Ozone in the Marine Boundary Layer Over the Pacific and Indian Oceans: Latitudinal Gradients and Diurnal Cycles

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Ozone concentrations in the atmospheric boundary layer of the Pacific and Indian Oceans were measured on four separate oceanographic research cruises (July 1986, May to August 1987, April to May 1988). These measurements show a distinct zone of near zero (≤ 3 ppb) ozone concentration in the central equatorial Pacific in April-May, with ozone increasing in this region over the next 4 months. The seasonal observed change in the latitudinal gradient of ozone is consistent with previous ozone measurements at Hilo and Samoa by *Oltmans and Komhyr* [1986] and predictions from an atmospheric general circulation model study [*Levy et al.*, 1985]. A significant diurnal cycle of ozone was found in almost all locations with a maximum near sunrise, a minimum in the late afternoon, and a peak-to-peak amplitude of 1 to 2 ppb (10–20%), similar to that predicted by a photochemical model in the low NO_x limit [*Thompson and Lenschow*, 1984].

INTRODUCTION

Ozone is one of the most important trace species in the troposphere. The photolysis of ozone produces OH radicals which oxidize most biogenic and anthropogenic reduced gases. Perturbations in ozone concentration can change the atmospheric distribution of the OH radical [*Liu et al.*, 1980] which can cause further changes in the atmospheric distributions of oxidizable trace species such as CH_4, CO, CH_3Cl, $(CH_3)_2S$ (DMS) and hydrocarbons. All of these perturbations have the potential of altering the Earth's climate. Ozone can also directly affect climate through the absorption of infrared radiation [*Fishman et al.*, 1979].

Increasing tropospheric ozone concentrations, likely due to anthropogenic influences, have been observed in the northern hemisphere in recent times. *Logan* [1985] suggested that ozone concentrations have increased 20 to 100% over the last 40 years at land sites in rural North America and Europe. *Angell and Korshover* [1983], using ozonesonde data, reported increases of middle troposphere ozone concentrations of 1% per year between 1970 and 1981. *Oltmans and Komhyr* [1986] reported increases of ozone concentrations of 1.4% per year over the period 1973 to 1984 at Mauna Loa, Hawaii, a site in the free troposphere above the boundary layer. These recently measured concentration increases emphasize the need to understand the behavior of ozone in all regions of the atmosphere.

The marine boundary layer is an important region of atmospheric photochemical reactions. The ocean is a source of a number of photochemically active gases such as CH_4, light

hydrocarbons, DMS, NO, methyl halides, and CO. The ocean is a sink for other gases produced photochemically in the atmosphere such as SO_2, HNO_3, H_2O_2, and H_2CO. All of these gases are climatically important species and must pass through the marine boundary layer as they enter or exit the sea surface.

We present here measurements of ozone concentrations in the marine boundary layer from oceanographic research ships on four separate cruises between 1986 and 1988 over the Pacific and Indian oceans as part of the NOAA Radiatively Important Trace Species (RITS) program and as part of the joint Soviet American Gases and Aerosols (SAGA) experiment.

MEASUREMENTS

The 1986 cruise, RITS 86, occurred on the NOAA ship *Oceanographer* between June 30 and July 23, from Honolulu Hawaii, to Kodiak Alaska. The first 1987 cruise, SAGA 87, occurred on the Soviet research ship *Akademik Korolev* between May 1 and July 6, from Hilo, Hawaii, to Kamchatka, Wellington, New Zealand, 90°E 30°S in the Indian Ocean, and Singapore. The second 1987 cruise, RITS 87, occurred on the *Oceanographer* between July 13 and August 20 from Townsville, Australia, to Dutch Harbor, Alaska. The 1988 cruise, RITS 88, occurred on the *Oceanographer* from April 5 to May 5 between Dutch Harbor, Alaska, and Pago Pago, Samoa. The portions of the cruise tracks where ozone data were collected are shown in Figure 1.

On each cruise a Dasibi model 1003-AH ultraviolet photometer was used to measure ozone. The three RITS cruises on the *Oceanographer* used Dasibi photometers maintained by NOAA-GMCC which had been calibrated relative to an NBS standard ultraviolet ozone photometer. Over the 0 to 50 ppb (parts per billion by volume) range of interest, the uncertainty in the calibration of each Dasibi photometer was approximately ±3 ppb [*Oltmans*, 1981; *Oltmans and Komhyr*, 1986]. During each of the RITS cruises, at intervals of 1 to 4 days a charcoal filter was placed in the sampling line for 1 hour to determine a zero, which was subtracted from the ozone signal.

During the RITS 86 cruise the ozone photometer was located in the ship's aft laboratory and a 90-m-long 1/4" ID Teflon sample line was used to draw air samples from an inlet at the

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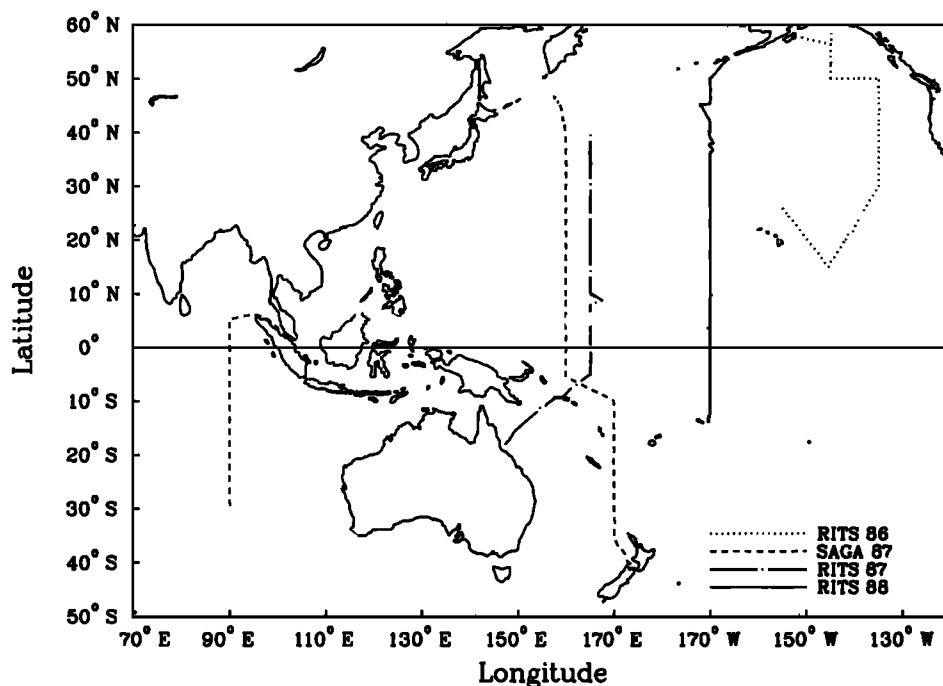
Fig. 1. Cruise tracks along which ozone data were collected on RITS cruises on the NOAA ship *Oceanographer*, and on the SAGA cruise on the R/V *Academik Korolev*. Only the segments of the cruise tracks are shown where ozone data are displayed in Figure 2.

bow of the ship. On the RITS 87 cruise the Dasibi photometer was mounted on the upper deck, just behind the navigational bridge, with a 10–15 m long 1/8" ID Teflon sample line which had an inlet just above and forward of the ship's bridge. During the RITS 88 cruise the Dasibi photometer was located in a van mounted directly on the flying bridge, with a 5-m-long 1/8" ID Teflon sample line which had an inlet directly forward and above the navigational bridge. On this cruise a chemiluminescent ozone detector (Monitor Labs) was also placed in the van and used the same sampling line as the Dasibi photometer.

Our experience has shown that the loss of ozone in a Teflon sample line is approximately 5% per 30 m, implying that the losses were close to negligible (<3%) on the RITS 87 and RITS 88 cruises, but may have been ≈15% on the RITS 86 cruise. There were also sample artifacts due to pressure drops in the sampling line. The Dasibi photometers that were used did not correct for the absolute pressure in the measurement cell. On the RITS 86 cruise the pressure loss in the 90 m sample line was 5% of atmospheric. On the RITS 87 and 88 cruises the pressure losses were 2 to 3%. The RITS 86 data has been corrected by dividing by 0.8 to correct for a 15% sample line loss and a 5% pressure loss. The RITS 87 and 88 data have not been corrected as the total losses were likely less than 6%.

The SAGA 87 cruise used a 15-m-long, 3-cm ID, PVC sample line in which air was drawn from the top of a forward mast into a stainless steel sampling plenum at 200 L/min, resulting in a 3-s residence time in the line, and a similar period in the plenum. A 1-m-long, 1/8" ID Teflon line was used to draw sample air into a Dasibi 1003-AH photometer maintained by Washington State University. This Dasibi was calibrated against another Dasibi that is used as the WSU laboratory standard. The WSU laboratory standard Dasibi was found to have an accuracy of 1% during an EPA audit in 1986.

Because of the PVC and stainless steel surfaces in the sampling stream, surface losses were suspected and were tested at the beginning and end of the cruise. These tests were conducted during wind conditions when clean air was clearly located at the window of the laboratory in which the Dasibi photometer was located. Ozone was measured with a short (several meters) Teflon line going directly from just outside the laboratory to the Dasibi. This measurement was compared to the ozone concentration in air drawn through the long sampling line. The absolute difference was not consistent, but the percentage difference (19%) was within 1% each time, even though the ambient concentrations differed by a factor of 4.5. The ozone data from the SAGA 87 cruise have been corrected by multiplying by 1.19.

DATA ANALYSIS

The Dasibi photometers operate on a 10- to 24-s cycle time with a new value produced during each cycle. On each cruise the analog signal from the Dasibi photometer was digitized and recorded with a microcomputer system and 1-min averages of the raw signal were stored in digital form. The 1-min averages of the ozone data were further averaged into 6-min averages. One minute averages of condensation nuclei (CN) concentrations and wind speed and direction relative to the ship, were also recorded in digital form. During periods of high CN counts, very low relative wind speed or relative wind angles behind the beam of the ship, the ozone 6-min averages were examined by eye for spurious departures which were deleted. The deleted data for each cruise were always less than 10% of the total. The remaining data were then aggregated into 1-hour averages. The hourly averages for each cruise were then placed into 1° latitude bins. Median values for each bin are shown in Figures 2a–e, with the north-south sections from the SAGA 87 cruise in the Pacific Ocean and the Indian Ocean separated into two latitude series. The position of the ITCZ as
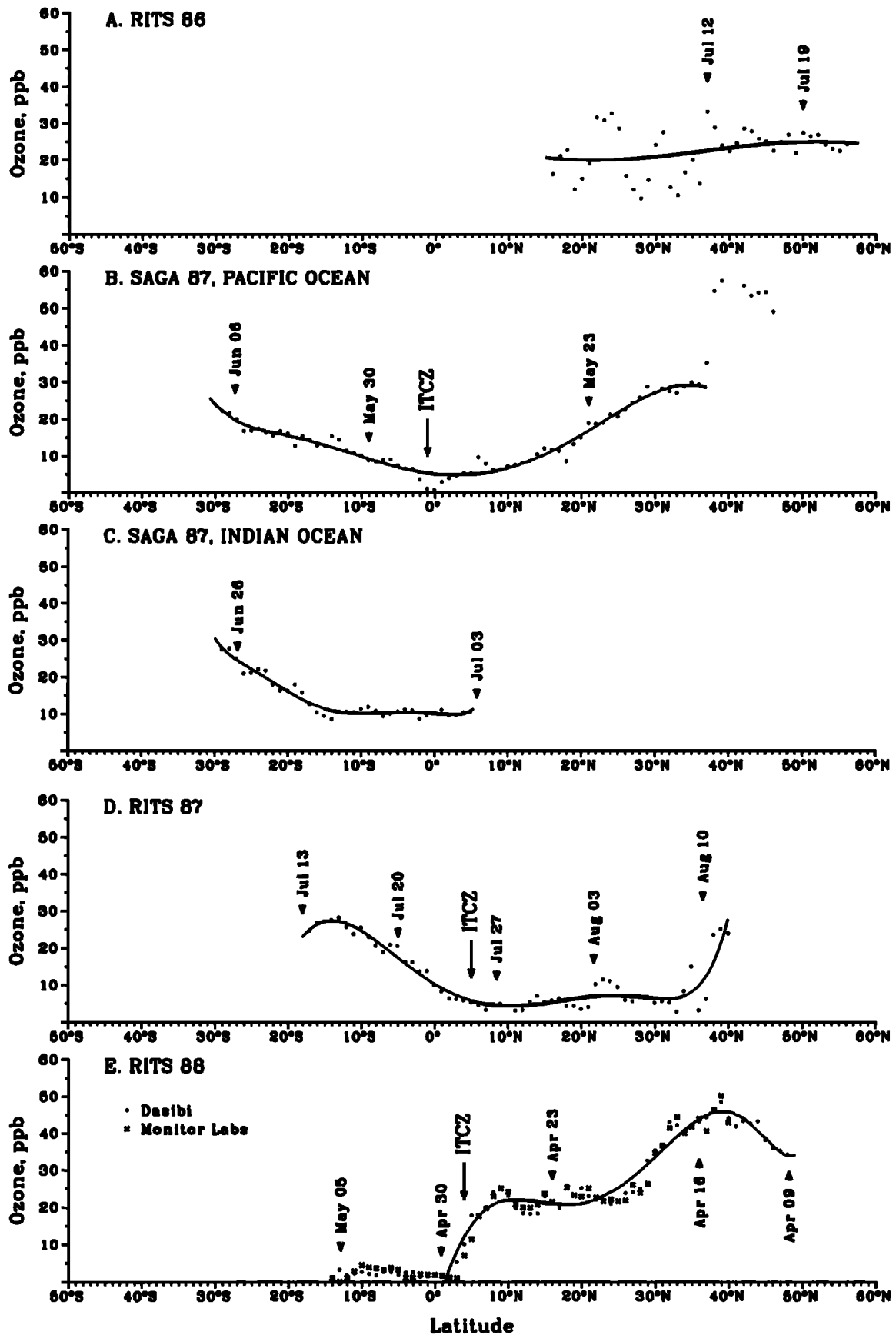
Fig. 2. Latitude profiles of the ozone concentration data in parts per billion by volume as measured by the Dasibi ozone photometers. The points represent the median value in 1° wide latitude bins of the hourly mean points, the smooth lines are from ninth-order polynomial least squares fits. Negative latitude indicates degrees south. The position of the ITCZ is shown for the SAGA 87 Pacific Ocean, RITS 87, and RITS 88 cruises. Ozone measurements from RITS 88 with a chemiluminescent ozone detector (Monitor Labs) are also shown.

determined by concurrent measurements of atmospheric CO_2, CO and CH_4 (K. Kelly, private communication, 1989) is shown for the SAGA 87 Pacific Ocean, RITS 87, and RITS 88 cruises.

The RITS 86 cruise is the only one that did not extend across the equator, and the latitudinal gradient of ozone was the weakest of all the data sets.

The SAGA 87 data record did not include the initial Hilo to Kamchatka leg, so the data record started on May 15. This section was relatively close to Asia, and the unusually high ozone values ($\approx$60 ppb) from 50°N to 40°N, were observed to be coincident with elevated carbon monoxide and particulate soot levels. Back trajectory analysis (J. Harris, private communication, 1989) of the surface wind field has shown that a likely origin of this air mass was a massive forest fire in northeastern China which burned for 25 days and consumed 1 million hectares. It is likely that the NO_x level in the smoke plume was elevated as well; the several-day transport time of the air mass to the ship off the Asian coast could have allowed photochemical production of the high ozone levels observed. Ozone decreased to near zero ($\leq$3 ppb) between 0 and 1°N latitude, approximately 1° north of the ITCZ. South of the equator, the ozone slowly increased to levels around 25 ppb near New Zealand (31°S).

The ozone data for the marine boundary layer over the Indian Ocean from the New Zealand to Singapore leg of the SAGA 87 cruise are shown in Figure 2c. Ozone decreased from 25 to 10 ppb between 2°S and 15°S along 90°E. The equatorial minimum in the Indian ocean (90°E) was broader and not so deep (10 ppb) as that observed in the Pacific Ocean (170°E) the previous month ($\leq$3 ppb).

The following month (August), the RITS 87 cruise occurred in the Pacific on the 170°E meridian. On this cruise there was also no minimum observed at the equator, however, there was a region of low ozone (5–15 ppb) that extended from the equator to 35°N. The sudden increase at 35°N was coincident

with a wind shift with easterly trade winds to the south and westerlies to the north. Although the cruise extended further north, the Dasibi photometer malfunctioned, and the reliable data record ends at 40°N.

The RITS 88 cruise, Figure 2e, occurred in April and had very high ozone concentrations between 35 and 45°N, and a very sharp gradient between 3° and 4°N where ozone went from 20 ppb to near zero ($\leq$3 ppb). Concurrent measurements of CO showed that this strong gradient coincided with the position of the ITCZ (K. Kelly, personal communication, 1989). South of the ITCZ to about 11°S, the ozone concentration remained within several ppb of zero. The chemiluminescent instrument that was used on this cruise had not been calibrated for several years and was found to be a near constant 30% higher than the Dasibi record. The entire chemiluminescent data was then reduced by this ratio and plotted in Figure 2e, where it is seen to agree very well with the Dasibi record.

In almost all ozone data from the tropics (except in regions of near zero ozone), a diurnal cycle was immediately observable by eye. For example, Figure 3 is a 4.5-day section from the ozone time series during the RITS 87 cruise, presented with a concurrent record of sunlight as measured by an Epply radiometer. It is very clear that ozone decreases during daylight hours, with subsequent restoration during the night.

To isolate the diurnal variation from the latitudinal variation we assume that for each cruise the ozone concentration, $C(\theta,t)$, was a function of latitude, θ, and local time-of-day, t. Local time in hours is related to universal time T, by $t = \lambda/15 + T$, where λ is longitude in degrees. All other observed variability in ozone is then assigned to a noise term, C_n. The concentration of ozone for each cruise can therefore be written as

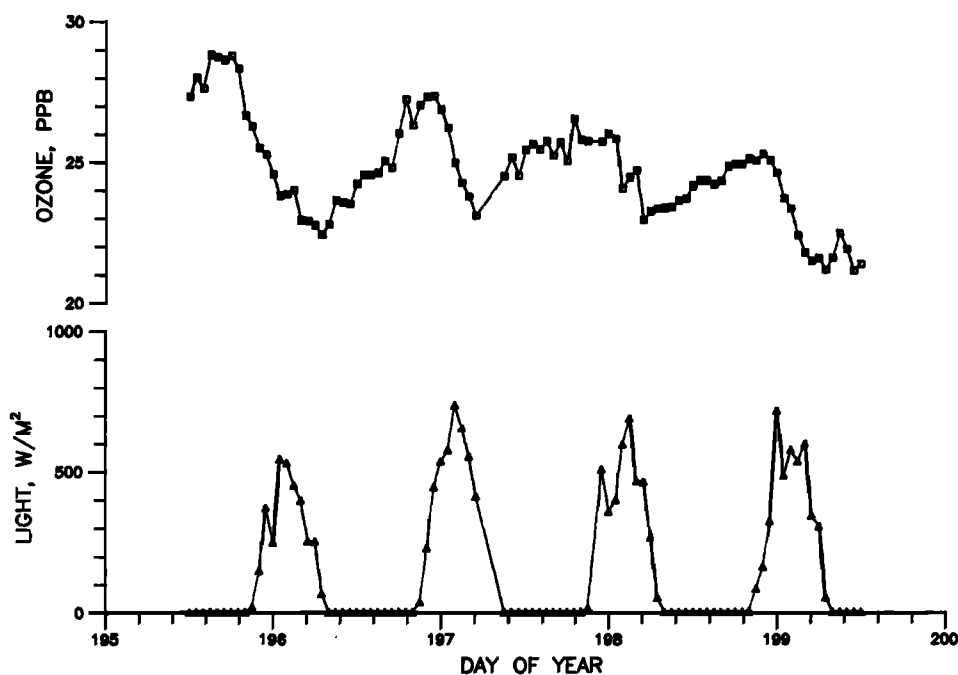$$C(\theta,t) = C_o(\theta) + C_d(t) + C_n(\theta,t)$$

Fig. 3. A 4-day time series of ozone concentration taken on days 1 to 5 of the RITS 87 cruise (July 14 to 18). The solar radiation as measured by an Epply radiometer is also shown. The diurnal cycle in ozone is clearly evident.

The latitudinal variation C_0 was estimated by first computing the median of the data in 1° latitudinal bins in order to reduce the time variations. A low-order power series (nine terms) was then fitted by damped least squares to these binned values in order to determine a smooth representation of ozone concentration in the latitude domain for each cruise. (The polynomial fits were not made to the SAGA 87 data north of 37°N or to the RITS 88 data south of 1°N due to numerical difficulties with the abrupt concentration changes.) These smooth functions in latitude are shown in Figure 2 and compare well with the observed latitude averages.

For each time series, the latitudinal trend and the mean were removed by subtracting from each hourly point the ozone predicted by the latitude function. Line spectra (periodograms) of these corrected time series for each cruise are shown in Figure 4. In three of these line spectra (SAGA 87 Indian Ocean, RITS 87, and RITS 88) the diurnal frequency of 1 cpd (cycle per day) is at least twice the height of the background, which satisfies the test for significance at the 95% level.

The low-frequency variations, due to the synoptic scale weather, and the frequencies greater than 3.5 cpd were removed by filtering the corrected time series. The corrected and filtered time series were then converted to local time. The diurnal variations, grouped by 20° latitude bins, were
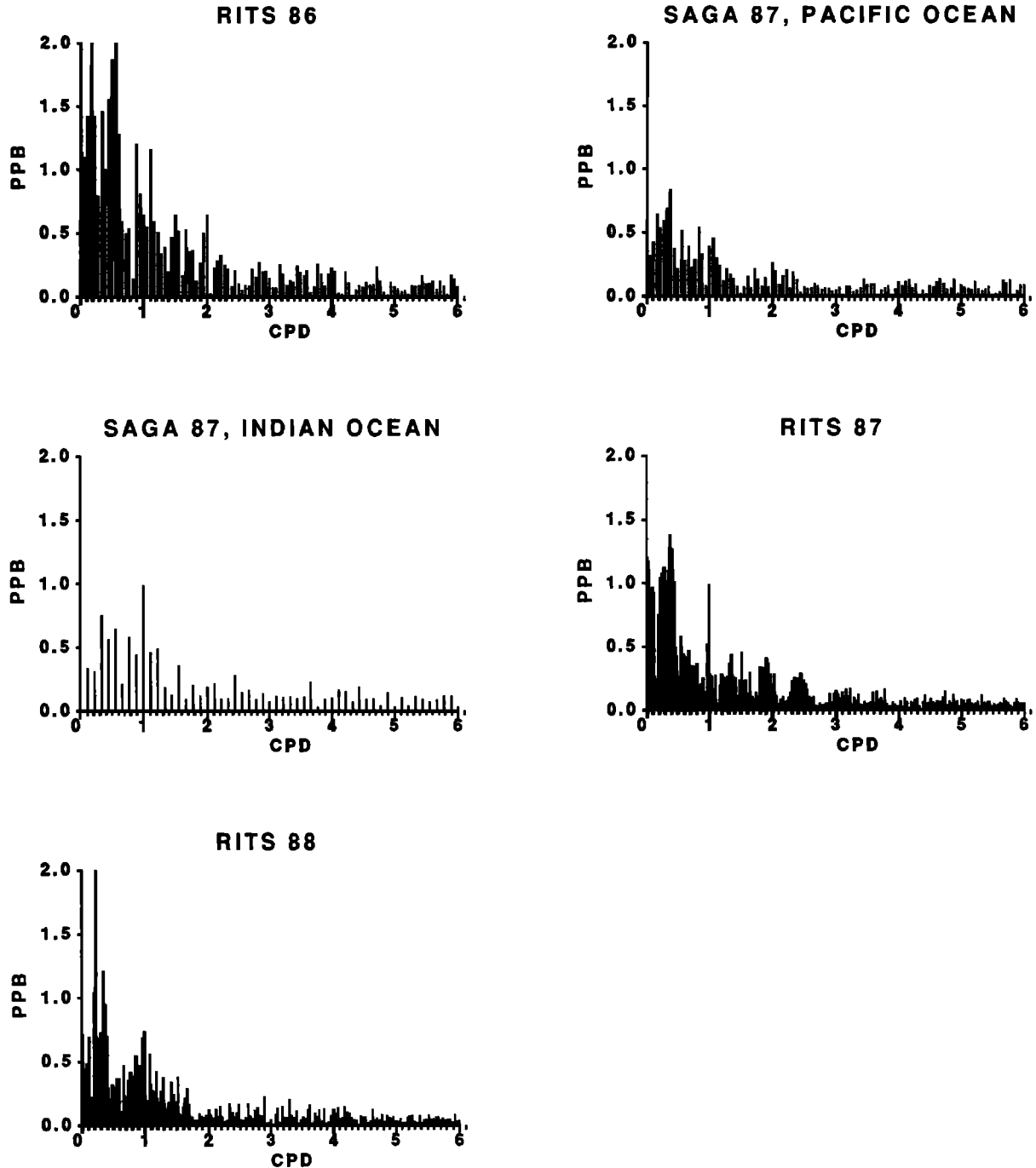

Fig. 4. Line frequency spectra (periodograms) of the ozone record from each cruise.

determined by least squares, assuming the diurnal variation could be adequately described by three harmonics, 1, 2, and 3 cpd. These smooth diurnal variations are plotted as functions of local time in Figure 5 for each cruise and latitude bin. The standard error in each record is about 1 ppb, so that the diurnal variation is statistically barely discernable. With the small size of each data record (2 to 7 days), a relatively large standard error is expected. A comparison between cruises shows, however, a reasonable consistency with ozone decreasing during daylight hours and increasing at night. The variations generally show a maximum value around 0600–0900 hours (local time) and a minimum value around 1500–1800 hours with a peak-to-peak amplitude of about 2 ppb. This consistency indicates that the diurnal variation is a real effect, and that there is no significant latitudinal dependence in the magnitude of the diurnal modulation, although the equatorial region does suggest a slightly smaller range. Although the observed amplitude was fairly constant and independent of latitude, the mean ozone concentrations were about a factor of

2 higher in mid-latitudes than in the tropics. This indicates that the relative magnitude of the diurnal cycle was latitude dependent and varied from ≈20% in the tropics to <10% in the higher latitudes, consistent with a photochemical lifetime of order 5–10 days.

It is possible that a diurnal temperature oscillation in the Dasibi photometers could produce an artifact in the data record that would resemble a diurnal cycle in ozone. However, since the Dasibi ozone photometers respond to ozone molecular density, a typical diurnal cycle of 5°C should only lead to a 1.5% effect, much less then the measured diurnal amplitudes of 10 to 20%.

We further looked at possible temperature-caused anomalies during the RITS 88 cruise, when the sampling van containing the Dasibi also contained a chemiluminescent ozone detector. The temperature in the van was also recorded on the data system. We have examined data records from April 19 through April 27 (28°N to 5°N), a period where there was minimal latitudinal gradient in ozone. The average values for each hour
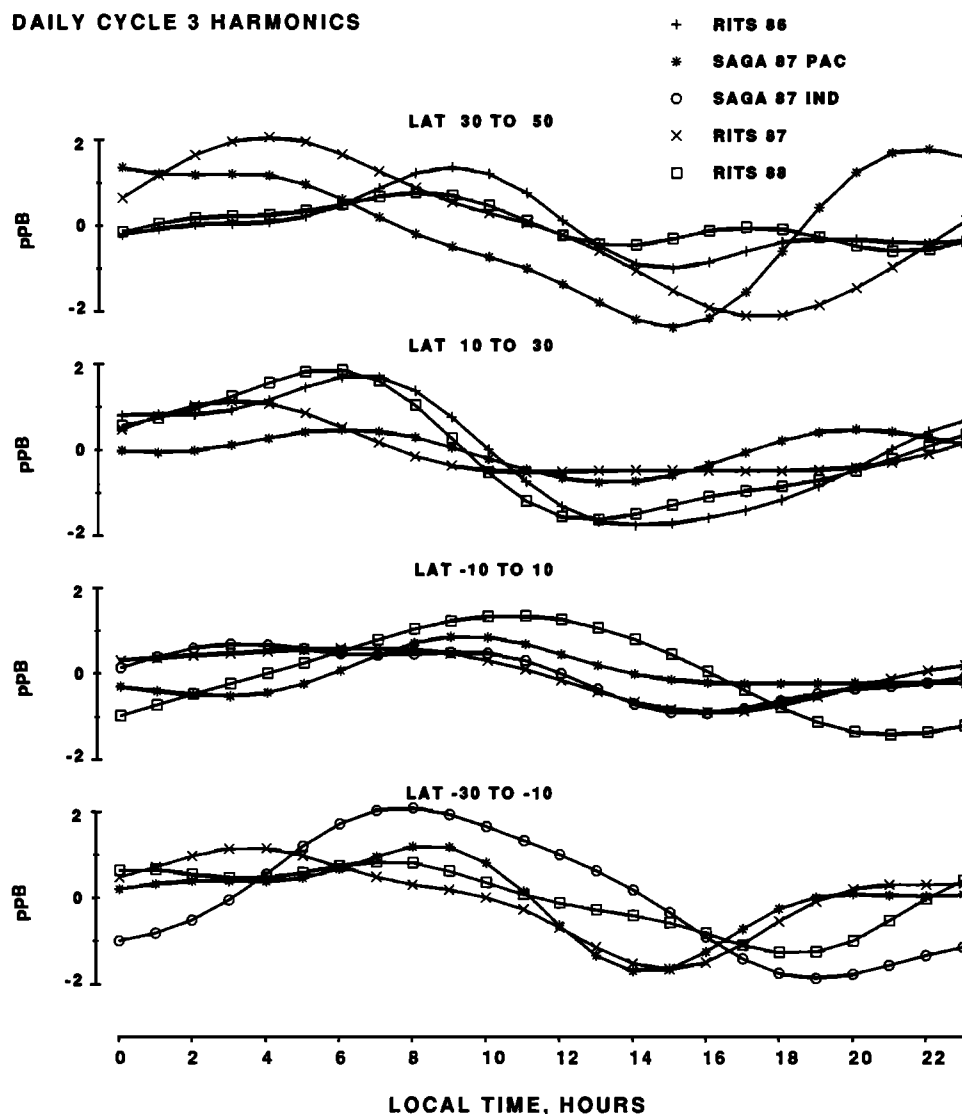

Fig. 5. Diurnal cycles in ozone by 20° latitude bins for each cruise. The plots are fits in a least squares sense of sine functions with harmonics at 1, 2, and 3 cpd. Before the fitting procedure, the latitude trend in each cruise for each latitude bin was removed and frequencies <0.5 and >3.5 cpd were filtered out.

of the day for this period are shown in Figure 6 for sunlight, van temperature, and Dasibi and chemiluminescent ozone. It is seen that the average diurnal cycle as measured by the Dasibi was very similar to the average cycle from the chemiluminescent instrument. The sample vans also contained eight electric pumps (800 W each) that were turned off each morning so that filter packs could be changed. During this interval the air conditioning system in the van was able to lower the van temperature an average of 4°C. This morning temperature perturbation was much larger than the diurnal cycle induced by solar heating and had minimal effect on the ozone data records. We thus assume that the observed diurnal effect is real and not an instrumental artifact.

DISCUSSION

Latitudinal and Seasonal Distributions

Many workers have noted seasonal and latitudinal variations in near surface ozone concentrations. *Chatfield and Harrison* [1977] examined northern hemisphere ozonesonde data from
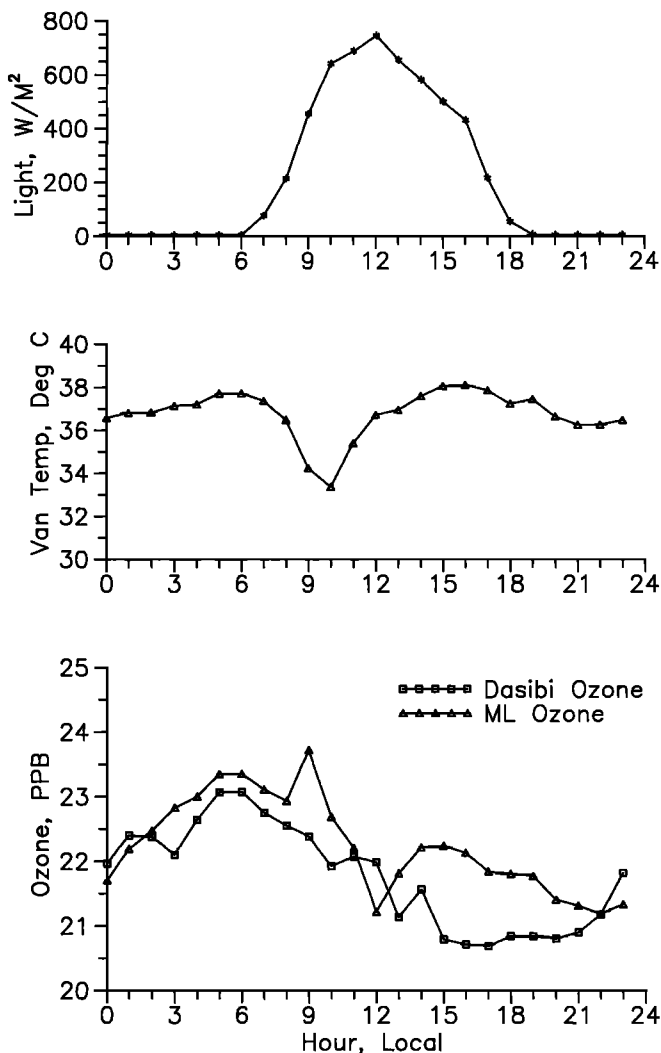

Fig. 6. Mean diurnal cycles of sunlight, van temperature, and ozone as measured by a Dasibi photometer and a chemiluminescent detector (Monitor Labs) from April 19 through April 27 (28°N to 5°N) from the RITS 88 cruise. The van temperature is the temperature of the van containing both ozone instruments.

1966–1969 from a meridional band near 75°W. At all levels in the troposphere, and during all seasons they found greater ozone in the temperate latitudes than in the tropics. They also found a seasonal cycle with a maximum in May–July and an amplitude that increased with increasing latitude.

Winkler [1988] reported marine boundary layer ozone measurements from 32 ship cruises in the Atlantic Ocean between 80°N and 80°S. In his time-averaged latitudinal data, he found a northern hemisphere ozone concentration maximum between 25°N and 65°N of 30 ppb, a small minimum at the equator of about 14 ppb, and a small southern hemisphere maximum between 20°S and 40°S of about 17 ppb. Winkler also found seasonal maxima in ozone concentrations in the temperate latitudes of each hemisphere during each hemisphere's spring.

Oltmans and Komhyr [1986] measured ozone at four land-based stations at Barrow, Alaska; Mauna Loa, Hawaii; American Samoa; and the South Pole. The Mauna Loa and Samoa record, being geographically the closest to our measurements are the most relevant to this study. The Samoa station is located on the windward side of Tutuila Island near sea level in the marine boundary layer. The Mauna Loa station is located at an altitude of 3400 m, above the trade wind inversion, and is more representative of the free troposphere. Ozonesonde observations at Hilo from 1985 through 1987 give an annual average boundary layer (surface) value of 22 ppb compared with a value at 700 mb (near the Manua Loa altitude) of 43 ppb, so the monthly means should perhaps be divided by ≈2 to be representative of surface ozone. Oltmans and Komhyr's data clearly show the seasonal cycle in each hemisphere with a maximum at Mauna Loa in April and a maximum at Samoa in September. The monthly mean data from these two stations from the years 1976–1984 are shown in Figure 7.

The marine boundary layer ozone measurements made during the April–May expeditions confirm a latitudinal distribution with higher ozone in the northern mid-latitudes, a pronounced equatorial minimum, and increasing ozone levels from the equator southward. The latitudinal gradient is also strongly affected by the seasonal ozone cycle in each hemisphere. As seen in Figure 7, the phase offset between the two hemispheres is not 6 months; rather, the two hemispheres have their maxima only 4 months apart. Our three North-South Pacific cruise tracts, which crossed the equator, span this interval between the maximum in the northern hemisphere and the maximum in the southern hemisphere. July/August is the time of maximum ozone in the South Hemisphere tropics, and minimum ozone in the North Hemisphere tropics. The RITS 87 cruise, which occurred at this time, clearly shows more ozone in the southern tropics than in the northern tropics. The SAGA 87 Pacific transect, which occurred 3 months earlier, was close to the midpoint of the seasonal cycle between maximum ozone in the northern hemisphere and maximum ozone in the southern hemisphere. Although the higher latitude northern hemisphere has more ozone than the higher latitude southern hemisphere, the tropical section is nearly symmetric. The RITS 88 data, taken during the next year and from 25° further east, show a dramatically different ozone picture with 20–30 ppb ozone between 5°N and 25°N and 0–3 ppb ozone between 10°S and 3°N. This cruise occurred in April and was near the time of the maximum North-South gradient in ozone.

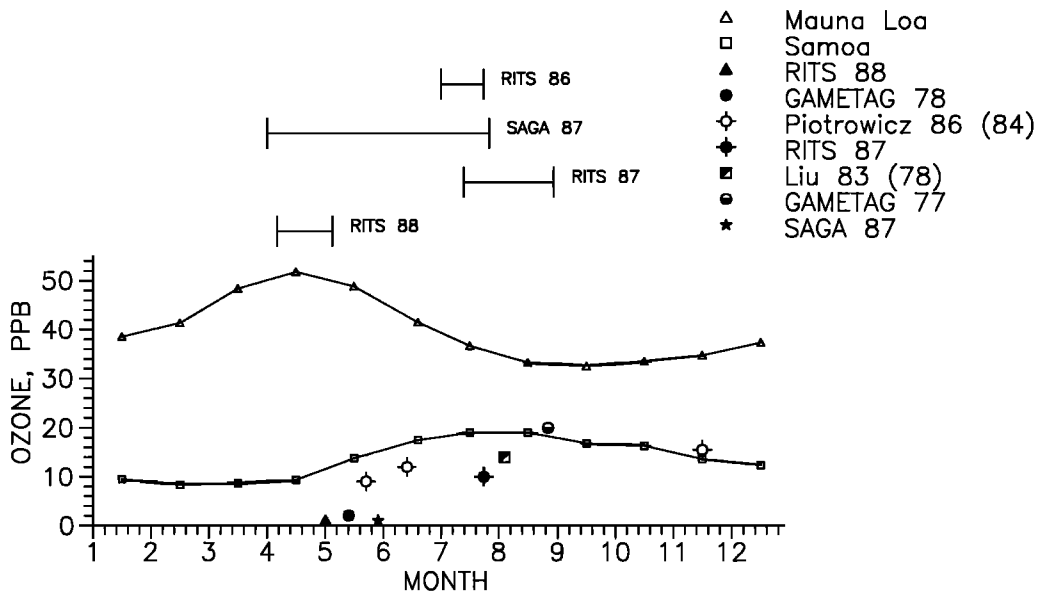*Levy et al.* [1985] examined the importance of transport in

Fig. 7. Monthly mean ozone concentrations as measured at Samoa (1976–1984) and Mauna Loa (1974–1984), taken from *Oltmans and Komhyr* [1986]. The Mauna Loa data are during conditions of downslope winds, when land surface contamination is at a minimum. The concentration of ozone from the marine boundary layer of the equatorial central Pacific is shown from our data as well as from other investigators. The time span of our cruises is also shown.

determining the tropospheric distribution of ozone by using a general circulation model in which stratospheric injection was the only ozone source and deposition to the surface, V_d, was the only ozone sink. Both high and low values of V_d were considered, in each case with an order of magnitude greater loss rate to land surface than to ocean. Although photochemical production and destruction of ozone within the troposphere were excluded from their model, photochemical destruction of ozone in the marine boundary layer would have appeared as if it were surface deposition. The strongly seasonal injection of ozone from the stratosphere, together with the relatively inefficient loss to the sea surface, led to a model prediction of a pronounced April ozone maximum over the North Pacific (H. Levy, private communication, 1989). This feature is observed in our springtime meridional transects near the dateline (see Figures 2b and 2e) for the SAGA 87 (May) transect along 160°E and the RITS 88 (April) transect along 170°W. The measured latitudinal distribution of ozone on these lines agrees much better with the model prediction for the high surface deposition velocity (land, $V_d = 1.0$ cm/s; water, $V_d = 0.1$ cm/s) than for the low deposition case, with peak ozone levels of 30–40 ppb near 40°N. The low deposition model case, using realistic values of oceanic V_d (0.02 cm/s; *Galbally and Roy* [1980]; *Lenschow et al.* [1982]), produces surface ozone values more than a factor of 2 greater than we observe, particularly in the tropical latitudes and even the high deposition flux ($V_d = 0.1$ cm/s) to the sea surface cannot account for measured low concentrations. However, the addition of a marine boundary layer photochemical sink, appearing as surface destruction, would reconcile our low ozone concentration values, the direct measurements of low ozone deposition velocity, and the high deposition velocity required by the *Levy et al.* [1985] model.

Equatorial Ozone Minima

Routhier et al. [1980] first reported the existence of a distinct equatorial ozone concentration minimum in the boundary layer of the Pacific during the Gametag experiment.

They found that during April/May of 1978, a latitude zone existed between 13°S and 2°N along 170°W, which was virtually devoid of boundary layer ozone. They did not see a similar minimum zone 8 months earlier in August/September of 1977 at 170°E.

Liu et al. [1983] measured ozone on a ship along 170°W, between 8°N and 10°S during July/August of 1978. Liu reported ozone concentrations of 7–15 ppb, well above the near-zero levels reported during the 1978 Gametag flight, which had occurred just 2 months earlier.

Piotrowicz et al. [1986] measured ozone from a ship in the equatorial Pacific in 1984. They had two cruise tracks which crossed the equator at the 150°W meridian, one in May-June, and one in mid-June. On their first cruise, although they did not see near zero ozone at the equator, they reported a sharp gradient coincident with the ITCZ at 5°N where the ozone concentration went from 25 ppb in the north to 10 ppb in the south. On their second cruise they found the ozone concentrations had risen several ppb over the equator and decreased about 5 ppb north of the ITCZ so that the gradient was much smaller. They also measured ozone in November of 1984 near the dateline, some 30° further west and found ozone at the equator had risen to the 15–20 ppb level.

As seen in Figure 2, our data show a very sharp latitudinal gradient in ozone at the ITCZ from the RITS 88 cruise in April 1988 at 170°W. South of this gradient the ozone level dropped to within three ppb of zero. During the SAGA 87 Pacific leg, which crossed the equator at 165°E on May 28 of the previous year, ozone concentrations went to near zero (≤ 3 ppb) at the equator, but the belt of near zero ozone concentration was only about 3° wide. The RITS 87 cruise which crossed the equator at 165°E on July 22 saw no ozone minimum at the equator and no significant ozone gradient at the ITCZ.

We have taken our equatorial Pacific marine boundary layer ozone concentrations, along with other published equatorial ozone concentrations from the Pacific, and plotted them as a function of time-of-year in Figure 7. Although the data set is rather small and the measurements were separated in longitude,

the data seem to be consistent with the seasonal ozone cycle in the southern hemisphere tropics, as measured at Samoa. The only measurements which show near zero ozone are those made in the April–May period. All measurements made in the June–November period show ozone levels of 10 to 15 ppb. Although this is a small data set and covers only a few years, it is plausible that an equatorial ozone "minima," defined to have observed concentrations $\leq$3 ppb, exists between 5–10°S and the ITCZ in the central Pacific during the February to April period of minimum ozone in the Southern Hemisphere Tropics. It is unfortunate that there are no reported boundary layer ozone measurements on the equator between December and March.

The cause of the very low equatorial ozone concentrations has yet to be established; however, there may be several photochemical explanations. The simplest explanation may be in the reaction of ozone with uv radiation ($\lambda < 310$ nm) and the subsequent reaction of the excited oxygen atom (O^1D) with water vapor to produce hydroxyl radical. In a low NO_x environment, the hydroxyl radical will not recycle ozone, so this pathway represents a net sink for ozone [Crutzen, 1988]. In the remote marine tropical atmosphere there is both a large uv flux, due to the diminished stratospheric ozone layer that occurs naturally near the equator, and a maximum water vapor concentration due to high evaporation rates from warm surface waters. Both of these conditions favor a much lower lifetime of atmospheric ozone. Recent measurements of ozone, water vapor and solar uv flux over the tropical Atlantic by Smit et al. [1988] found that a region near 10°S had the highest ozone loss rate, and that the photochemical lifetime of ozone due to the uv-water vapor reaction was as short as 4 days. In the annual record from Samoa, Figure 7, it is seen that the ozone concentration minimum occurs between February and April, coincident with the warmest sea surface temperatures, the highest atmospheric water vapor concentrations, and maximum insolation.

The prevailing atmospheric circulation patterns will tend to maintain the ozone minimum at the equator. The ITCZ is generally located between 5 and 10°N. From the southern side of the ITCZ, during February through April, the air mass that is converging at the ITCZ originates near 10° to 20°S, a region already low in ozone, as the Samoa record shows. If the tropical marine boundary layer in the southern hemisphere is a photochemical sink for ozone, then further photochemical reactions may lead to near zero ozone concentration in the boundary layer over the equator in this season.

Diurnal Cycles

It has been long recognized that the photochemical oxidation of CO, CH_4, and other hydrocarbons in the atmosphere will produce ozone, provided NO_x concentrations are above some critical limit, while these same photochemical oxidation reactions will destroy ozone if the NO_x concentration is below this critical limit. The predicted critical NO_x limit is in the 5–10 ppt range [Liu et al., 1983, 1980]. Over continental regions combustion processes produce large amounts of NO_x, so that the continental boundary layer NO_x concentrations are generally well above this critical limit. Most rural continental ozone concentration records show diurnal cycles with sunrise minima and afternoon maxima [Parrish et al., 1986; Fehsenfeld et al., 1983]. These diurnal cycles are driven by photochemical ozone production in daylight hours with loss to surfaces dominating at night. The nighttime depletion in ozone is enhanced by the formation of a thin, cool, and stable surface

layer, across which vertical mixing is suppressed.

Over the ocean, these same factors contributing to the diurnal cycle in continental ozone are reversed. First, surface cooling over the sea at night is likely less than 0.1°, preventing development of a stable surface layer. Second, the destructive flux of ozone to the ocean surface is a factor of 10–100 lower than the flux to land surfaces [Galbally and Roy, 1980; Lenschow et al., 1982]. Third, in the remote marine boundary layer, well away from continental influences, NO_x concentrations are generally found to be under the 10 ppt threshold [Fehsenfeld et al., 1988; Ridley et al., 1987; Davis et al., 1987; McFarland et al., 1979], so that daytime photochemical processes destroy rather than create ozone. Daytime photochemical destruction of ozone in the marine boundary layer has been confirmed by Chameides et al. [1987] from their analysis of simultaneous measurements of ozone, NO, CO, H_2O, and temperature from the GTE/CITE 1 aircraft program in the central North Pacific Ocean.

Thompson and Lenschow [1984] examined the photochemistry of the remote marine troposphere with a time dependent model. With NO_x levels near 9 ppt they found photochemical destruction of ozone in the marine boundary layer occurring during daylight hours. In the particular case they described, their model produced 12 ppb of ozone with a maximum at sunrise, a minimum in late afternoon and a 0.8 ppb (7%) peak-to-peak amplitude.

Our measurements show a persistent diurnal cycle in ozone concentration in the tropics that is very similar in phase and amplitude to the model predictions of *Thompson and Lenschow* [1984]. In the marine boundary layer, because of minimal change in the meteorology between the night and day, the diurnal cycle of ozone is probably due to photochemical processes. Although we did not make concurrent measurements of the ambient NO_x levels, it is reasonable to assume that NO_x was below the photochemical threshold for ozone production during all of the tropical measurements. We base this assumption on the few measurements of marine boundary layer NO_x which have been made to date [McFarland et al., 1979; Fehsenfeld et al., 1988], as well as on any reasonable budget of NO_x in the marine boundary layer [Thompson and Lenschow, 1984]. The phase of the diurnal ozone cycle is likely a reflection of the NO_x concentration, with low NO_x leading to daytime depletions of ozone. These cycles are easier to see in the tropics than in the mid-latitudes, where synoptic scale storms, occurring about every 2–5 days, produce more variability in ozone. It is interesting to note that two of the diurnal cycles shown in Figure 5 (RITS 86, 30°N to 50°N; SAGA 87, 30°S to 10°S) show an initial increase in ozone concentration just after sunrise. These two sections were relatively close to land (North America and Australia) and may have been influenced by continental sources of NO_x with subsequent early morning photochemical ozone production.

Our diurnal ozone cycles are similar to several reported measurements in the marine boundary layer. Oltmans [1981] found a diurnal cycle in the March–May Samoa record with phase (maximum at 0900, minimum at 1600) and amplitude (1.2 ppb, 13%) similar to ours. He also found a diurnal cycle in the Mauna Loa record; however, the diurnal cycle in wind regime, which changes from downslope during nighttime to upslope during daytime, complicates the picture.

Stallard et al. [1975] measured ozone in the marine boundary layer on a ship cruise in the South Atlantic between Cape Town and Dakar. Although they did not plot a

composite diurnal plot, on each day they saw ozone decrease between 0800 and 1500, with a subsequent increase during the night. *Piotrowicz et al.* [1990] also found a diurnal cycle in ozone concentrations in the marine boundary layer over the tropical Atlantic Ocean. The phase and amplitude were similar to ours with a maximum at 0600, a minimum at 1600, and a peak-to-peak amplitude of 3 ppb ($\approx$10%).

CONCLUSIONS

Over large regions of the remote Pacific and Indian Oceans, a significant diurnal oscillation exists in the concentration of ozone at both tropical and mid-latitudes. This oscillation has a maximum near sunrise and a minimum near sunset. The absolute peak-to-peak amplitude (2 ppb) over these regions is less variable than the relative amplitude (10–20%). This diurnal cycle of ozone is clear evidence of a photochemical sink for ozone in the low NO_x (<10 ppt) regime.

Equatorial minima in boundary layer ozone concentration were encountered over the central Pacific Ocean during April through May. They may also occur during January through March, as suggested by the seasonal pattern at Samoa. These minima are most likely the result of photochemical depletion caused by low NO_x, high solar *uv* flux and high water vapor concentration.

Between the months of April and August, the latitudinal gradient of ozone in the tropics (30°S to 30°N) changes dramatically. Much greater ozone occurs in the northern hemisphere in April, while greater ozone is present in the southern hemisphere in August.

Further ozone measurements are needed in the equatorial Pacific marine boundary layer during December through March. Concurrent measurements of NO_x and reactive light hydrocarbons would also be very helpful in improving our understanding of the cycle of ozone in the marine boundary layer of the remote oceans.

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