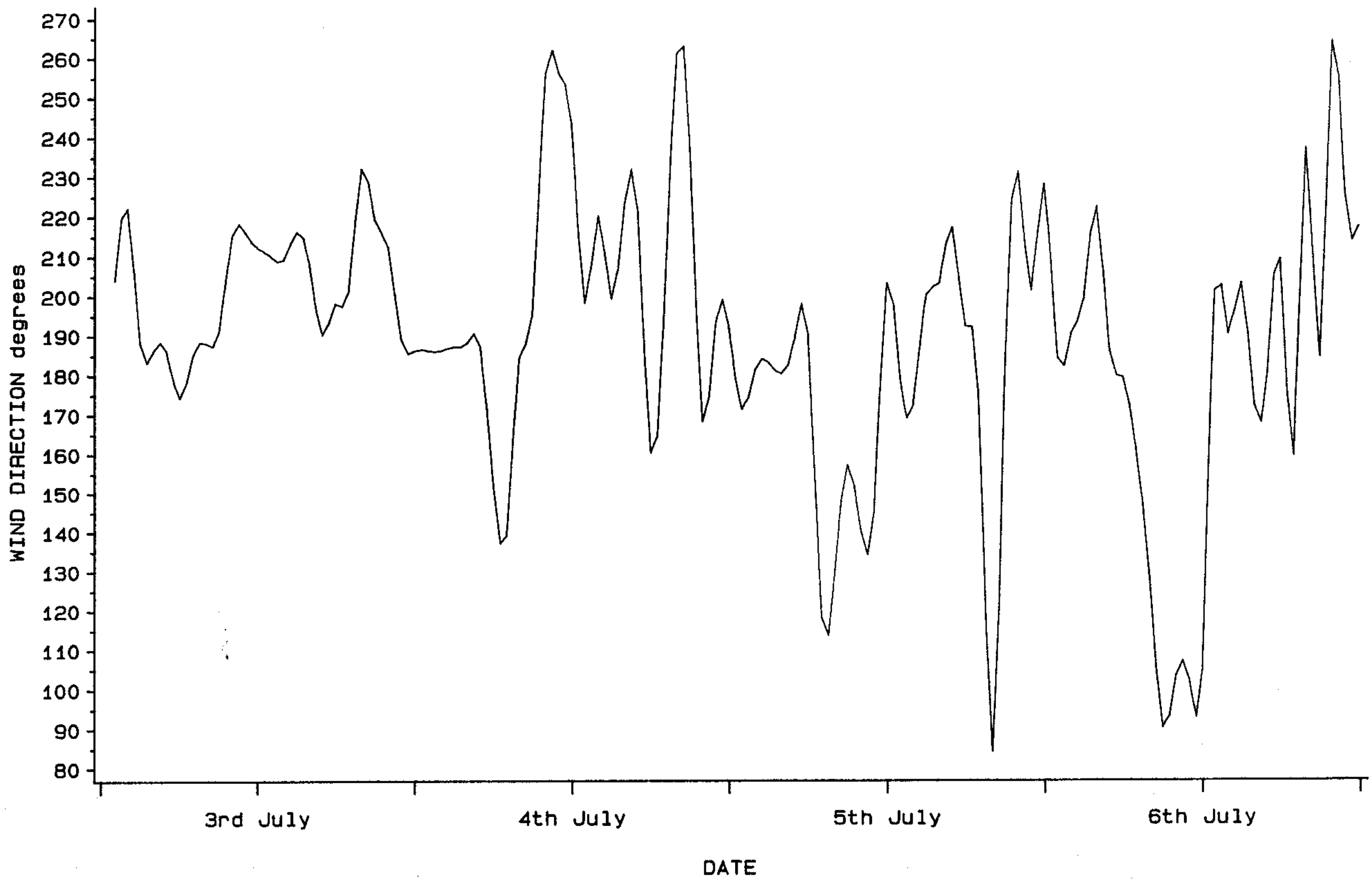


FIGURE 15.

HOURLY AVERAGED SOLAR RADIATION VALUES FOR BUSH FROM 3-6 JULY 1989

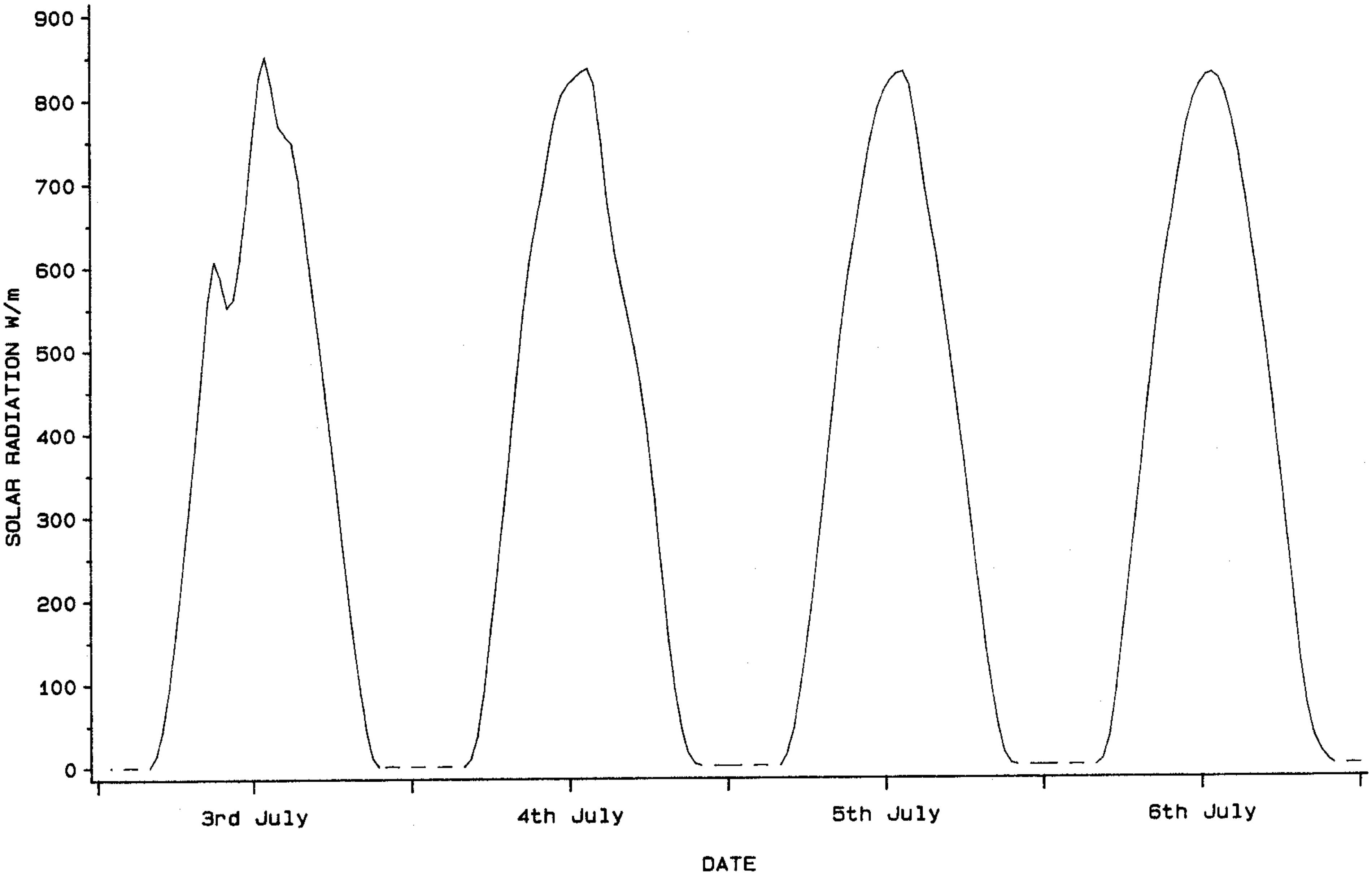


FIGURE 16.

DAILY MEAN WINDSPEED VALUES (m/s) FOR BUSH IN 1988 & 1989

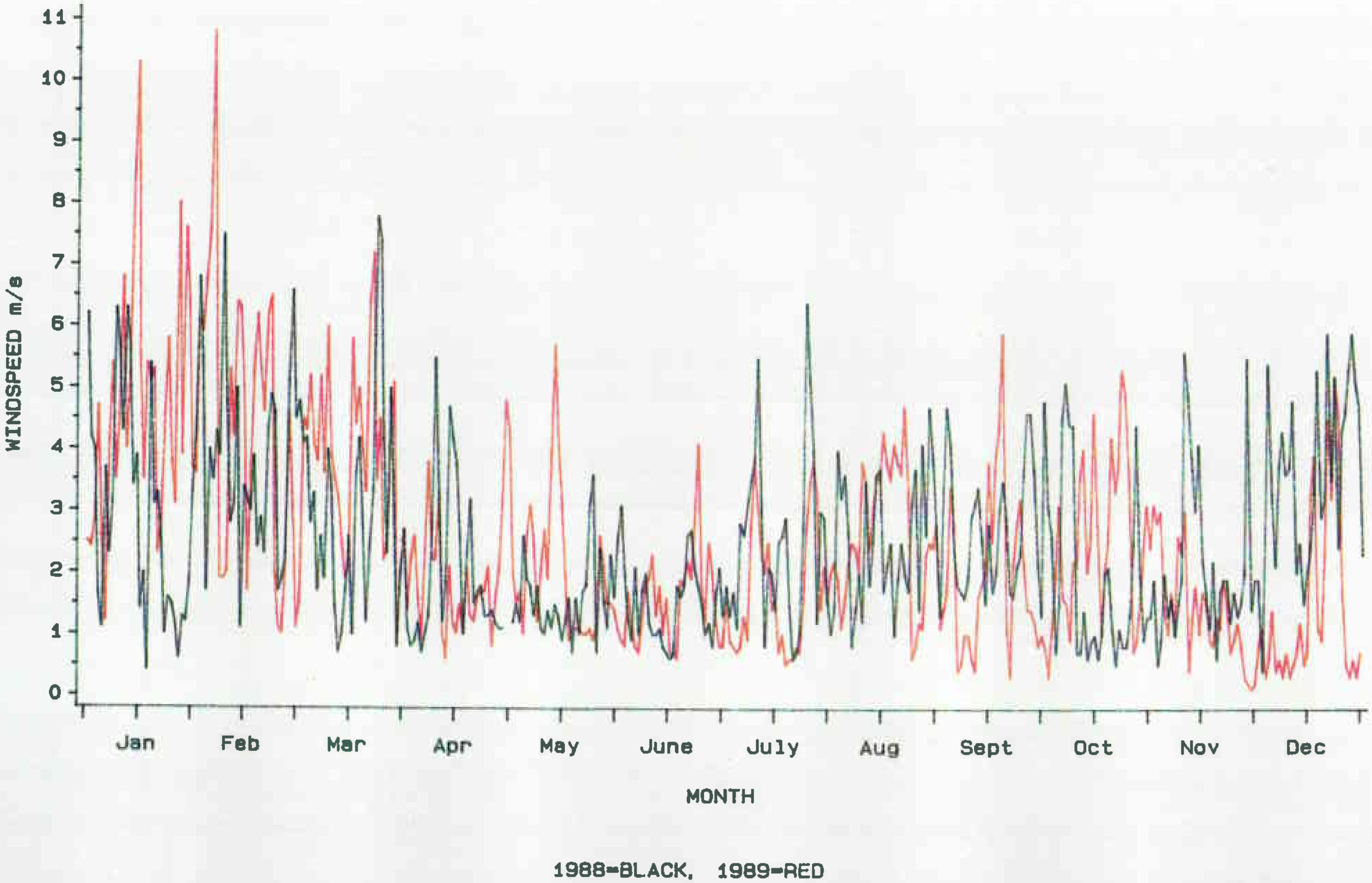


FIGURE 17.

DAILY MAXIMUM WINDSPEED VALUES FOR BUSH IN 1988 & 1989

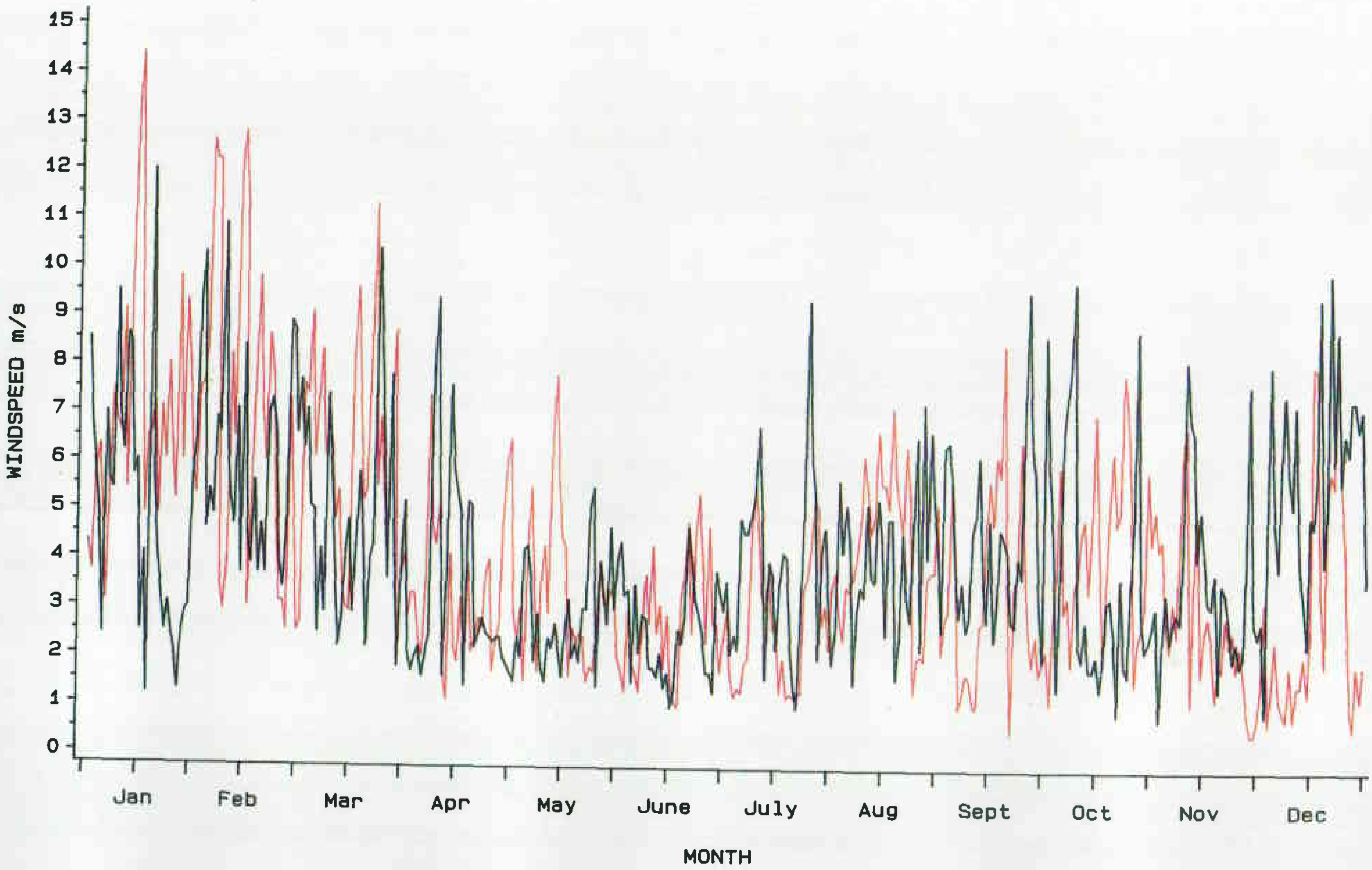
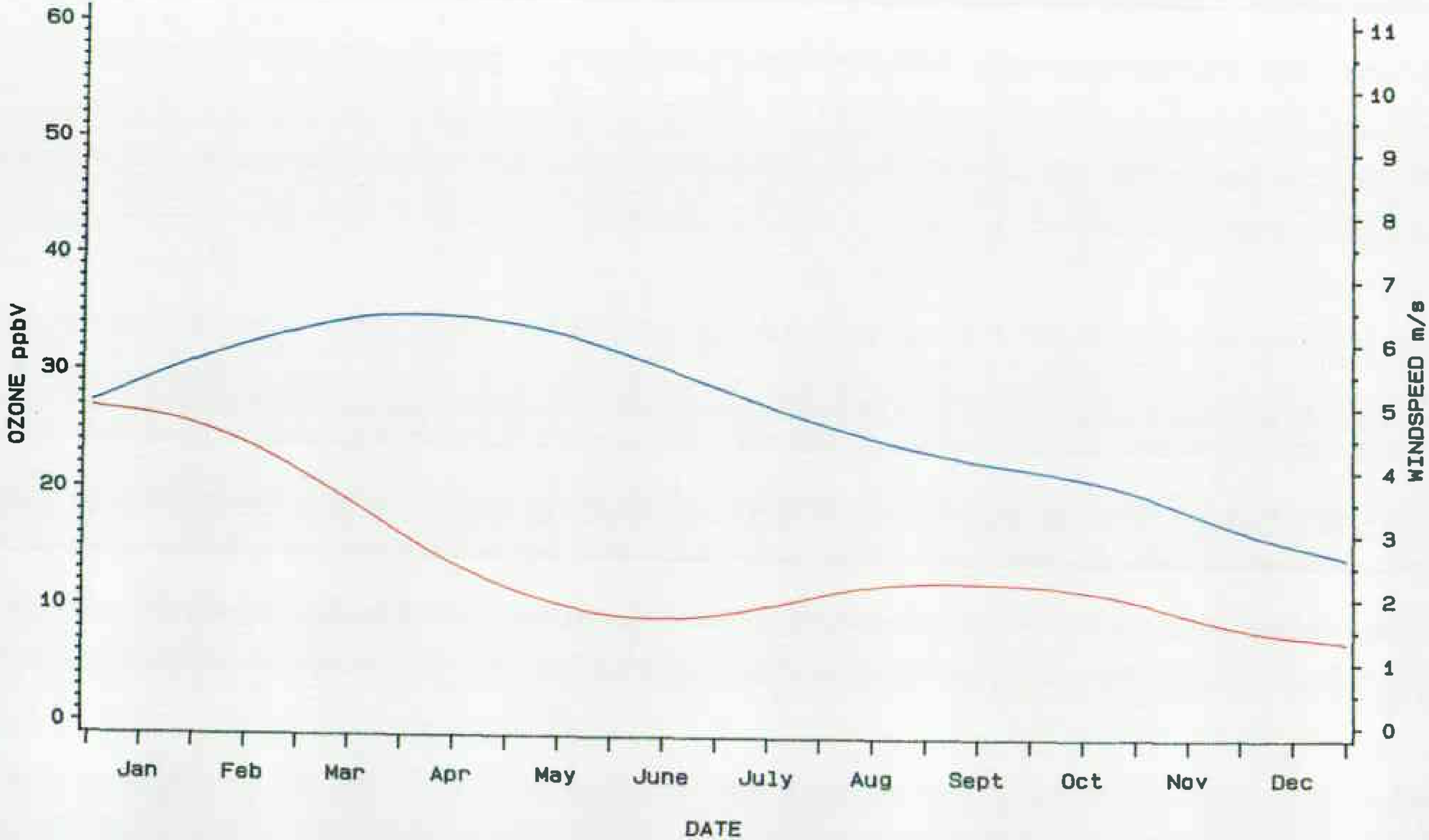


FIGURE 18.

SMOOTHED PLOT OF DAILY MEAN OZONE & WINDSPEED VALUES FOR BUSH IN 1989



BLUE=OZONE
RED=WINDSPEED

During the period January to March in particular, when windspeeds average 4 to 5 m/s at the Bush Estate site, the surface air is well coupled to the bulk of the mixing layer and ozone is continually transported downwards. Vertical mixing in these conditions hanmpers the destruction of ozone by the dry deposition process to such an extent that ozone concentrations can remain at the free tropospheric concentrations of 30-35 ppb for several days at a time. When windspeeds fall below 3 m/s during the winter months of the year, lack of photochemical activity results in the decrease of surface ozone concentrations to only a few ppbV. The above effects are clearly illustrated in Figure 19 which shows the variation in ozone concentrations with windspeed at the Bush Estate site, on an hourly basis, from 4-6 January 1989.

The factors described above linking ozone with windspeed during the winter months also explain the larger daily mean and maximum ozone concentrations observed from January to March 1989 than from January to March 1988. Monthly windspeed values from January to March 1989 were approximately 30% larger than those recorded from January to March 1988. The same factors also explain the lower ozone concentrations noted from August to December 1989 compared with those observed during the same period in 1988. Table 5 shows that monthly windspeeds over this period in 1988 were significantly higher than in 1989.

The prevalence of anticyclonic conditions in the summer months (from April to September) in any calendar year can result in considerable photochemical ozone formation at the Bush Estate site. A feature of these meteorological conditions is the large frequency of windspeed values in the range 1 to 3 m/s. These low windspeeds which can last for several days, allow well defined boundary layers to persist which in turn permit high concentrations of photochemical ozone and its precursors to develop. At night, radiative cooling of the ground leads to the formation of a shallow nocturnal inversion layer below which ozone is rapidly destroyed by dry deposition. In these conditions ozone:windspeed ratios, on an hourly basis, can range from 90:1 during the daytime to 5:1 in the evening. Figure 20 shows this situation for windspeed values and ozone concentrations over the episoidal period from the 3-6 July 1989.

The strong correlation between ozone and windspeed in the winter months at the Bush Estate site may be summed up by considering ozone frequency distributions at the site. It is known [4] that high altitude sites exhibit reasonably normal frequency distributions since they are generally unaffected by low level nighttime inversion layers. These layers, as discussed previously, result in the depletion of surface ozone to a few ppbV at the Bush Estate site by dry deposition. Indeed the effects of such depletion are observable in the large percentage of hourly ozone data at concentrations less than 15 ppb which are apparent in the frequency distribution for calendar year 1989 at the bush Estate site, see Figure 21.

When the Bush Estate ozone data are separated into summer (April to September) and winter (October to March) daytime (1000-1800) and nighttime (2200-0600) data sets, to exclude periods of impeded vertical mixing and hence loss of ozone by dry deposition, significantly different seasonal features emerge. Figures 22 and 23 show that the distribution for the summer daytime period is reasonably normal but that for the winter daytime period continues to exhibit a certain percentage of low ozone concentrations.

Windspeed, however, has a major effect on the shape of this winter daytime distribution. Exclusion of 8 hourly averaged ozone data (1000-1800) when the 8 hourly averaged windspeed is less than 2 m/s results in a normal frequency distribution which is typical of that for a site situated in free tropospheric air. This resulting distribution is shown in Figure 24.

NO_x MONITORING AT THE BUSH ESTATE SITE.

Detailed discussions and summaries of NO_x data from various UK sites and including the Bush Estate site have recently been compiled.[5]

NO and NO_2 concentrations at Bush Estate are generally unaffected by local, vehicular emissions of NO_x. The largest NO and NO_2 concentrations which have been recorded at the site are observed in the winter months of the year; usually between October and December. On many occasions these occur when windspeeds are very low (<0.1 m/s) and they are normally the result of the advection of N0 and NO_2 plumes from the city of Edinburgh and its environs. In other instances large NO and NO_2 concentrations are due to the advection of plumes from the industrial areas of England. Very occasionally, depending on meteorological conditions, they may be due to advection of plumes from the European continent.

FIGURE 19.

HOURLY AVERAGED OZONE & WINDSPEED VALUES FOR BUSH FROM 4–6 JANUARY 1989

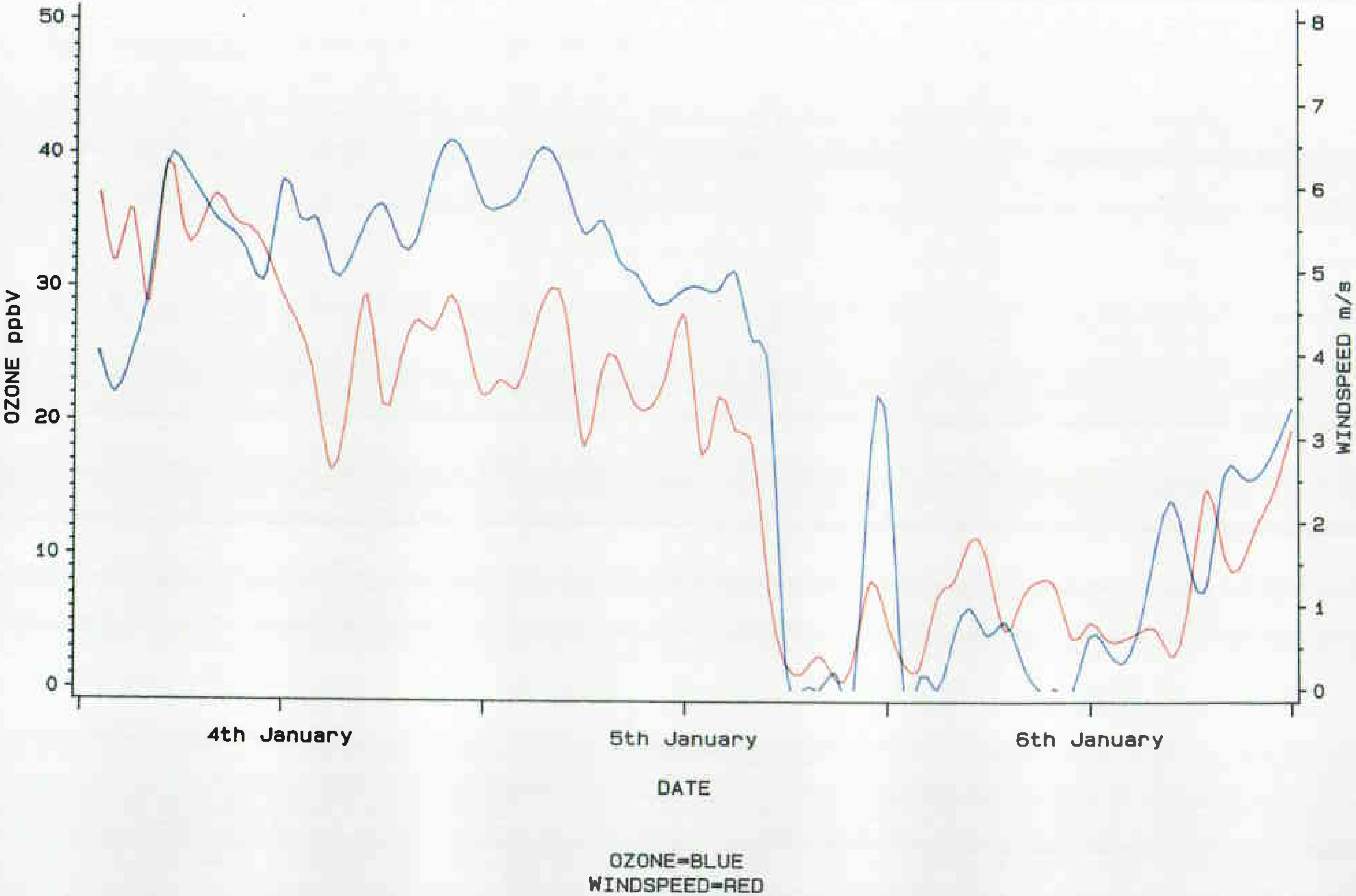
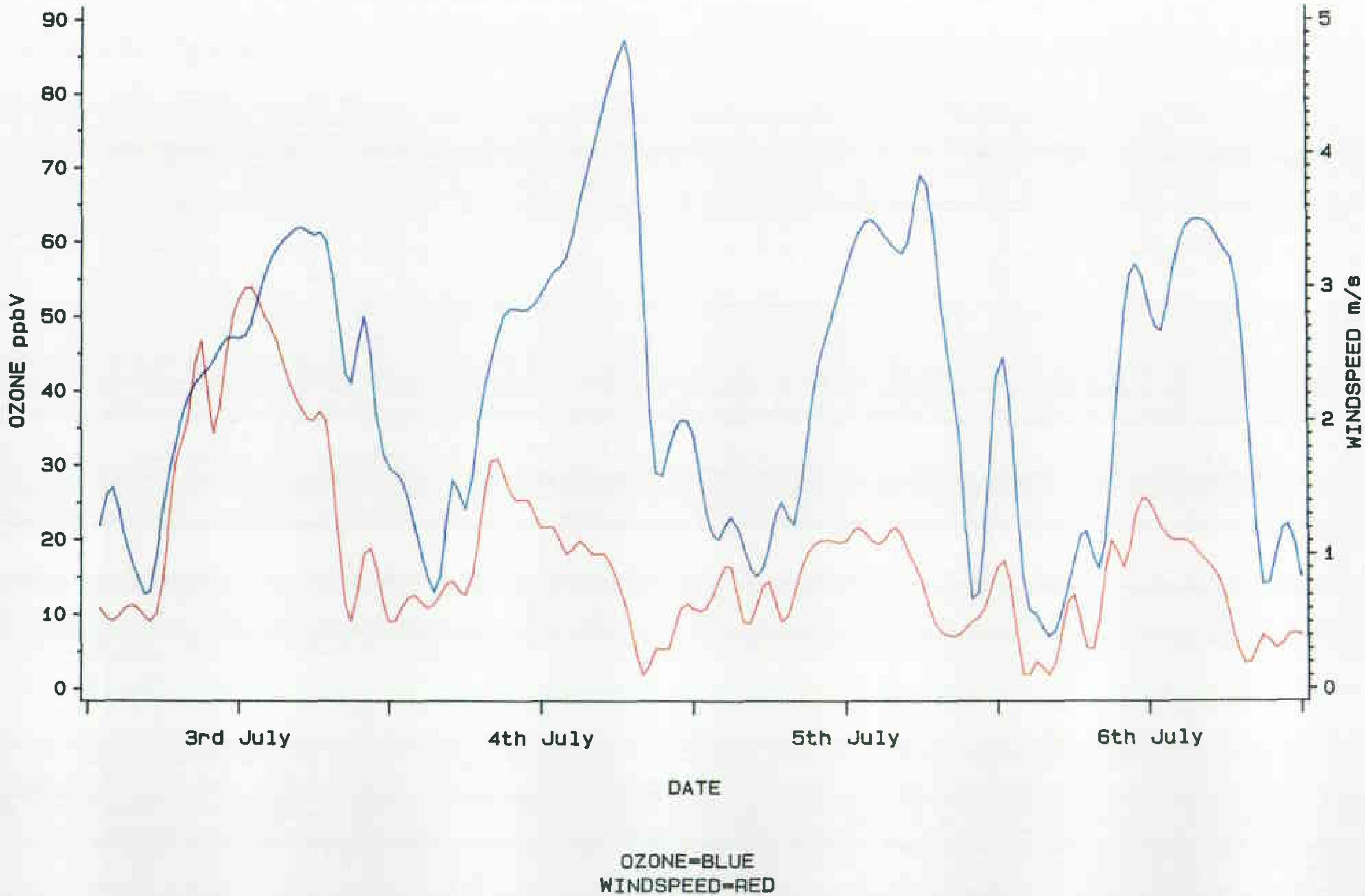
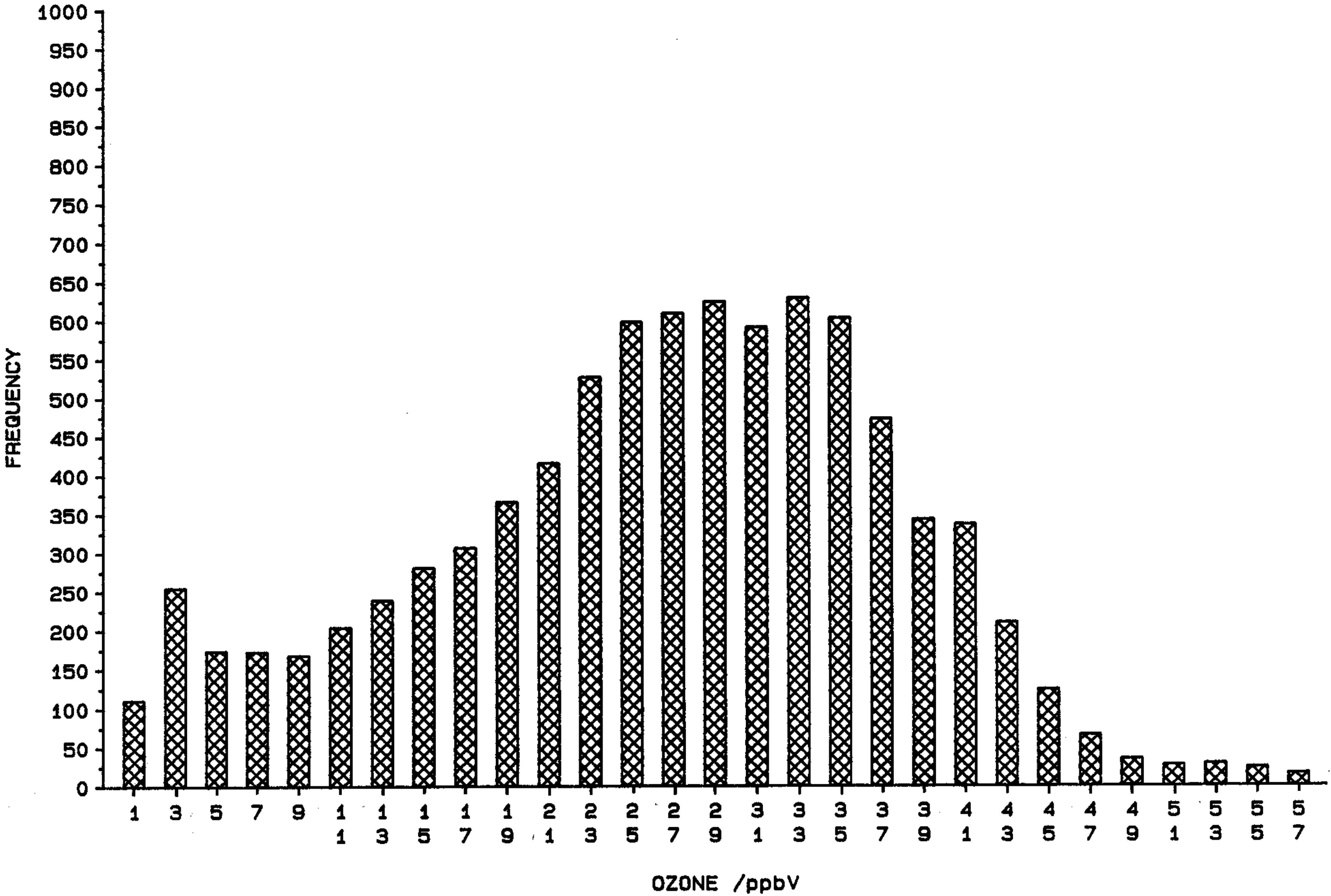


FIGURE 20.

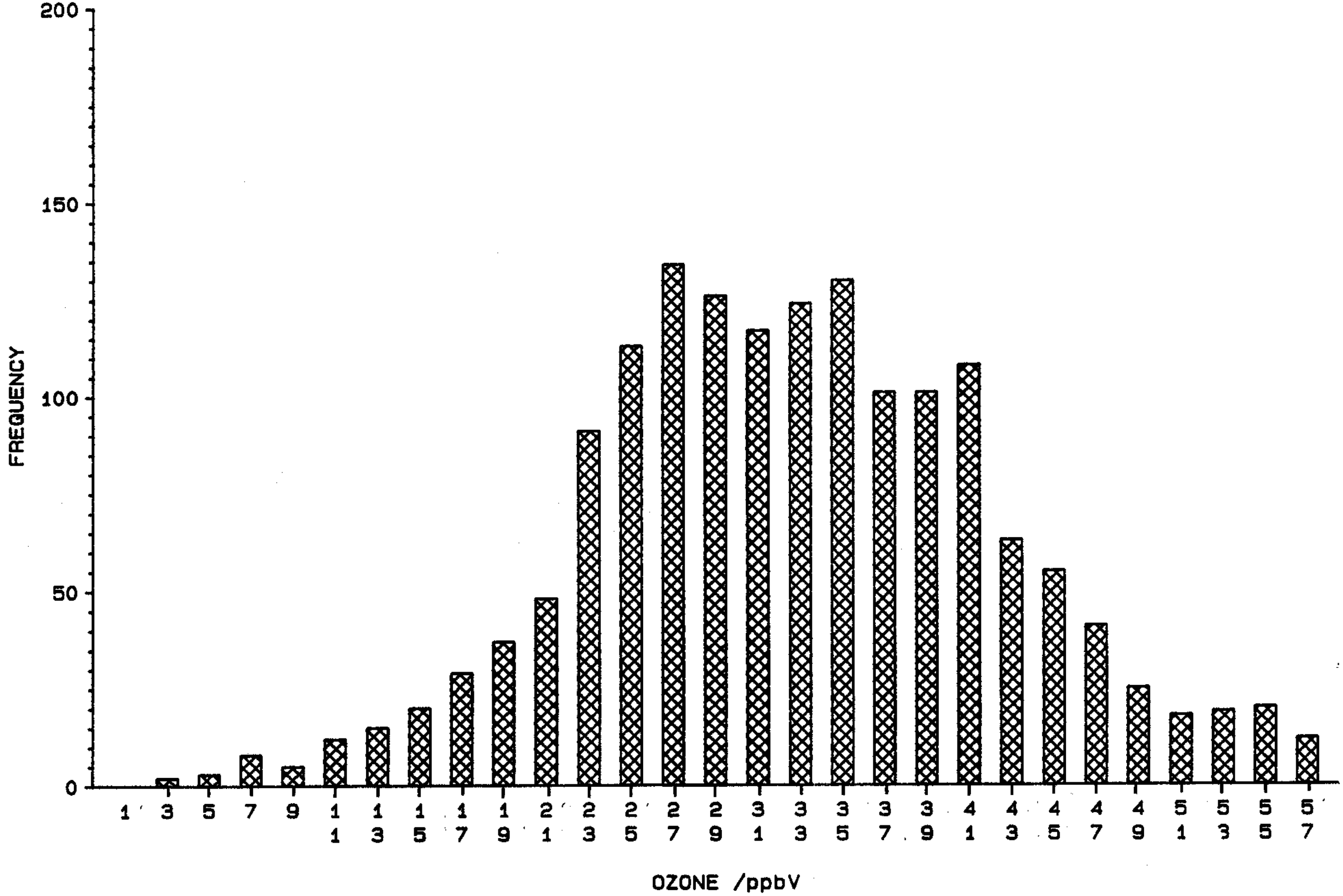
HOURLY AVERAGED OZONE & WINDSPEED VALUES FOR BUSH FROM 3-6 JULY 1989



OZONE FREQUENCY DISTRIBUTION FOR BUSH FOR CALENDAR YEAR 1989



OZONE FREQUENCY DISTRIBUTION FOR BUSH SUMMER DAY (1000–1800) 1989



OZONE FREQUENCY DISTRIBUTION FOR BUSH WINTER DAY (1000–1800) 1988–89

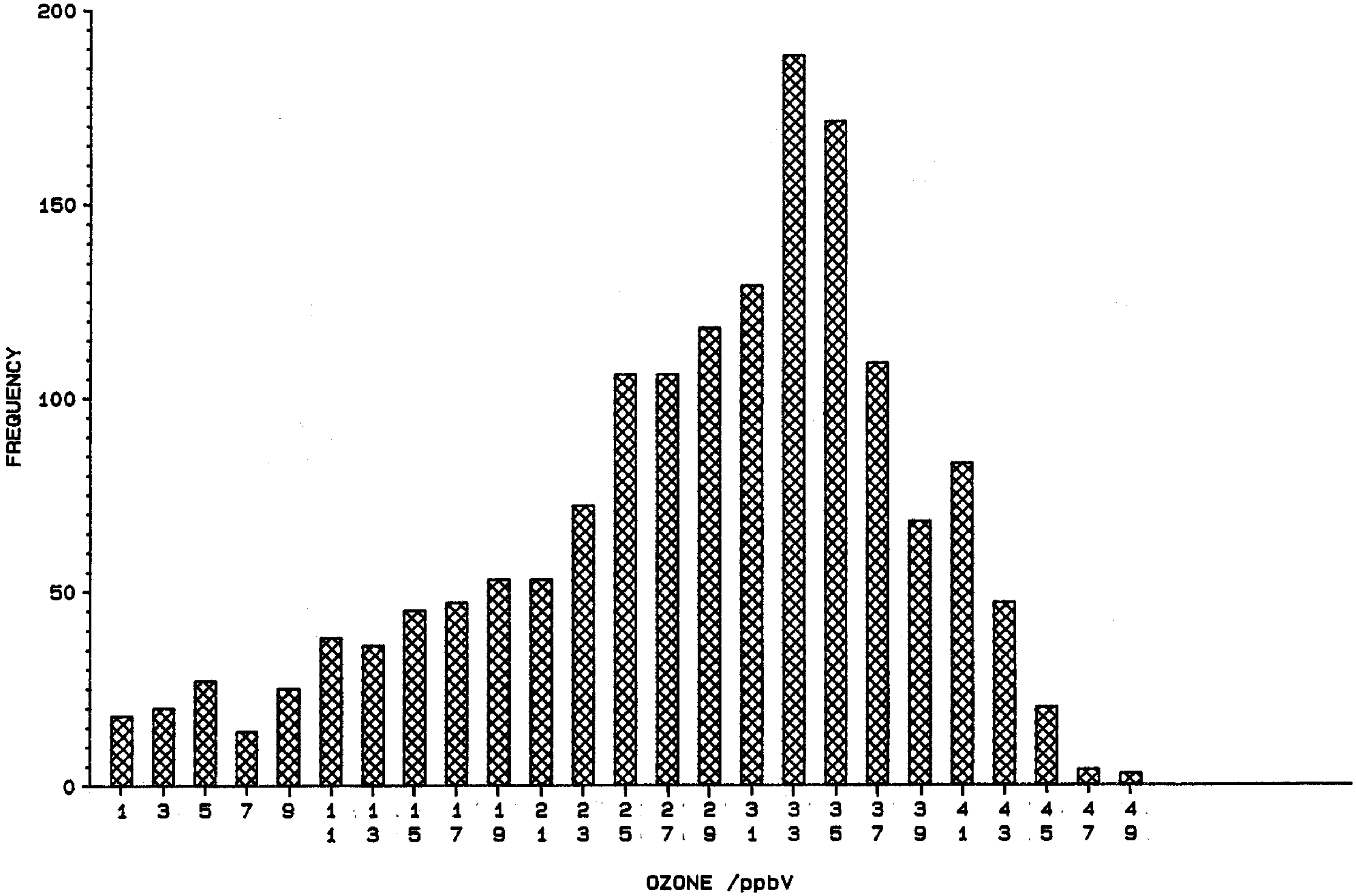
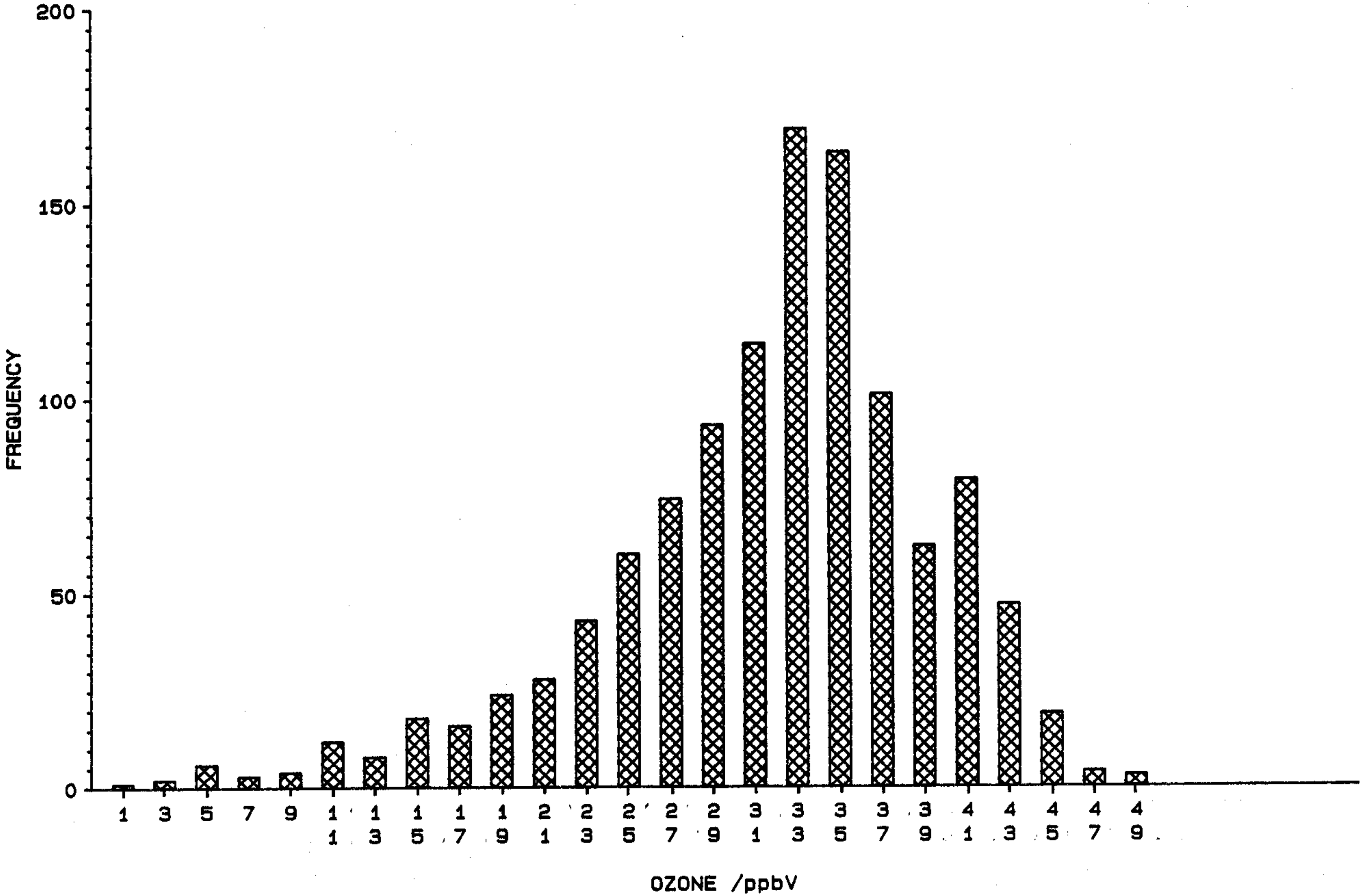


FIGURE 24.

WINTER DAY DISTRIBUTION EXCLUDING DAYS WITH WINDSPEED < 2m/s



Figures 25 to 28 show plots of daily mean and daily maximum NO, NO_2 and 0_3 concentrations for the year 1988 and 1989. The data illustrated in the plots were all recorded by Monitor Labs analysers. The calendar year mean value for N0 is 1 ppb in both years and is close to the detection limit of the NO_x analyser. The calendar year mean concentration for NO_2 in 1988 and 1989 is 6 ppb. The NO:NO_2 ratio for Bush Estate is approximately 1:6 which reflects the rural nature of the monitoring site and its remoteness from NO emissions. At roadside sites which record NO and NO_2 concentrations only metres from heavy traffic flow, the NO concentrations are extremely large compared with NO_2 concentrations. This is well illustrated in Table 6 which lists NO:NO_2 ratios for a range of site environments.

Table 6. <u>NO:NO_2 ratios for roadside, urban background, suburban and rural sites.</u>

Site	Description	Annual Means NO	Annual Means NO_2	Ratio	Year
Bush Estate	rural	1	6	1:6	1988
Bottesford	rural	12	24	1:2	1987
Harwell	rural	4	11	1:2.8	1986
Stevenage	suburban	39	23	1:0.6	1984
Central London	urban background	34	43	1:1.3	1984
Cromwell Road	urban kerbside	188	46	1:0.23	1982

In 1988, the calendar year maximum for NO at Bush Estate was 62 ppb. In 1989 the maximum value was 142 ppb. The values observed for NO_2 in 1988 and 1989 were 43 ppb and 45 ppb. From October to December 1989, the frequency with which NO concentrations greater than 60 ppb occurred was significantly greater than in 1988. NO_2 concentrations were reasonably similar in both years.

It is apparent from Figures 25 to 28 that, on a few occasions, very low 0_3 concentrations are co-incident with large NO concentrations. These are a likely result of the chemical depletion of 0_3 by NO via the reaction $NO + 0_3 \rightarrow NO_2 + 0_2$. As an earlier study showed however,[6] dry deposition accounts for much of the 0_3 depletion at the Bush site throughout most of the year.

The similarity in daily NO and NO_2 concentrations from January to September in 1988 and 1989 is also apparent in Figures 25 to 28. This suggests that the comparatively larger 0_3 concentrations recorded from January-March 1989 than in the same period during 1988 are unlikely to be directly due to the effects of NO_x.

<u>COMPARISON OF OUTPUT FROM DIFFERENT NOx ANALYSERS</u>

Table 1 lists the 3 different (continuous) instruments which have been in operation over the past 2 years at the Bush Estate site. Highest data capture has been obtained using the Monitor Labs chemiluminescent analyser which determines NO_2 concentrations from the (NO_x-NO) calculation. Reasonably high data capture has also been obtained using the Scintrex chemiluminescent analyser which monitors NO_2 directly. A comparison of their NO_2 data is discussed in the following paragraphs.

Figures 29 and 30 show the daily mean and maximum NO_2 concentrations in 1988 and 1989 which were recorded by the Scintrex analyser. Data capture is lower in 1989, but the data in both years exhibit a similar range of values throughout the various months of each year. The fact that the largest NO_2 concentrations occur during the winter months of the year are distinctly obvious in these two figures.

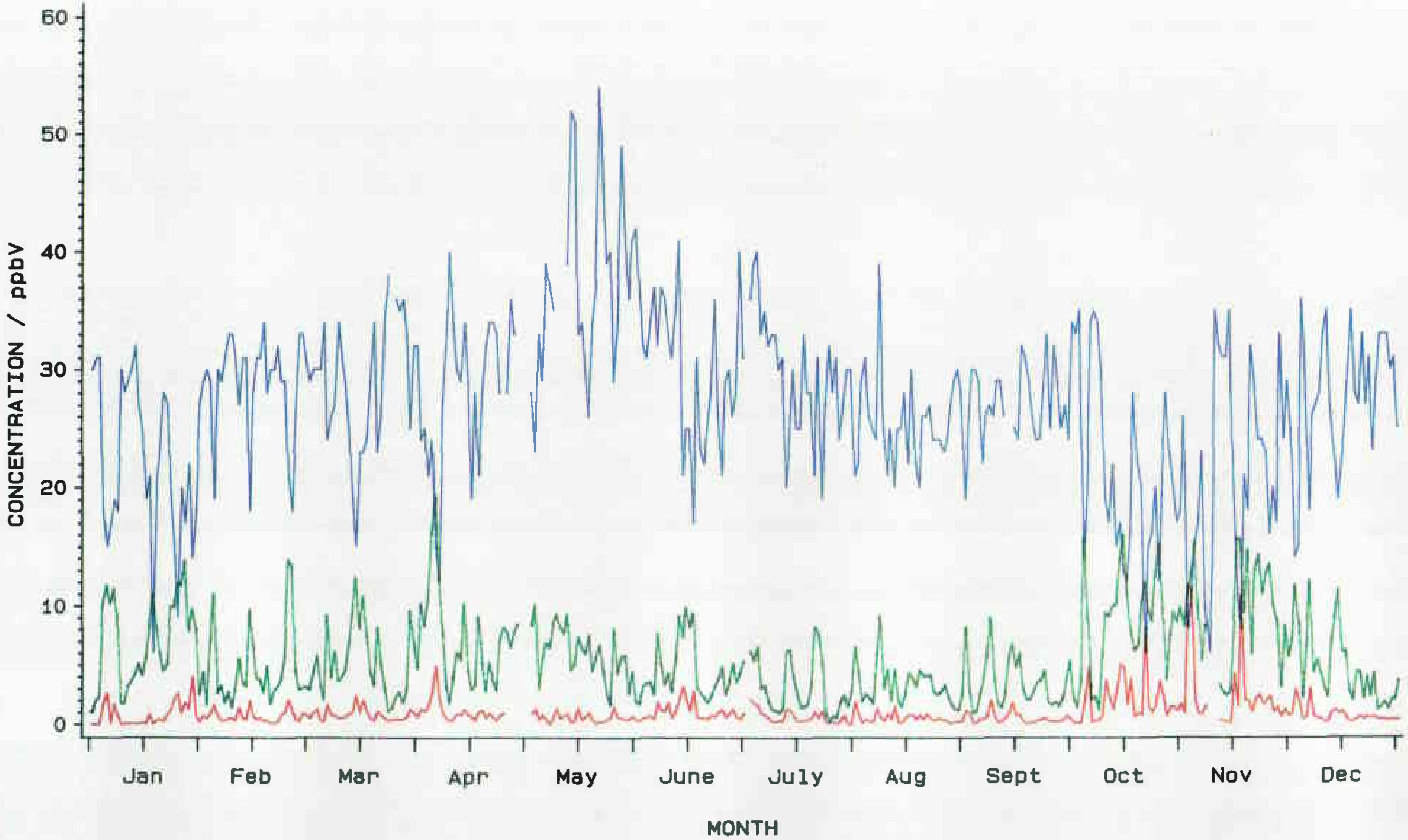
A comparison of the daily mean and daily maximum NO_2 data obtained at the Bush Estate site for calendar year 1988 using a Scintrex and Monitor Labs instrument are shown in Figures 31 and 32. The correlation in the daily data over the period is very good but the Figures fail to emphasize the difference in sensitivity limits of the two instruments. This is better illustrated in Figure 33 which shows the cumulative frequency plots of the hourly mean data for the two instruments in 1989. The Monitor Labs instrument which measures NO_2 from (NO_x-NO) is sensitive down to 1 ppbV. The Scintrex analyser gives a linear response to NO_2 down to several pptV.

<u>CUMULATIVE FREQUENCY DISTRIBUTIONS FOR NO2</u>

The log-normal distribution of pollutant concentrations is related to the dispersion of pollutants from sources. The primary pollutants (SO_2, NO and primary NO_2) fit a log normal distribution reasonably well, especially at sites close to sources. Secondary

FIGURE 25.

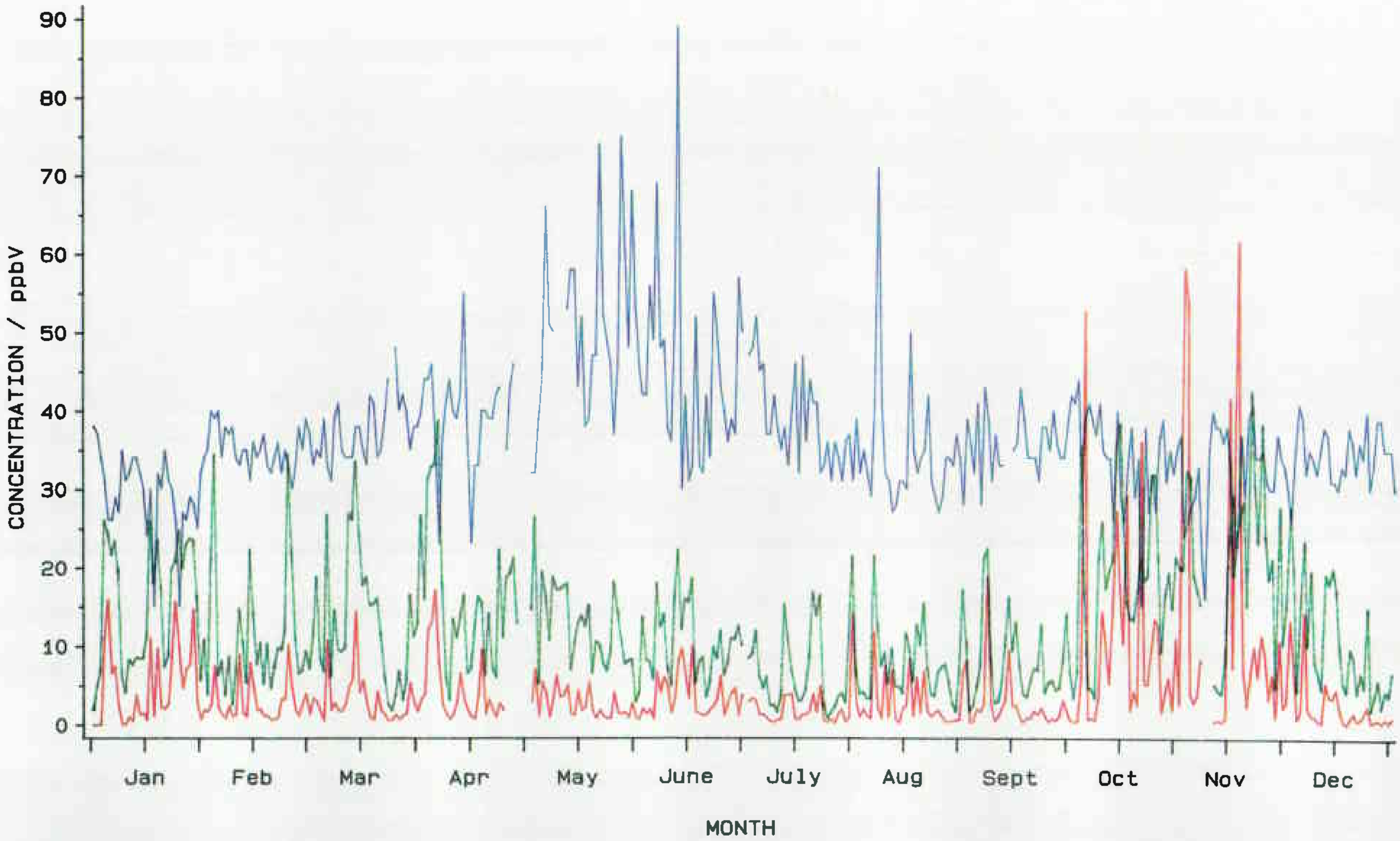
DAILY MEAN NO,NO2 & O3 VALUES FOR BUSH IN 1988



NO= RED, NO2= GREEN, O3=BLUE

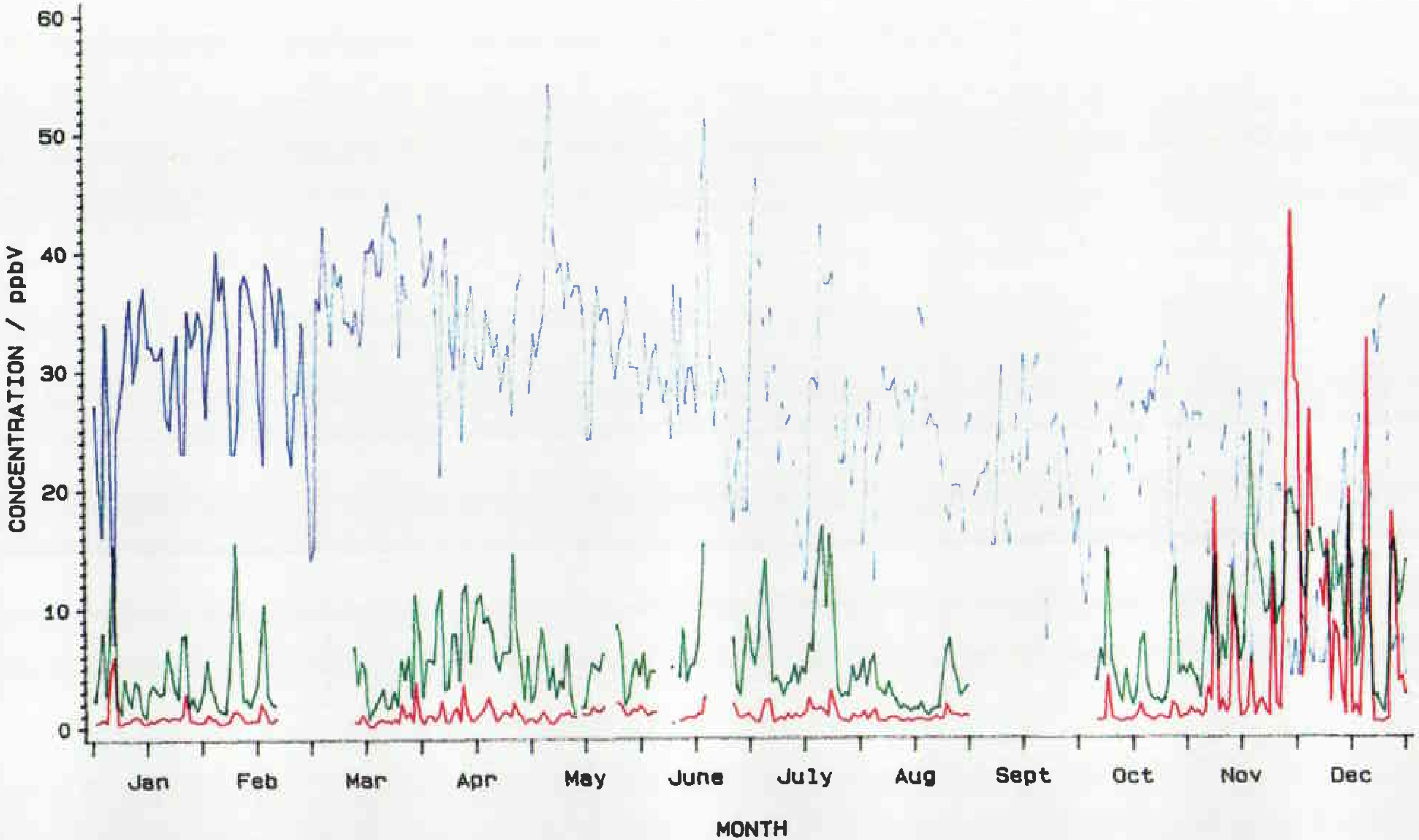
FIGURE 26.

DAILY MAXIMUM NO,NO2 & O3 VALUES FOR BUSH IN 1988



NO= RED, NO2= GREEN, O3=BLUE

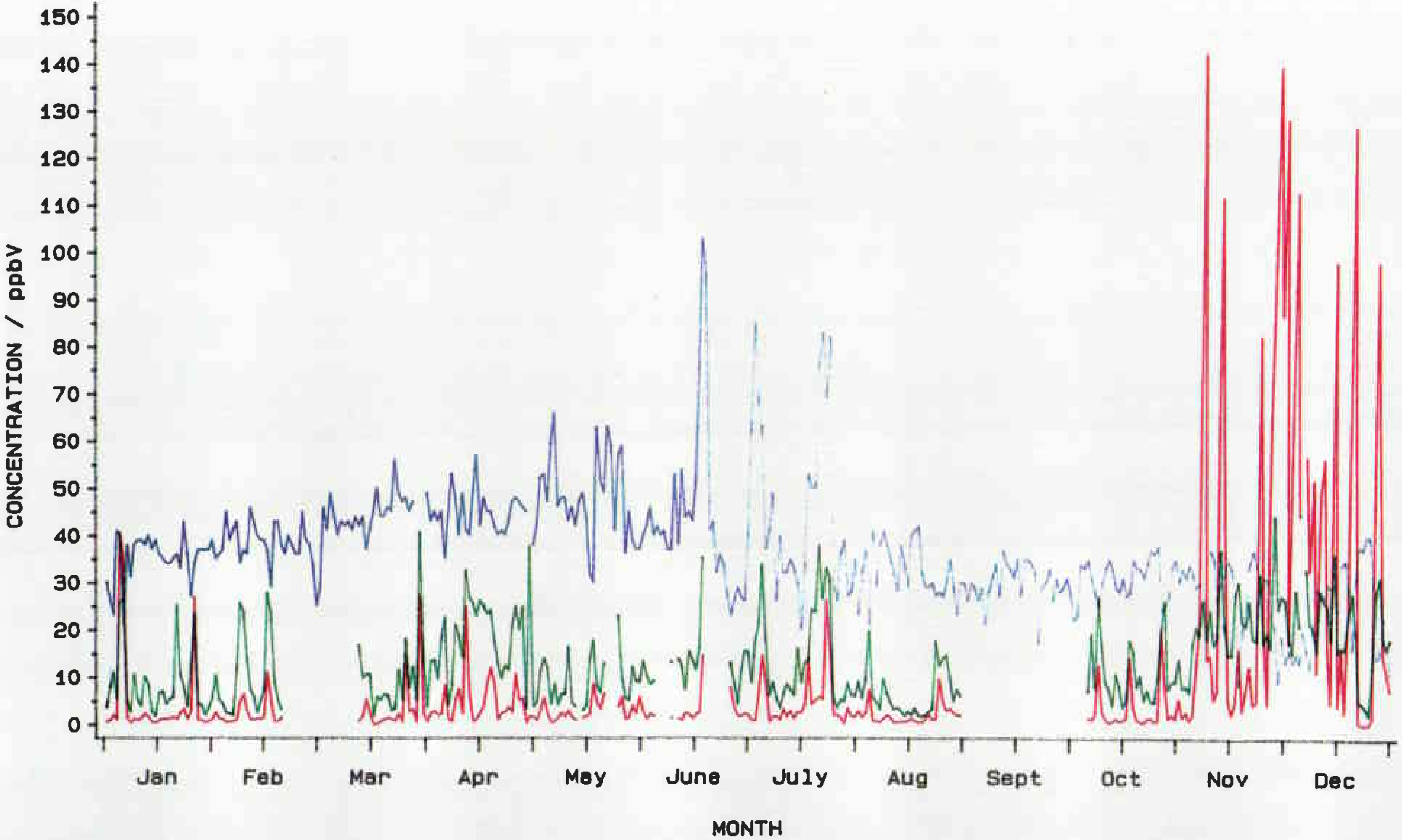
DAILY MEAN NO,NO2 & O3 VALUES FOR BUSH IN 1989



NO= RED, NO2 = GREEN, O3=BLUE

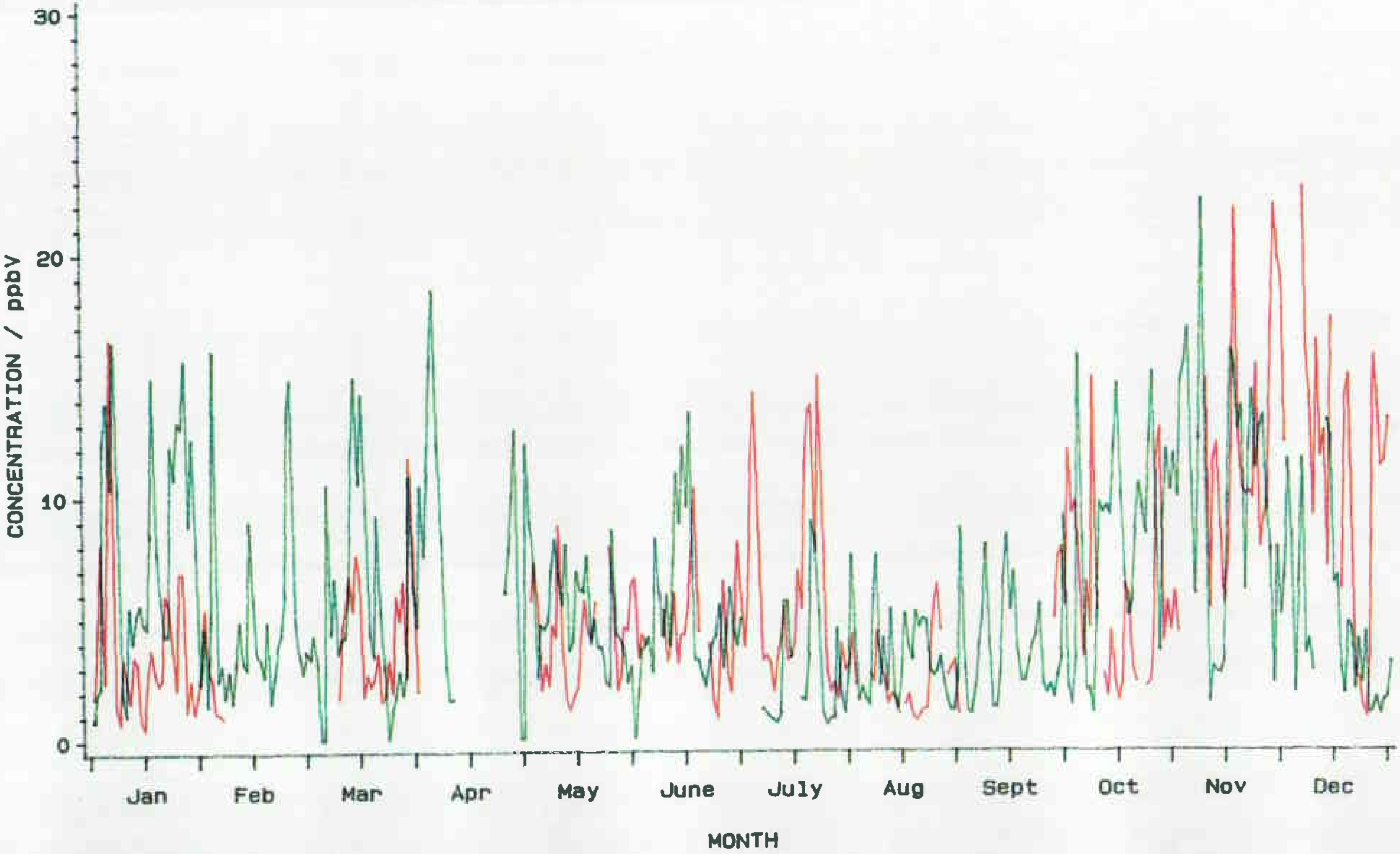
FIGURE 28.

DAILY MAXIMUM NO,NO2 & O3 VALUES FOR BUSH IN 1989



NO= RED, NO2 = GREEN, O3=BLUE

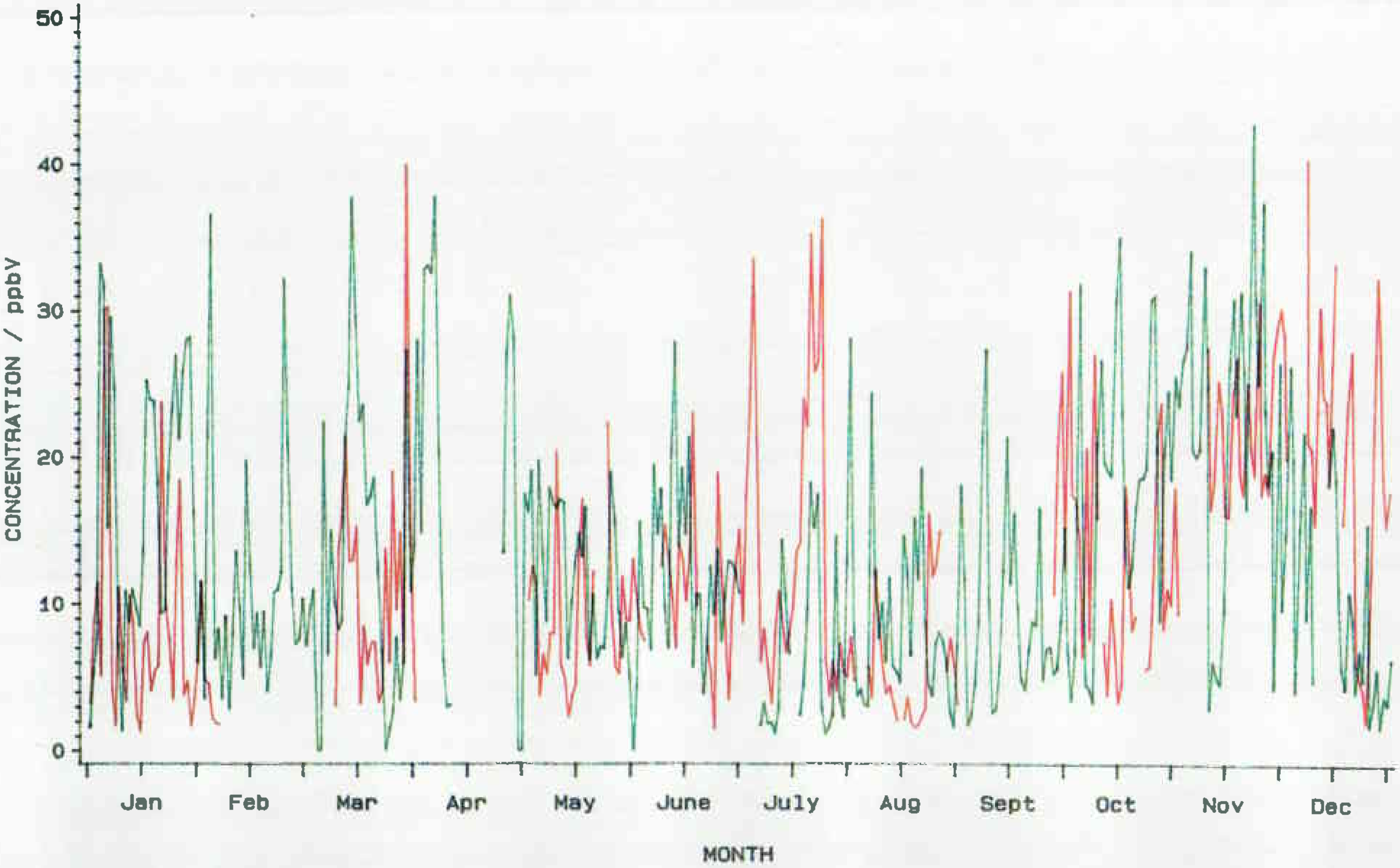
DAILY MEAN NO2 VALUES FOR 1988 & 1989 USING A SCINTREX ANALYSER



1989- RED. 1988 - GREEN

FIGURE 30.

DAILY MAXIMUM NO2 VALUES FOR 1988 & 1989 USING A SCINTREX ANALYSER



1989= RED. 1988 = GREEN

DAILY MEAN NO2 VALUES (ppbV) FOR BUSH IN 1988

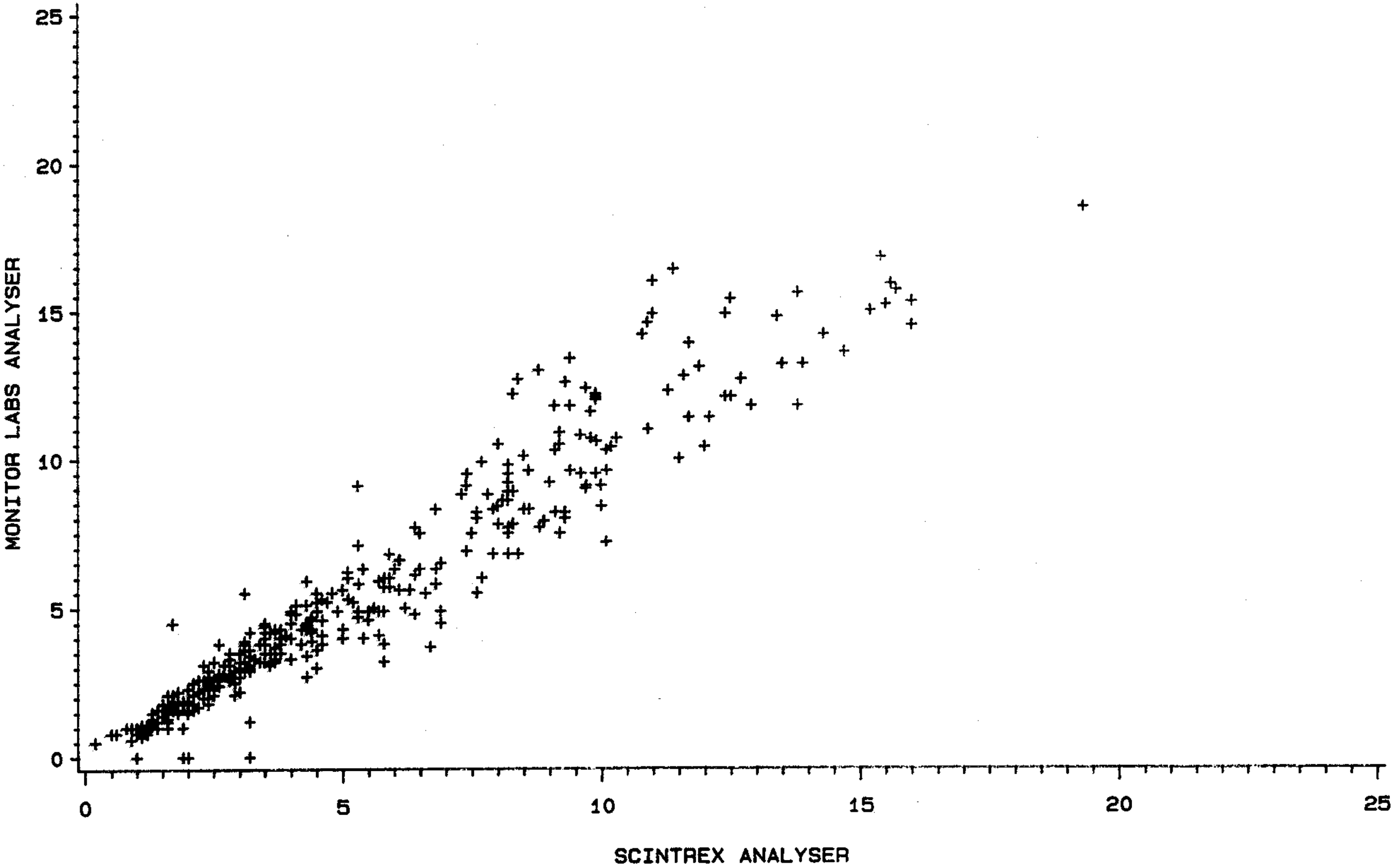
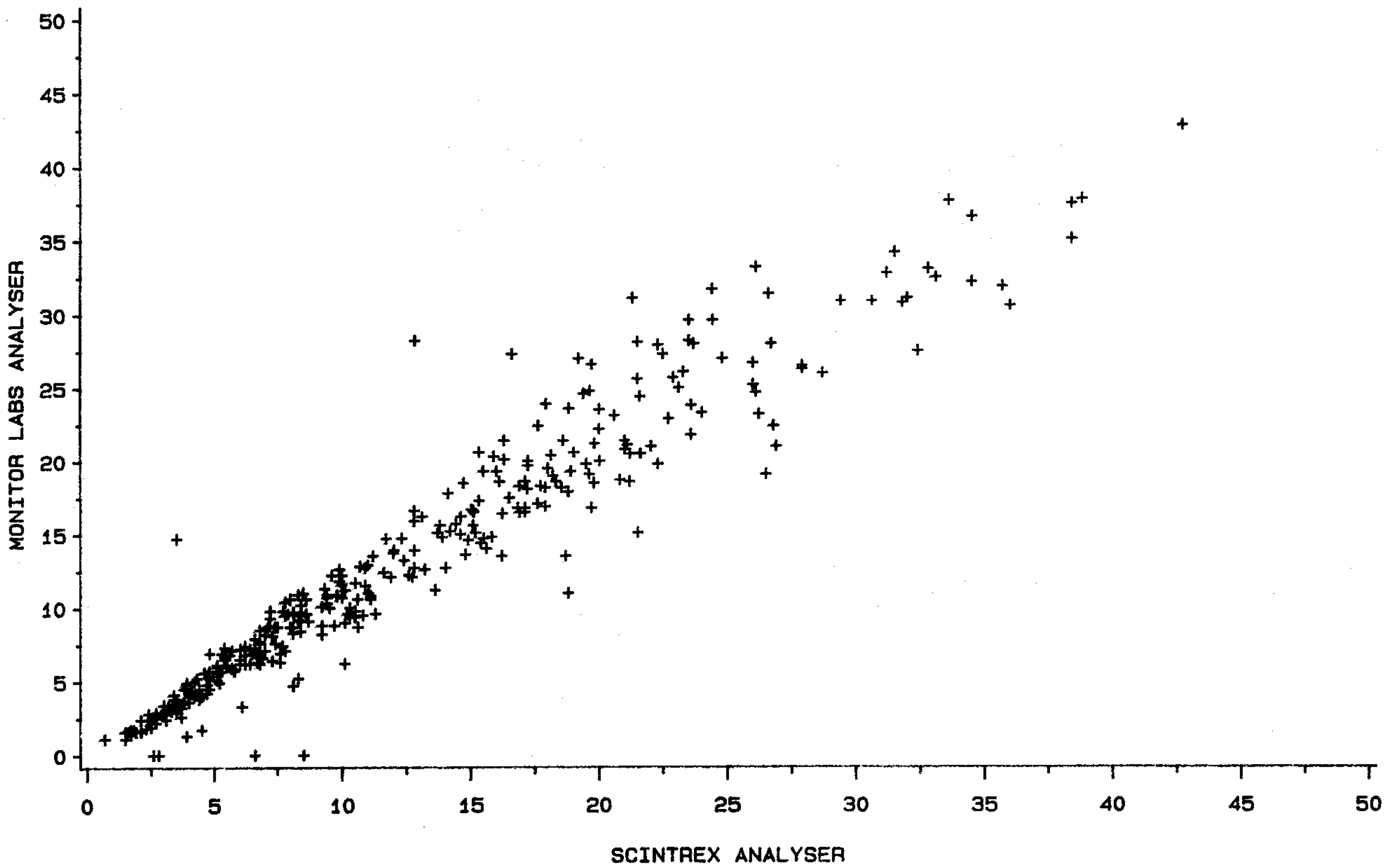


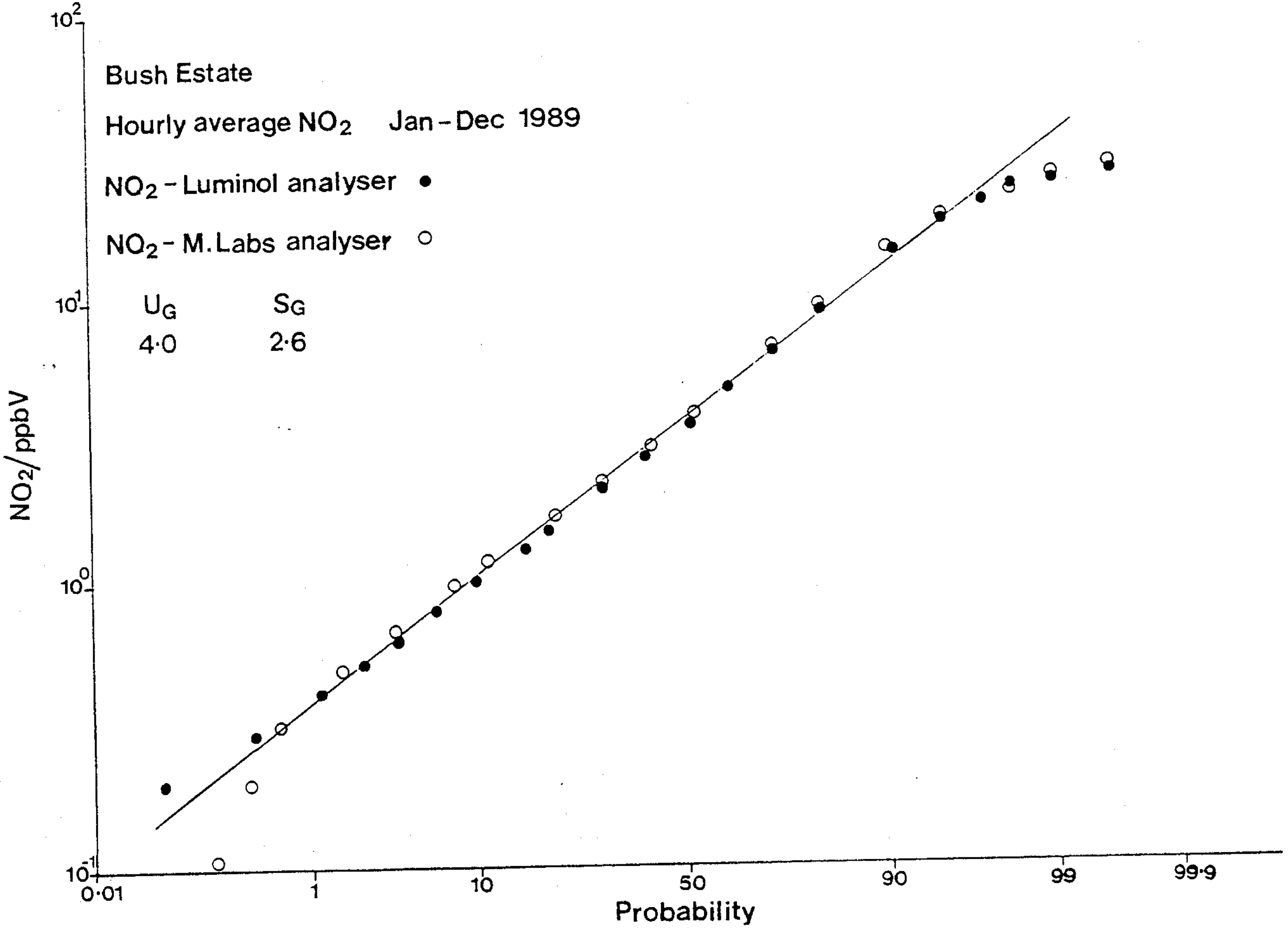
FIGURE 32.

DAILY MAXIMUM NO2 VALUES (ppbV) FOR BUSH IN 1988



Cumulative frequency distribution for NO2 at the Bush Estate site.

FIGURE 33.



pollutant concentrations are less well described by the log-normal distribution, because their concentrations may depend on chemical processes rather than atmospheric dispersion. For rural sites and remote sites, the distributions for NO_2 data may deviate from log normality at high percentiles, reflecting the influence of secondary processes.

This influence is observable in Figure 34 which shows a comparison of the distributions for NO_2 data which were recorded at Bush Estate and at Bottesford. The latter site is located in the East Midlands of England and is situated considerably closer to larger NO_x emissions than those observed at the Bush Estate site. The Bottesford data deviates from log normality at about the 70th percentile, whereas the Bush Estate data deviates at about the 90th percentile. The medians and standard geometric deviations calculated from the frequency distributions (over the 20th to the 70th percentile range) for the two sites are listed below in Table 7 along with those for other UK sites.

Table 7. Medians and Standard Geometric Deviations for a range of site environments.

Site	Description	Year	Median	SgD
Bush Estate	rural	1988	4	2.6
Bottesford	rural	1987	17	2.2
Wray	rural	1985	3.7	2.5
Devilla	rural	1979	12	1.9
Stevenage	suburban	1984	21	2.1
Cromwell Road	urban, road side	1984	46	1.6
Central London	urban, back ground	1984	42	1.4

The geometric standard deviations for Bush Estate and Wray are large and are a reflection of substantial periods when NO_2 concentrations are very low (~ 2 to 3 ppb) at the sites. At the Devilla and Bottesford sites, the geometric standard deviations are smaller. These results indicate the presence of higher background NO_2 concentrations. The standard geometric deviations observed at urban sites are significantly lower than those for rural sites.

The range of values displayed by the standard geometric deviations calculated over the log linear area of the distributions for rural, suburban and urban sites indicate that differentiation of site environment may be feasible using statistics of this type.

At the percentile values where deviations from log-normality occur, the parameters of the log-normal distribution fitted to the whole data set results in overestimates of the peak concentrations. The overestimation of peak values from the mean properties of the whole data set have been examined[7] and it has been shown that the application of extreme value statistics provides much better estimation of peak values.

EVIDENCE OF PAN AT THE BUSH ESTATE SITE

PAN and 0_3 are closely related components of photochemical air pollution. Measurements at ground level show that PAN and 0_3 follow very similar diurnal variations. This fact is well illustrated in Figure 35.

In the UK, the most extensive PAN measurements have been made at Harwell, Oxfordshire where data were collected on a semi-continuous basis between 1974 and 1981. At such a rural location, concentrations of PAN are known to rise to greater than 1 ppb in the summer months and to fall to lower than 0.1 ppb in the early months of winter. The concentration ratio for ozone:PAN lies between 50:1 and 30:1.

PAN is normally measured by gas chromatography in conjunction with electron capture detection. PAN can also be measured using the luminol detector system devised for NO_2. In this technique, luminol replaces the electron capture detector and PAN is separted from NO_2 on the chromatographic column.

No specific monitoring of PAN is presently carried out at the Bush Estate site. During ozone episodes however, close comparison of 15 minute averaged data recorded by the Monitor Labs instrument (NO_x + NO_y) and the Scintrex (NO_2) analyser reveal the presence of a pollutant which exhibits the concentration patterns of PAN. Figures 36 and 37 show plots of 15 minute averaged 0_3 data and (Monitor Labs-Scintrex) 'NO_2' data for the 18 to 21 June 1989 and for the 3 to 6 July 1989. The 'NO_2' concentration difference is zero when 0_3 concentrations are less than 50 ppb. When the 0_3 concentration lies in the range 60 to >80 ppb the 'NO_2' concentration difference rises to between 2 ppb and 3 ppb.

FIGURE 34. Cumulative frequency ditributions for NO2 at the Bush Estate and Bottesford sites.

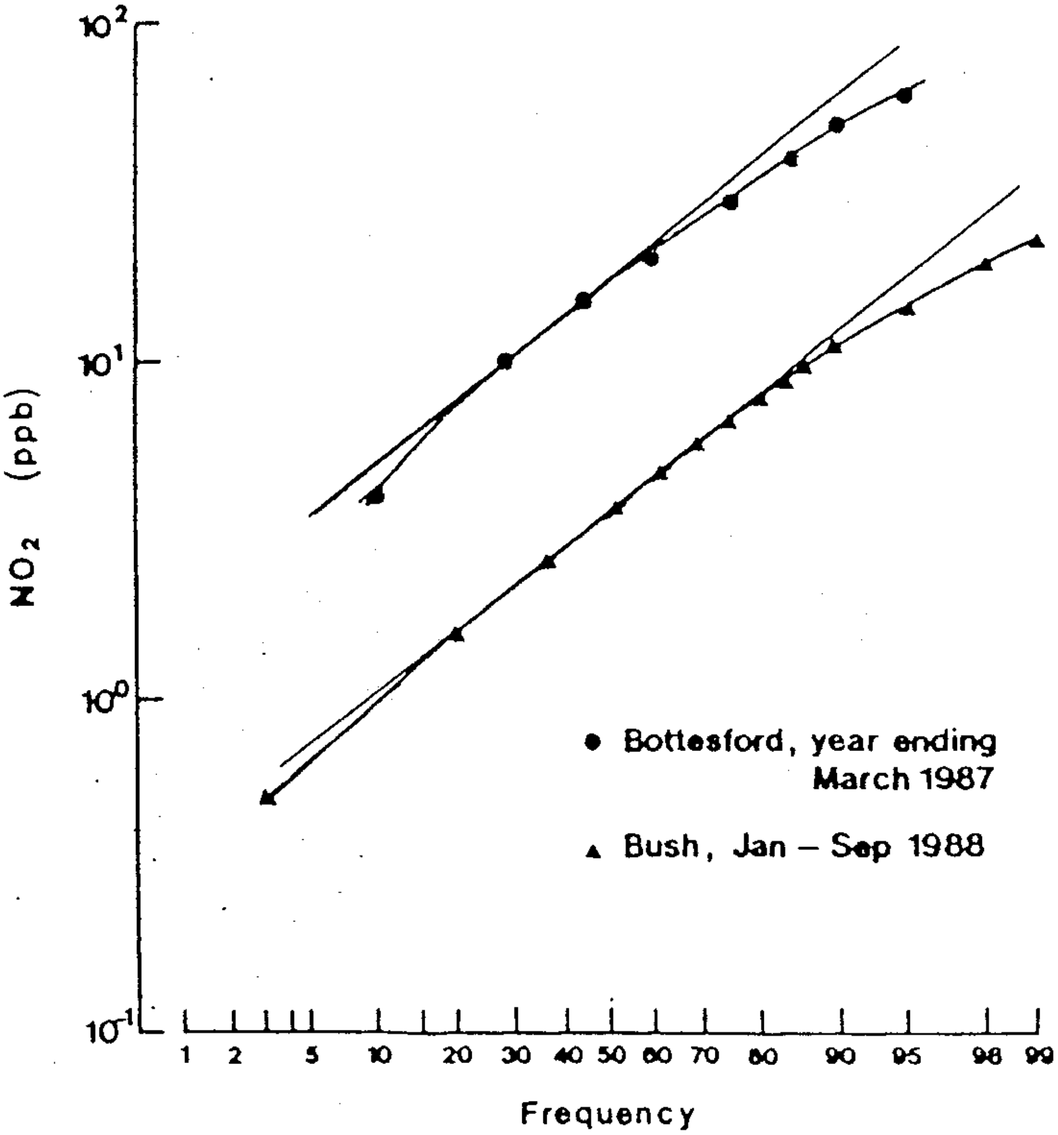


FIGURE 35. Diurnal variation in ozone and PAN concentrations at Harwell, Oxfordshire.

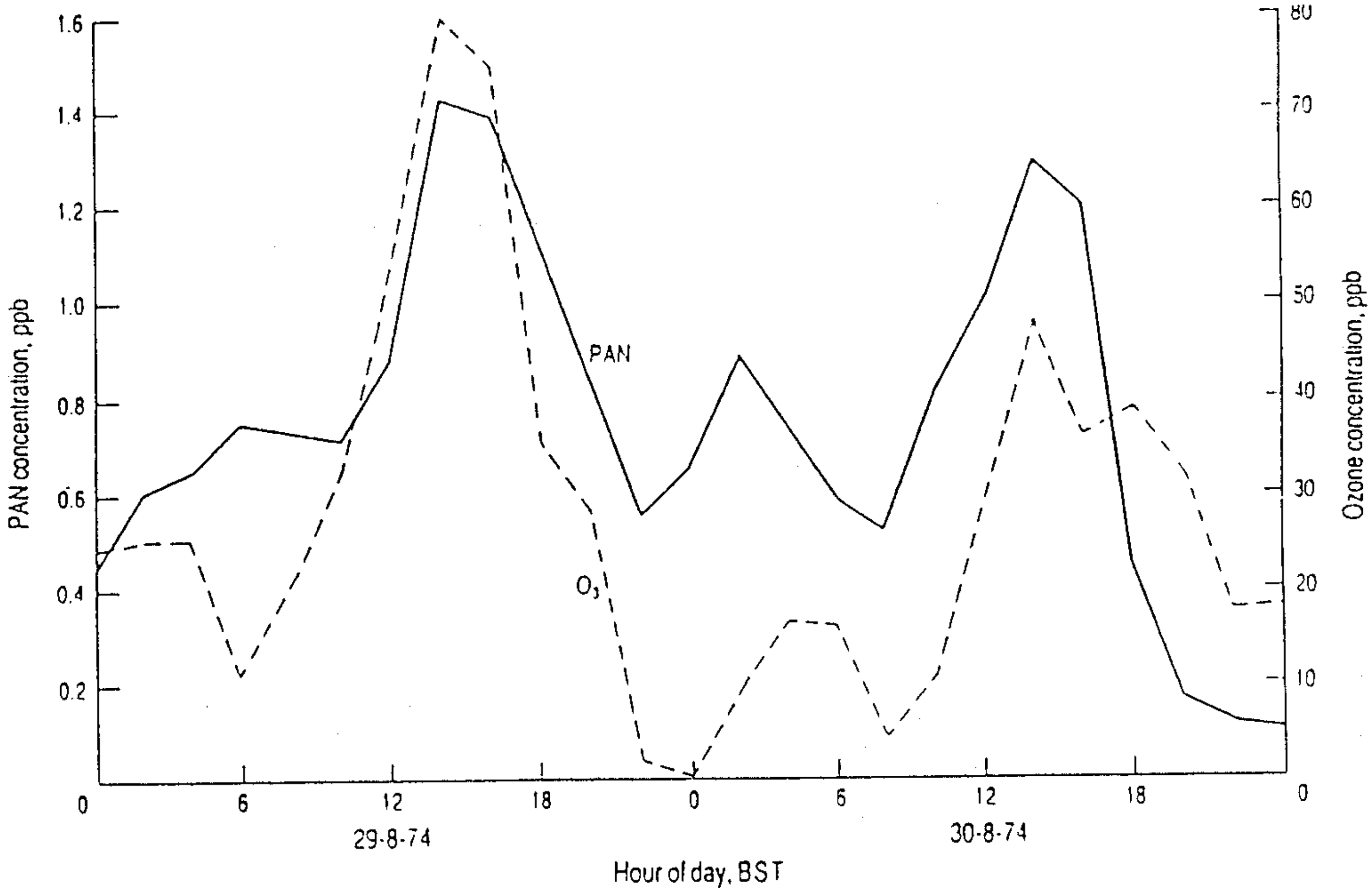
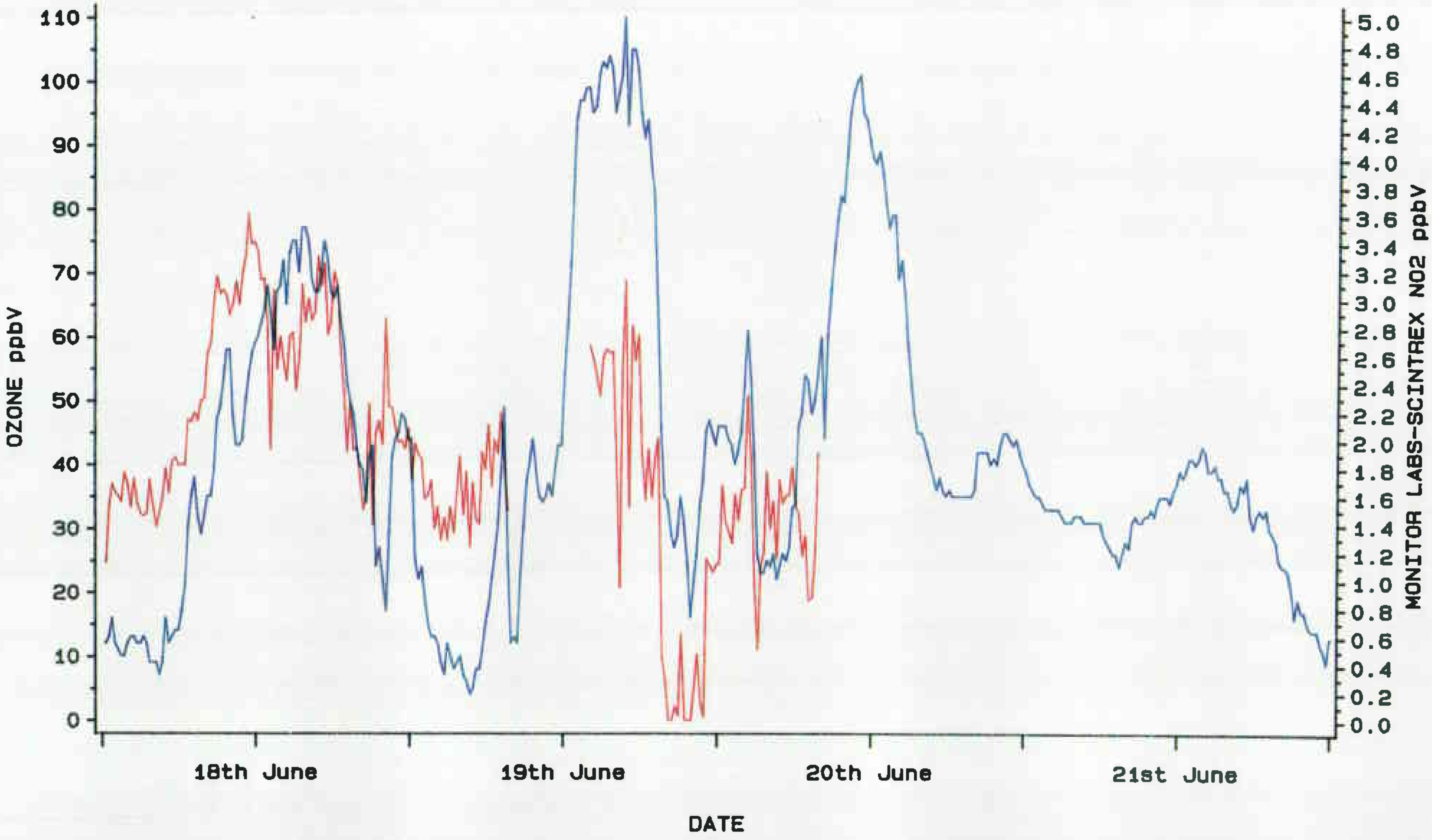


FIGURE 36.

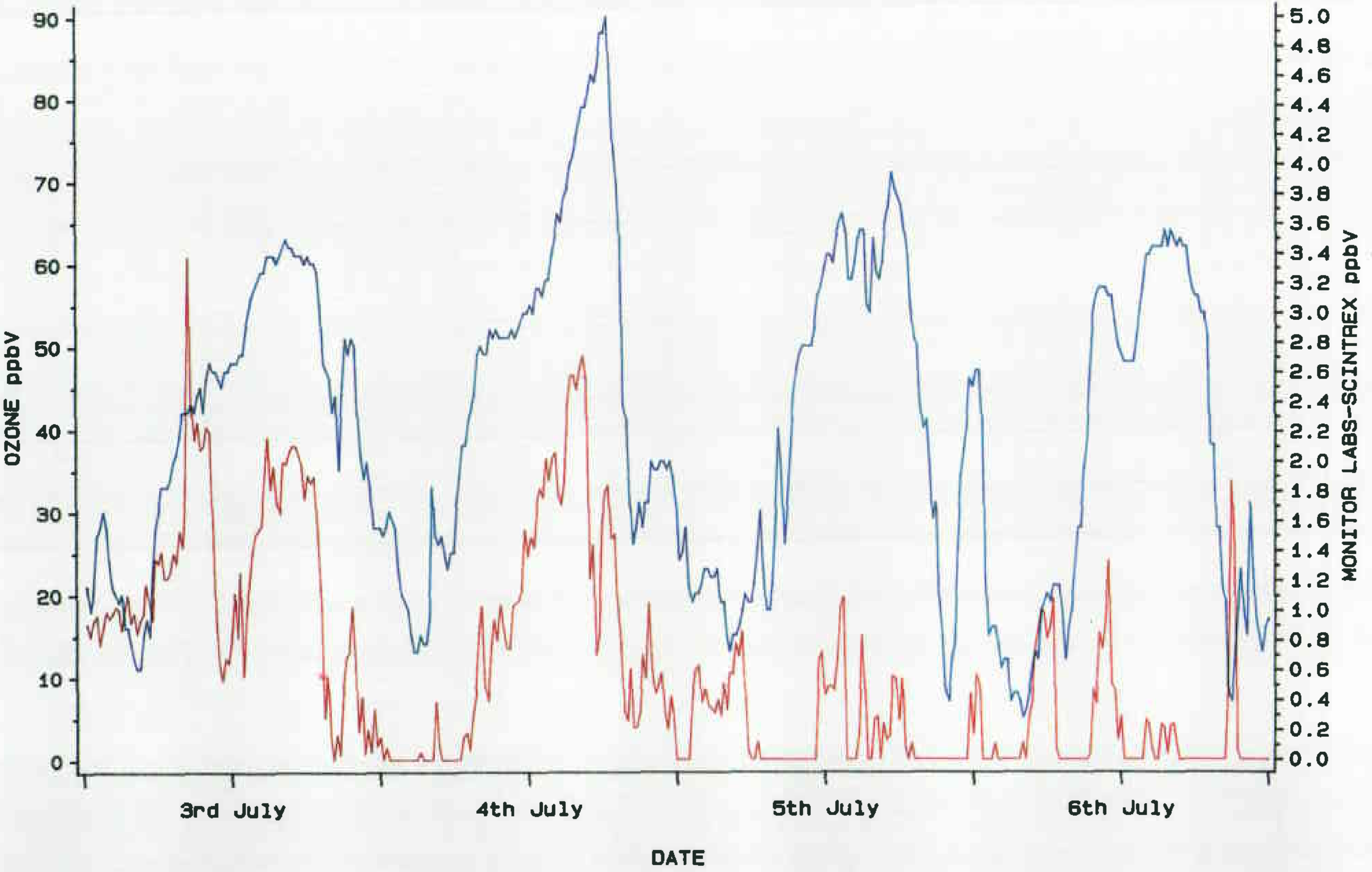
OZONE & (MONITOR LABS–SCINTREX) NO2 VALUES FROM 18–21 JUNE 1989



BLUE=OZONE
RED= (MONITOR LABS-SCINTREX) NO2

FIGURE 37.

OZONE & (MONITOR LABS-SCINTREX) NO2 VALUES FROM 3-6 JULY 1989



A plot of 15 minute averaged ozone data against (Monitor Labs-Scintrex) 'NO_2' data for the 19th to 20th June 1989 indicates a linear relationship between the two parameters with a ratio of approximately 30:1. This is shown in Figure 38.

The ratio and concentrations observed for the 'NO_2' concentration difference are therefore in close agreement with those described above for PAN. These results do indicate the presence of PAN but clearly specific PAN measurements at the site are necessary for proof of its presence.

SO_2 MONITORING AT THE BUSH ESTATE SITE

SO_2 has been monitored since 1987 at Bush Estate and there are now 3 full years of data for the site. In 1988 and 1989, the calendar year mean values were 2 ppbV and 3 ppbV respectively. The extreme values for each year are 51 ppbV and 45 ppbV respectively.

In 1989, two analysers monitored SO_2 at Bush Estate; a Teco and a Monitor Labs instrument. Figure 39 plots the daily maximum SO_2 values, monitored by each of the analysers. The Monitor Labs analyser operated over a shorter period than the Teco instrument but over the period when both were in operation, the data correllate extremely well. As with the NO_2 data which were recorded at the Bush Estate site, the largest SO_2 concentrations are observed from October to December during periods when windspeeds are very low and SO_2 plumes are advected from the city of Edinburgh.

Figure 40 shows the cumulative frequency distribution of hourly averaged SO_2 values which were recorded at the Bush Estate site in 1989. Unlike the plot of NO_2 data shown in Figure 33 and which deviates from log-linearity at about the 90th percentile, the SO_2 data shows only minimal deviation from log-linearity over the entire range of its frequency distribution. This is a result, which was discussed earlier, of the primary nature of the SO_2 pollutant.

The ratio of SO_2:NO_2 at the Bush Estate site is approximately 1:2.5.

COMPARISON OF 0_3, NO_2 AND SO_2 CONCENTRATIONS AT BUSH ESTATE

Various air quality guidelines have been set for ambient NO_2 and 0_3 concentrations, with particular regard for human health[1,5]. There is considerable interest at the present time, however, in the synergistic effect of pollutants; particularly their combined effects on crops and vegetation. At present, research in this area, is at a very early stage.

The World Health Organization has proposed Air Quality Guidelines for SO_2, NO_2 and 0_3 in combination. Their limit value is an annual mean concentration for NO_2 of 16 ppb in the presence of an annual mean SO_2 concentration of 10 ppb and a summer mean 0_3 concentration of 30 ppb. Figures 41 to 44 show the daily mean and maximum concentrations of NO_2, SO_2 and 0_3 at the Bush Estate site in 1988 and 1989. These Figures clearly indicate that the WHO guideline for the presence of the 3 pollutant gases in combination is not exceeded at the site in either year.

FIGURE 38.

OZONE & (M.LABS-SCINTREX)NO2 DATA FOR BUSH FOR 19-20 JUNE 1989

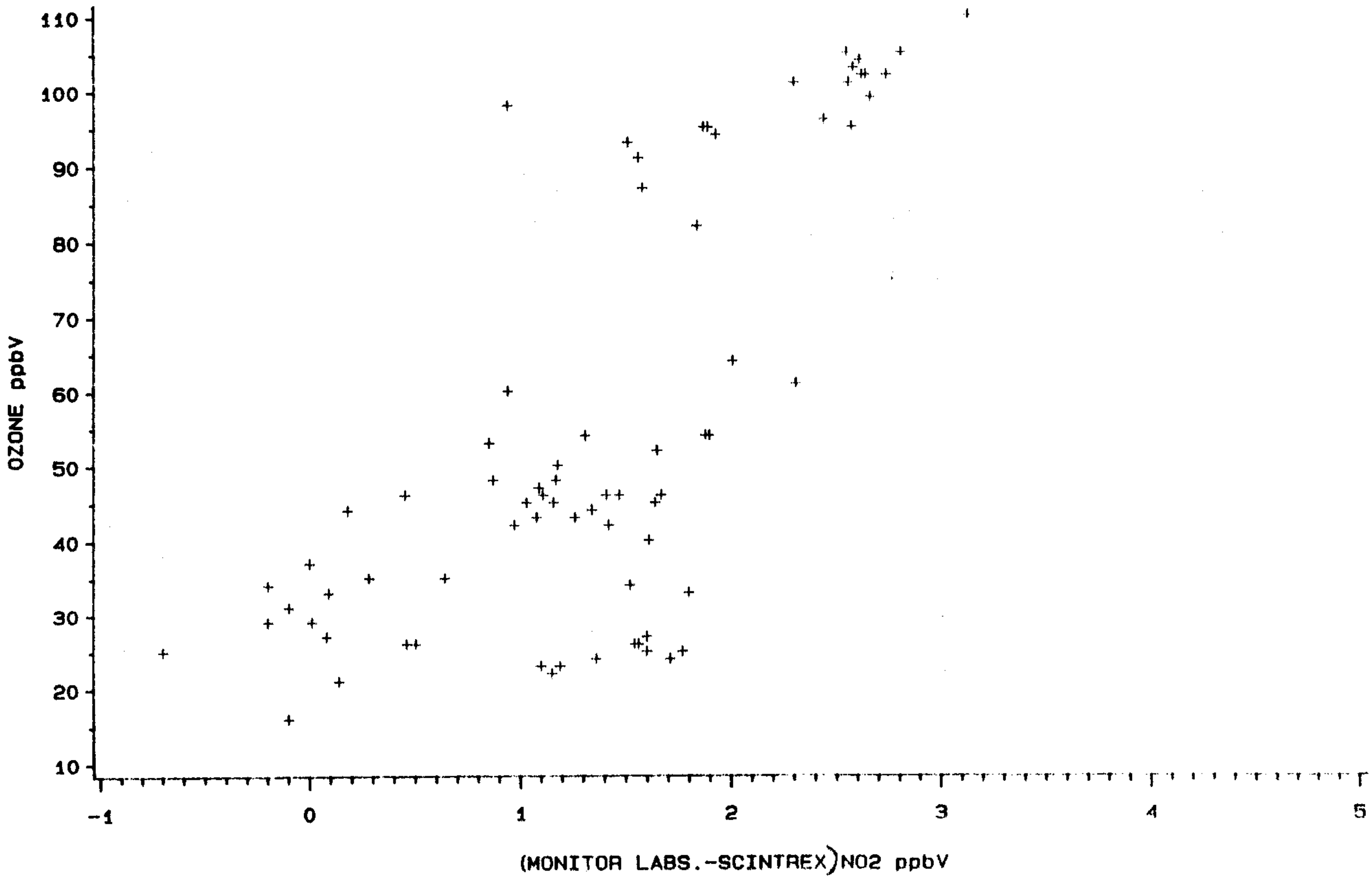
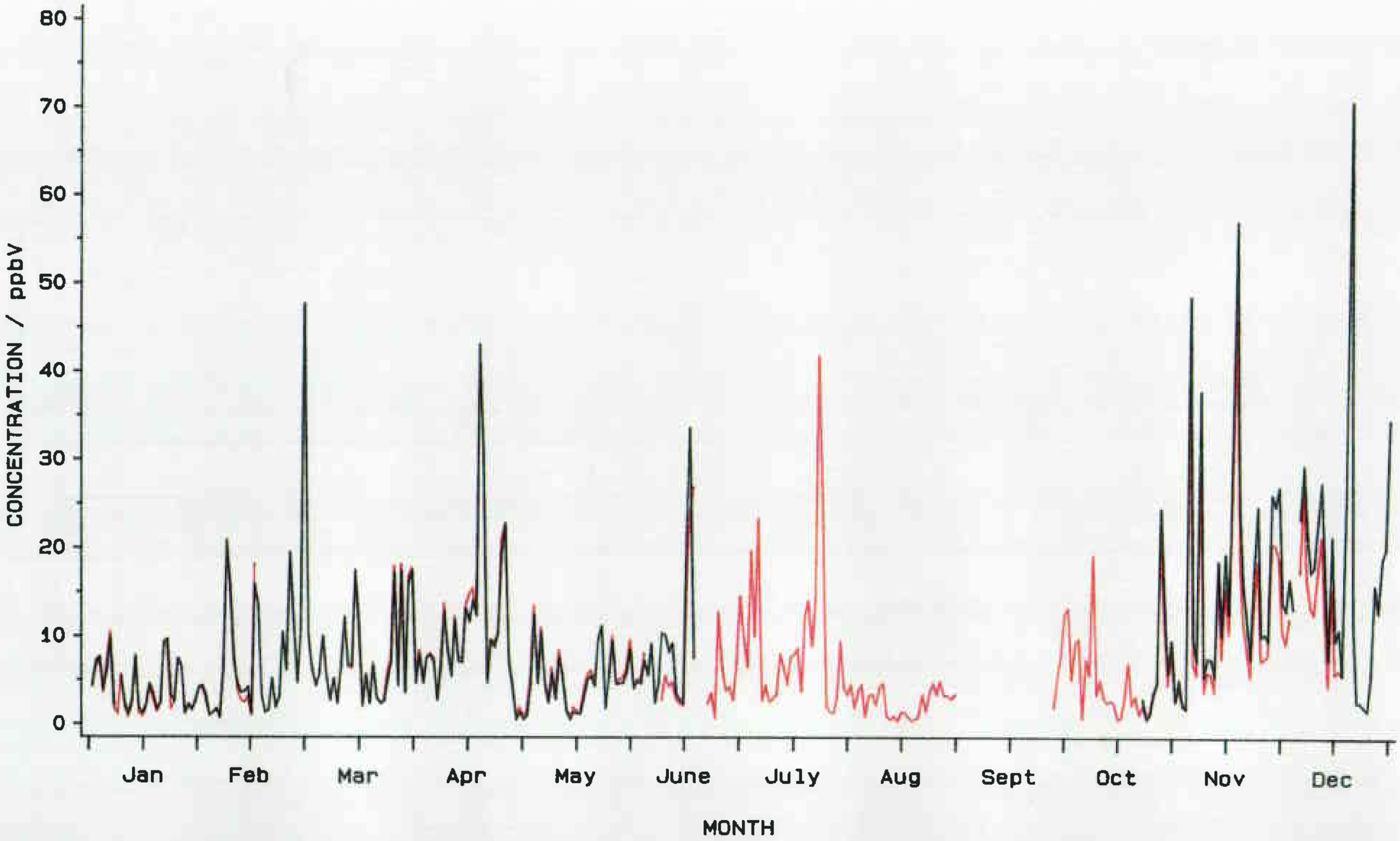


FIGURE 39.

DAILY MAXIMUM SO2 VALUES FOR BUSH IN 1989



MONITOR LABS SO2=BLACK, TECO SO2=RED

FIGURE 40. Cumulative frequency distribution for SO2 at the Bush Estate.

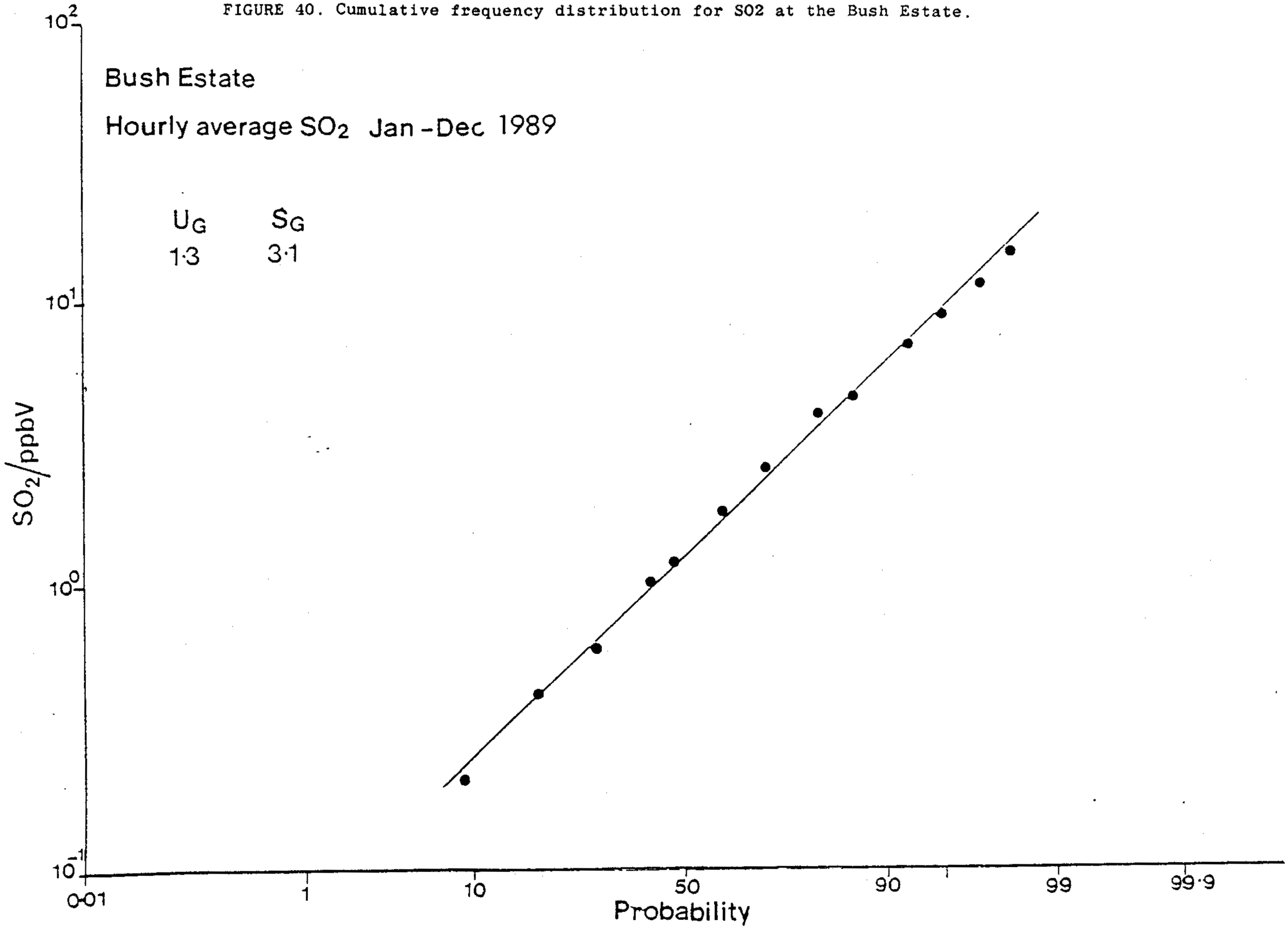
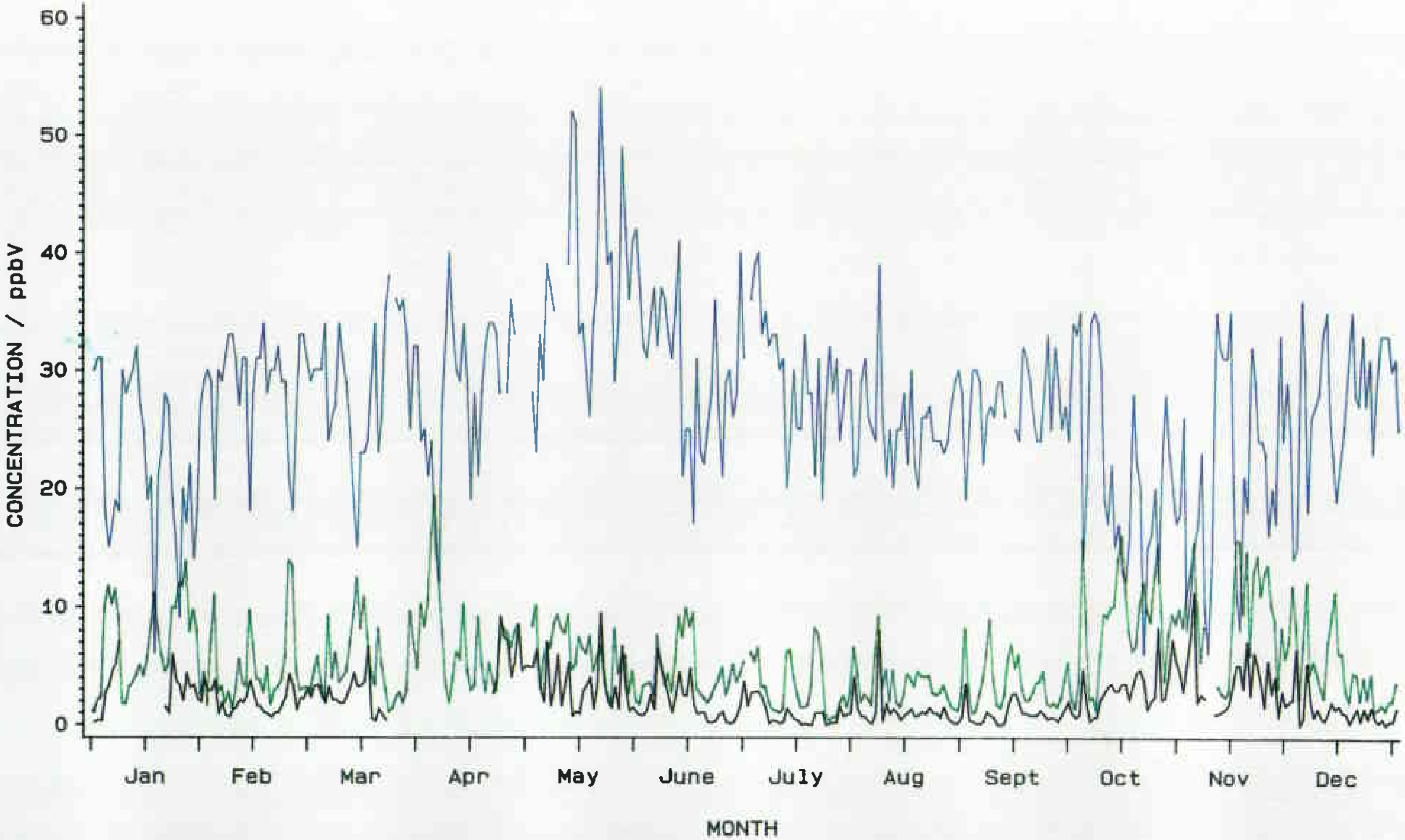


FIGURE 41.

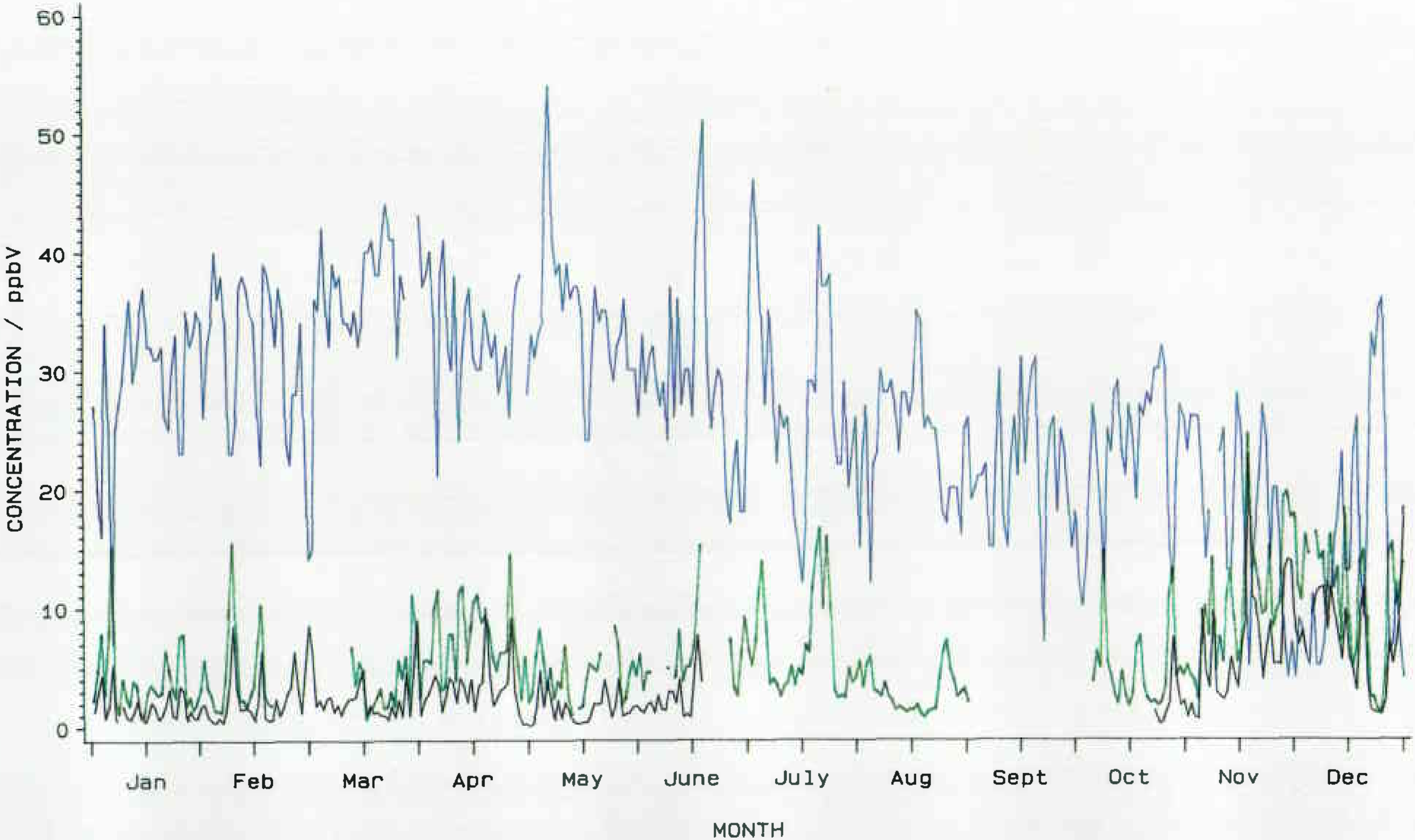
DAILY MEAN SO2,NO2 & O3 VALUES FOR BUSH IN 1988



NO2= GREEN, SO2=BLACK, O3=BLUE

FIGURE 42.

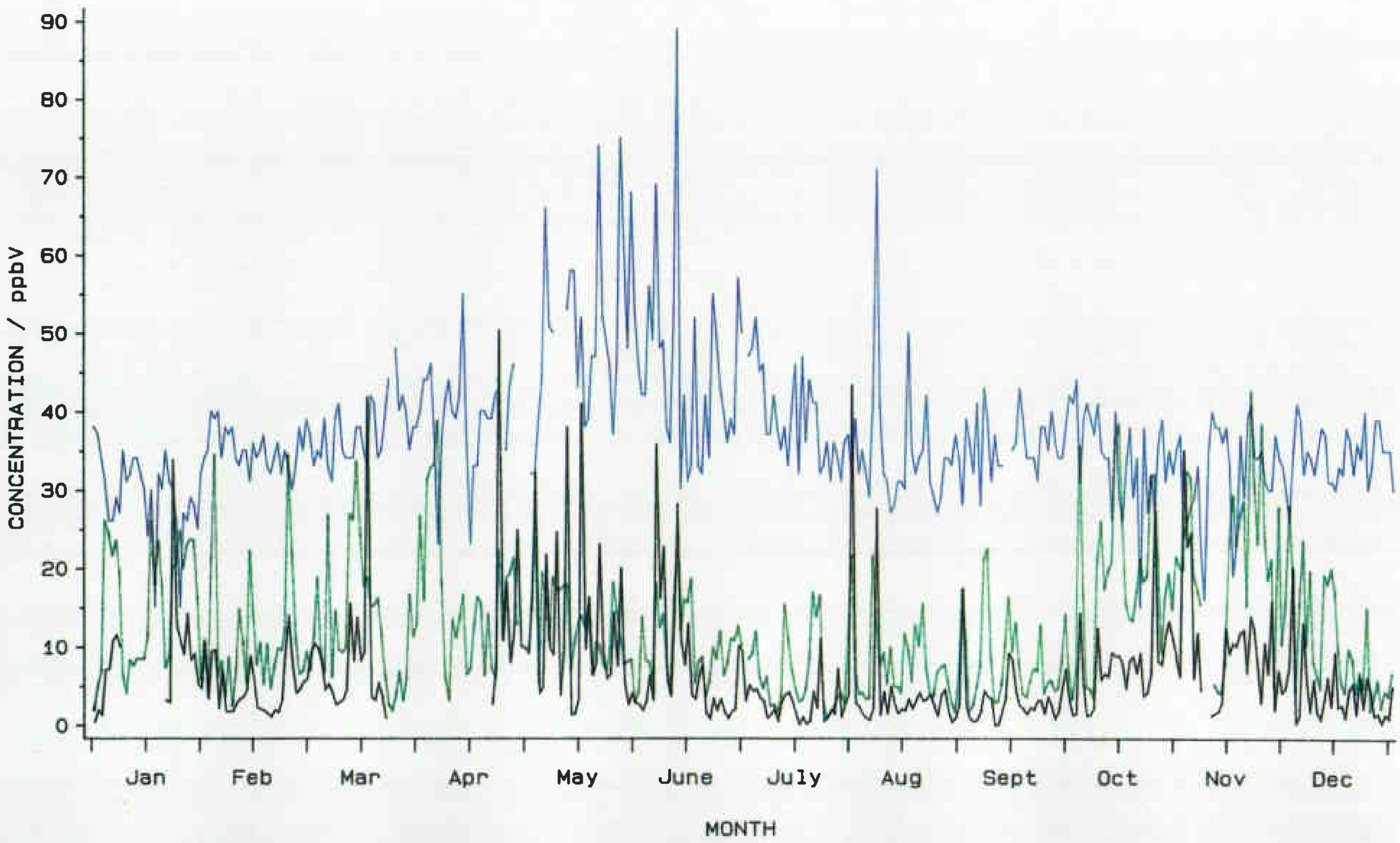
DAILY MEAN NO2,SO2 & O3 VALUES FOR BUSH IN 1989



NO2=GREEN. SO2=BLACK. O3=BLUE

FIGURE 43.

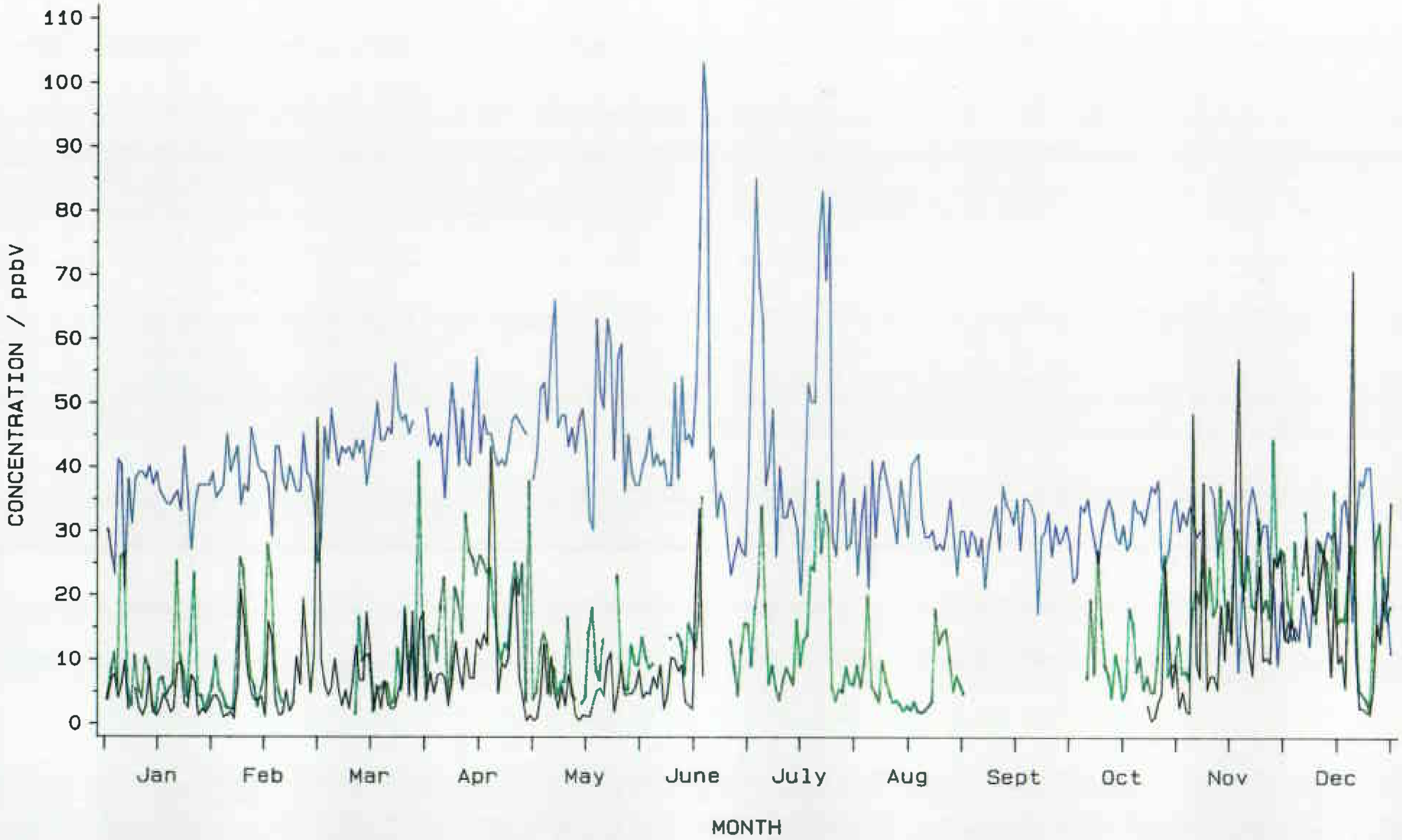
DAILY MAXIMUM SO2,NO2 & O3 VALUES FOR BUSH IN 1988



NO2= GREEN, SO2=BLACK, O3=BLUE

FIGURE 44.

DAILY MAXIMUM NO2,SO2 & O3 VALUES FOR BUSH IN 1989



NO2=GREEN. SO2=BLACK. O3=BLUE

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