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Ozone in the Pacific tropical troposphere from ozonesonde observations

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Abstract. Ozone vertical profile measurements obtained from ozonesondes flown at Fiji, Samoa, Tahiti, and the Galapagos are used to characterize ozone in the troposphere over the tropical Pacific. There is a significant seasonal variation at each of these sites. At sites in both the eastern and western Pacific, ozone mixing ratios are greatest at almost all levels in the troposphere during the September-November season and smallest during March-May. The vertical profile has a relative maximum at all of the sites in the midtroposphere throughout the year (the largest amounts are usually found near the tropopause). This maximum is particularly pronounced during the September-November season. On average, throughout the troposphere, the Galapagos has larger ozone amounts than the western Pacific sites. A trajectory climatology is used to identify the major flow regimes that are associated with the characteristic ozone behavior at various altitudes and seasons. The enhanced ozone seen in the midtroposphere during September-November is associated with flow from the continents. In the western Pacific this flow is usually from southern Africa (although 10-day trajectories do not always reach the continent) but also may come from Australia and Indonesia. In the Galapagos the ozone peak in the midtroposphere is seen in flow from the South American continent and particularly from northern Brazil. High ozone concentrations within potential source regions and flow characteristics associated with the ozone mixing ratio peaks seen in both the western and eastern Pacific suggest that these enhanced ozone mixing ratios result from biomass burning. In the upper troposphere, low ozone amounts are seen with flow that originates in the convective western Pacific.

1. Introduction

The tropical Pacific is often considered to be a region remote from major polluting influences because of its isolation from heavily industrialized landmasses. Recent field campaigns [*Hoell et al.*, 1999] have emphasized that though this is often the case, the signature of pollution, particularly from biomass burning, makes a significant imprint on the air chemistry of the region [*Singh et al.*, 2000]. In a number of instances, layers of enhanced ozone (mixing ratios >80 ppbv) were found in the midtroposphere in the remote western Pacific [*Stoller et al.*, 1999]. These layers in addition to having enhanced ozone were replete with markers of biomass burning such as carbon monoxide, ethane, ethyne, and notably methyl chloride [*Gregory et al.*, 1999].

Beginning in August 1995 as part of the Pacific Exploratory Mission (PEM) Tropics A, ozone vertical profile measurements were begun at Pago Pago, American Samoa (14.3°S, 170.6°W), and Papeete, Tahiti (18.0°S, 149.0°W). At Samoa, profiles were also obtained as part of an earlier measurement program from 1986 to 1989. These earlier profiles provide an opportunity for comparison with measurements during the more recent period. Profile measurements were continued at Tahiti and Samoa through PEM Tropics B with the program at Tahiti completed in December 1999. At Samoa, weekly soundings continue as part of the Southern Hemisphere Additional Ozonesondes (SHADOZ) project (A.M. Thompson et al., The 1998-2000 SHADOZ (Southern Hemisphere Additional Ozonesondes) tropical ozone climatology: Seasonal patterns, the zonal wave-one, and comparison with TOMS and ground-based measurements, submitted to *Journal of Geophysical Research*, 2001, hereinafter referred to as A.M. Thompson et al., submitted manuscript, 2001). During most of the measurement period, soundings were

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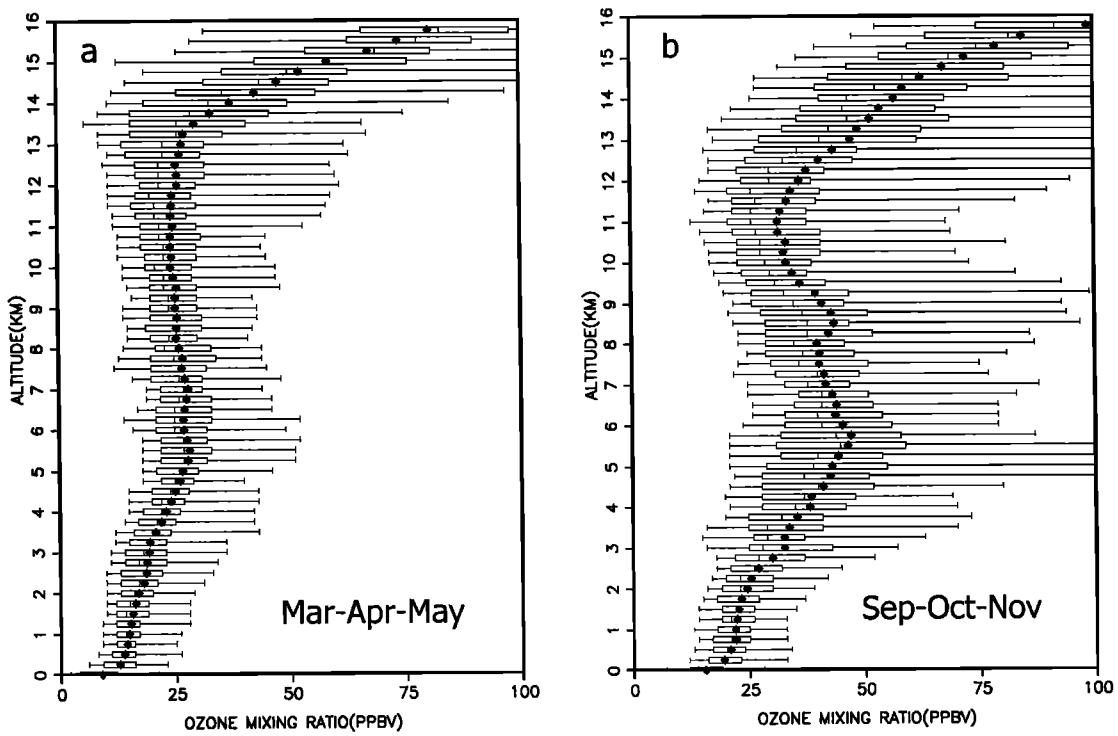

Figure 1. The average ozone profile and variability for 0.25 km layers at Tahiti for two seasons (a) March-May and (b) September-November for the period 1995-1999. The median is the vertical line inside the box, and the box represents the inner 50th percentile of the data. The "whiskers" represent the inner 90th percentile of the data. The solid diamond is the mean.

done weekly. During the aircraft field campaigns in September-October 1996 (PEM Tropics A) and March-April 1999 (PEM Tropics B) soundings were done twice a week. In January 1997, weekly soundings were begun at Suva, Fiji (18.1°S, 178.2°E) in anticipation of PEM Tropics B. As part of the Soundings of Ozone and Water Vapor in the Equatorial Region (SOWER) project ozone profile measurements were started on a campaign basis in March 1998 at San Cristobal, Galapagos (0.9°S, 89.6°W),

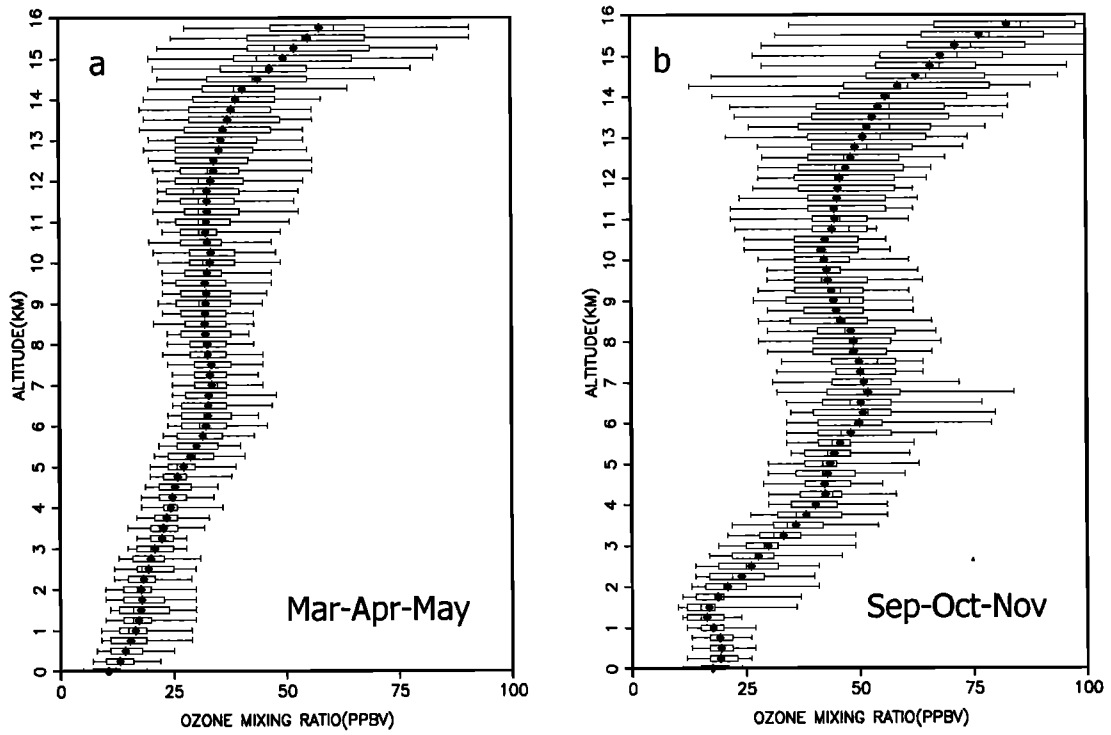

Figure 2. The average ozone profile and variability for 0.25-km layers at Galapagos for two seasons (a) March-May and (b) September-November for the period 1998-2000.

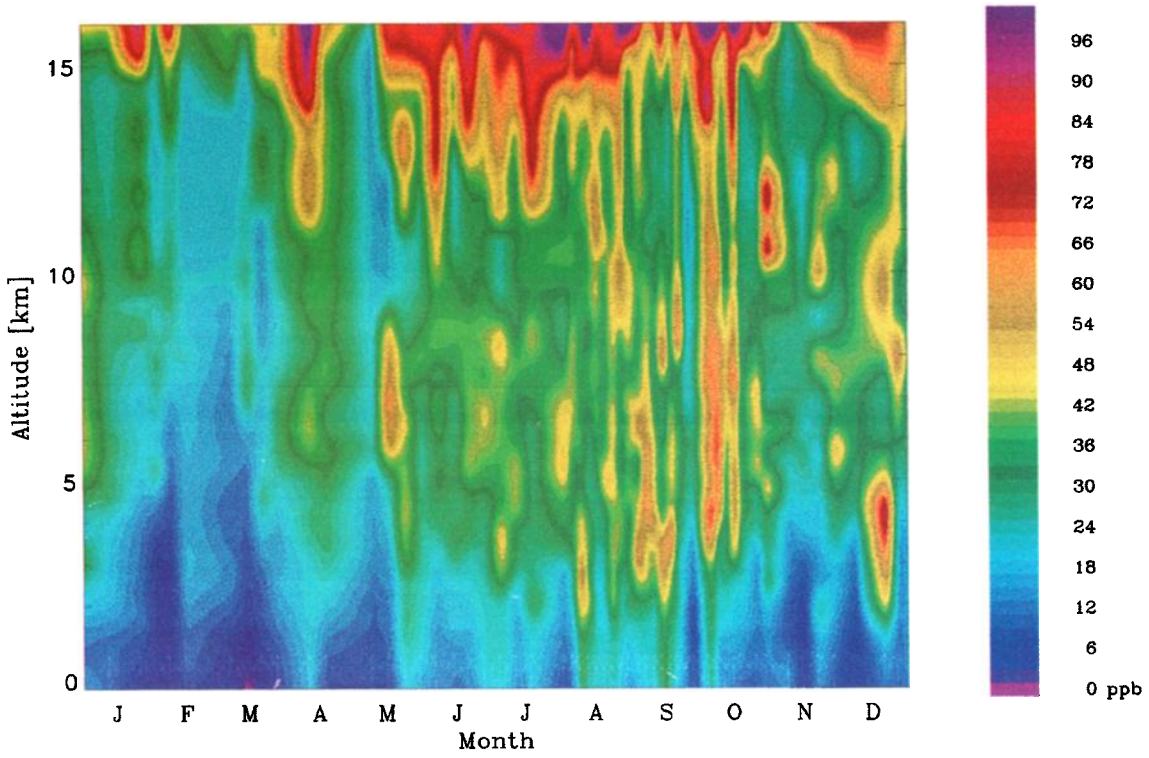

Plate 1. Time-height cross section of ozone mixing ratio at Pago Pago, American Samoa (14.3°E, 170.6°W), for 1996. Soundings are weekly except during the Pacific Exploratory Mission (PEM) Tropics A intensive measurement period from August-September when soundings were done twice weekly.

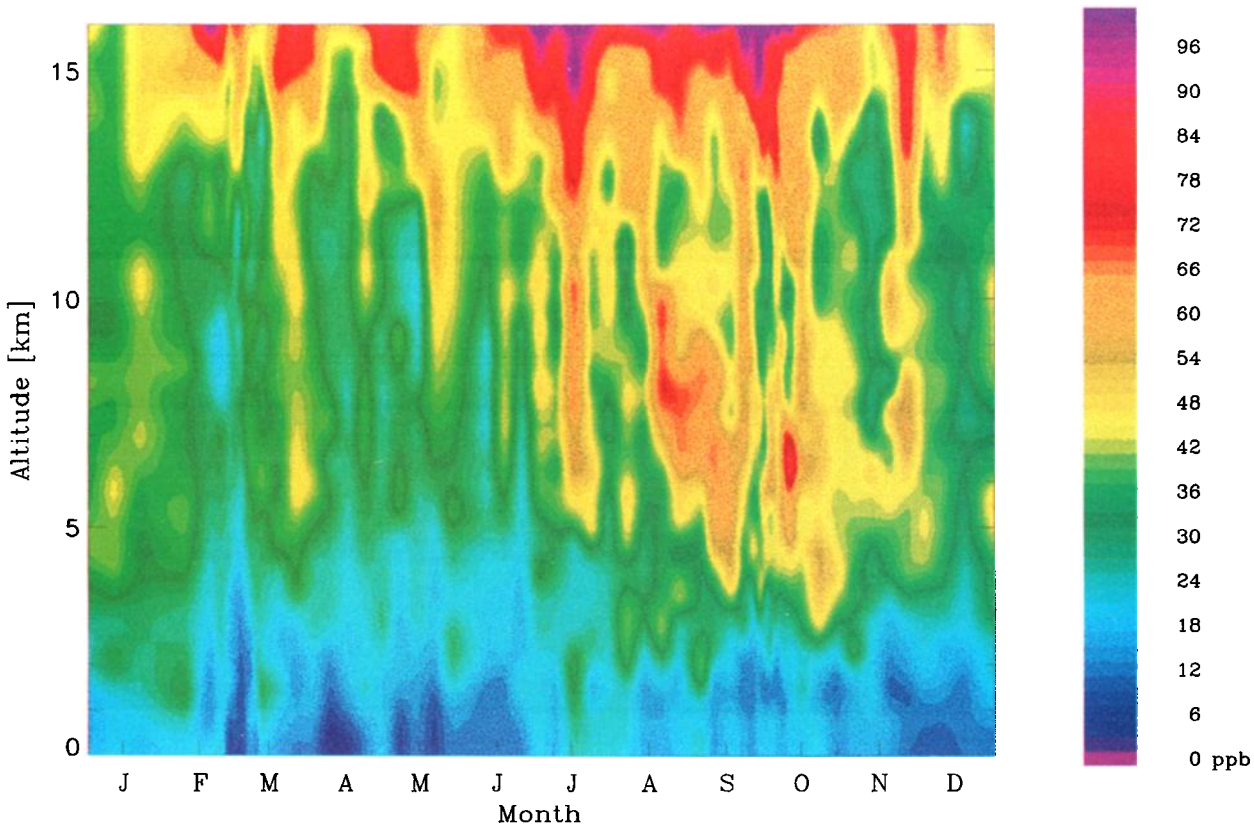

Plate 2. Time-height cross section of ozone mixing ratio from weekly soundings at San Cristobal, Galapagos (0.9°S, 89.6°W) for 1999.

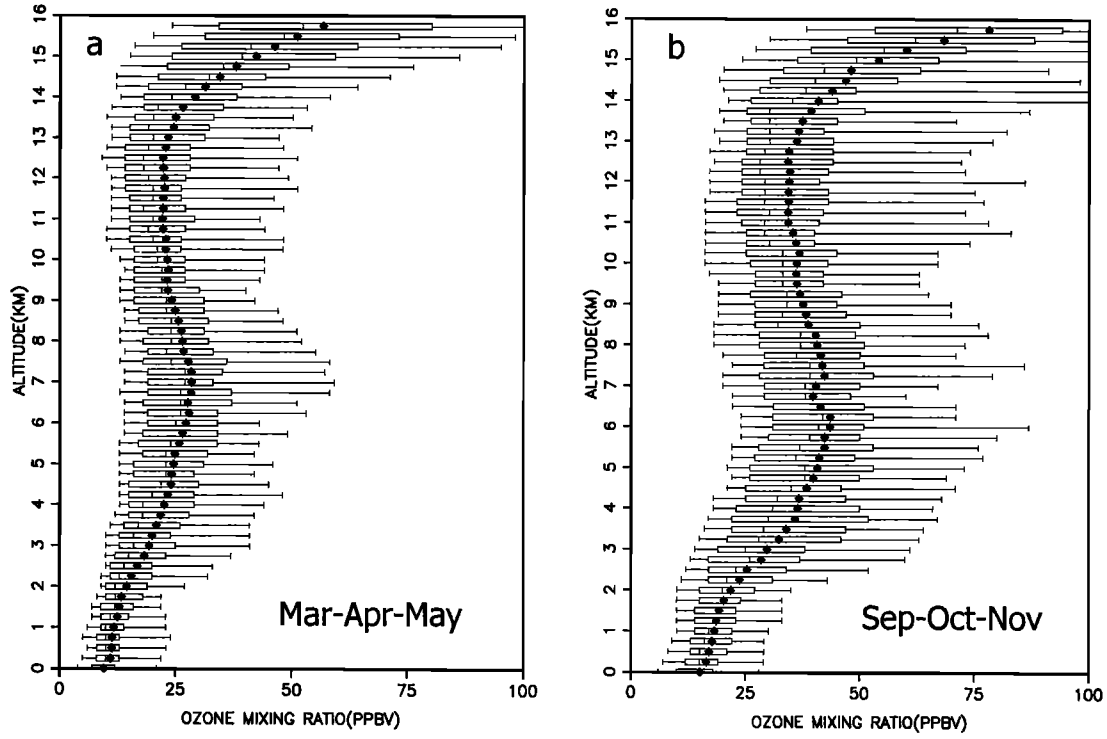

Figure 3. The average ozone profile and variability for 0.25-km layers at Samoa for two seasons (a) March-May and (b) September-November for the period 1995-2000.

were increased to biweekly soundings in September 1998 and to weekly soundings as part of SHADOZ early in 1999. Soundings continue at Fiji and the Galapagos in 2000 as part of SHADOZ and SOWER.

This set of ozone profiles obtained using balloon-borne ozonesondes provides information on the distribution of ozone throughout the troposphere of the tropical Pacific that has not been available in the past. In particular, new insights on the short-term and seasonal variability of ozone in this region as well as differences between the eastern and western Pacific are revealed in these data. In addition, isentropic trajectories are used to look at the transport associated with particular features of

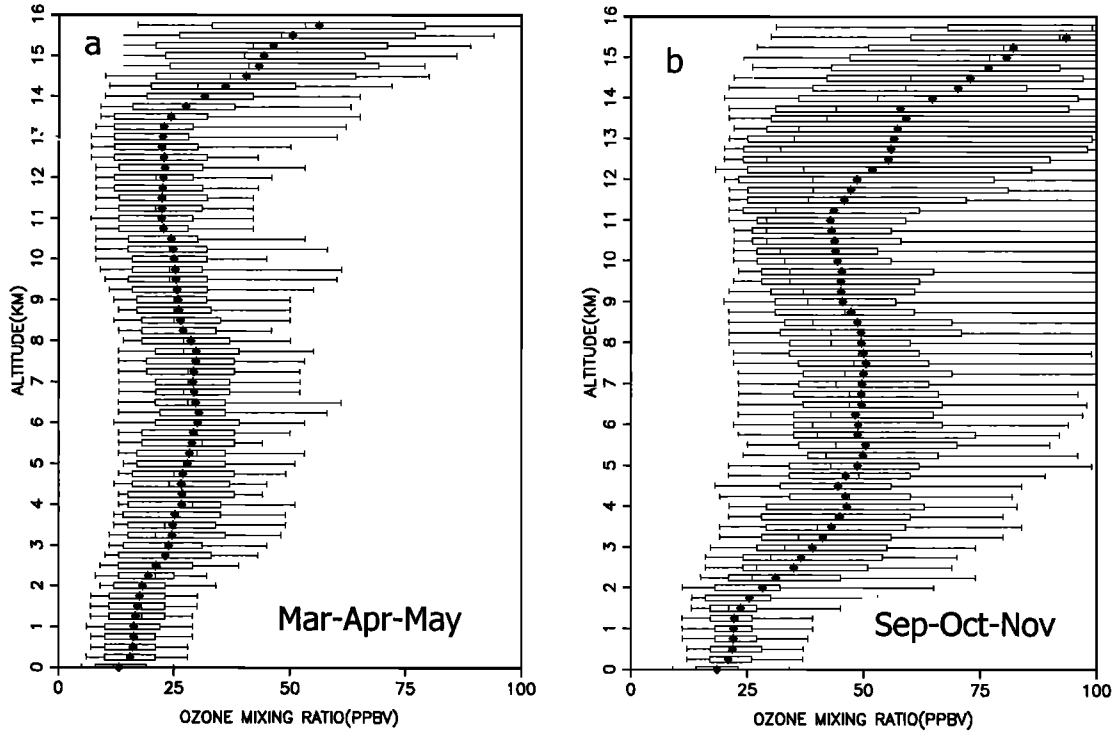

Figure 4. The average ozone profile and variability for 0.25-km layers at Fiji for two seasons (a) March-May and (b) September-November for the period 1997-2000.

individual profiles and also at the influence of climatological transport patterns on the principal features of the ozone distribution in the tropical troposphere in this region.

2. Methods

2.1. Ozonesondes

The ozone vertical profiles were obtained using the electrochemical concentration cell (ECC) ozonesonde [*Komhyr et al.*, 1995]. This has become a standard technique for obtaining ozone profiles with high vertical resolution in both the troposphere and stratosphere to altitudes of ~35 km. The measurements of ozone have an accuracy of ±5% through most of the troposphere with somewhat more uncertainty (±10%) for very low mixing ratios (<10 ppbv) encountered occasionally in the tropics. The only important interferent in the measurement technique, which is based on the oxidation reaction of ozone with potassium iodide in solution, is sulfur dioxide that is not encountered at these sites at sufficient concentrations to be of significance. One exception is the presence of a layer of zero ozone measured at the Galapagos in a single profile shortly after a volcanic eruption in Ecuador. The data were obtained with an altitude resolution of ~50 m but for the analysis performed here were averaged into 250-m layers. Only at Samoa are total column ozone measurements from a collocated Dobson spectrophotometer available for comparison with the integrated total ozone from the ozonesonde. These comparisons give an average ratio of 1.04 ± 0.05 between the Dobson total ozone measurement and the integrated total ozone from the ozonesonde, giving confidence that the ozonesonde measured ozone amounts from all of the sites can be compared with each other. During the course of the measurement program a change was made in early 1998 in the sensing solution recipe (B.J. Johnson et al., ECC ozonesonde pump efficiency measurements and sensitivity tests of buffered and unbuffered sensor solutions, submitted to *Journal of Geophysical Research*, 2001) at all of the sites except the Galapagos where the new recipe was used from the beginning. From comparison flights made at these sites, as well as laboratory tests, an empirical correction has been derived, and the earlier data have been corrected using this relationship. This correction is largest in the stratosphere. It leaves values for the earlier data at the surface unchanged and reduces amounts by ~2% at 100 hPa. Data placed in the Global Tropopshere Experiment (GTE) archive for PEM Tropics at NASA Langley and in the SHADOZ archive have this correction applied.

2.2. Trajectories

For the purposes of characterizing the tropospheric airflow patterns influencing transport to the tropical sites, insentropic trajectories have been calculated. The trajectories are computed from the European Centre for Medium-Range Weather Forecasts (ECMWF) analyses using the model described by *Harris and Kahl* [1994]. The limitations in such trajectories must be recognized in interpreting the results that are obtained, but they do provide a useful tool for obtaining a picture of the flow patterns that may influence ozone behavior at these sites. In particular for this work the role of convection needs to be considered as a possible influence on the air parcel path. For individual trajectory paths the outgoing longwave radiation (OLR) maps available from the NOAA-CIRES Climate Diagnostics Center, Boulder, Colorado, Web site (http://www.cdc.noaa.gov/HistData/), that are constructed from NCEP operational OLR data, were inspected for each of the 10 days to see if low OLR values indicative of convection were found at the air parcel location. The computed trajectories are used both to investigate individual cases and by grouping the

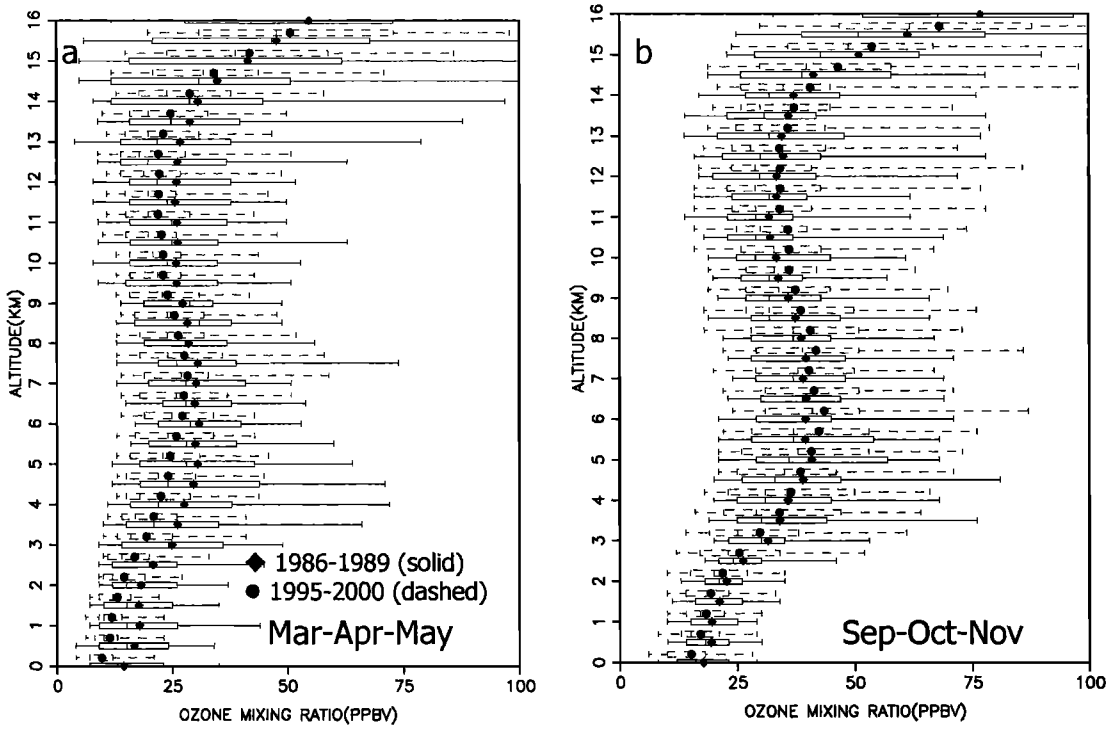

Figure 5. Comparison of the ozone mixing ratio profiles at Samoa for the periods 1986-1989 and 1995-2000 for (a) March-May and (b) September-November.

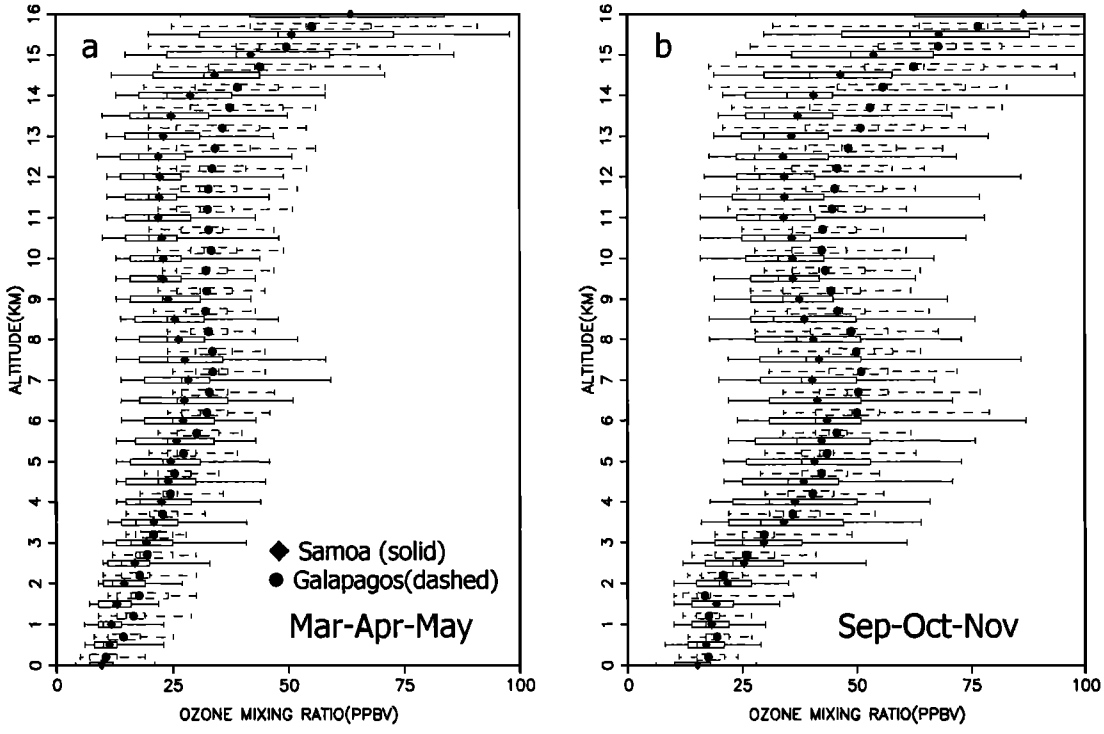

Figure 6. Comparison of the ozone mixing ratio profiles at Samoa (1995-2000) and the Galapagos (1998-2000) for (a) March-May and (b) September-November.

trajectories using an objective clustering technique [*Moody*, 1986; *Harris and Kahl*, 1990] that gives an indication of the primary flow regimes influencing a particular location at a given altitude. The trajectories are computed twice daily (0000 and 1200 UT) for 10 days backward in time. During 10 days of travel, air parcels may have undergone diabatic processes that are not accounted for in the model used here, and these are an important contribution to the uncertainty in the computed pathway of the air parcel [*Merrill*, 1996]. Transport from sources or sinks more than 10 days travel time from a particular site could also have a significant influence on ozone levels measured at the site.

3. Day-to-Day Variations

Variations on a timescale of several days are a large source of the variability seen in tropospheric ozone at the Pacific tropical sites studied here as will be shown in the analysis in this section. These variations have been studied using surface observations at Samoa [*Harris and Oltmans*, 1998]. The surface variations were found to result from changes in airflow to the site that tapped different sources and sinks. During all seasons, air coming from higher latitudes and altitudes has ~50% more ozone than air with a tropical origin [*Harris and Oltmans*, 1998]. Although the ozone soundings are done on an approximately weekly schedule compared to the continuous observations at the surface, the variability from sounding-to-sounding captured in the time-height cross section of ozone mixing ratio for 1996 at Samoa (Plate 1) is also apparent. During 1996 at Samoa the soundings were done twice a week during August and September so that the variability is well represented during this time of the year. This can also be seen in the plot of the average profiles at 0.25-km increments for individual seasons at Tahiti (Figure 1). The median is the vertical line inside of the box, and the box represents the inner 50th percentile of the data. The whiskers represent the inner 90th percentile of the data. The solid diamond is the mean. The September-November period has greatly enhanced variability especially in the 2-10 km layer when compared to the March-May period. These seasonal profiles are based on several years of data and represent the variability that is primarily contributed by the short-term fluctuations within a season.

In the Galapagos the time-height cross section for 1999 (Plate 2), the only complete year available for this site, shows many of the same features seen at Samoa. The seasonal profiles for the Galapagos (Figure 2) show similar behavior to Tahiti with a maximum in the variability in September-November and a minimum in the March-May season. The variability is greater at Tahiti in September-November than it is in the Galapagos. At Samoa (Figure 3) the variability in September-November is also larger than at the Galapagos but not quite as large as at Tahiti. Since Fiji (Figure 4) also shows greater variability than that of the Galapagos during this September-November, this feature is likely a real difference between the eastern and western Pacific.

4. Seasonal Variation

As can be seen in Figures 1 - 4, not only is the variability of ozone in the troposphere greater in September-November than in March-May, but also the mean (and the median) values are greater as well. Time-height cross sections based on 14-day averages over the entire record of measurements (which varies somewhat for each site) are shown in Plate 3. Although there are unique features at each site, a pattern is discernable that is reflected at all sites. In the western Pacific, there is a prominent layer of enhanced ozone in the midtroposphere in September and October. There also seems to be a distinct pulse in June and July of somewhat smaller magnitude with a relative minimum in late

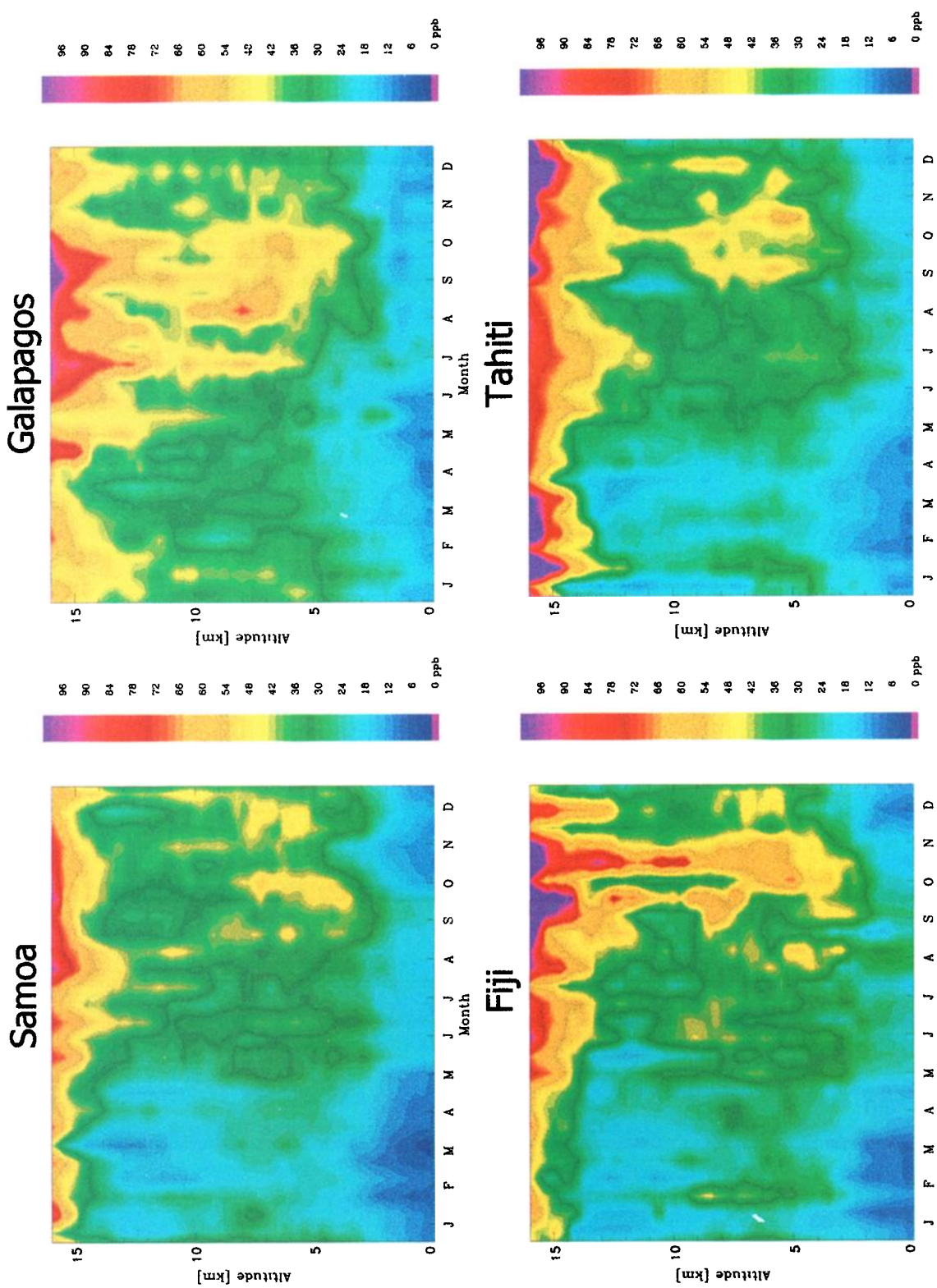

Plate 3. Time-height cross sections of ozone mixing ratio based on 14-day averages over the entire record of measurements at Samoa, Galapagos, Fiji (18.1°S, 178.2°E), and Tahiti (18.0°S, 149.0°W).

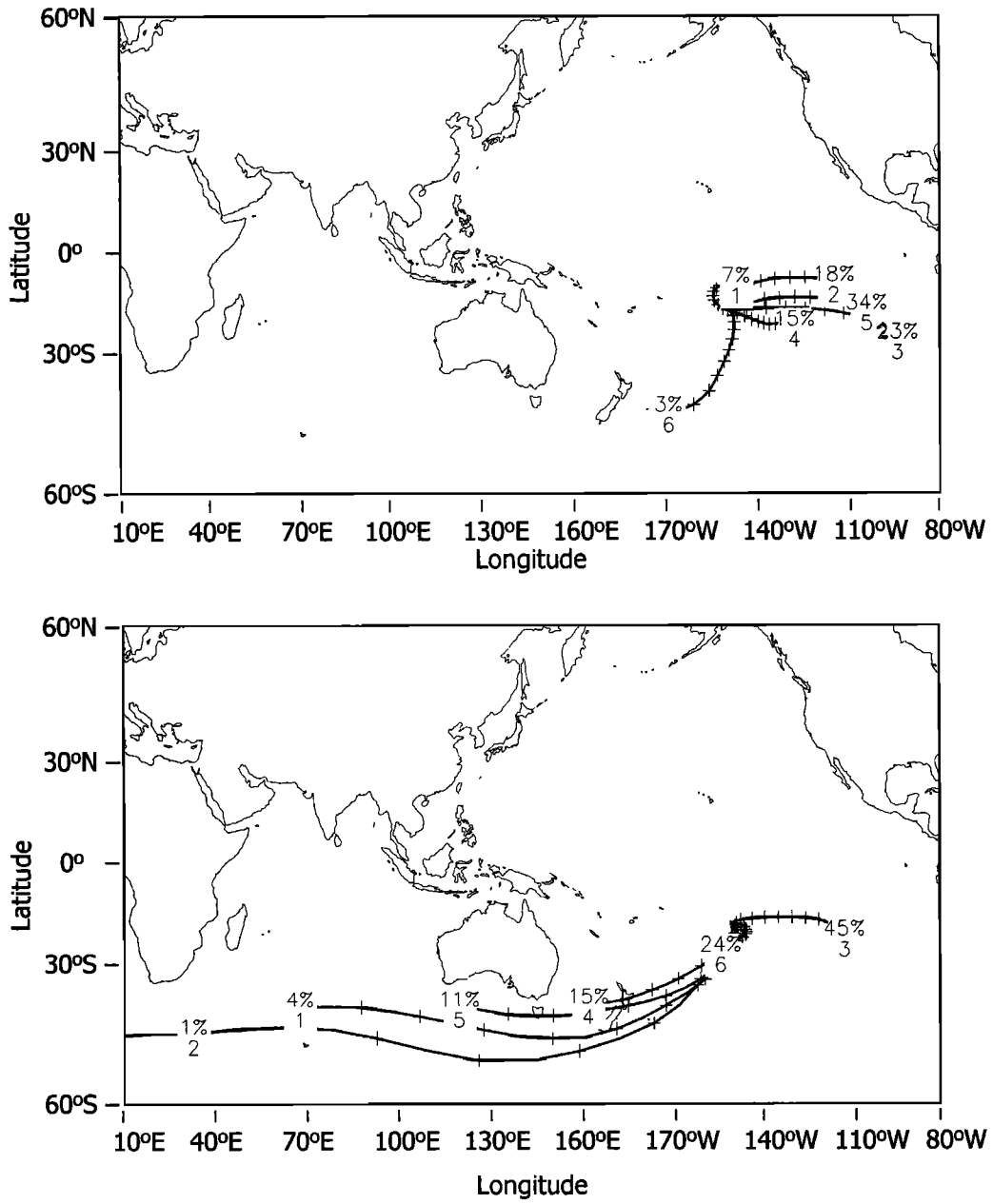

Figure 7. Clusters of trajectories arriving at Tahiti at 1 km for (a) December-February and (b) September-November for the period 1990-1999. The clusters are numbered 1-6, and the percentage of the total number of trajectories in each cluster is also shown.

July and August. Associated with this June-July enhancement in the midtroposphere, ozone in the boundary layer also increases, and this produces a seasonal maximum near the surface that occurs earlier than the peak in the midtroposphere. During austral winter and spring, greater ozone amounts descend to ~10-12 km. This seems to be associated with ozone in the lower stratosphere. In January-May, ozone at all altitudes is almost always less than at a corresponding altitude during the rest of the year. Also, at this time of year, ozone in the upper troposphere has smaller mixing ratios, approaching those seen at the surface which are almost always quite small (<15 ppbv) in this season.

An earlier set of profiles obtained at Samoa from August 1986 to January 1990 (Figure 5) show similar characteristics to those seen in the more recent 5-year data set. For March-May the 1986-1990 period has somewhat more ozone than in the 1995-2000 period that appears to be driven by several profiles with greater ozone amounts, particularly in the low and mid-troposphere (Figure 5a). In September-November, however, the amounts and variability are very similar during the two periods (Figure 5b).

In the Galapagos the general picture is similar to the western Pacific sites (Figure 6), but with some important differences. The midtropospheric ozone maximum occurs earlier in the year and diminishes earlier as well (see Plate 3). Near the surface the seasonal variation is smaller. The most noticeable difference is the lack of very low mixing ratios in the middle and upper troposphere especially during the January-May time of year. This is consistent with the fact that the western Pacific is a more

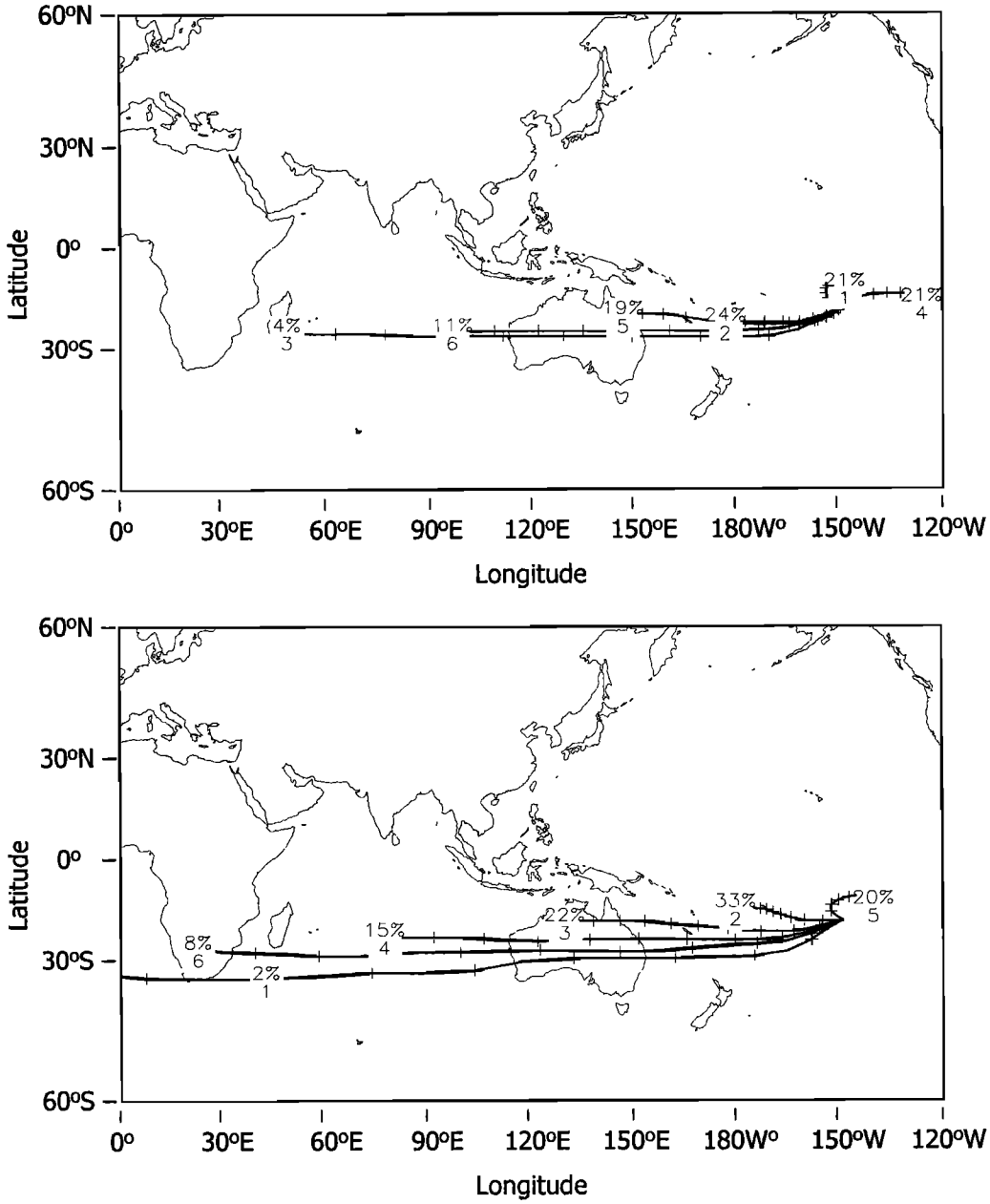

Figure 8. Clusters of trajectories arriving at Tahiti at 6 km for (a) March-May and (b) September-November for 1990-1999.

convective region where boundary layer air can be mixed into the upper troposphere. Other than this noticeable lack of low ozone amounts the differences among the western Pacific sites are similar to the differences between the eastern and western Pacific. It is also clear that in the Galapagos ozone amounts are greater than in the western Pacific above 4 km in September-November and above 5 km in March-May.

5. Flow Characteristics

Although the seasonal ozone behavior at all of the sites has some common features such as the maximum during the austral spring (September-November), this does not by itself imply that the sources and sinks influencing the measured ozone at the sites are the same. For example, the proximity of the Galapagos to South America suggests that this continent is likely to have the greatest influence on this site. The following analysis shows that while the airflow patterns at the western Pacific sites are quite similar, they are much different from those in the Galapagos. The differences in airflow direction with season are greatest in the boundary layer. Wind shear at all altitudes is somewhat greater in the Galapagos than in the western Pacific. To carry out this analysis, a 10-year climatology of 10-day back trajectories was computed at three levels (1, 6, and 13 km) for all four of the sites for each of four seasons. These trajectories were grouped into six clusters at each site for each altitude. The choice of six clusters was somewhat arbitrary, but it has been found that six clusters usually gives sufficient transport detail while not producing a cluttered figure or redundant transport types. Examples representative of various regimes are discussed here (Figures 7-12).

Because of the similarity in flow patterns at the western Pacific

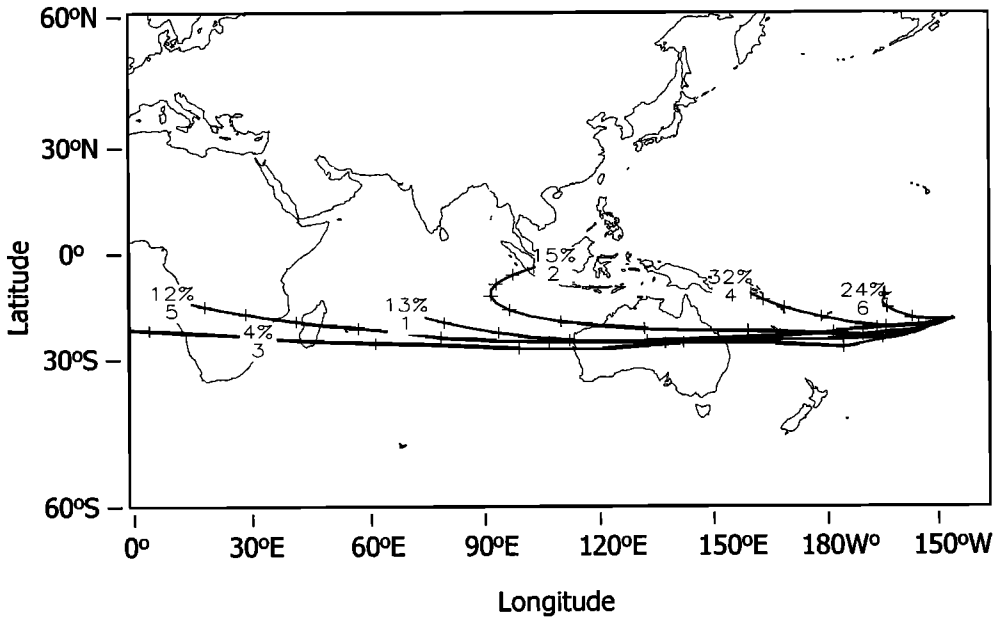

Figure 9. Clusters of trajectories arriving at Tahiti at 13 km for all seasons for 1990-1999.

sites the description of the behavior at Tahiti is used to indicate the western pattern with some differences from the other sites noted. At 1 km, a level in the marine boundary layer, the largest seasonal contrast is between December-February (Figure 7a) and June-August (Figure 7b). These are the seasons of minimum and maximum surface ozone at Samoa [*Harris and Oltmans*, 1998]. During the austral summer (December-February) flow at the 1-km level is predominantly from the tropical Pacific for all of the sites in the western Pacific. In the other seasons, 15-65% of the flow is from the west and more southerly latitudes with the largest percentage of flow from the south occurring in austral winter. At Fiji (not shown) this feature is most prominent with 65% of trajectories coming from the south and west during June-August, while at Tahiti and Samoa the percentage of southerly flow is closer to 30% (Figure 7b).

At 6 km above Tahiti airflow (Figure 8) is more uniformly from the west compared with low altitude flow, with only ~20% coming from the east on an annual basis. There is a southerly component to the airflow, but it usually does not extend south of 40°S within 10 days, in contrast to the low-level flow that reaches much higher latitudes. Throughout the austral winter and spring (June-November), at least 25% of the trajectories arriving at Tahiti come from as far west as the mid Indian Ocean and ~10% reach southern Africa (Figure 8b) within 10 days. To Fiji the

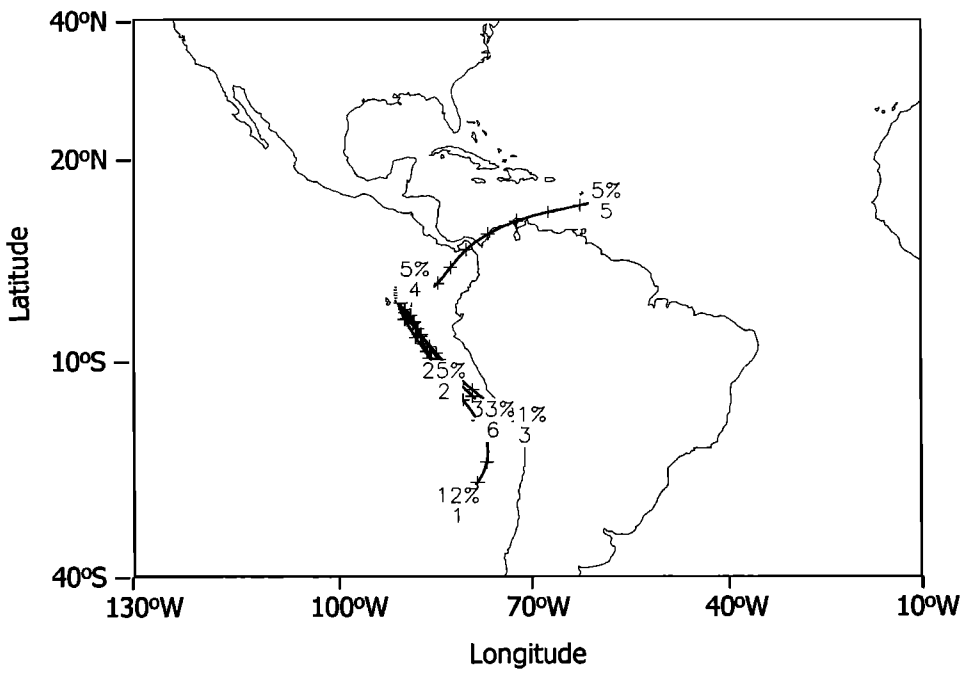

Figure 10. Clusters of trajectories arriving at the Galapagos at 1 km for all seasons for 1990-1999.

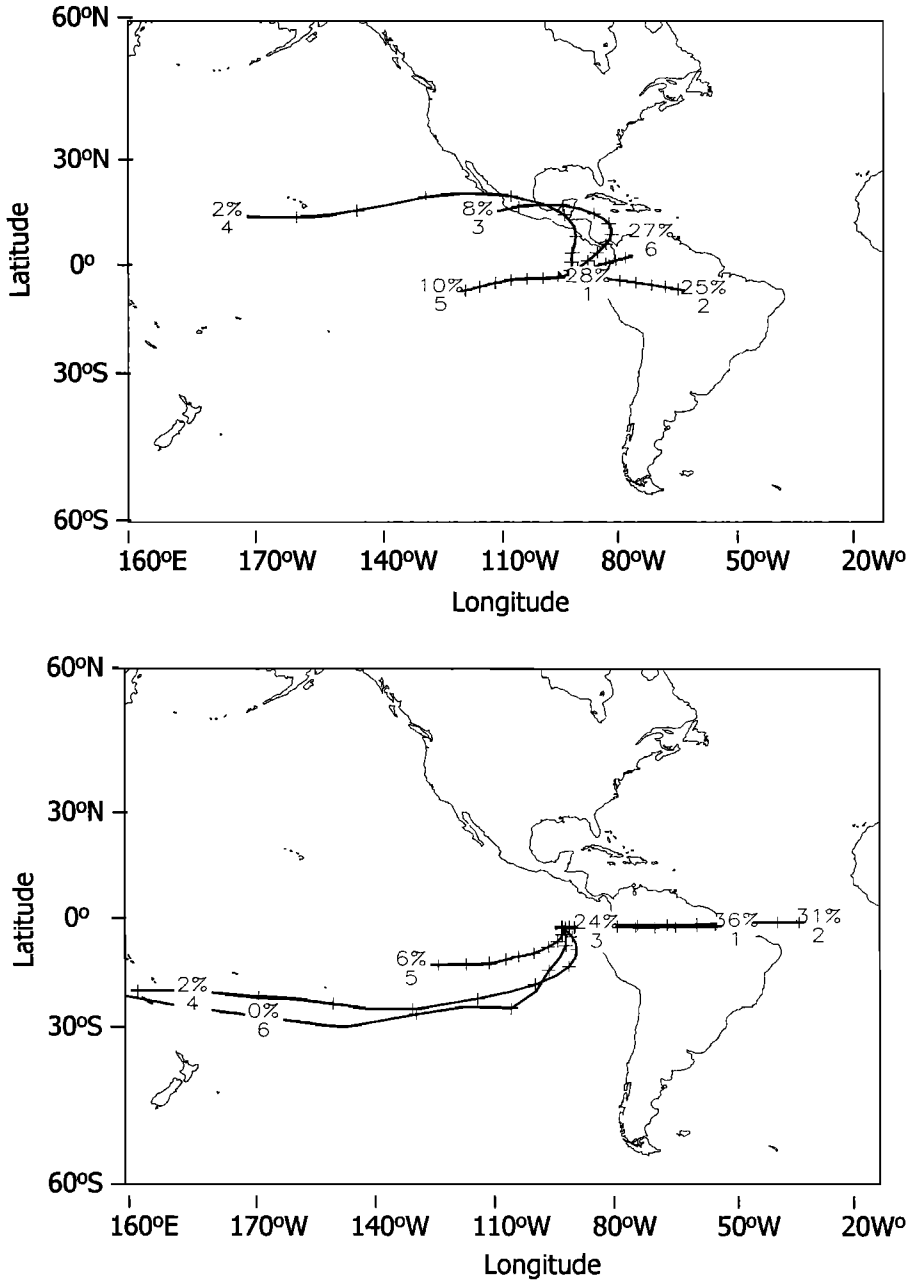

Figure 11. Clusters of trajectories arriving at the Galapagos at 6 km for (a) December-February and (b) June-August for 1990-1999.

flow is even more vigorous from the west and ~5% of the trajectories come from South America. A number of trajectories also have their 10-day origins over northern Australia. In the summer, flow is less vigorous and some trajectories have a northerly component.

In the upper troposphere (13 km), flow is from the west, but a majority of the trajectories also have a northerly component (Figure 9). This northerly flow brings air from near or even north of the equator and is strongest in September-November but is present in other seasons as well. As in the midtroposphere, a significant number of the trajectories come from the Indian Ocean and Africa.

The flow patterns in the Galapagos differ significantly from those in the western Pacific. At the lowest level (Figure 10) the flow is overwhelmingly from the south and over the ocean in all seasons. There is some variation with season (not shown) with December-May showing 10-15% of the trajectories coming from the Atlantic. In June-November the flow is exclusively from the south, often paralleling the South American coast. The flow at 6 km is in strong contrast to that in the boundary layer. On an annual basis, 75% of the trajectories arrive at San Cristobal from the east and have passed over the South American continent in the previous 10 days. In December-February (Figure 11a), ~10% of trajectories arrive from the tropical north Pacific, another 10% from the tropical south Pacific, and the remainder from the east off continental South America. During June-August (Figure 11b) and continuing through November (not shown), ~10-15% of the flow is from the tropical south Pacific with the remainder from the east or with little movement (cluster 3 in Figure 11b). At 13 km (Figure 12) the flow is about equally divided between weak

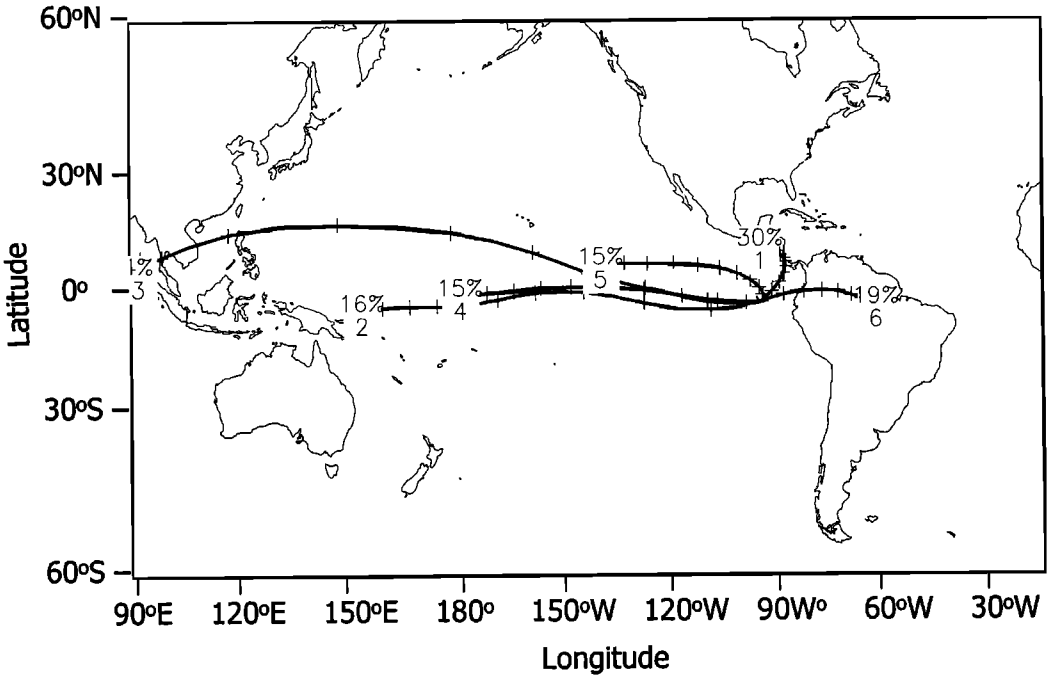

Figure 12. Clusters of trajectories arriving at the Galapagos at 13 km for all seasons for 1990-1999.

flow from the east or northeast and vigorous flow from the west. There is a fairly strong seasonality with December-May dominated by trajectories arriving from the west, but about half the trajectories during June-November come from the east and northeast.

6. Discussion

In the previous sections the short-term and seasonal variations have been described as well as the major air flow characteristics affecting the ozonesonde sites in the western and eastern tropical Pacific. In this section, important features of the ozone profile are linked to the trajectories to show how important source and sink regions for ozone may contribute to both the shorter-term and seasonal variations. Since the tropics are known to be a significant area of biomass burning (see TRACE-A and SAFARI special sections of the *Journal of Geophysical Research, 101*, 1996), particular attention is paid to characterizing the possible influence of burning on ozone at these sites by linking enhanced ozone layers with flow from potential source regions. It appears that several burning regions contribute to what is seen at these sites. The low ozone mixing ratios seen in the upper troposphere at the western Pacific sites also are discussed briefly.

It is clearly seen in Plate 3 that there is a persistent layer of enhanced ozone in the midtroposphere in the June-November season. The climatological trajectory analysis also shows this season to be one of regular occurrences of flow from potential burning related source regions in southern Africa and Australia for the western locations and South America for the Galapagos. Several individual profiles are examined that contain enhanced midtropospheric ozone along with the trajectories calculated for these cases. An event of very high ozone seen at Fiji and Samoa in November 1997 is investigated because the flow path suggests an Indonesian source for the enhanced ozone.

A profile with an enhanced midtropospheric layer characteristic of those seen during the September and October period in the western Pacific is shown in Figure 13 for a sounding done at Samoa on October 30, 1998. The peak in the ozone mixing ratio of 105 ppbv at 5-6 km has a trajectory (Figure 14) that reaches back to southern Africa 10 days prior to the sounding. As with all soundings in the tropical Pacific, the layer of enhanced ozone is also marked by a large depression between the frost point and ambient air temperatures, indicative of dry air.

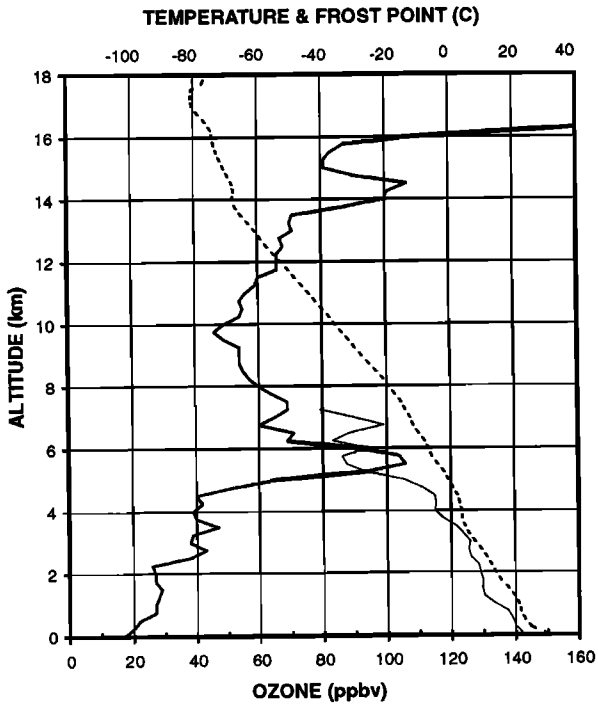

Figure 13. Ozone mixing ratio profile at Samoa on October 30, 1998. The thicker solid line is the ozone mixing ratio. The dashed line is the air temperature and the thinner solid line the dew/frost point temperature. At temperatures above 0°C the moisture profile is with respect to the liquid phase of water (dew point) and below freezing profile is for the solid phase (frost point).

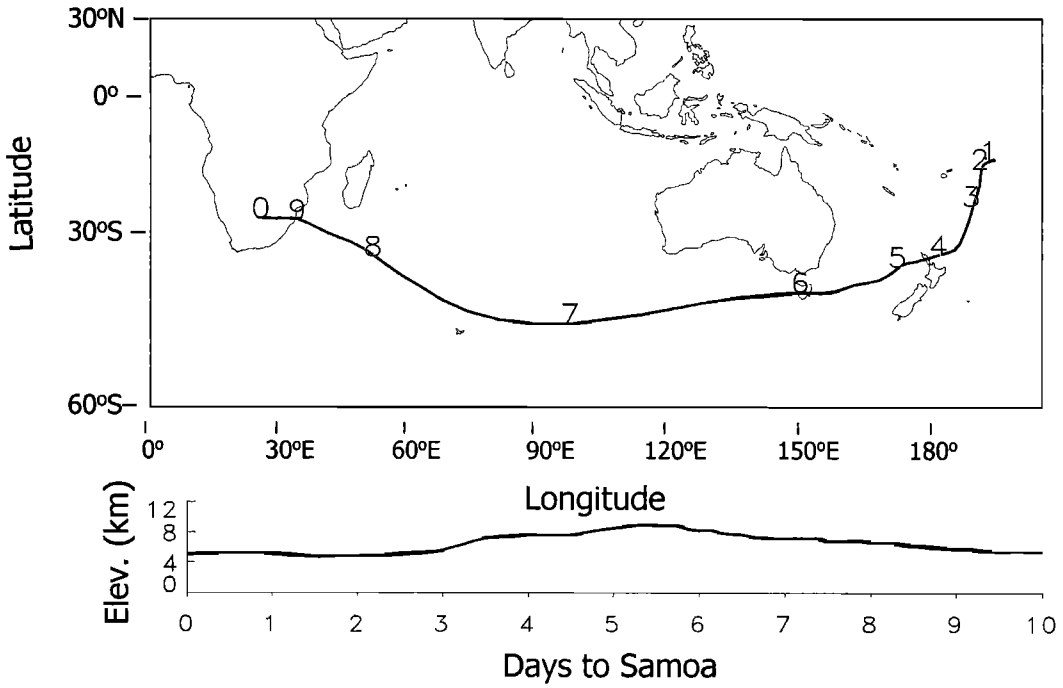

Figure 14. Ten-day back trajectory arriving at Samoa at 5 km at 0000 GMT on October 30, 1998. The numbers along the trajectory path mark the number of days back in time from the endpoint that the air parcel was located. The elevation change of the air parcel is shown in the bottom.

This suggests that air with large ozone amounts is not simply lifted from the surface at the source region and transported to Samoa. The change in the temperature lapse rate near 4 km at the bottom of the layer with enhanced ozone suggests that the air has subsided and warmed in its transit to Samoa. A significant subsidence of ~3 km can be seen in the air parcel based on the calculated trajectory (Figure 14). In order for a layer with such a prominent ozone peak to be transported over the distances suggested by the trajectory calculation it would likely have to remain relatively unmixed, both vertically and horizontally, with air from surrounding layers.

The preservation of the layer as well as the validity of the trajectory calculation is dependent on the air parcel not passing through a region of strong convection. Inspection of the OLR

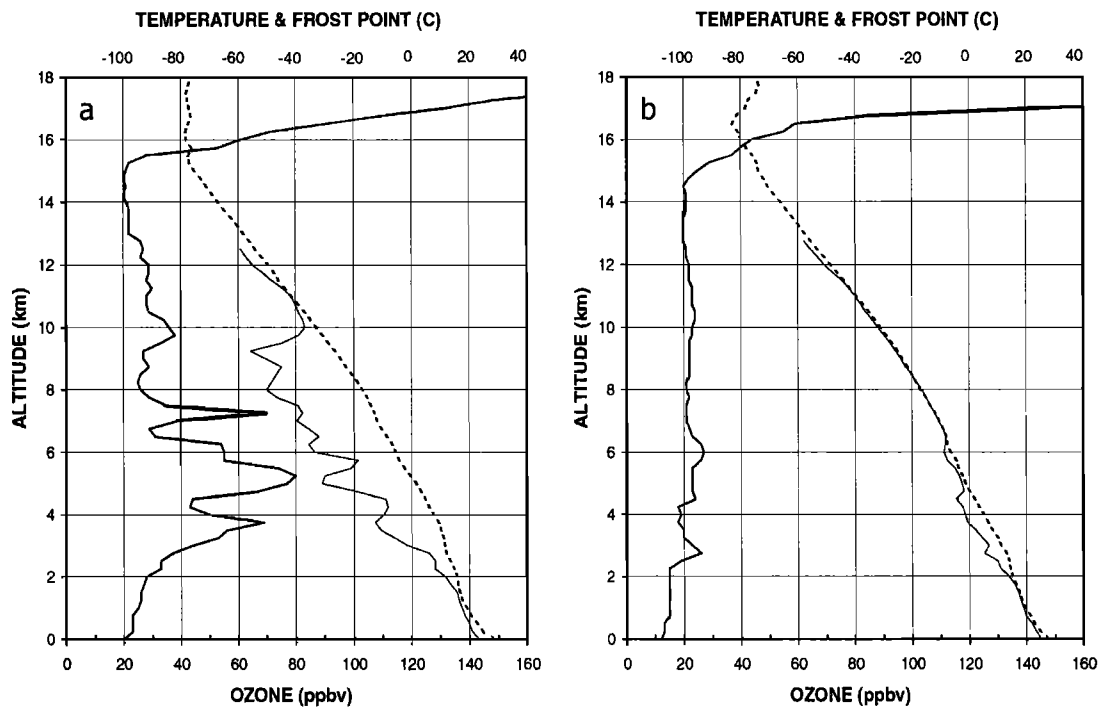

Figure 15. Ozone mixing ratio profiles at Samoa on (a) October 2, 1997 at 0000 GMT and (b) October 30, 1997, at 0000 and 1200 GMT.

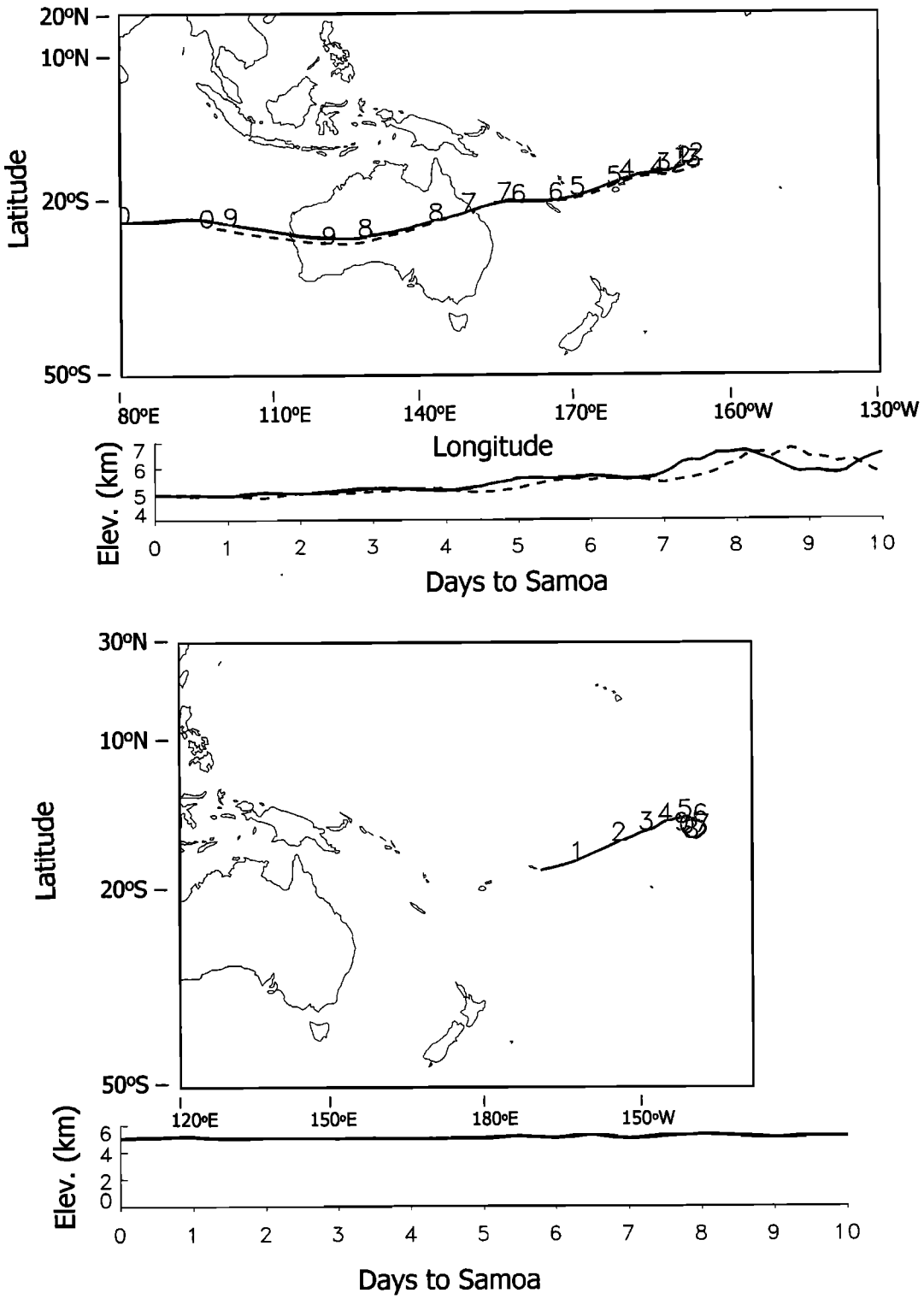

Figure 16. Trajectories to Samoa at 5 km on (a) October 2, 1997, at 0000 GMT (solid) and 12 GMT (dashed) and (b) October 30, 1997, at 0000 GMT.

maps for October 20-30, 1998, shows that indeed for the computed trajectory path the air parcel is not likely to have been strongly influenced by convection. The other needed ingredient in addition to a transport path for the appearance of the enhanced ozone layer over Samoa is a source of such large ozone concentrations. No ozonesonde data are available from southern Africa (the source region suggested by the trajectory) during this period. Soundings from Irene, South Africa (25.9°S, 28.2°E) were begun late in November 1998 so do not include the period of the Samoa sounding. Profiles from Irene in 1999 and 2000 from late October do show ozone levels of ~100 ppbv at altitudes below 10 km (*Thompson and Witte* 1[999], and the SHADOZ archive at http://code916.gsfc.nasa.gov/Data_services/shadoz/). At La Reunion, Madagascar (21.1°S, 55.5°E) there is a profile earlier in

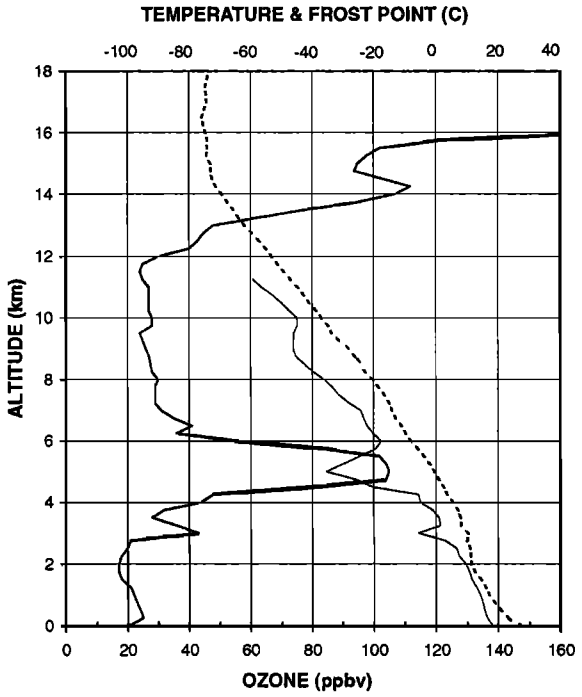

Figure 17. Ozone mixing ratio profile at Tahiti on October 31, 1995.

the month with midtropospheric mixing ratios near 100 ppbv. This is somewhat earlier, however, than when the trajectory for the Samoa profile indicates that the air parcel would have been over southern Africa. It is not unusual for La Reunion to see very large ozone enhancements during this time of the year that are often associated with biomass burning [*Randriambelo et al.*, 1999, 2000]. Maps of tropical tropospheric column ozone (TTO) derived from TOMS total ozone measurements [*Thompson and Hudson* [1999] and the Web site http://metosrv2.umd.edu/~tropo/) around October 20, 1997, show highly elevated ozone in the region to the north (0°-15°S) of the area indicated by the calculated trajectory. This technique does not produce reliable tropospheric data at more southerly latitudes. Given the somewhat uncertain nature of the trajectory calculation after 10 days and the indication of enhanced ozone amounts over southern Africa at this time year, it is reasonable that Africa was the source of the layer of high ozone concentrations over Samoa seen in the October 30, 1998, profile.

Ozone profiles with peaks greater than ~70 ppbv (Figure 15) do not always have trajectories (Figure 16) that extend back to Africa in 10 days, but they always have paths that have a strong westerly component so that 10-day origins are to the west of Australia into the Indian Ocean. On many occasions the trajectories pass over Australia, usually through the middle or southern part of the continent. The marked contrast that can occur during a month (see Figure 15) illustrates the dominant role that the airflow (Figure 16) to a site plays in the ozone profile, particularly during this season. For the profile obtained on October 30, 1997 (Figure 15b), the 10-day trajectory (Figure 16b) in the midtroposphere shows little air movement from the vicinity of Samoa and mixing ratios are 20-25 ppbv or less throughout the troposphere. This is in contrast to the near 80 ppbv mixing ratio seen at 5 km on October 2 (Figure 15a) when the flow was westerly (Figure 16a).

From Figure 8 it is clear that a large fraction of the air parcels reaching Tahiti (and also Samoa and Fiji) pass over Australia. From the data that are available from the ozonesondes and trajectories it is difficult to determine if trajectories that pass over Australia are influenced by burning in Australia rather than by burning in southern Africa [*Olson et al.*, 1999]. In some cases the trajectories show that the air moves more slowly (for example

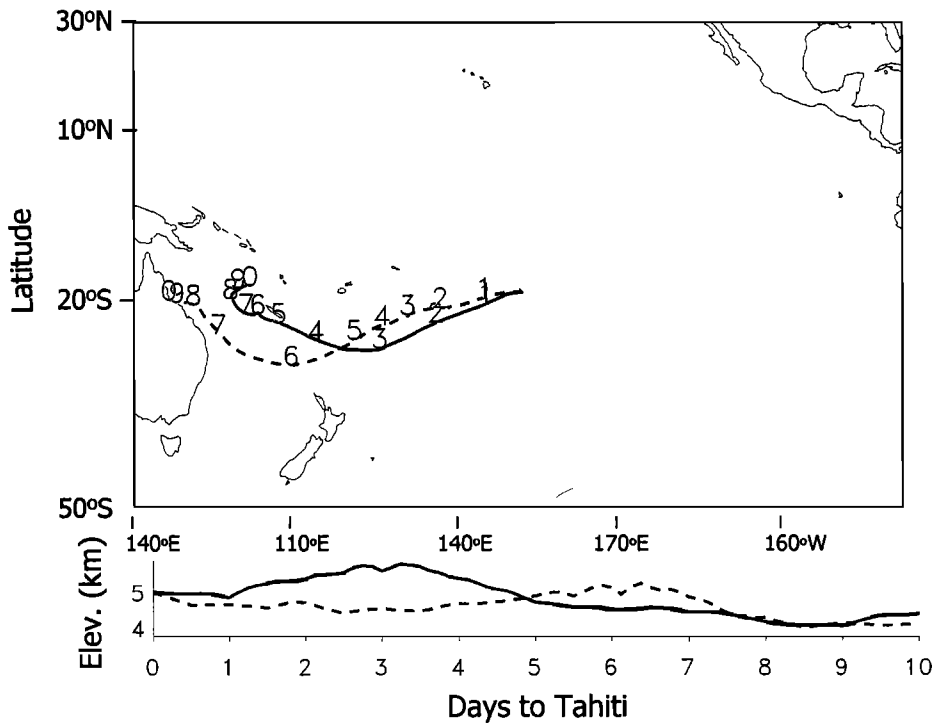

Figure 18. Trajectory to Tahiti at 5 km on November 1, 1995, at 00 and 12 GMT.

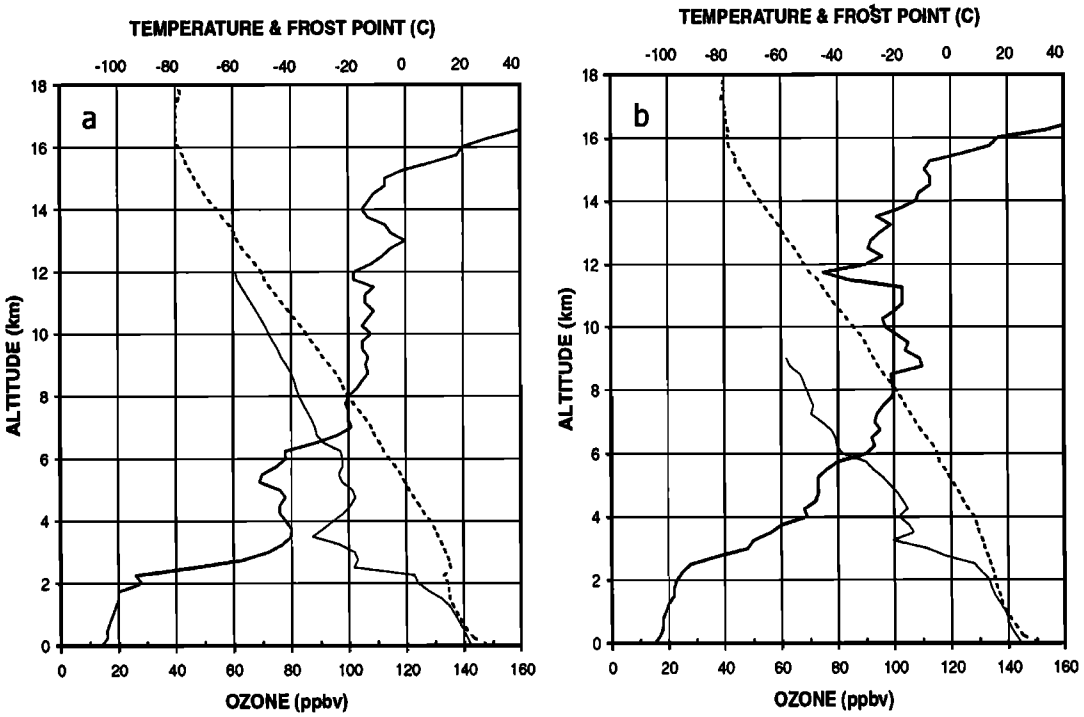

Figure 19. Ozone mixing ratio profile at (a) Fiji on November 19, 1997, and (b) Samoa on November 20, 1997.

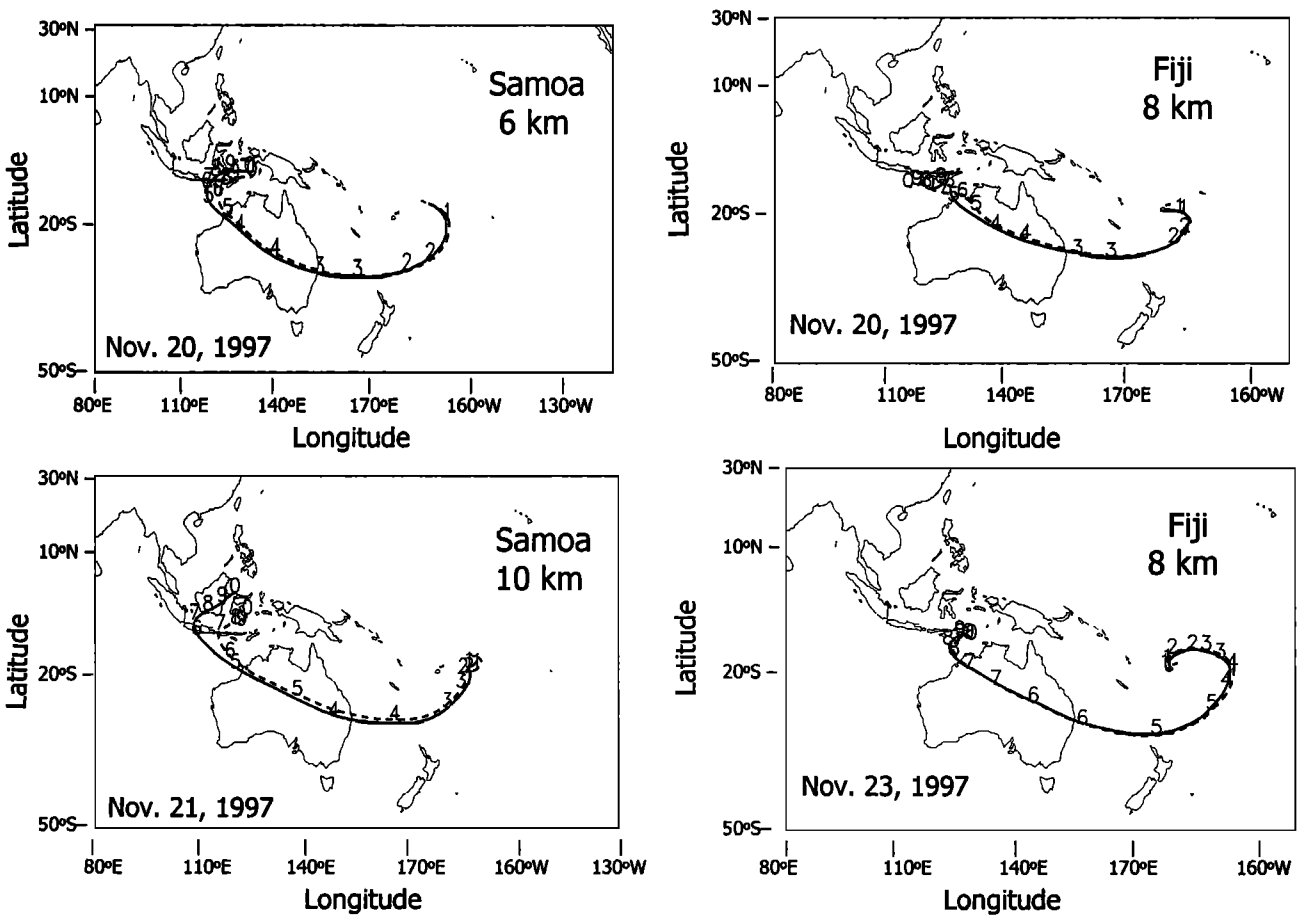

Figure 20. Trajectories to Samoa at 6 km on November 20, 1997, and at 10 km on November 21, 1997, and to Fiji at 8 km on November 20, 1997, and November 23, 1997.

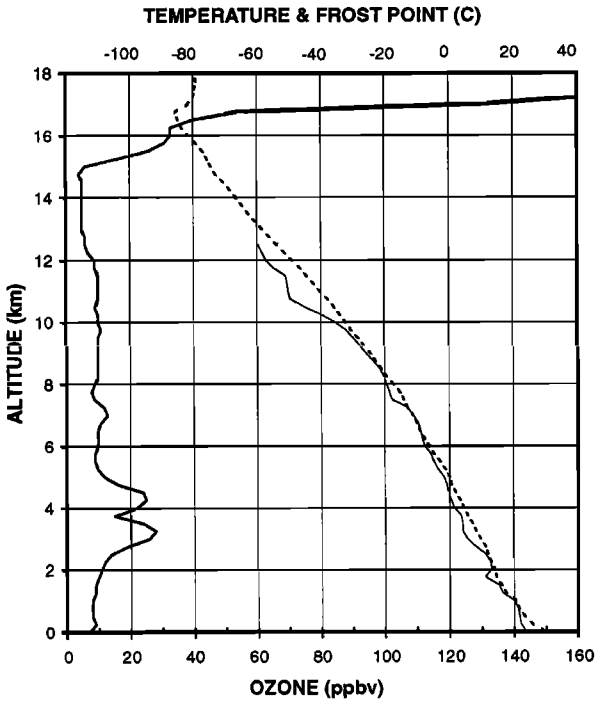

Figure 21. Ozone mixing ratio profile at Samoa on February 20, 1999.

cluster 3 in Figure 8b). An example of such a case is shown in the profile of October 31, 1995, at Tahiti (Figure 17). The corresponding trajectory just reaches the York Peninsula of Australia (Figure 18) in 10 days. The indication of relatively slow transport, the large peak mixing ratio, and the thin vertical extent of the layer suggest that the source of the elevated ozone seen at Tahiti may have been relatively nearby (i.e., Australia rather than southern Africa). Although burning is known to take place during this time of year in northern Australia [*Olson et al.*, 1999] there is not information from ozone profiles from this region to confirm that high ozone is produced in the region and in particular whether the high ozone amounts seen in the layer at Tahiti came from this source.

In 1997, extensive burning took place in Indonesia associated with drought conditions that were a consequence of the strong El Niño. Ozone profile measurements [*Fujiwara et al.*, 1999] and analysis of satellite data [*Thompson et al.*, 2001] found very high ozone amounts in Indonesia and Malaysia in connection with the burning in the region On November 19 and 20 at Fiji and Samoa (Figure 19) some of the highest tropospheric ozone amounts were seen for any event recorded at these sites. These enhancements, which encompassed the entire troposphere above the two sites, increased the total tropospheric column by ~20 DU, or more than 70% over average values for the month. The trajectories show that at both sites air was coming from Indonesia (Figure 20a-20d) throughout the depth of the tropospheric column. Although these profiles were the only ones measured during the event, trajectories show that a flow pattern nearly identical with the one during this large ozone enhancement persisted for ~5 days around the time that the profiles were obtained (Figure 20d). Although November was not the peak in the burning over the Maritime Continent, the presence of large ozone column amounts over the region can be seen from the TTO maps from the period (Plate 4) that the trajectories show air moving from this region toward Fiji and Samoa. Given the large vertical extent of the ozone enhancement seen in the profile measurements and the coherence of the trajectory path with altitude, it appears that a large plume of air with high ozone concentration slid southeastward from the Maritime Continent region over Fiji and Samoa. The TTO maps at the time of the profiles from Samoa and Fiji show very clearly an area of enhanced column ozone amounts of ~50 DU near the dateline and extending from ~7°S to15°S that lasted ~10 days.

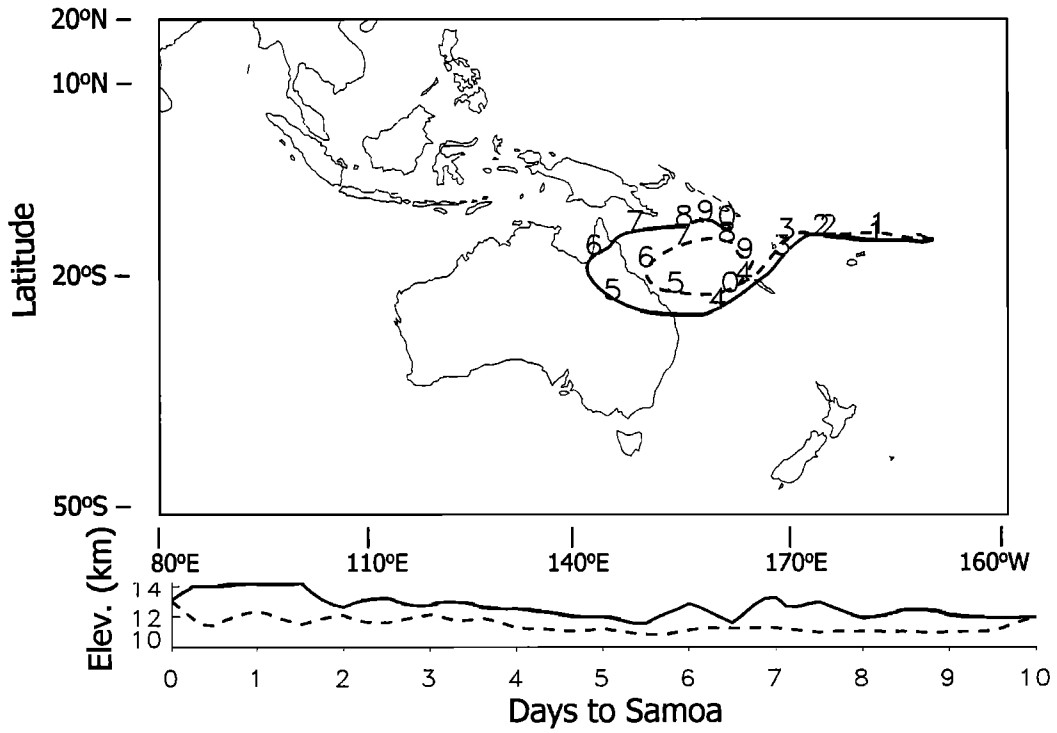

Figure 22. Trajectory to Samoa at 13 km on February 20, 1999, at 0000 GMT (solid) and 1002 GMT (dashed).

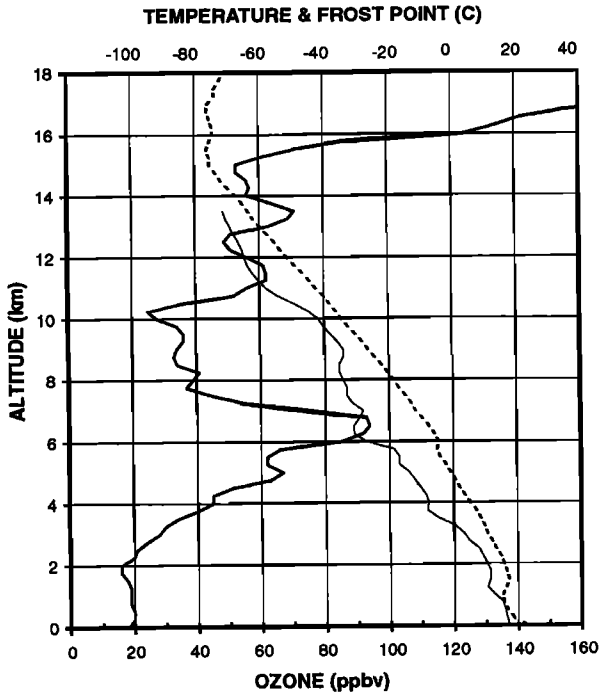

Figure 23. Ozone mixing ratio profile at the Galapagos on October 9, 1999. The thicker solid line is the ozone mixing ratio. The dashed line is the air temperature, and the thinner solid line is the dew/frost point temperature.

This is consistent with the column amounts measured in the profiles.

As was noted earlier, during the austral summer, ozone mixing ratios are generally small throughout the troposphere in the western Pacific. Values less than 10 ppbv are seen as in the profile for February 20, 1999, at Samoa (Figure 21), where in the 13-15 km layer ozone is ~5 ppbv similar to the very low values seen by *Kley et al.* [1996]. The trajectory at 13 km (Figure 22) shows that air originated 10 days earlier in northeastern Australia in a region associated with extensive convection during this time of year. The OLR map (Plate 5) for the period prior to the sounding shows that convection (evidenced by the very low OLR) was widespread in the region along the South Pacific Convergence Zone (SPCZ) through which the air parcel traveled based on the trajectory calculation. The validity of the trajectory calculation under these very convective circumstances is open to question, but since the calculation is for an altitude of 13 km, there is some reasonable expectation that the air parcel path is above the layer with the strongest vertical motions. At any rate it is clear that air reaching Samoa during this period is likely to have passed through a region influenced by convection. The low ozone mixing ratios are not usually a result of mixing directly from the surface near the site, although surface mixing ratios are low. This can be seen in Plate 3a, 3c, and 3d where the minima in the upper troposphere are not connected to the low values at the surface as illustrated by the individual profile shown in Figure 21. Instead, there is normally a relative maximum in the mixing ratio in the midtroposphere. It is more likely that air with very low ozone is mixed vertically by convection in the region of northern Australia and eastern Indonesia and transported to these sites in the upper troposphere [*Kley et al.*, 1997].

In the Galapagos many of the profiles during August-October also show pronounced midtropospheric peaks as seen on October 9, 1999 (Figure 23). The trajectory for this event (Figure 24) crosses Brazil in less than 10 days over a region that is heavily influenced by biomass burning during this time of the year [*Fishman et al.*, 1996]. Clear evidence for the enhancement of ozone over Brazil is seen in two profiles from Natal, Brazil (5.4°S, 35.4°W), on September 29 and October 6, 1999 (Figure 25), where ozone mixing ratios exceed 100 ppbv. Although the air parcel trajectory passes almost directly over Natal, it may be that both Natal and the Galapagos are influenced by the area to the west and south of Natal, where the burning actually takes place [*Kirchhoff et al.*, 1996]. This is strongly indicated by the TTO map for October 4-6, 1999 (Plate 6), that identifies the

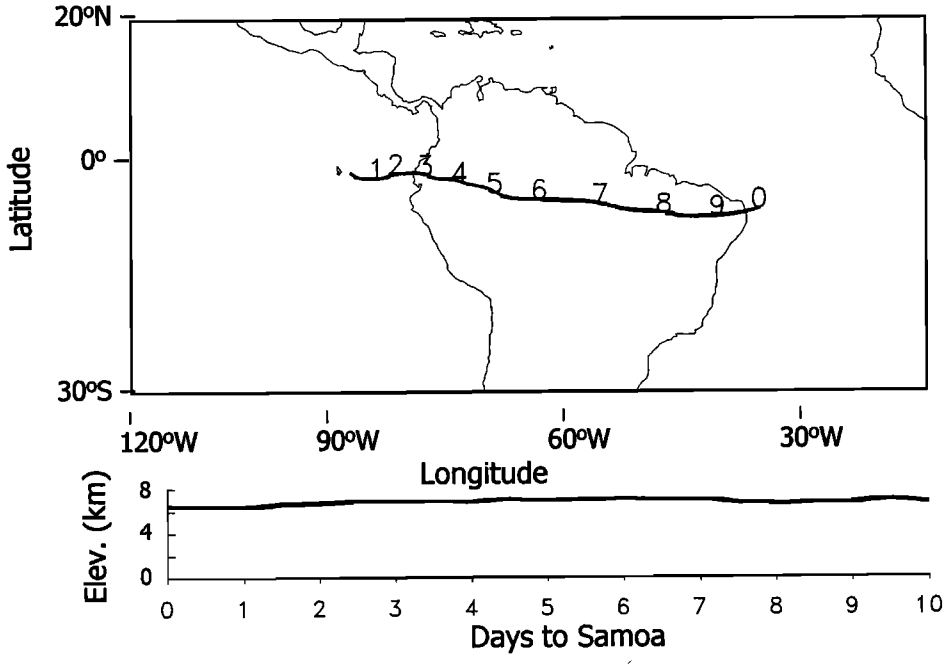

Figure 24. Trajectory to the Galapagos at 6 km on October 9, 1999, at 0000 GMT.

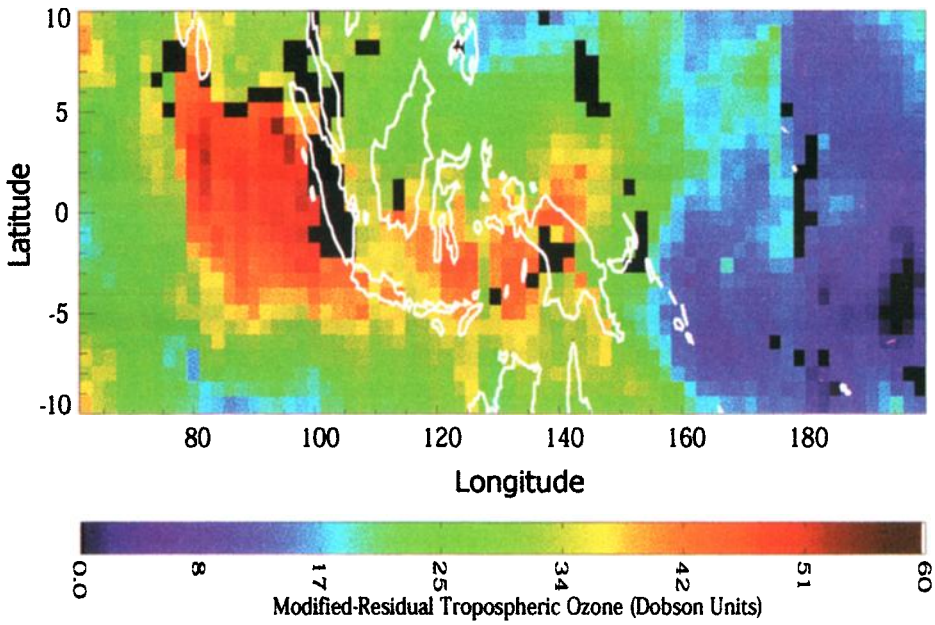

Plate 4. Map of the average tropical tropospheric ozone residual computed from the Total Ozone Mapping Spectrometer (TOMS) total column ozone for the period November 10-12, 1997.

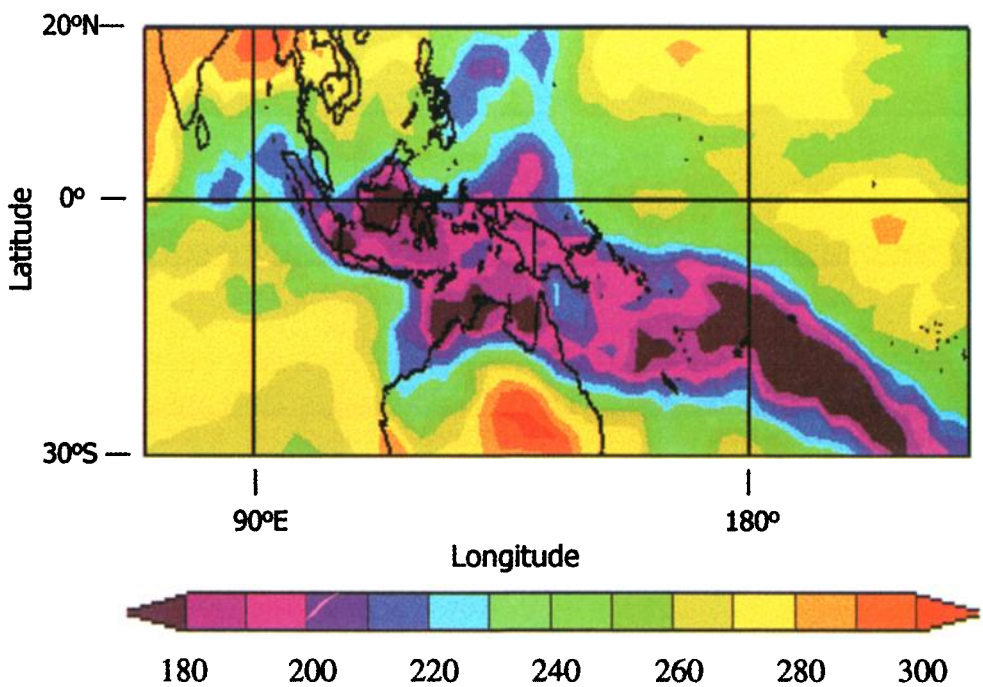

Plate 5. Map of the average outgoing longwave radiation (OLR) for the period February 12-20, 1999. Plot from the NOAA-CIRES Climate Diagnostics Center.

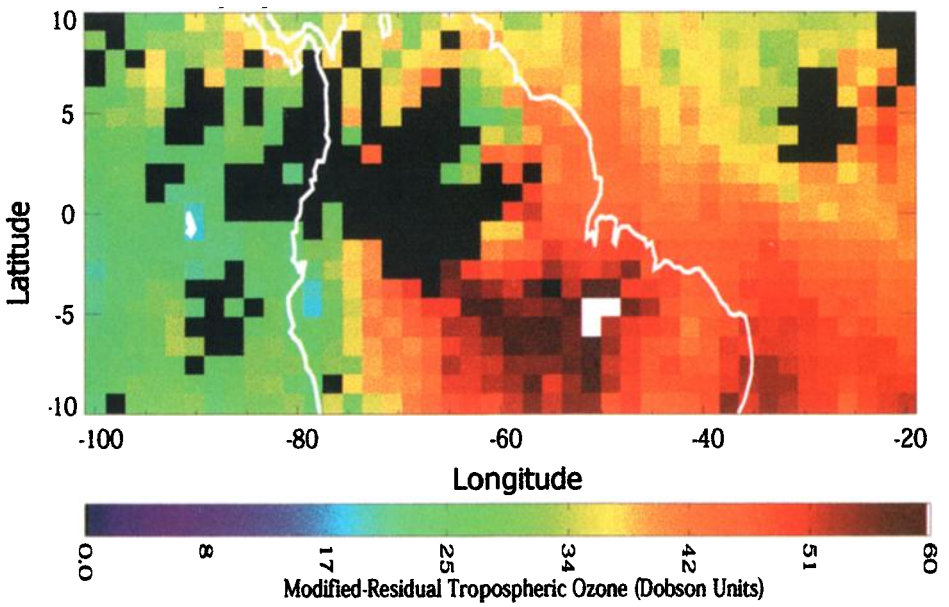

Plate 6. Map of the average tropical tropospheric ozone residual computed from the TOMS total column ozone for the period October 4-6, 1999.

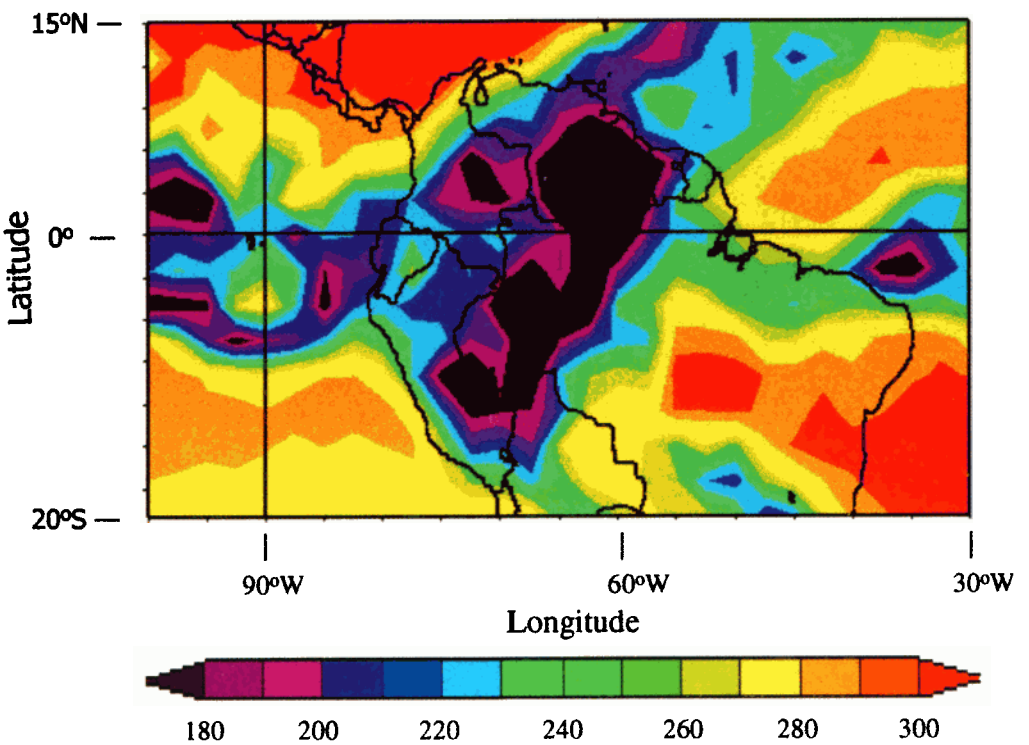

Plate 7. Map of the average OLR for the period March 31, 1998. Plot from the NOAA-CIRES Climate Diagnostics Center.

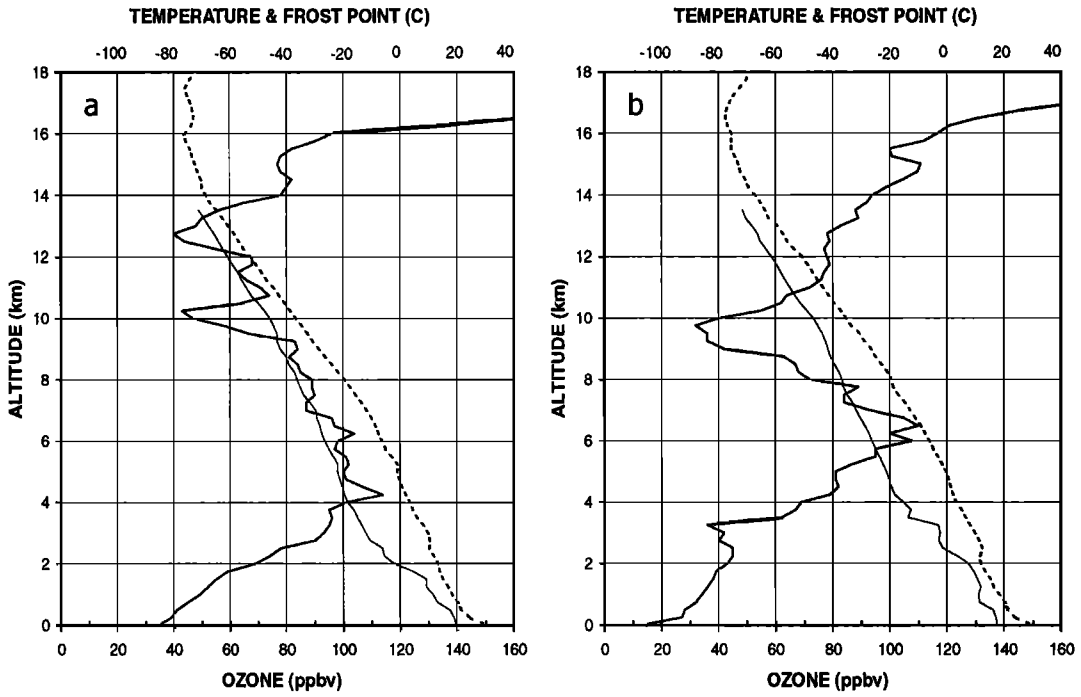

Figure 25. Ozone mixing ratio profiles at Natal on (a) September 29, 1999, and (b) October 6, 1999.

region of highest tropospheric column ozone as being over central Brazil. From the Galapagos and Natal soundings it is clear that enhanced ozone amounts resulting from biomass burning are transported both to the east [*Kirchhoff et al.*, 1996] where they appear at Natal and to the west reaching at least as far as the Galapagos. It is possible based on the case studied here that air reaching Natal from the region of burning may be recirculated back to the west toward the Galapagos or may be transported directly from the burning region to the Galapagos.

Investigation of each profile with an enhanced ozone layer in the midtroposphere during the August-October period showed a trajectory that passed over Brazil. At times of the year when burning is not occurring in Brazil, profiles at the Galapagos do not show pronounced tropospheric peaks (Figure 26). Profiles with mixing ratios near 50 ppbv in the midtroposphere are occasionally seen (Figure 26a). These higher amounts are generally associated with flow from continental South America (Figure 27a). However, flow from the continent may also have

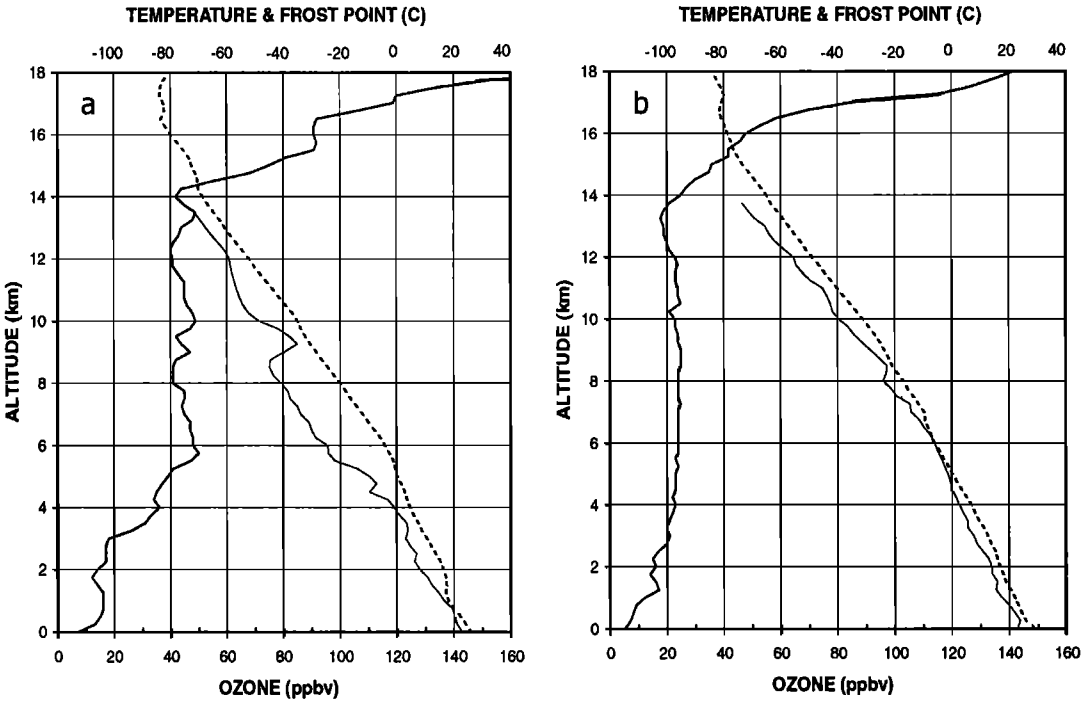

Figure 26. Ozone mixing ratio profiles at the Galapagos on (a) March 25, 1999, and (b) April 4, 1998.

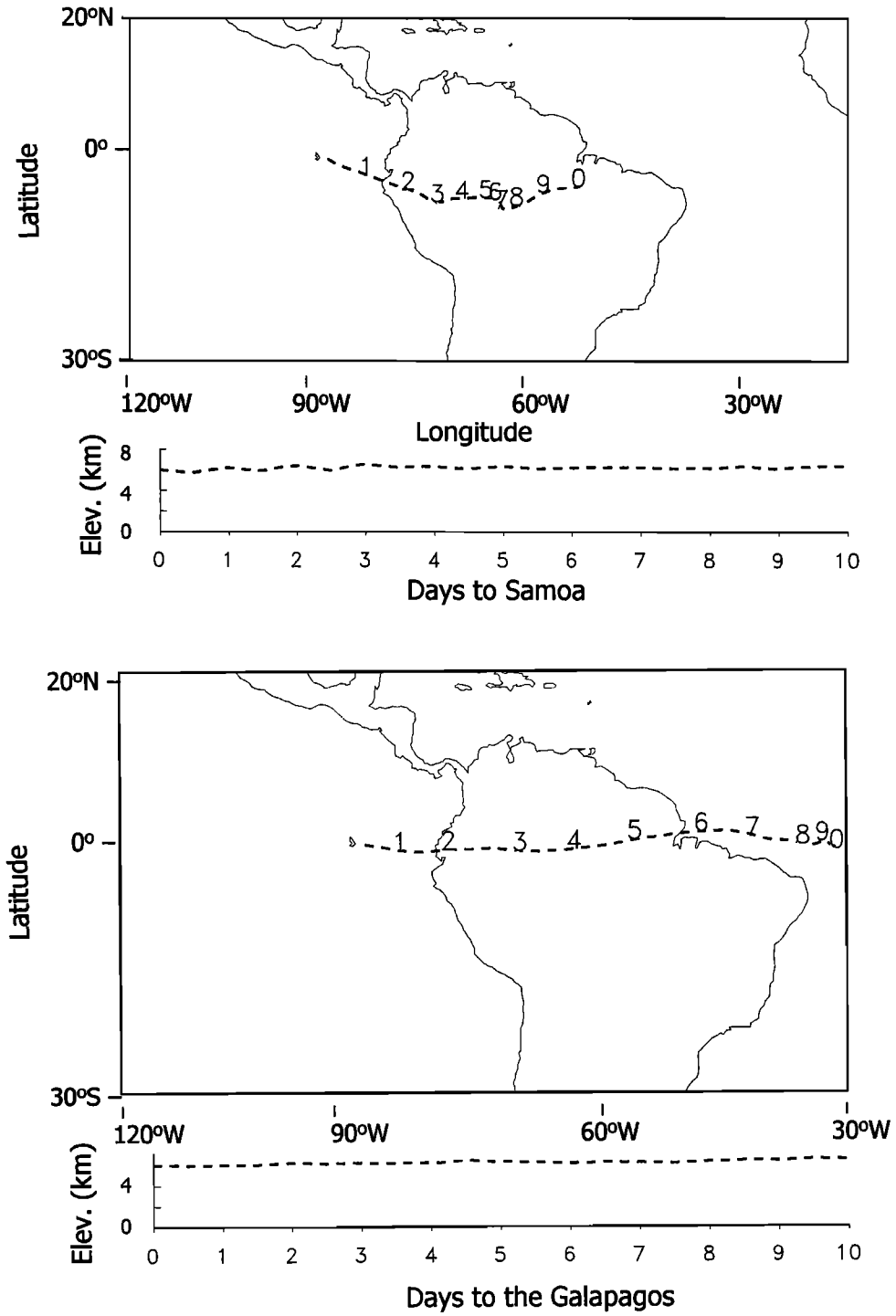

Figure 27. Trajectories to the Galapagos at 6 km on (a) March 25, 1999, at 1200 GMT and (b) April 4, 1998 at 120 GMT.

relatively low ozone amounts (Figures 26b and 27b). It appears that even though transport to the site is similar, that unless this flow taps a source region with higher ozone, the passage of air parcels over a continent is not sufficient (although it does appear necessary) to give enhancements in the ozone amount. The April 4, 1998, example (Figure 26b) was also near the end of the 1997-1998 El Niño-southern oscillation (ENSO) warm phase with well above normal precipitation both in the Galapagos and western equatorial South America. The profile of April 4 suggests that convection has influenced the profile since humidity is high up to ~9 km (the depression between the air temperature and frost-point temperature shown in Figure 26b is small). The convection that is responsible for the characteristics of this profile is likely to have occurred over equatorial South America where the trajectory (Figure 27b) shows the air parcel intersecting an area of very strong convection (Plate 7). Convection nearer to the

Galapagos may have influenced the characteristics of the ozone profile at lower levels (below ~6 km), but this cannot be discerned from the profile information.

7. Conclusions

From an extensive set of ozone profiles obtained over the past several years in the tropical Pacific, the picture emerges of a region of both very low tropospheric ozone amounts (~10 ppbv) and surprisingly large (~100 ppbv) mixing ratios at all of the sites studied. The low concentrations are expected in light of the strong photochemical sink in this region [*Kley et al.*, 1997], and the important role of convection, particularly during the austral summer. On the other hand, the ubiquitous presence of midtropospheric layers of enhanced ozone demonstrates that the influence of biomass burning is widespread throughout the tropical zone during August-November. In several examples a strong connection could be made between enhanced ozone amounts in the burning source region and layers of large ozone concentration in both the eastern and western tropical Pacific. On average, ozone at the equatorial Galapagos site in the eastern Pacific is greater than at the three western tropical Pacific sites. However, for individual profiles the midtropospheric enhancements seen in the western Pacific attain larger mixing ratios than those seen in the Galapagos. This is in spite of the fact that the Galapagos are located much closer to a potential source of biomass burning (Brazil) than are the western Pacific sites (southern Africa). The proximity of other sources in Australia and Indonesia may partially account for this by providing closer source regions for the western Pacific sites. Alternatively, the much greater amount of biomass burned in southern Africa may produce larger ozone enhancements [*Olson et al.*, 1999]. The extensive burning that took place in Indonesia and Malaysia during the latter half of 1997 appears to have been the source of very large ozone amounts seen in Samoa and Fiji in November 1997.

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