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SURFACE OZONE MEASUREMENTS FROM A GLOBAL NETWORK

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Abstract— From a network of sites, primarily in the Atlantic and Pacific Ocean regions, measurements of the surface ozone concentration yield information on the seasonal, synoptic, and diurnal patterns. These sites, generally removed from the effects of local pollution sources, show characteristics that typify broad geographical regions. At Barrow, AK; Mauna Loa, HI; American Samoa; and South Pole, data records of 15–20 years show trends that in all cases are a function of season. This dependence on season is important in understanding the causes of the long-term changes. At Barrow, the summer (July, August, September) increase of 1.7% per year is probably indicative of photochemical production. At South Pole, on the other hand, the summer (December, January, February) decrease is related to photochemical losses and enhanced transport from the coast of Antarctica.

At all the sites there is a pronounced seasonal variation. In the Southern Hemisphere (SH), all locations which run from 14 to 90°S show a winter (July–August) maximum and summer minimum. In the Northern Hemisphere (NH) most of the sites show a spring maximum and autumn minimum. At Barrow (70°N) and Barbados (14°), however, the maxima occur during the winter, but for very different reasons. At many of the sites, the transport changes associated with synoptic scale weather patterns dominate the day-to-day variability. This is particularly pronounced at Bermuda and the more tropical sites. In the tropics, there is a very regular diurnal surface ozone cycle with minimum values in the afternoon and maxima early in the morning. This appears to result from photochemical destruction during the day in regions with very low concentrations of nitrogen oxides. At Niwot Ridge, CO, and Mace Head, Ireland, there is clear evidence of photochemical ozone production in the summer during transport from known regional pollution sources.

Key word index: Ozone distribution, ozone trends, surface ozone, tropospheric chemistry.

1. INTRODUCTION

In order to assess the extent to which the ozone content of the troposphere may be changing and to what extent that change may be attributed to human influences, it is necessary to have a global picture of the distribution of ozone and its variations. As part of the Climate Monitoring and Diagnostics Laboratory (CMDL), surface ozone measurements have been made for 15–20 years at four sites. Beginning in 1988, the number of sites has been expanded as part of the Atmosphere/Ocean Chemistry Experiment (AEROCE) to include several locations in the North Atlantic region. Information on the location and period of data record is summarized in Table 1. The majority of these sites are generally free from local sources of contamination. At two of the sites—Barrow, AK, and Bermuda—the locally contaminated measurements can be screened using the local wind direction. At Mauna Loa, HI, and Izaña, Canary Islands, the strong mountain wind circulation separates the measurements into upslope and downslope conditions. During the daytime, upslope regime boundary layer air is mixed with the free tropospheric air, while during nighttime downslope flow, free tropospheric air is sampled. At Reykjavik, Iceland, the measurements are made within the city center and only by screening of the data, as discussed later, can the regional ozone behavior be extracted. Special considerations at other sites will be discussed briefly in the discussion of the data sets.

The purpose here is to show the significant variations including seasonal, day-to-day, and diurnal patterns and, for the four long-term records at Barrow, Mauna Loa, Samoa and South Pole, to look at the trends as well. For these longer records, this work is an update of several previous studies (Oltmans, 1981; Oltmans and Komhyr, 1986; Oltmans *et al.*, 1989).

2. INSTRUMENTATION

The vast majority of measurements discussed here were made using ozone monitors which use the absorption of

Table 1. Elevation, location, and period of observation for surface ozone measurement stations

Station	Elevation	Latitude	Longitude	Period of observation
Barrow, Alaska	11 m	71°N		3/73–2/92
Reykjavik, Iceland	60 m	64°N		9/91–9/92
Westman Islands, Iceland	100 m	63°N		9/92–12/92
Mace Head, Ireland	30 m	53°N		7/89–12/92
Niwot Ridge, Colorado	3000 m	40°N		7/90–12/92
Bermuda	40 m	32°N		10/88–12/92
Izaña, Canary Islands	2360 m	28°N		5/87–10/89
Mauna Loa, Hawaii	3397 m	20°N		10/73–9/92
Barbados	45 m	13°N		4/89–12/92
Samoa	82 m	14°S		1/76–12/91
Cape Point, South Africa	75 m	34°S		1/83–6/88
Cape Grim, Australia	94 m	41°S		1/82–12/91
Syowa, Antarctica	21 m	69°S		2/89–1/90
South Pole, Antarctica	2835 m	90°S		1/75–2/92

ultraviolet (UV) radiation at 254 nm as the principle of measurement. Most of the measurements reported here are tied to a network standard maintained by CMDL, which is in turn linked by intercomparison with the standard ozone photometer maintained by the U.S. National Institute of Standards and Technology. Several sets of data taken from the literature are not directly linked to this standard, but it has been found that most of the UV absorption type instruments that we have purchased give ozone amounts within 5% of our standard when using the monitor as received from the manufacturer.

At the four long-term CMDL measuring sites an electrochemical concentration cell ozone meter was used for several years prior to 1976 before the UV absorption type instruments were introduced. The two types of equipment were run simultaneously at each site for several years. The comparability of the measurements has been documented (Oltmans and Komhyr, 1986).

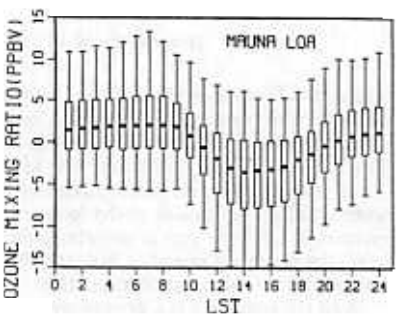

Fig. 1. Median departure (dot), inner 50th percentile of the departure (box), and inner 90th percentile of the departure (whiskers) from the daily mean for each hour of the day of the ozone mixing ratio at Mauna Loa, Hawaii.

3. DIURNAL VARIATION

The variation of ozone within a day may be helpful in delineating the processes responsible for ozone formation or loss at a particular location. At Barrow, AK, and South Pole, no diurnal cycle is detected as was reported in earlier studies (Oltmans, 1981). At Mauna Loa and Izaña the diurnal cycle is dominated by the mountain induced wind flow regime (Oltmans, 1981). This is illustrated in Fig. 1, which shows the median departure from the daily mean for each hour, along with the dispersion at Mauna Loa. Ozone values drop markedly during the day as upslope winds carry boundary layer air with less ozone (Oltmans and Komhyr, 1986) up to the observatory. Ozone amounts gradually build up during the night, reaching a peak in the morning. These nighttime values are representative of the free tropospheric ozone behavior based on comparison of the Mauna Loa surface data and ozone vertical profile measurements (Oltmans and Komhyr, 1986). The downslope data, designated as the period from midnight to 8 a.m., LST, are used in subsequent analyses.

At Reykjavik, the ozone measurements were made for one year from the Meteorological Office which is located within the city of approximately 100,000 population. Recently, a site was established at a location in the Westman Islands, a group of small volcanic islands just to the south of the main island. As can be seen in Fig. 2a, there is a very strong daily cycle at Reykjavik with low values during the day and highest values late at night and early in the morning. This pattern, which is most pronounced in the autumn and winter, appears to be closely tied to traffic patterns with strong ozone loss due to titration with automobile emitted NO.

Although only two months of data are available from the remote sampling site at Westman Islands (Fig. 2b), it is clear that this diurnal loss seen at Reykjavik is not present. Comparing Reykjavik data for the 03–07 LST period with the daily average (since there is no daily cycle) at Westman shows that the nighttime values at Reykjavik are representative of the background seasonal trend. Based on this, the daily average using the 03–07 LST values will be used to determine the basic seasonal pattern in the region.

The site at Mace Head, Iceland, is seldom influenced by local emissions but does see emissions from England and the European continent. Even winds from the clean sector off the ocean may occasionally

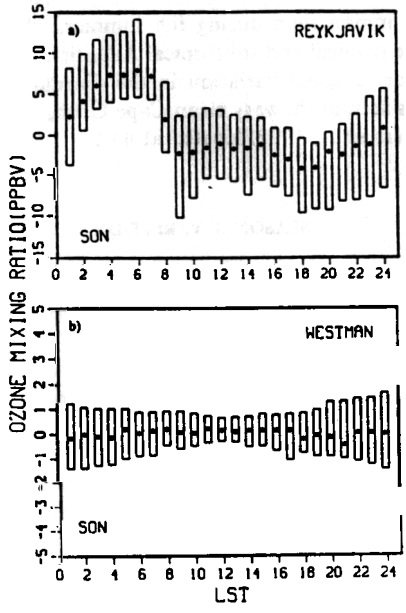

Fig. 2. The diurnal ozone variation as in Fig. 1 for (a) Reykjavik, Iceland, and (b) Westman Islands, Iceland.

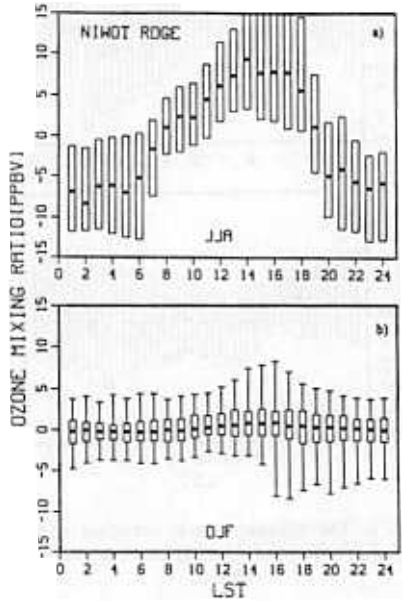

Fig. 4. The diurnal ozone variation as in Fig. 1 for Niwot Ridge, Colorado, (a) summer and (b) winter.

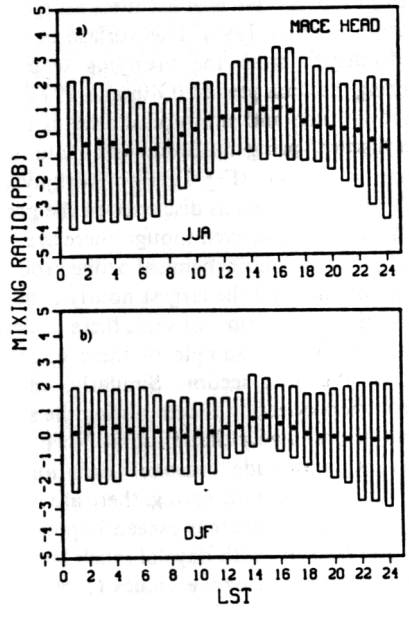

Fig. 3. The diurnal ozone variation as in Fig. 1 for Mace Head, Iceland, during (a) summer (J–J–A) and (b) winter (D–J–F).

have trajectories that reach back to the European continent in 2–3 days. During the spring and summer, there is a clear diurnal cycle (Fig. 3a); while in the autumn and winter (Fig. 3b), there is no readily discernible daily variation. This variation becomes most pronounced during stagnation episodes that show up as very high daily maxima and reflect very strong photochemical production. These occur primarily between May and August, which is also the time of strongest solar insolation.

Niwot Ridge, even though it is a high altitude site, shows a much different diurnal pattern (Fig. 4) than seen at the other mountain locations (Mauna Loa and Izaña). During the summer (Fig. 4a), there is a marked diurnal variation with a maximum in the afternoon. Given the season of the year and time of day, it is clear that the peak results from photochemical production under polluted conditions. Unlike the condition at Mauna Loa, during the daytime upslope conditions, air—laden with ozone and ozone precursors—is swept up from the populated front range of Colorado into the mountains. Studies at this site (Fehsenfeld *et al.*, 1983) have shown that ozone can be efficiently produced. During the winter, on the other hand, when solar insolation is low and the very strong westerly winds dominate the air flow, there is almost no diurnal variation (Fig. 5b).

At the subtropical location of Bermuda, we begin to see the pattern that appears to be typical of subtropical and lower latitude oceanic sites (Oltmans and Levy, 1992). Ozone amounts reach a maximum during the early morning and a minimum in the afternoon (Fig. 5). At Bermuda, this variation is quite seasonally dependent, with the largest variation during the summer (Fig. 5a) and a much weaker variation in the winter (Fig. 5b). At the two more tropical stations of Barbados (13°N) and Samoa (14°S), there is much less seasonal dependence. The summertime variation at Bermuda has a similar amplitude to those at Barbados (Fig. 6a) and Samoa (Fig. 6b). This diurnal variation

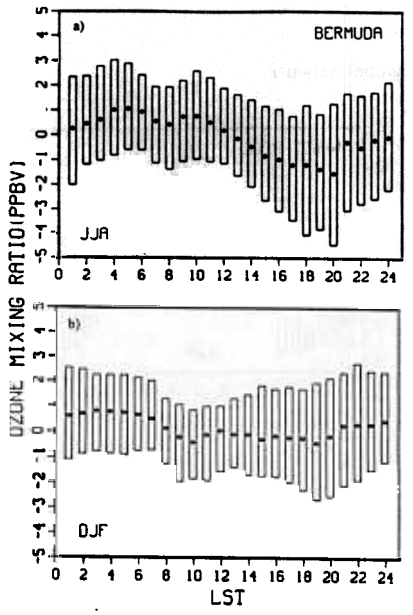

Fig. 5. The diurnal ozone variation as in Fig. 1 for Bermuda for (a) summer and (b) winter.

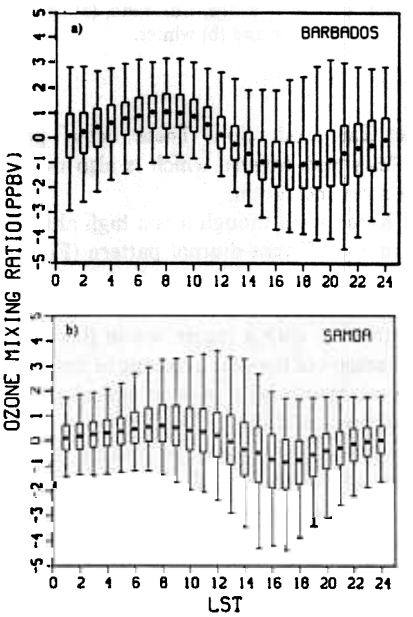

Fig. 6. The diurnal ozone variation as in Fig. 1 for (a) Barbados and (b) Samoa.

appears to be a result of photochemical ozone destruction during daylight hours in a regime with very low nitrogen oxide (NO_x) concentrations (Oltmans and Levy, 1992; Oltmans, 1981; Liu *et al.*, 1983). The seasonal variation in the amplitude of the diurnal cycle at Bermuda is consistent with this picture since there is a much wider range of solar insolation experienced over the course of a year at Bermuda than is found at the lower latitude locations and hence much weaker destruction during the winter. NO_x concentrations may also be somewhat higher at Bermuda during the winter when flow from North America is more common than during the summer, when flow from the tropical and subtropical Atlantic dominates. A similar seasonal variation in the diurnal cycle of ozone is seen at the very clean Cape Grim, Australia, site (Ayers *et al.*, 1992) located at 43°S.

4. SEASONAL VARIATION

Every surface ozone record investigated here has a prominent seasonal cycle (Fig. 7). The nature and course of this seasonal variation is quite different at different locations, however. This section will discuss the unique characteristics of a site or group of sites with emphasis on how this pattern may represent a broader scale phenomena.

At Barrow, AK, located on the Arctic Ocean coast, there is a distinct spring minimum (Oltmans *et al.*, 1989) that has been reported at other Arctic basin locations (Barrie *et al.*, 1989; Oltmans, 1992; Oltmans, 1993). This phenomenon, which is not seen at other high latitude locations removed from the Arctic Ocean (Oltmans, 1993), occurs in conjunction with a strong spring pulse in atmospheric bromine. It is not clear, however, whether the bromine is the cause of the strong ozone depletion, although several mechanisms have been proposed (Barrie *et al.*, 1989; Sturges, 1989; Finlayson-Pitts *et al.*, 1990). This surface ozone pattern is decoupled from the overlying troposphere where spring maxima prevail (Oltmans, 1993).

For mid-latitude and subtropical sites in the NH, there is a distinct spring maximum and a late summer or autumn minimum (Fig. 7). For Reykjavik, the 03–07 LST data are used as discussed in the previous section. At Mace Head, even though there are clearly periods of enhanced photochemical ozone production during the summer and the largest hourly concentrations occur during this time of year, there is clearly a spring maximum. An example of these episodes is discussed in the next section. Similarly, enhanced photochemical production is seen during the summer at the continental, high altitude site at Niwot Ridge.

The largest amplitude seasonal variation is at Bermuda where, during the spring, there are episodes where daily average values may exceed 70 ppb (Fig. 8). These are interspersed with days of much lower concentration. The highest ozone values (>50 ppb) always occur when airflow is from the mid-troposphere over North America (Oltmans and Levy, 1992; Moody *et al.*, 1993). The lower ozone concentrations occur when flow is from more tropical latitudes. During the summer, under the influence of a semi-permanent anticyclone (the Bermuda High), flow from the continent of North America is restricted and air reaching the station spends long periods over the ocean where reactions with abundant hydroxyl and peroxy radicals

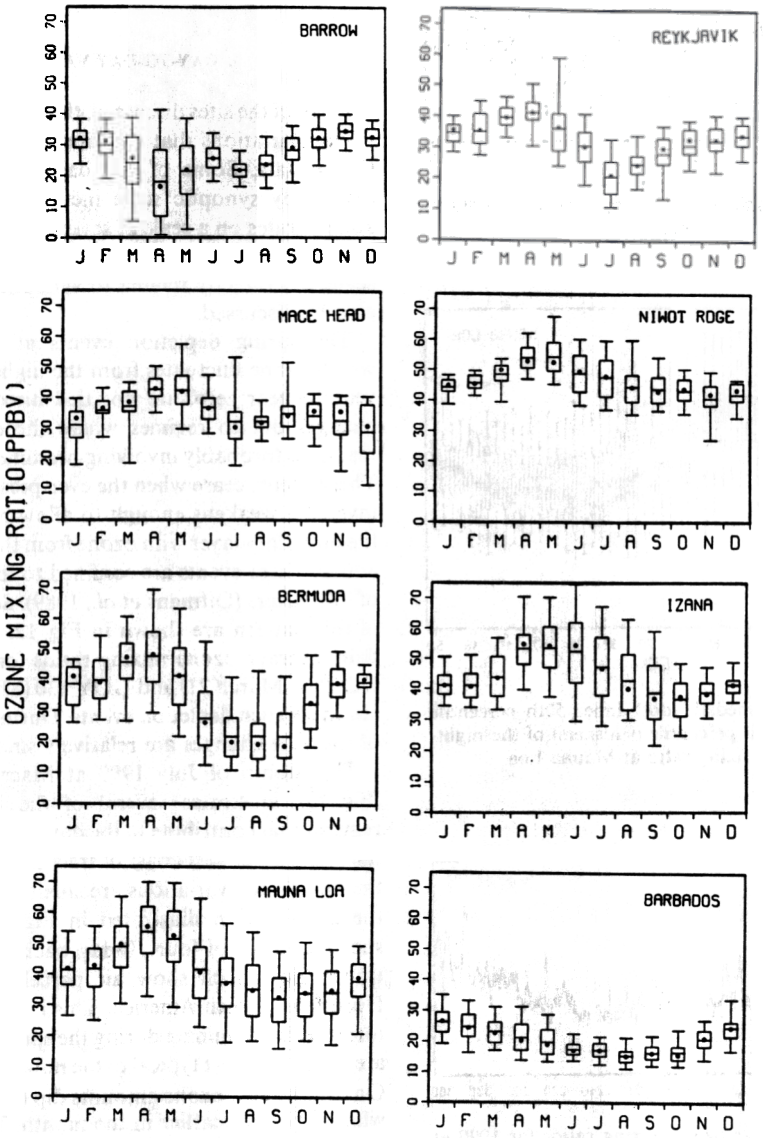

Fig. 7. The monthly median (dot), mean (bar), inner 50th percentile (box), and inner 90th percentile (whiskers) of the surface ozone mixing ratio for sites in the NH.

lead to ozone destruction. Such processes appear to be the main sink for ozone over the ocean where surface deposition is low (Galbally and Roy, 1980). The Bermuda location, approximately midway between strong source and sink regions, is the reason for large day-to-day variability as well as a large seasonal amplitude.

At both Izaña and Mauna Loa, which are oceanic locations, their higher elevation means that they are less likely to see air from the lowest levels where ozone destruction is strongest. The weekly nighttime, downslope data from Mauna Loa (Fig. 9) shows that the summer minima are only 60% of the spring maximum and that low values below 20 ppb are reached during the summer. This suggests that in the downslope flow, which is representative of the free troposphere at about 3 km, there is still a significant summer drawdown.

At Izaña, the summer minimum is not nearly as deep as that at Mauna Loa. The seasonal maximum at Izaña extends into early summer. The transport of enhanced ozone concentrations from the European continent during this period (Schmidt *et al.*, 1988) has been noted. A very strong correlation between ozone and ^{7}Be and anti-correlation with ^{210}Pb suggest that transport from the upper troposphere and lower stratosphere may also make a very significant contribution to the summer ozone enhancement at Izaña (J. Prospero, private communication).

The seasonal cycle at Barbados is quite different in character from those in the rest of the NH with a winter rather than spring maximum (Fig. 10), al-

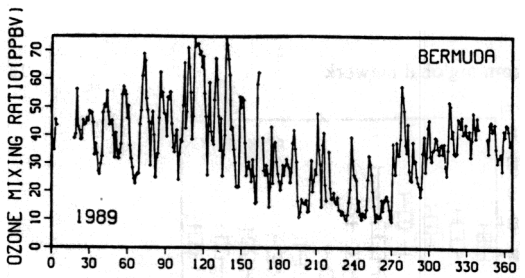

Fig. 8. Daily average ozone mixing ratios for 1989 at Bermuda.

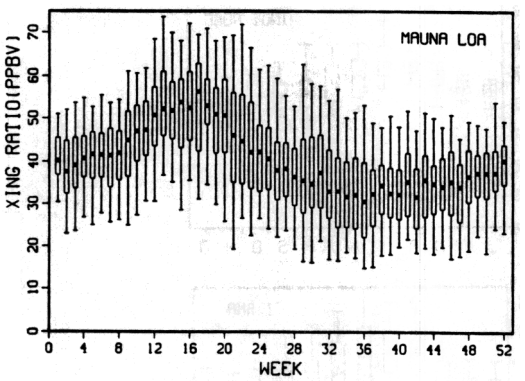

Fig. 9. The weekly median (dot), inner 50th percentile (box), and inner 90th percentile (whiskers) of the nighttime ozone mixing ratio at Mauna Loa.

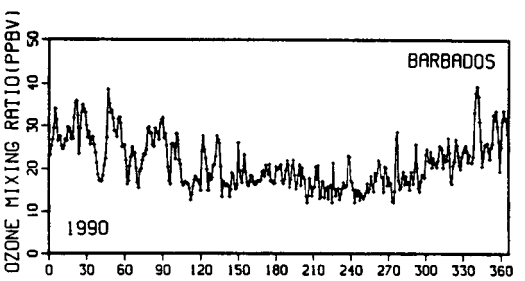

Fig. 10. Daily average ozone mixing ratios for 1990 at Barbados.

though there is still a summer minimum. This summer minimum is very similar in its depth to that at Bermuda and must reflect the widespread sink for ozone over the tropical oceans. The higher winter values are associated with transport from higher latitudes and altitudes (Oltmans and Levy, 1992; Savoie *et al.*, 1992) and will be discussed more fully in the next section on day-to-day variations.

In the SH, the seasonal variation at the surface (Fig. 11) has a similar phasing at all latitudes with a winter maximum and summer minimum. At Samoa, this cycle is exactly 6 months out-of-phase with Barbados. At South Pole, which is at an elevation of nearly 3 km, the variation is very similar to that at Syowa and the other sea level locations. Over Antarctica this pattern has prevailed for at least 30 years (Oltmans and Komhyr, 1976).

5. DAY-TO-DAY VARIATIONS

At all of the sites discussed, there are significant day-to-day variations that contribute significant variance to the data. Some of this day-to-day variability is caused by synoptic scale meteorological variations and operates on a scale of several days. Examples will be shown for some of the sites. Other changes on this scale, not directly related to synoptic variations, will also be discussed.

The spring depletion events at Barrow, during which ozone fluctuates from the highest values of the year to near zero, are not tied directly to air mass changes but to regimes where the ozone depleting reactions (probably involving bromine) can take place. These events cease when the ever-present temperature inversion weakens enough to allow replenishment of the boundary layer with ozone from the large reservoir above. These events are confined to the lowest couple of kilometers (Oltmans *et al.*, 1989). Several examples of this pattern are shown in Fig. 12, which gives the daily average ozone mixing ratios for 1988. Between DOY 80 (March 21) and DOY 130 (May 10), there are about six such depletion events. During the remainder of the year changes are relatively small.

The month of July 1990 at Mace Head, Ireland (Fig. 13), illustrates several of the important flow regimes that contribute to the day-to-day variations at this site on the west coast of Ireland. Early and late in the month, the variations are small and are typical of the flow pattern illustrated in Fig. 14a. This figure shows a series of four 10-day backward, isenstropic trajectories which show air parcels reaching Mace Head from North America. This is not unlike trajectories which dominate during the spring (Fig. 14b) and are probably most typical of the flow reaching this site. On 6 and 7 July ozone amounts dip to less than half of what they were earlier in the month. The trajectories during this period (Fig. 14c) come from subtropical latitudes and remain over the ocean at relatively low levels. Such over ocean trajectories are seen often at Bermuda with ozone amounts very similar to the 15 ppb seen during this period at Mace Head. The month is dominated, however, by the very large peaks exceeding 75 ppb. The period 22–27 July shows rising daytime concentrations with a pronounced diurnal variation. This pattern is one where there is strong ozone production. The flow pattern (Fig. 14d) shows air, which is reaching the site after having circulated over Great Britain and northern Europe, where abundant ozone precursor chemicals are expected to be present. Under conditions with transport from the European continent during months of reduced sunlight, there is a large ozone deficit (e.g. around DOY 292 in Fig. 15) indicating significant ozone destruction

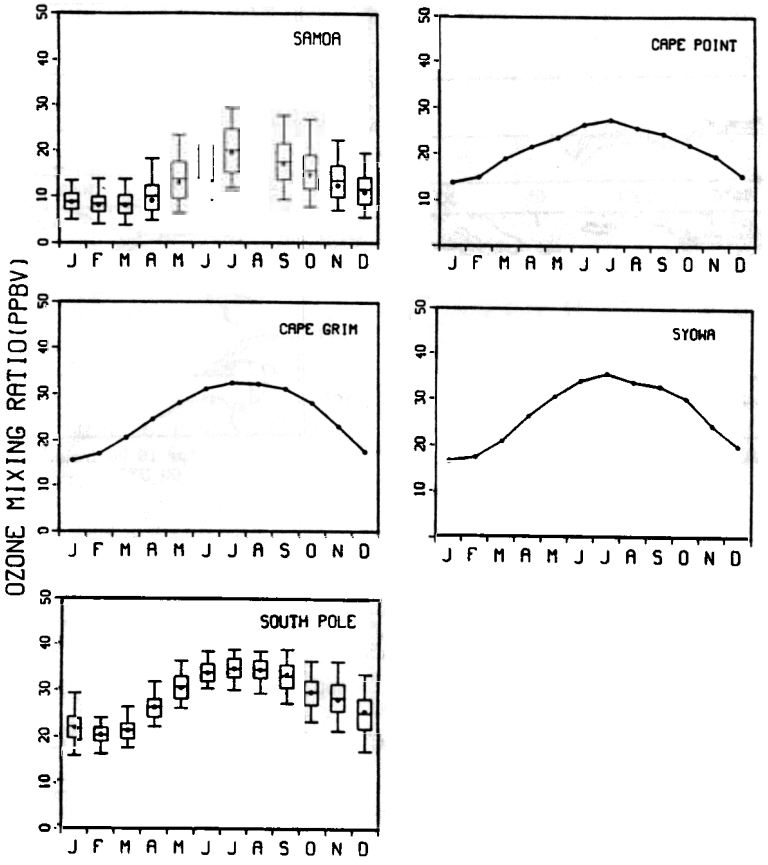

Fig. 11. Average monthly ozone for sites in the SH. Data for Cape Point are from Scheel *et al.*(1990),for Cape Grim from Elsworth *et al.*(1988),and for Syowa from Murayama *et al.* (1993).

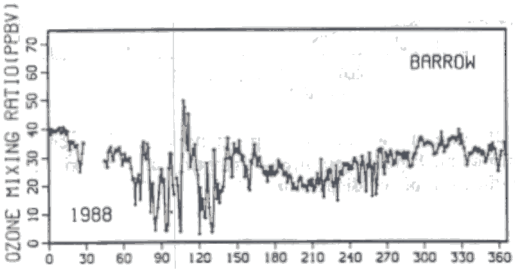

Fig. 12. Daily average ozone mixing ratios for 1988 at Barrow, AK.

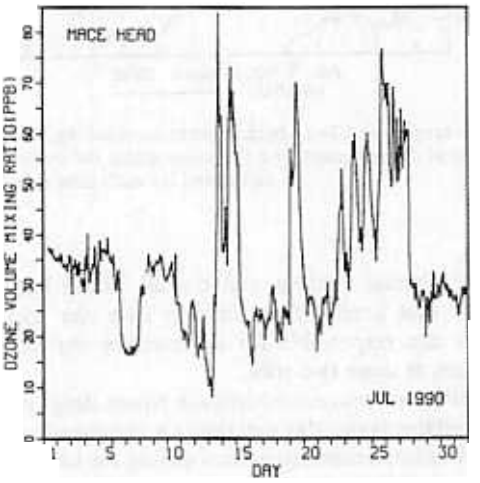

Fig. 13. Hourly average ozone mixing ratios for July 1990 at Mace Head.

possibly due to titration by NO. During such conditions low ozone amounts are closely associated with elevated CO concentrations (Doddridge *et al.*, 1993). The daily average ozone amounts for the entire year of 1990 (Fig. 15) show that the large excursions associated primarily with transport of pollution directly from Europe or occasional transport from subtropical latitudes only modify slightly the underlying seasonal pattern, which seems to be driven primarily by the much more frequent prevailing flow from over the Atlantic north of about 40°N as illustrated in Fig. 14b.

At Reykjavik, where there are some limitations in the data record as mentioned previously, the day-to-day changes resemble those at Mace Head without the large excursions associated with the pollution events from continental Europe. This, along with the very

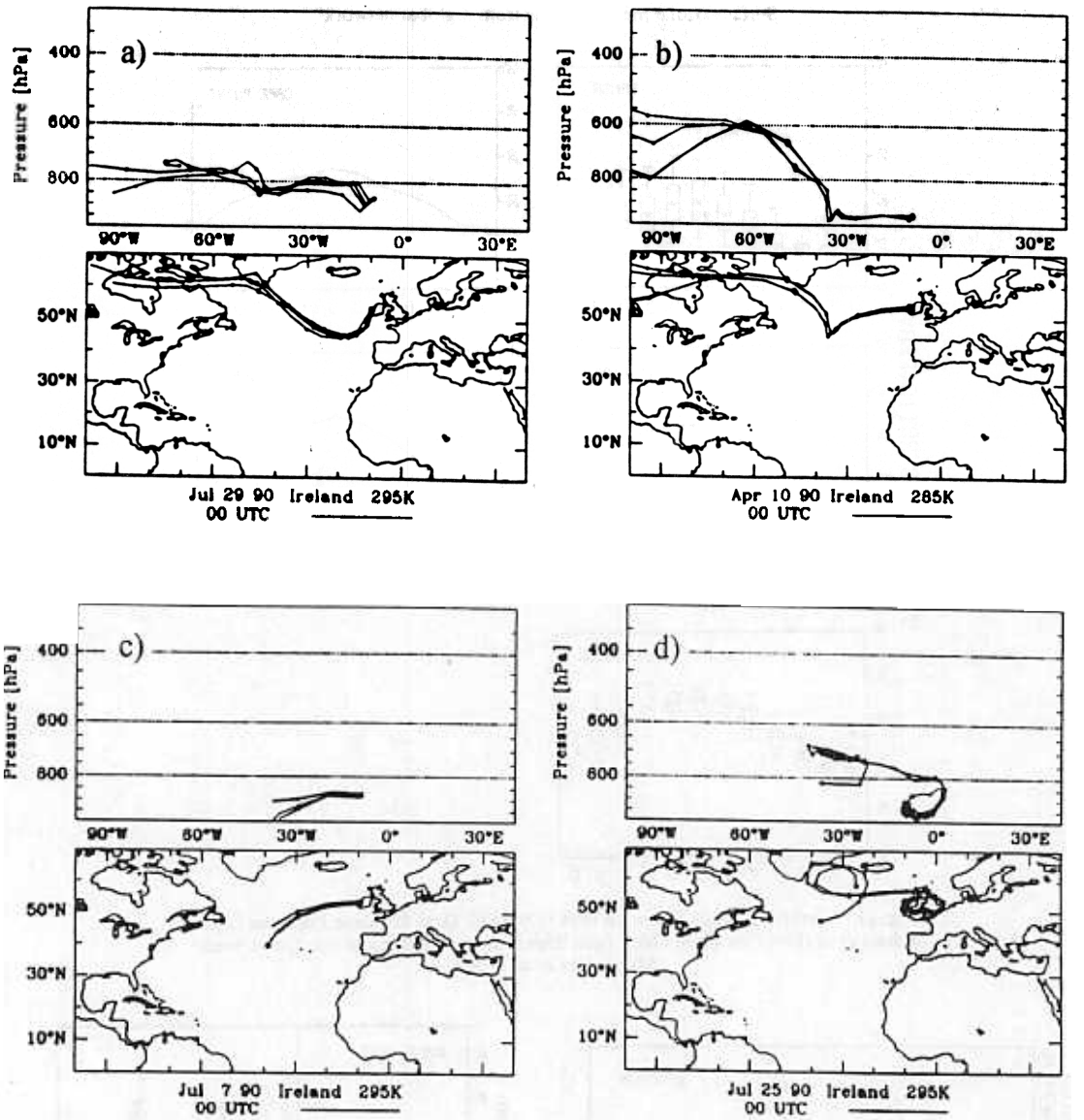

Fig. 14. Isentropic 10-day back trajectories reaching Mace Head on the dates indicated. The upper panel for each set shows the vertical displacement and the lower panel the horizontal displacement. Four trajectories originating near the site are calculated for each time to give some indication of the dispersion.

similar seasonal pattern and overall ozone levels, suggests that similar flow patterns over the north Atlantic are responsible for determining the basic variations at these two sites.

For the continental, mid-latitude Niwot Ridge site, almost all the day-to-day variability is associated with photochemical ozone production during the summer, associated with orographic upslope flow. During the winter, the much less frequent upslope flow produces events depleted in ozone. This pattern is seen by examining the 5th and 95th percentile "whiskers" in Fig. 7, where for November–March the 5th percentile extends further below the median than the 95th extends above it. During the summer this is reversed.

The subtropical sites (Bermuda, Izaña, Mauna Loa) show the largest day-to-day variations and these are most closely tied to air mass changes. At Bermuda, daily values during the spring often exceed 60 ppb. An example for 1990 shows three events for 18 May–2 June with alternating high and low ozone (Fig. 16). A trajectory from each of these periods is shown in Figs 17a–f. During the low ozone events on 19, 23, 29 May, air parcels remain over the tropical or subtropical ocean at altitudes below 800 mb. On days with high ozone—21 and 26 May, 2 June—the trajectories all come from north of 50°N and altitudes near 600 mb. Although the trajectories cannot be taken as an unequivocal determination of an air parcel

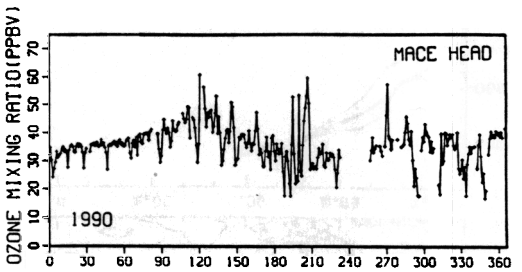

Fig. 15. Daily average ozone mixing ratios for 1990 at Mace Head.

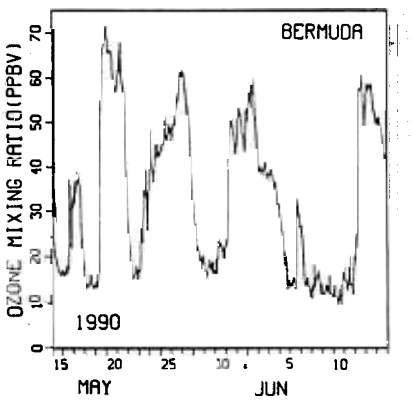

Fig. 16. Hourly average ozone at Bermuda during the period 15 May–14 June 1990.

origin or history, there is a great deal of consistency in this pattern when looking at a large number of cases (Moody *et al.*, 1993).

The higher altitude sites at Izaña and Mauna Loa rarely see the very low ozone concentrations seen at Bermuda but do show strong variability, on the scale of a few days, that can be seen in Fig. 18, which shows the daily downslope ozone values for a year at each site. Only during late autumn and winter are the fluctuations somewhat reduced, especially at Izaña.

At the tropical sites of Barbados and Samoa, the day-to-day variations are not as dramatic as those seen at subtropical latitudes, but particularly in the winter and spring, show relatively (compared to the much lower average concentration) large changes. These can be seen from the daily values for a year at each site in Figs 10 and 19. During the winter and spring at Barbados, variations with a period of 5–15 days are seen that are related to changes in air flow patterns. During high ozone episodes, air reaches Barbados from more northerly latitudes in the mid-troposphere, while during the low ozone events, air parcels remain at lower latitudes and altitudes. An example of this pattern is shown in Fig. 20. On 12 March (DOY 71) ozone values are relatively low (15 ppb) and trajectories remain well south of 30°N and at low altitudes (Fig. 20a). Ozone amounts gradually rise over the next 6 days, eventually reaching nearly 30 ppb. By 18 March (DOY 77), the air flow has shifted to the north and from mid-tropospheric levels (Fig. 20b). These changes of air flow also affect a number of other atmospheric constituents (Savoie *et al.*, 1992) during this time of the year. For example, low ozone amounts are associated with high particulate nitrate and high ^{210}Pb concentrations and vice versa. At Barbados, high nitrate and ^{210}Pb are closely related to transport from continents, primarily Africa (Savoie *et al.*, 1992). This indicates that the high ozone amounts at Barbados are generally associated with air from higher tropospheric levels with little signature of recent interaction with air from near land surface.

At Samoa, where the seasonal pattern is strikingly similar to that at Barbados, there are some significant differences in the day-to-day variability. While both locations (Fig. 10 and 19) show major events separated by about 5–15 days, at Samoa this pattern continues throughout the year, even during the seasonal minimum. At Barbados, on the other hand, such events are much reduced in amplitude during the summer minimum. This greater variability during the summer seasonal drawdown may occur because of the more frequent interruption of trade wind flow by air from the south and occasionally by air reaching Samoa from the Northern Hemisphere (NH) (Bortniak, 1981). These intrusions of NH air at Samoa are confined to the December–April period.

Only during late spring and summer at South Pole do marked day-to-day variations take place (Fig. 21). During this time of year, the general seasonal decline is punctuated with periods of higher concentration. This is also the season of high ^{7}Be concentrations (Feely *et al.*, 1988). This radionuclide has its origin in the lower stratosphere and upper troposphere. During the summer, the decreased thermal stability of the lower troposphere allows enhanced vertical mixing of air from higher levels in the troposphere (Feely *et al.*, 1988).

6. LONG-TERM VARIATIONS

Four of the sites (Barrow, AK; Mauna Loa, HI; American Samoa; and South Pole) have surface ozone records ranging from 16 to 20 years. As was discussed earlier, the surface record at Barrow (Fig. 22a) reflects the unique conditions in the boundary layer around the Arctic Ocean basin. During the spring, the surface is often decoupled from the overlying free troposphere. Long-term changes at the surface, therefore, may not reflect changes even in the rest of the lower troposphere. There has been a significant increase in ozone at the surface ($0.67 \pm 0.30\%$/yr). Because the increase has taken place during months of significant sunlight at Barrow (see Table 2 for seasonal trends), the question may be raised as to the possibility of enhanced photochemical ozone production. A known large source of ozone precursors, particularly of the

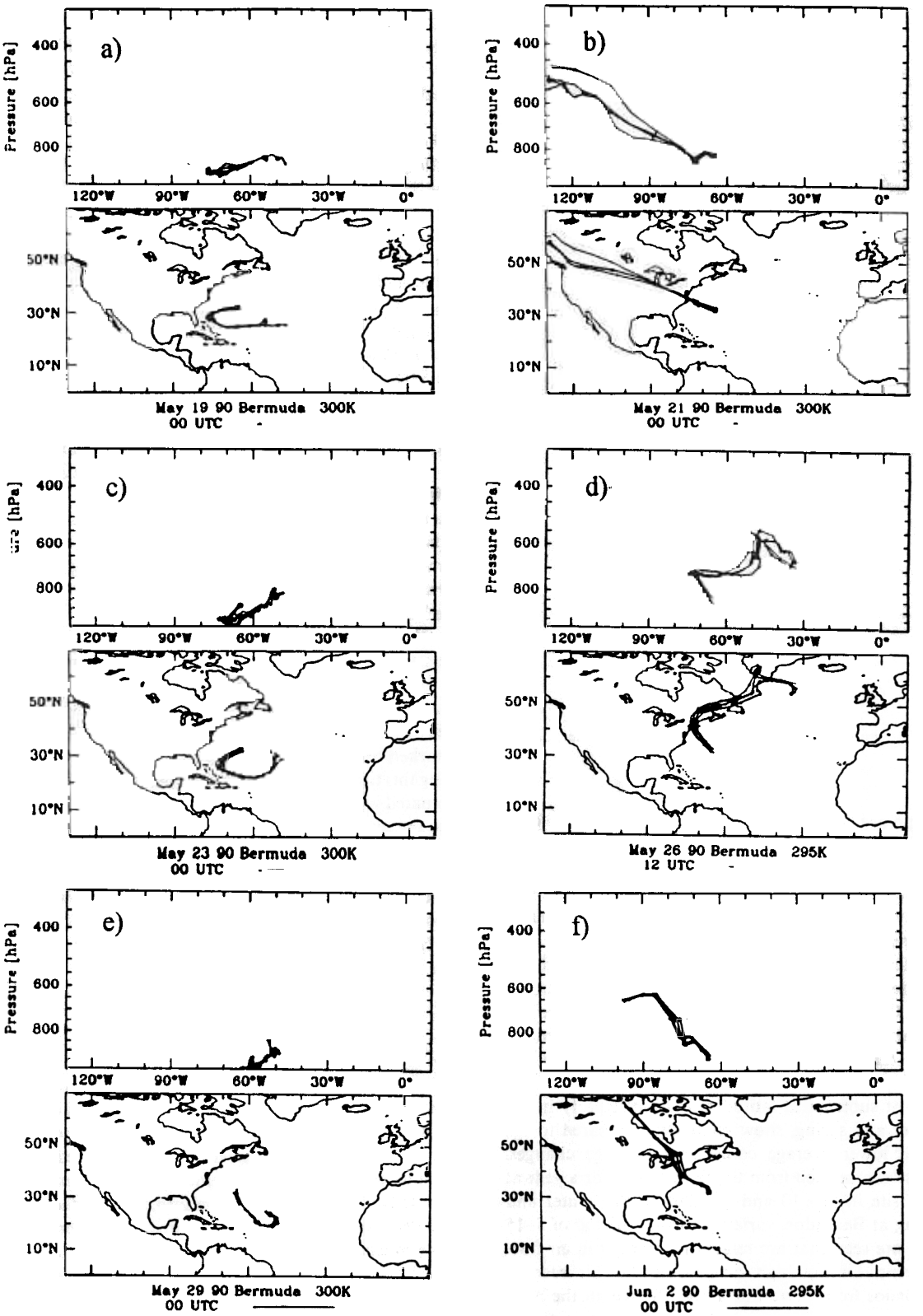

Fig. 17. Trajectories as in Fig. 14 for Bermuda.

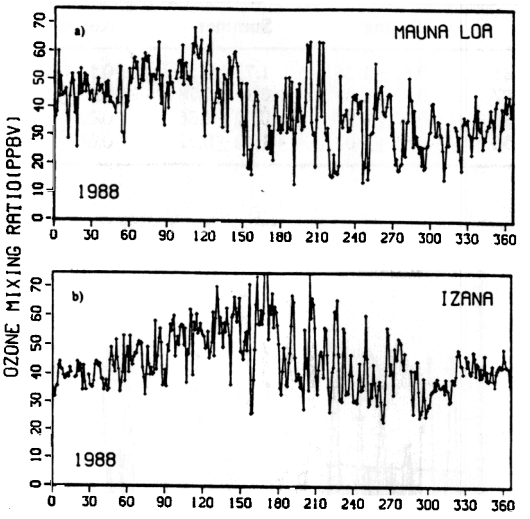

Fig. 18. Daily average ozone mixing ratios for 1988 at (a) Mauna Loa and (b) Izaña.

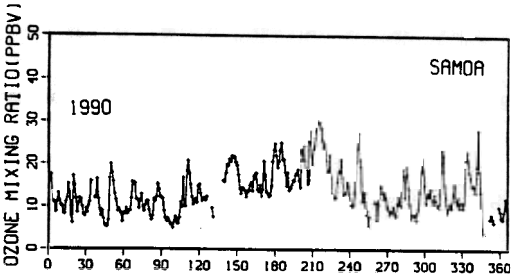

Fig. 19. Daily average ozone mixing ratios for 1990 at Samoa.

required nitrogen oxides (NO_x), is the petroleum extraction activities located on the North Slope of Alaska in the vicinity of Prudhoe Bay (Jaffe, 1991), located ~300 km to the east of Barrow. Limited summer NO and total reactive nitrogen (NO_y) measurements at Barrow (Honrath and Jaffe, 1990) give no clear indication of elevated concentrations. Transport from Prudhoe Bay during the measurement period was, however, seldom observed. If Prudhoe Bay is, in fact, the source of the rising concentrations of summertime ozone at Barrow, this increase should begin to decline as the petroleum extraction reaches peak production, then levels off, and begins to decline. In fact, this may have already occurred since the greatest increase took place between 1976 and the early 1980s. It is not clear from the ozone record (Fig. 22b) whether such a leveling off has begun in the ozone record, however.

During the nighttime, downslope wind regime at Mauna Loa, air generally representative of the free troposphere at the observatory level (~3 km) is sampled. Such a record should be representative of this region of the subtropical Pacific, where air parcels have a long fetch over the ocean before reaching the site. Based on 20 years of observations (10/73–9/92), there has been a small but statistically significant increase (Fig. 23) in ozone of $0.37 \pm 0.26\%$/yr measured at the site, where the 95% confidence interval is based on Students t-test. The bulk of the increase is during the winter and spring (see Table 2) and the largest increases are in January ($1.02 \pm 0.78\%$) and April ($0.74 \pm 0.99\%$/yr). The very high value for winter 1982–83 may reflect the strong ENSO event although anomalous flow patterns to Mauna Loa are not readily apparent (Harris and Kahl, 1990). Removal of this value has no impact on the trend calculation here, although earlier estimates of the trend based on data only through 1984 (Oltmans and Komhyr, 1986) were strongly influenced by the high values near the end of the record. This very clean site has not likely been affected by local or even regional changes. During the winter and spring, there are a significant number of cases where air reaching the observatory has passed

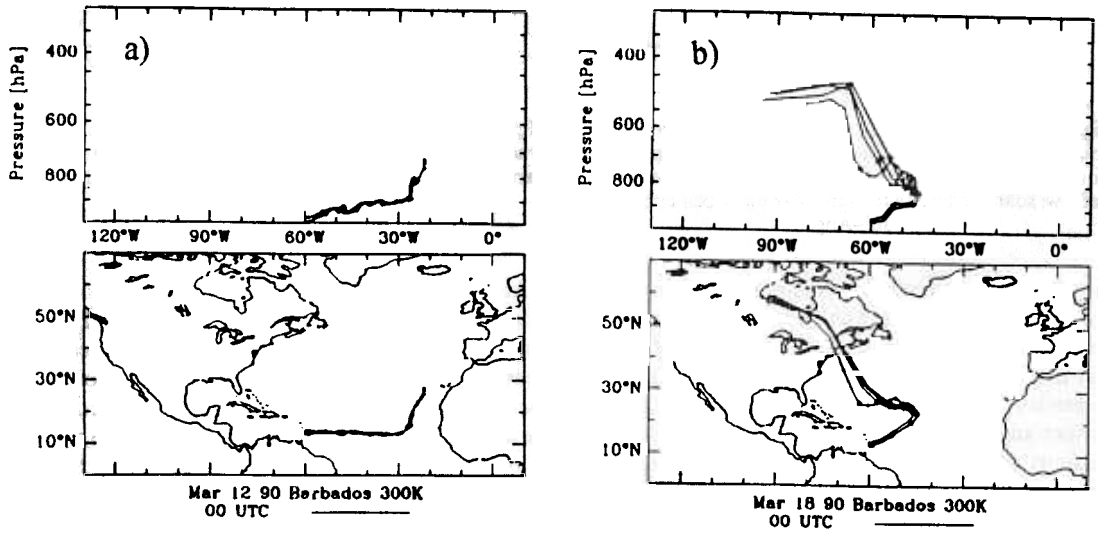

Fig. 20. Trajectories as in Fig. 14 for Barbados.

Table 2. Trends in deseasonalized surface ozone mixing ratio in percent per year. Ninety-five percent confidence interval is based on Student's t-test

Station	Period	Annual	Winter	Spring	Summer	Autumn
Barrow	3/73–2/92	0.67 ± 0.30	-0.07 ± 0.81		1.73 ± 0.58	0.50 ± 0.61
Mauna Loa	10/73–9/92	0.37 ± 0.26	0.56 ± 0.67		0.34 ± 0.78	0.04 ± 0.63
Samoa	1/76–12/91	0.03 ± 0.44	0.22 ± 0.86		-0.82 ± 1.36	0.22 ± 1.35
South Pole	1/75–2/92	-0.68 ± 0.23	-0.22 ± 0.56		-1.42 ± 0.72	-0.66 ± 0.73

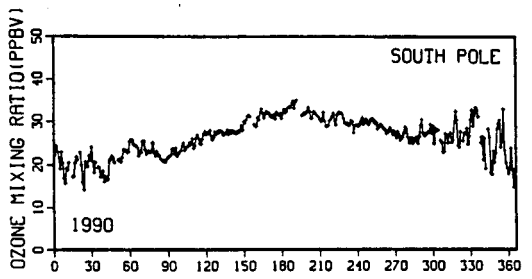

Fig. 21. Daily average ozone mixing ratios for South Pole.

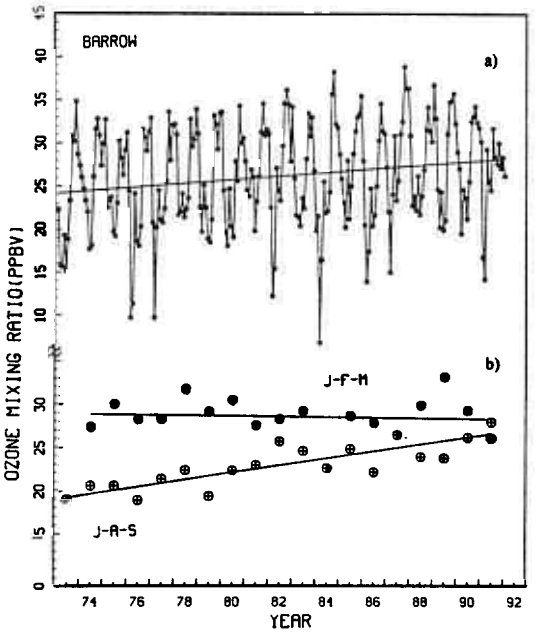

Fig. 22. (a) Monthly mean surface ozone at Barrow. The linear least squares fit is based on the monthly departures from the long-term monthly mean. (b) Seasonal trends for Barrow, solid circles are for Jan–Mar and open circles for Jul–Aug.

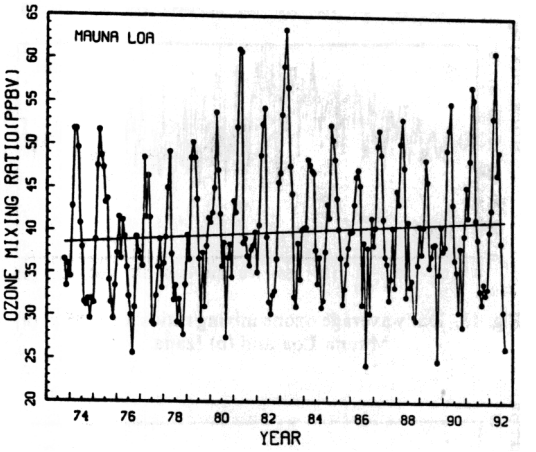

Fig. 23. Monthly mean downslope (00–08 LST) surface ozone at Mauna Loa with the linear trend.

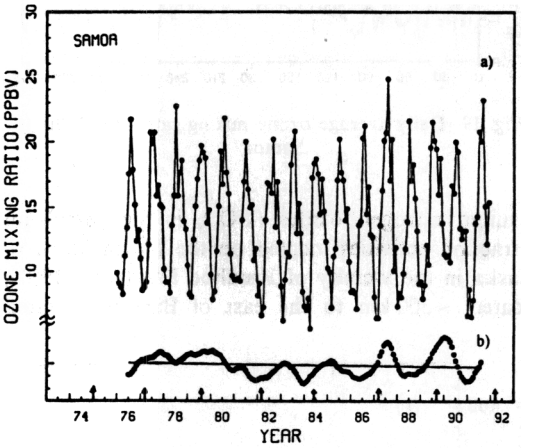

Fig. 24. (a) Monthly mean surface ozone at Samoa with the linear trend. (b) Smoothed monthly departures and arrows showing the time of the 30 mb east wind maximum at Singapore.

over the Asian continent or Japan within the past 10 days, although this is more common in the winter than the spring. To date it has not been possible to identify long-term changes in ozone with these trajectories originating over Asia. Given the relatively small ozone changes and the large variability in both ozone and transport, this approach is probably not sensitive enough to pinpoint causes of the long-term change.

At American Samoa (Fig. 24), there are no long-term trends in the overall record ($0.13 \pm 0.42\%$/yr). This site is probably one of the more isolated and clean locations in terms of effects from pollution source regions (Prospero and Savoie, 1989). Although the lifetime of ozone near the surface at this site should be quite short, based on the strong reverse diurnal variation and very low ozone amounts during the

seasonal minimum, there is a remarkable quasi-biennial variation that appears to be linked to the tropical stratospheric wind QBO. Figure 22b shows the smoothed ozone amounts resulting from applying an 11-point weighted filter to the monthly anomalies. The ~2 ppb amplitude of this variation represents about 15% of the mean and also about 15% of the average seasonal variation. Also shown with an arrow in Figure 24b are times of the maximum east wind at 30 mb over Singapore, which is often used as an index of the stratospheric wind QBO. The maximum in ozone generally follows the east wind maximum by several months, except during 1982–83 when the maximum in ozone appears to be delayed by about 6 months. This may be related to the effect of the very strong warm event of the ENSO that occurred during this time. It is not clear what property of the stratospheric wind QBO could influence the surface ozone distribution.

Ozone at the surface at South Pole has declined markedly since measurements began in 1975 (Fig. 25a). This decline ($-0.68\pm0.23\%$ yr^{-1}) is largest during the summer ($-1.42\pm0.72\%$ yr^{-1}), although all seasons show some decline. This summer decrease represents a 25% change over the 16 years of measurement. This decrease during the seasonal minimum (Fig. 25b) is coincident with the dramatic decline in stratospheric ozone during the spring over Antarctica (Schnell *et al.*, 1991). As mentioned earlier, the summer seasonal minimum at South Pole results from the transport of air with low ozone from the coast of Antarctica (Schnell *et al.*, 1991) during the summer ozone drawdown (Fig. 11; Ayers *et al.*, 1992). The dramatic decline in spring stratospheric ozone which

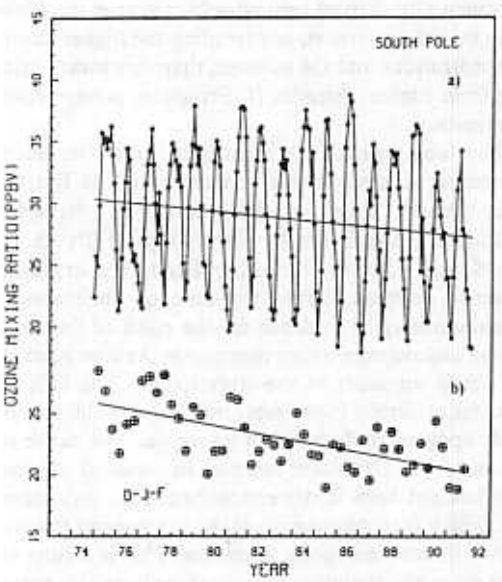

Fig. 25. (a) Monthly mean surface ozone at South Pole with the linear trend. (b) Summer monthly (D–J–F) means and trend.

persists well into the summer and extends beyond the periphery of the continent allows greater penetration of UV to the surface. Under the very low NO_x conditions prevailing in the region, this will lead to enhanced surface ozone loss (Schnell *et al.*, 1991). A second important factor leading to the decline appears to be enhanced transport from the coast of Antarctica to South Pole, which brings with it ozone depleted air. The primary evidence for such enhanced transport is an increase in cloudiness and subsequent decrease in solar radiation, both of which have been measured (Schnell *et al.*, 1991; Dutton *et al.*, 1991). It has been suggested that even this enhanced poleward transport is a consequence of the stratospheric ozone loss (Neff, 1992), through the overall change in atmospheric stability.

7. DISCUSSIONS AND CONCLUSIONS

From the pattern of the diurnal variation found here and in other studies (Johnson *et al.*, 1990; Oltmans and Levy, 1992; Ayers *et al.*, 1992), there is evidence that over almost all of the ocean in the SH and over much of the NH ocean, conditions with low NO_x concentrations prevail, and hence ozone production is weak. This is based on a diurnal cycle in which the highest ozone amounts are seen before sunrise and lowest values in the afternoon. This variation results from a series of reactions (see, e.g. Crutzen 1988; Levy II, 1971) where

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \quad (\lambda < 310\,\text{nm})$$

$$O(^1D) + H_2O \rightarrow 2\,OH.$$

The OH radicals can then react directly with ozone or with carbon monoxide and methane, when NO_x concentrations are low, to form peroxy radicals, which in turn can react with ozone, leading to further ozone destruction through

$$OH + O_3 \rightarrow HO_2 + O_2$$

$$HO_2 + O_3 \rightarrow OH + 2O_2.$$

At Samoa, Barbados, and Bermuda and Cape Grim during the summer, this reverse diurnal variation prevails. For high latitude sites such as Barrow and South Pole and probably Westman Islands in Iceland, there is no real sign of a diurnal variation reflecting the lack of daily varying solar insolation for all or much of the year, and probably the low NO_x concentrations as well.

For a continental site (Niwot Ridge) or one in near proximity to a major continent (Mace Head) clear evidence for strong photochemical ozone production is evident in the diurnal pattern on many days during the summer. This results in summer afternoon ozone concentrations that are the highest of the year at these sites.

The seasonal cycle at the surface in the SH also appears to reflect the important role of ozone destruction in a low NO_x regime. Although summer minima

prevail at all latitudes (Fig. 11), at the South Pole low ozone amounts are associated with transport of ozone-poor air from lower latitudes. Also in the NH, the winter maximum at Barbados and the spring maximum in Bermuda are both clearly linked to the transport from higher latitudes and altitudes of air with higher ozone concentration. At Barbados, the maximum is shifted to the winter. In the spring, the events represented by flow over the tropical Atlantic (Fig. 20a) show lower minima, and peak amounts also decline. In Iceland and Ireland, the spring maximum is not associated with the dramatic events seen at Bermuda but with a gradual increase through the winter, peaking in the spring. Summer and early autumn minima are the rule in the NH, as well as the SH, at most of the sites studied. Even at places such as Niwot Ridge and Mace Head, where there is a clear signature of enhanced photochemical production, this does not on the average counteract the influence of the general summer decline. This is in contrast to sites in Europe where the strong production often shifts the seasonal maximum into the summer (Lefohn *et al.*, 1992). At Mauna Loa, on the other hand, which is also a high altitude site, the seasonal maximum is distinctly in April (Fig. 9) and concentrations fall rapidly as summer approaches. The seasonal variation in transport as well as the seasonally varying source and sink strengths play a major role in determining the seasonal surface ozone variation. A study now in progress of the seasonal cycle throughout the troposphere will also help to better define the roles of these processes.

In addition to differences in the phasing of the seasonal ozone cycle between the NH and SH, there is a clear difference in the amount of ozone, with greater concentrations at a comparable latitude in the NH than in the SH (compare Figs 7 and 11). This result has been observed consistently in both surface (Winkler, 1988) and vertical profile measurements (Fishman *et al.*, 1979; Oltmans *et al.*, 1989). The source of this hemispheric differences is not clear. The NH, because of the greater degree of industrialization, has much larger sources of NO_x emissions, and there is a clear signature of enhanced photochemical ozone production at some of the sites investigated here. On the other hand, at Barbados, which has about 50% higher ozone concentrations than Samoa, which is at a similar latitude in the SH, the regular reverse diurnal cycle suggests very low NO_x concentrations. This short lifetime of ozone observed at the surface, which suggests no local or regional sources, does not preclude a source of photochemically produced ozone in the free troposphere (Fishman *et al.*, 1991). Satellite data (Fishman *et al.*, 1990) indicate that the tropical Atlantic troposphere contains more ozone than is seen over the tropical Pacific. At least a portion of this difference has been attributed to biomass burning, primarily in Africa (Fishman *et al.*, 1990, 1991). The seasonal pattern in the troposphere over Barbados, inferred from the satellite measurements, is markedly different from the surface variation, with the highest amounts occurring in the summer. This difference is apparent over Bermuda as well (Fishman *et al.*, 1990). This suggests differences between the free troposphere and boundary layer behavior, that detailed vertical profile measurements of ozone would be very valuable in sorting out. Other sites, such as Bermuda and Mauna Loa, can also be characterized as low NO_x regimes based on the ozone daily cycle and, in the case of Mauna Loa, extensive measurements of nitrogen species [see *Journal of Geophysical Research*, Vol. 97—dedicated issue on the Mauna Loa Observatory Photochemistry Experiment (MLOPEX)]. Measured NO_x concentrations at Bermuda, when air flow is from tropical or subtropical Atlantic, are $\sim$20 ppt, but are considerably higher ($\sim$250 ppt) when rapid flow brings air from North America (Dickerson *et al.*, 1993). If the measurements here can be taken as representative of large areas over the NH oceans, it appears that much of this region during much of the year exhibits little or no enhanced photochemical ozone production. This means that the larger ozone concentrations in the NH result from the enhanced production over and near polluted continental regions, possible *in situ* production in the free troposphere, or a significant difference in the flux from the stratosphere (Levy *et al.*, 1985). However, concentrations at an elevated continental site (Niwot Ridge) or an elevated island site, occasionally impacted by continental pollution (Izaña), are not significantly different during the time of the seasonal maximum than at the lower latitude, very clean site at Mauna Loa. At Izaña and Niwot Ridge, however, the summer decline is less rapid than at Mauna Loa. In the case of Niwot Ridge, this is clearly related to the availability of ozone precursors transported to the site in the orographic upslope flow and the availability of abundant solar isolation. At Izaña, on the other hand, the occasional transport of European air masses, high in ozone, and continentally derived emissions (Schmidt *et al.*, 1988) may be less important, in extending the higher ozone concentrations into the summer, than downward mixing from higher altitudes (J. Prospero, private communication).

The long-term ozone records at four sites show increasing summer ozone concentrations at Barrow that may be linked to the increase in petroleum extraction activities on the North Slope of Alaska. At the South Pole, on the other hand, the dramatic summer decrease during the time of the seasonal minimum may be evidence for the effect of the huge spring and summer ozone decrease in the stratosphere on ozone amounts in the troposphere. The lack of changes at Samoa is probably indicative of the lack of anthropogenic influence in this region. The cause of the small but significant increase in ozone at Mauna Loa has not been firmly established. This very clean site, which is representative of the subtropical Pacific, shows winter and spring increases. This is a time of year when the signature for transport from the Asian continent has been seen in atmospheric particles (As-

ian dust) (Bodhaine *et al.*, 1981) and other gases (Harris *et al.*, 1992).

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