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OZONE MEASUREMENTS FROM A GLOBAL NETWORK OF SURFACE SITES

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ABSTRACT

From a network of surface ozone monitoring sites distributed primarily over the Atlantic and Pacific Oceans, the seasonal, day-to-day, and diurnal patterns are delineated. At most of the NH (northern hemisphere) sites there is a spring maximum and late summer or autumn minimum. At Barrow, AK (70°N) and Barbados (14°N), however, there is a winter maximum, but the mechanisms producing the maximum are quite different. All the sites in the SH (southern hemisphere) show winter maxima and summer minima. At the subtropical and tropical sites there are large day-to-day variations that reflect the changes in flow patterns. Air of tropical origin has much lower ozone concentrations than air from higher latitudes. At the two tropical sites (Barbados and Samoa) there is a marked diurnal ozone variation with highest amounts in the early morning and lowest values in the afternoon.

At four of the locations (Barrow, AK; Mauna Loa, HI; American Samoa; and South Pole) there are 15- through 20-year records which allow us to look at longer term changes. At Barrow there has been a large summer increase over the 20 years of measurements. At South Pole, on the other hand, summer decreases have led to an overall decline in surface ozone amounts.

1. INTRODUCTION

As part of the Climate Monitoring and Diagnostics Laboratory, surface ozone measurements have been made for a number of years at four sites. Beginning in 1988 the number of sites has been expanded as part of the Atmosphere/Ocean Chemistry Experiment (AEROCE). Information on the location and period of data record is summarized in Table 1. In the discussion of the seasonal cycle, monthly mean data from three locations in the SH are taken from the literature to give better geographic coverage.

2. SEASONAL VARIATION

Figure 1 displays the monthly median ozone and its dispersion for eight sites spanning the latitude range 71°N-14°N. At all but the most northerly (Barrow) and southerly (Barbados) there is a spring maximum. At high arctic locations such as Barrow at the surface, the expected spring maximum is missing because of strong ozone depletion that is linked to the presence of high bromine concentrations. (Barrie et al., 1988, Oltmans, 1991). In fact immediately above the boundary layer, there is a spring maximum (Oltmans, 1991). At Barbados the maximum in early winter is a result of the cutoff of flow from northerly mid-latitudes that occurs much earlier in the year at low latitudes than it does at Bermuda for instance (Oltmans and Levy, 1992). Niwot Ridge, Mauna Loa, and Izana are all high altitude sites at elevations of ~3,000 m. Expectedly, these sites have the highest ozone concentrations.

The largest seasonal variation is at Bermuda. During the winter and especially in the spring, there are numerous events where transport from mid-tropospheric levels over North America reaches Bermuda (Oltmans and Levy, 1992). During these events, hourly average ozone mixing ratios fall in the 50-70 ppb range. During the summer, however, flow from more southerly latitudes dominates with concentrations of 15-25 ppb. At the higher altitude site of Izana near the same latitude, summer values do not dip nearly so low

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

Station	Elev.	Lat.	Long.	Period of Observ.
Barrow, AK	11m	71°N	157°W	3/73-2/92
Reykavik, Iceland	60m	64°N	22°W	9/91-5/92
Mace Head, Ireland	30m	53°N	10°W	7/89-4/92
Niwot Ridge, CO	3000m	40°N	106°W	7/90-5/92
Bermuda	40m	32°N	64°W	10/88-5/92
Izana, Canary Is.	2360m	28°N	16°W	5/87-10/89
Mauna Loa, HI	3397m	20°N	156°W	10/73-3/92
Barbados	45m	13°N	59°W	4/89-5/92
Samoa	82m	14°S	171°W	1/76-12/91
Cape Point, S. Africa	75m	34°S	18°E	1/83-6/88
Cape Grim, Australia	94m	41°S	145°E	1/82-12/86
Syowa, Antarctica	21m	69°S	40°E	2/89-1/90
So. Pole, Antarctica	2835m	90°S	--	1/75-2/92

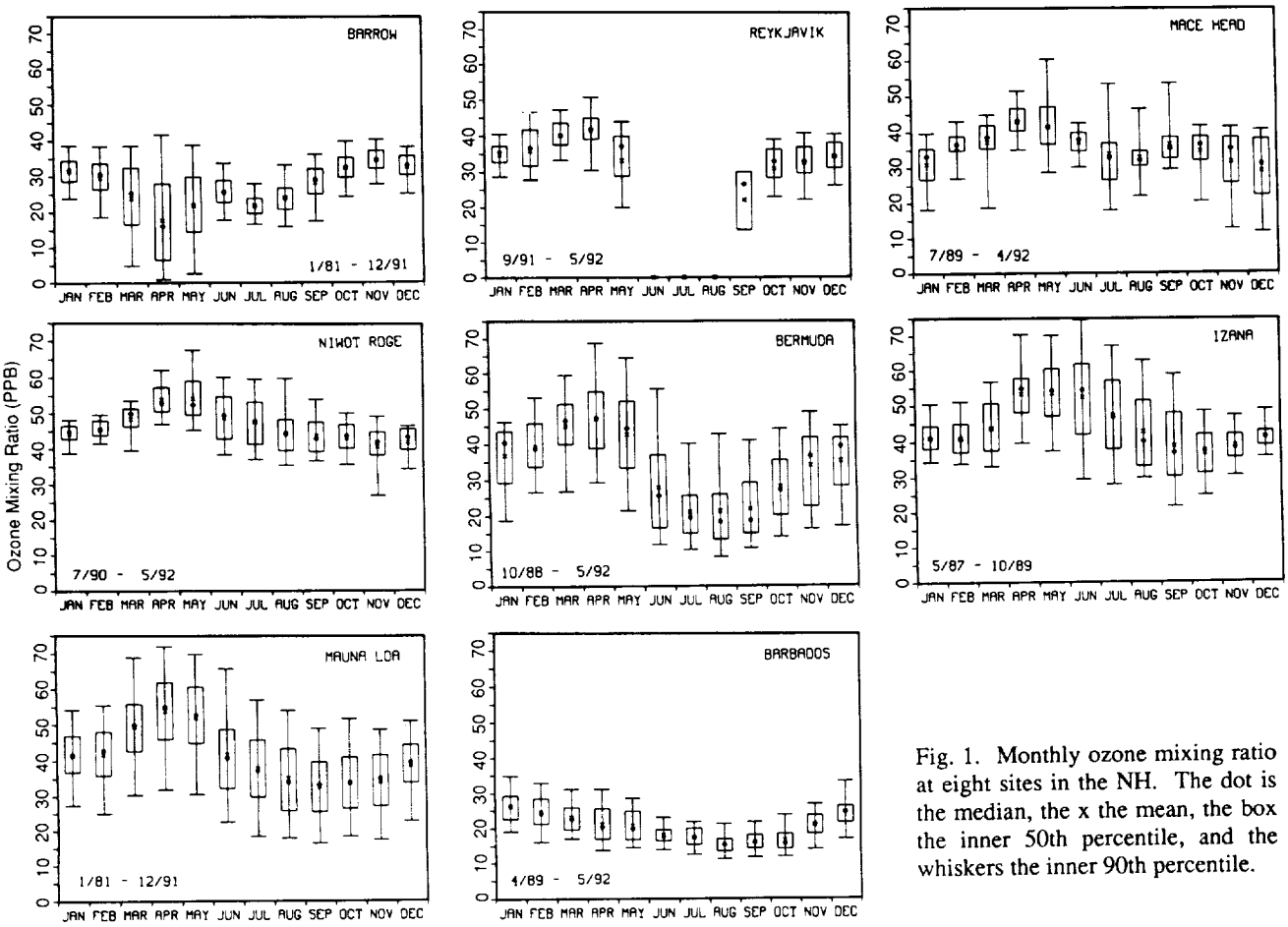

Fig. 1. Monthly ozone mixing ratio at eight sites in the NH. The dot is the median, the x the mean, the box the inner 50th percentile, and the whiskers the inner 90th percentile.

indicating much of the loss may result from ozone destruction in the boundary layer (Oltmans and Levy, 1992).

At Izana, unlike Mauna Loa, the spring maximum extends well into the summer. This difference results from transport from continental Europe to Izana (Schmitt et al., 1988). Generally the more southerly sites in the NH have larger seasonal variations. This is because the subtropical sites in particular are influenced in the winter and spring by flow from more northerly latitudes while during the summer are under the influence of more tropical flow with correspondingly lower ozone (see data for Barbados).

In the SH (Figure 2) there is a clear winter maximum and summer minimum at all locations from 14°S-90°S. At Cape Grim the maximum extends into early spring. There is a relatively smooth gradient from lower to higher values going from tropical to polar latitudes. South Pole is at an altitude of ~2800 m so cannot be compared directly with the other sites which are at sea level. Comparison of sites in the SH with locations at similar latitudes and altitudes in the NH shows higher concentrations in the NH (Fishman et al., 1979, Oltmans et al., 1989).

The phasing of the seasonal cycle is also different in the two hemispheres with the exception of Samoa and Barbados where the two stations are exactly six months out of phase with both having winter maxima and summer minima. This seems to be at least partially related to the strong photochemical ozone destruction in the boundary layer in the tropics, with the greater ozone destruction during times of greatest solar UV input.

3. DIURNAL VARIATION

In some cases the character of the diurnal variation is useful in determining to what extent the site experiences photochemical production or destruction during the day. At two of the high altitude sites (Mauna Loa and Izana) the mountain wind regime gives highest ozone amounts at night associated with downslope flow. At Mace Head and Niwot Ridge there is often a strong diurnal variation during the summer with the largest values of the year seen during the daylight hours. Such events are typical of conditions with ozone production from anthropogenic precursor emissions. At Barbados and Samoa, on the other hand, there is a very regular diurnal variation at all times of the year with a maximum early in the morning and minimum in the afternoon. This is consistent with a low nitrogen oxides regime in which ozone is destroyed during the day (Oltmans, 1981; Oltmans and Levy, 1992). At Bermuda the pattern

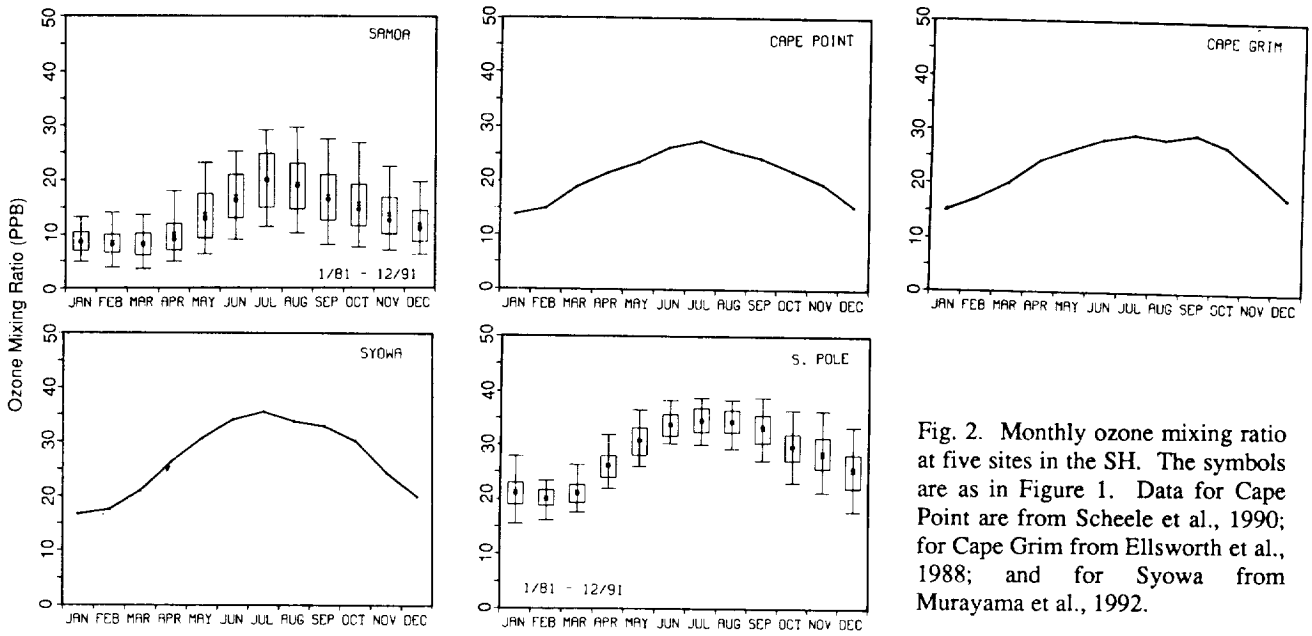

Fig. 2. Monthly ozone mixing ratio at five sites in the SH. The symbols are as in Figure 1. Data for Cape Point are from Scheele et al., 1990; for Cape Grim from Ellsworth et al., 1988; and for Syowa from Murayama et al., 1992.

appears to be similar but the much larger day-to-day variability makes the result less definitive. At Barrow and South Pole there is no discernable diurnal variation.

4. LONG-TERM VARIATIONS

At Barrow (Figure 3a) there has been a significant overall increase in surface ozone that has been driven primarily by the large (1.73±0.58%/yr) summer (JUL-AUG-SEP) increases. By contrast there has been little change during the winter. Smaller, statistically non-significant increases are seen in spring and autumn (Table 2). The observed increases are consistent with the increase in petroleum extraction activities on Alaska's North Slope (Jaffe, 1991).

At Mauna Loa (Figure 3b) there has been a small but marginally significant increase over the nearly 20 years of measurement. No individual season shows a statistically significant increase but during the half-year from DEC-MAY the increase is 0.58±78%/yr. In recent years (beginning in 1984) the overall increase has been small (0.10±0.71%/yr) but the spring increase has continued (1.15±2.42%/yr) though over this short period the increase is not statistically significant. The Mauna Loa trend prior to 1984 was influenced strongly by the anomalously high winter and spring values during the 1982-83 ENSO event but the 20-year trend computed when omitting this period is little affected except to decrease the variance. Since spring is the seasonal maximum, the increases may be linked to processes responsible for this peak.

There is no overall long-term trend at Samoa (Figure 3c). The summer decrease is fairly large (-0.82 ±1.36%/yr) but not statistically significant. The smoothed monthly anomalies at Samoa (Figure 3d) show a nearly 2-year fluctuation with a peak-to-peak amplitude of ~2 ppb which is about 15% of the mean value and about 15% of the average seasonal variation. The maximum in surface ozone follows the maximum in the stratospheric east wind component (largest negative zonal wind) at 30 mb over Singapore by approximately 6 months. For the six QBO cycles covered, this relationship fails only during 1982-83 when the maximum in surface ozone is delayed about 6 months. This may be related to the effect of the very strong warm event of the ENSO that occurred during this time.

South Pole surface ozone amounts have declined significantly during the 16 years of observations. The drop

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	0.85±1.26	1.73±0.58	0.50±0.61
Mauna Loa	10/73-3/92	0.37±0.26	0.56±0.67	0.49±0.98	0.28±0.88	0.04±0.63
Samoa	1/76-12/91	0.03±0.44	0.22±0.86	0.00±0.94	-0.82±1.36	0.22±1.35
So. Pole	1/75-2/92	-0.68±0.23	-0.22±0.56	-0.66±1.03	-1.42±0.72	-0.66±0.73

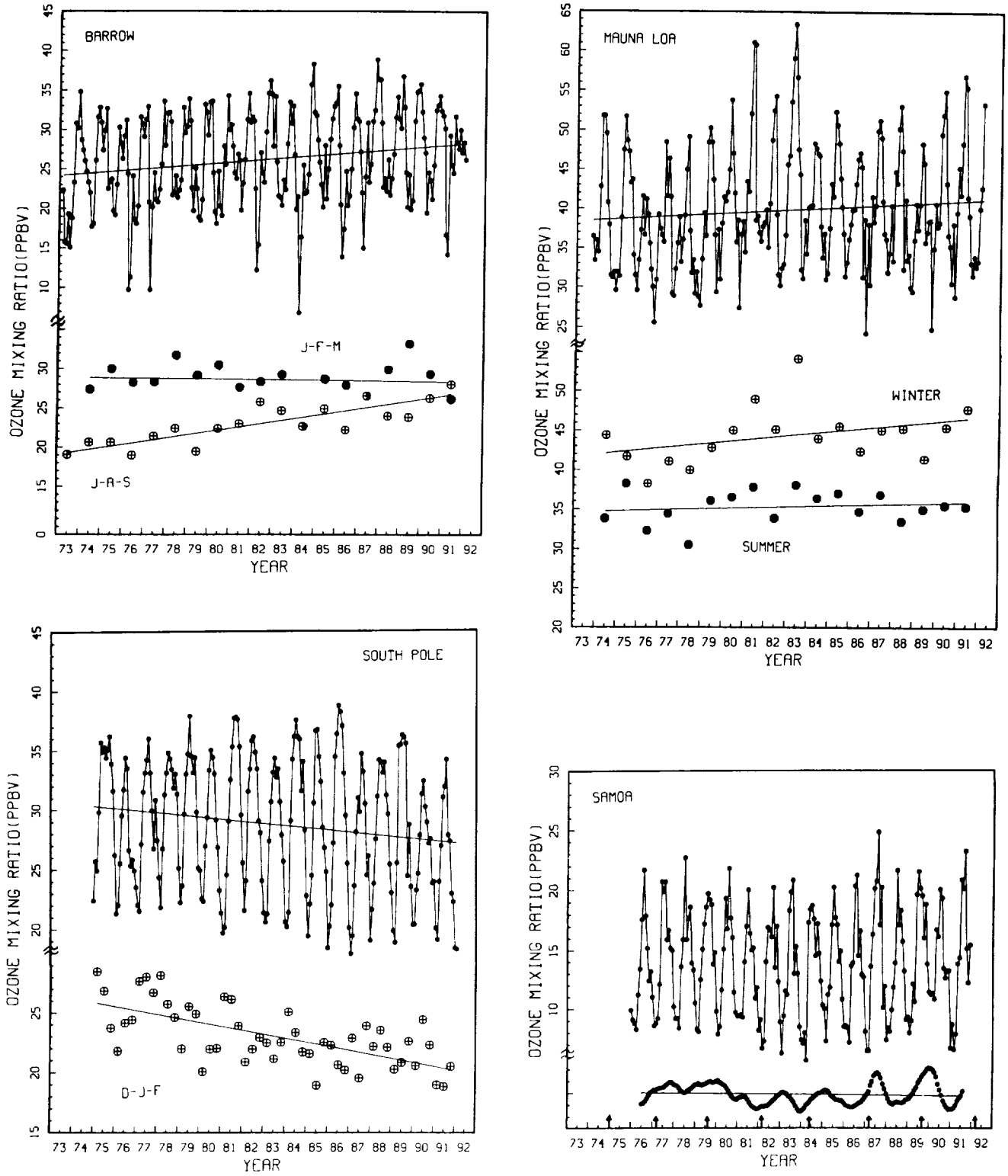

Figure 3. Monthly surface ozone mixing ratios with linear least squares trend derived from monthly anomalies. For Barrow, Mauna Loa, and South Pole various seasonal values and trends are shown. For Samoa the smoothed monthly anomalies are shown with the time of the Singapore 30 mb east wind maximum marked with an arrow.

has been very significant during the summer (Figure 3d, Table 2) with each of the months (DEC-JAN-FEB) showing significant declines (-1.44, -1.45, -1.32%/yr). This represents a nearly 25% decrease for this season over the measurement period. Two processes seem to be at work producing this decline (Schnell et al., 1991). The decline in stratospheric ozone in the spring which persists well into the summer allows for greater penetration of UV to the surface leading to enhanced surface ozone loss for the very low $NO_x(NO+NO_2)$ conditions prevailing in this region. Secondly, enhanced transport from the coast of Antarctica increases the number of events of lower ozone that reach South Pole (Schnell et al., 1991).

The trend results from this network can be compared with some of the long-term results reported from Europe (Low et al., 1992). In particular the results from the high altitude site at the Zugspitze can be compared with those at Mauna Loa. The increase is much larger over Europe, and at both sites there has been some moderation of the rise after about 1983.

5. CONCLUSIONS

All of the surface ozone records presented here show strong seasonal variations. In the NH, for a variety of locations, spring maxima and autumn minima prevail. The largest seasonal variation is in the subtropics. In the SH there is a consistent winter maximum and summer minimum at all latitudes. Surface ozone mixing ratios in the NH are consistently higher than for the corresponding latitude in the SH.

At tropical latitudes of both hemispheres there is a regular diurnal variation with highest amounts early in the morning and minima in the afternoon. This is consistent with a low NO_x regime and ozone photochemical loss during daylight hours.

In the polar regions, there have been large summer increases at Barrow while at South Pole summer ozone amounts have declined by nearly 25% over the 17-year measurement period. A smaller but significant increase at Mauna Loa, a location generally representative of lower free tropospheric air in the region, has occurred primarily in the spring during the time of the annual maximum. At Samoa there is a small but detectable quasi-biennial variation which is closely related to the stratospheric wind QBO.

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