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Summer and spring ozone profiles over the North Atlantic from ozonesonde measurements

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Abstract. Ozone profiles obtained by near-daily ozonesonde observations during campaigns at several sites in the North Atlantic are used to construct time-height cross sections of ozone concentration through the troposphere. Strong day-to-day ozone variability on the scale of synoptic meteorological disturbances is found both in the spring and in the summer throughout much of the troposphere. Layers of high ozone concentration (~100 ppb) are frequently seen in the middle and upper troposphere and are invariably associated with transport characteristics that strongly support a stratospheric source for these layers. Regions of low ozone (<40 ppb) are seen in the middle and upper troposphere associated with higher relative humidity. The connection of these events with low surface mixing ratios suggests that convective processes mix air low in ozone up through the troposphere. Vertical layering of ozone mixing ratio, which is seen at all of the observing locations, is a result of differing sources of air in the different layers.

Introduction

The significant role of ozone as an atmospheric oxidizing agent and greenhouse gas and the important part that human pollution sources can play in modifying its distribution provide strong motivation for a more complete understanding of ozone's behavior in the atmosphere. Because of its impact on human health and plant life, ozone has been most intensively observed near the surface. The limitations of observing ozone and other constituents primarily at the surface have long been recognized. Many components of the North Atlantic Regional Experiment (NARE) were designed to provide the necessary profile information for understanding the chemical behavior of the troposphere over the North Atlantic [*Fehsenfeld et al.*, this issue].

One goal of the vertical profiling measurement program within NARE was to obtain ozone vertical profiles throughout the troposphere and lower stratosphere using balloon-borne ozonesondes. During the NARE intensive in August 1993, ozone profiles were obtained from Keflavik, Iceland; Bermuda; and Lages, Azores. In addition, intensive series of spring profiles were obtained in April/May 1993 in Bermuda and May 1994 in the Azores. We will also report on profiles obtained at Cape Race, Newfoundland, in July/August 1991 and soundings from Tenerife in the Canary Islands in August 1993 and May 1994 (see Figure 1 for map of ozonesonde launch locations). The near daily soundings from several of these campaigns give us the opportunity to investigate the processes responsible for the very strong day-to-day variability that was regularly seen during the intensive profiling protocol. Several events in which high ozone amounts were seen in the midtroposphere over Bermuda are analyzed in detail in accompanying papers [*Merrill et al.*, this issue; *Moody et al.*, this issue]. In this paper as well as the two accompanying papers, the strong role of synoptic scale meteorological events will be noted. The ozone vertical profiles along with the analyzed meteorological fields provide an important tool for understanding ozone behavior in the troposphere. There are also some significant limitations to this approach. Ozone precursor gases are not measured with the ozone profile. Useful tracers of anthropogenic influence such as carbon monoxide are also not obtained from the balloon sounding. Water vapor amount is measured with the ozone concentration, so this does provide a useful but not always unambiguous indicator of air parcel history. In some cases the ozone profile and meteorological information are sufficient to make a strong case for a natural source (the stratosphere) for the observed elevated ozone amounts. In other instances a source is not easily identified and, in particular, the anthropogenic contribution may be suggested by the airflow to the site but cannot be unambiguously identified with this data set alone.

The time history of the ozone profiles from the periods of near daily soundings is displayed in the time-height cross sections. Mean characteristics for each site and season are

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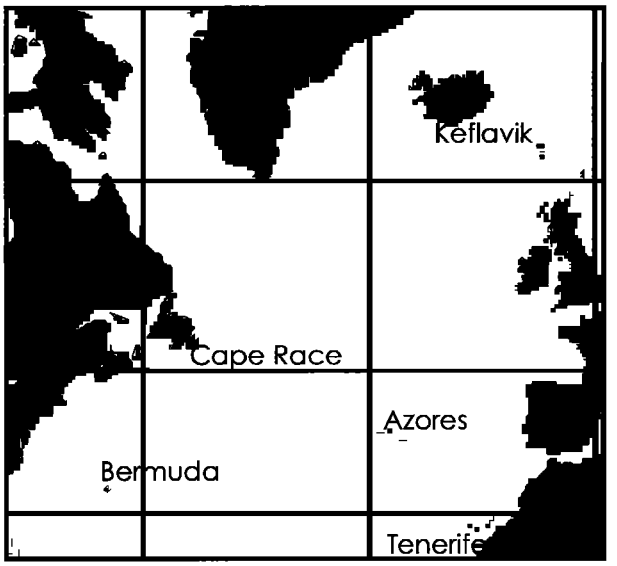

Figure 1. Map of the North Atlantic region showing locations where ozonesonde launches were made.

used to summarize the numerous soundings and for comparison of the ozone behavior at the various locations. Several representative ozone "events" are investigated at the various sites in relation to the changes in transport to the sampling location.

Measurements

The ozone vertical profiles in this study were obtained from balloon-borne ozonesondes. The ozonesonde consists of an ozone sensor (the electrochemical concentration cell), a noncontaminating air pump, an electronic interface board, and a model RS-80 Vaisala radiosonde. The electrochemical concentration cell (ECC) sensor [*Komhyr*, 1969] is widely used and has been extensively tested and compared with other techniques [*Komhyr et al.*, 1995]. The principle of measurement is the reaction of ozone with potassium iodide in solution which produces a small current in the cell. This current is quantitatively proportional to ozone with one ozone molecule producing a flow of two electrons. This reaction is not specific to ozone, so that other oxidants and reductants also produce a response. The primary interfering nonozone oxidant is NO_2 which responds with about 10% the efficiency of ozone. In the atmospheric regime considered here, the NO_2 concentration is in the sub-ppb range and thus is not a significant interferent. The primary atmospheric reductant affecting sensor response is SO_2 which acts with equal efficiency but in the opposite direction to ozone. Again SO_2 concentrations are in the sub-ppb range. The Teflon pump of the sonde is noncontaminating and does not destroy ozone. Since ozone is measured quantitatively by the ECC ozonesonde, it is not necessary to "normalize" the integrated ozone profile amount to an independent measure of column ozone such as the Dobson or Brewer spectrophotometers. This is important since other column ozone measurements are not available at all of the sites. The small instrument package (~2 kg) is carried aloft on a small helium or hydrogen-filled rubber meteorological balloon (1200 g) which normally reaches altitudes in excess of 30 km. Temperature, humidity (to ~12 km), and pressure are obtained from the accompanying Vaisala radiosonde. Data are sampled every 8 s. The sensor gives a 1/e response to a step change in ozone in 20 s, which translates to a vertical resolution of approximately 100 m. The normal data product and the one which will be used here is a 250-m height average. The sonde accuracy is 10% for tropospheric mixing ratios except in the case of very low mixing ratios (<10 ppb) when the accuracy may be degraded to 15%. Most of the launches were done in the morning local time which corresponds to 0900-1500 UT.

The trajectories used in this work are isentropic 10-day back trajectories. The trajectory model [*Harris and Kahl*, 1994] uses gridded analyses produced by the European Centre for Medium-Range Weather Forecasts (ECMWF). The trajectories do not pinpoint the origin of an air parcel but rather are indicative of the airflow path under the assumption of adiabatic displacement of the air parcels. For most of these sites in the mid-Atlantic, upper air observations in the surrounding region are sparse so that even close to the trajectory starting point there is significant uncertainty in the calculated representation of the air parcel motion. Under certain circumstances, such as when a synoptic scale front is encountered, the flow is probably not well resolved in the gridded analysis and the path represented by the trajectory may be suspect. We routinely calculate the trajectories back 10 days, which in some cases gives an unwarranted impression of our knowledge of the air parcel motion. The 10-day period is chosen primarily for computational uniformity when a large number of cases are being studied.

Time-Height Cross Sections

The time-height cross sections of ozone mixing ratio displayed in Plates 1-6 summarize the profile information during the periods of intensive observations and dramatize the kinds of changes seen throughout the troposphere. We first discuss the results from August 1993 when measurements were carried out simultaneously at Iceland, the Azores, and Bermuda (Plates 1-3). In Iceland (Plate 1a) the most striking feature is the large changes with time in tropopause height and hence the varying depths to which large ozone mixing ratios extend. The tropopause is marked in each cross section with the thick white line. The tropopause is determined from the temperature profile following the standard meteorological convention (the altitude where the average lapse rate first falls below 2°C/km for at least 2 km). The dips to lower altitude of high ozone concentration (e.g., Julian days 239-241 (August 27-29)) do not represent penetration of these large values into the troposphere but simply changing tropopause height. The periods of largest ozone mixing ratio in the middle and lower troposphere are all associated with the highest, not the lowest, tropopause heights. This is seen on Julian days 219, 230, 236, and 243 (August 7, 18, 24, and 31), where ozone amounts between 40 and 50 ppb extend down to altitudes below 2 km. Except for Julian day 243 (August 31), these were days of relatively larger ozone concentration at the surface. Although most of the tongues of large ozone mixing ratio stretching from the stratosphere down to the lower troposphere are associated with very dry air (e.g., Julian days 236 and 237 (August 24 and 25)), Julian day 230 (August 18) is not particularly dry (Plate 1b). It is also clear that

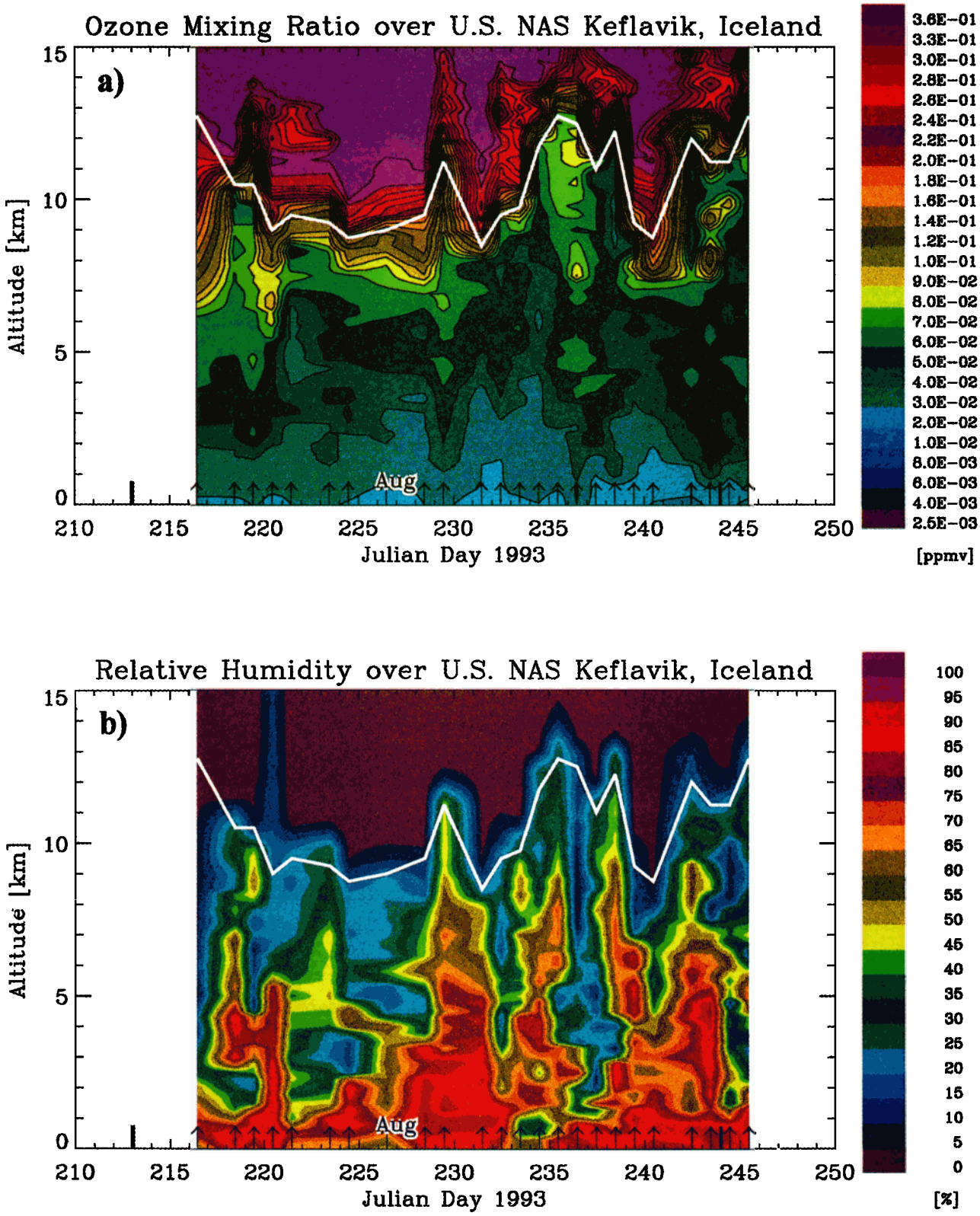

Plate 1. Time-height cross sections at Keflavik Air Base, Iceland, for August 1993 for (a) ozone mixing ratio (ppmv) and (b) relative humidity (%). The tick marks for the day denote the beginning of the day. The heavy tick mark denotes the first day of the month. The arrows along the lower axis are at the time of the sounding. The white, solid line marks the tropopause height based on the temperature profile using the standard meteorological convention to define the tropopause.

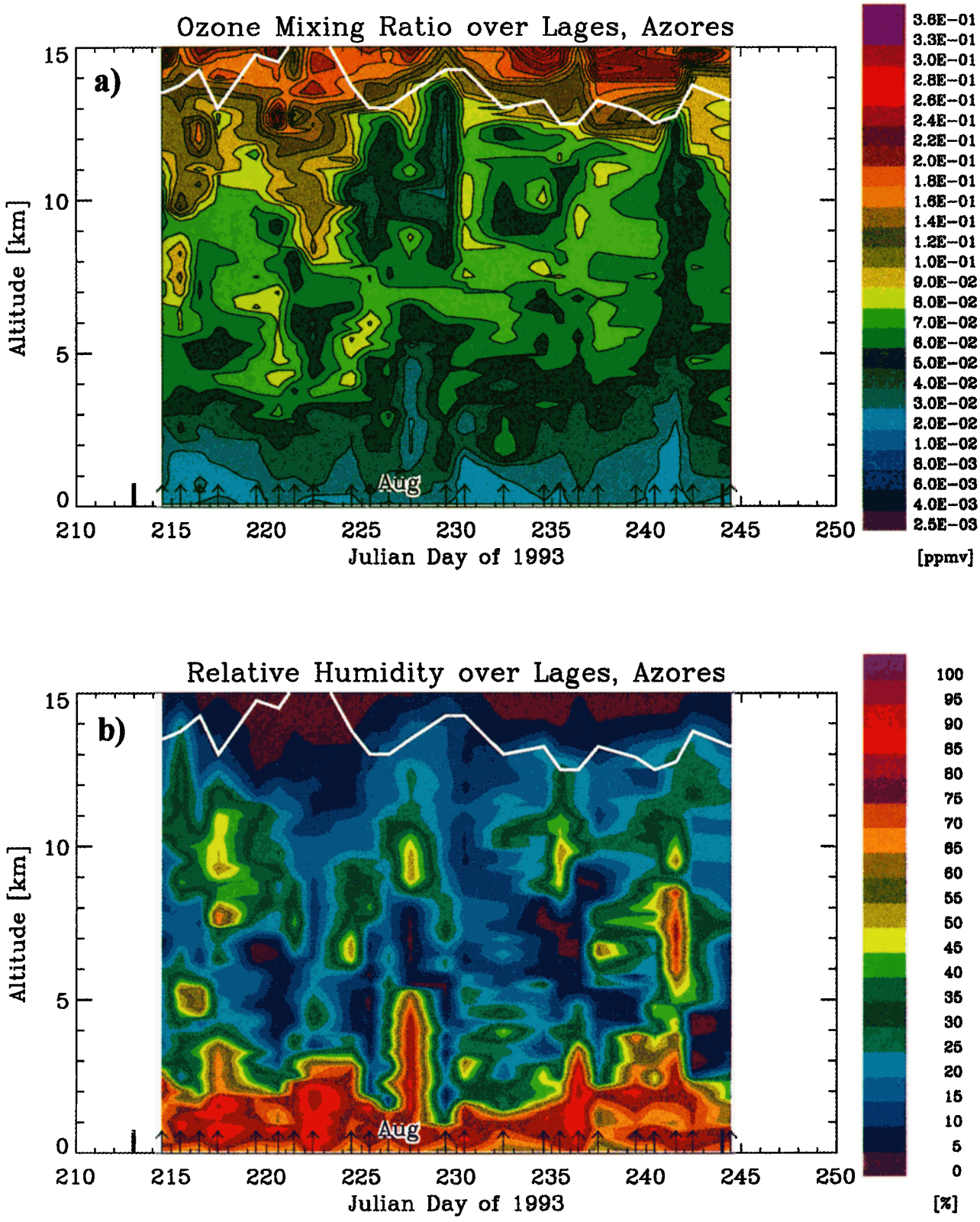

Plate 2. As Plate 1 but for Lages Air Base, Azores, in August 1993.

relatively smaller ozone amounts (<40 ppb) are found in the middle and upper troposphere. The humidity in these regions is invariably higher, implying this air had a source near the surface. Through the month there is a gradual decrease in the near-surface amounts, but this trend does not seem to be present in the midtroposphere.

In the Azores (Plate 2a) during August, the tropopause is usually between 12 and 14 km and larger ozone amounts (>90 ppb) extend into the upper troposphere (e.g., Julian days 216 and 222 (August 4 and 10)). At Bermuda (Plate 3a) the tropopause is near 15 km, and there are also several events where ozone amounts over 90 ppb extend into the

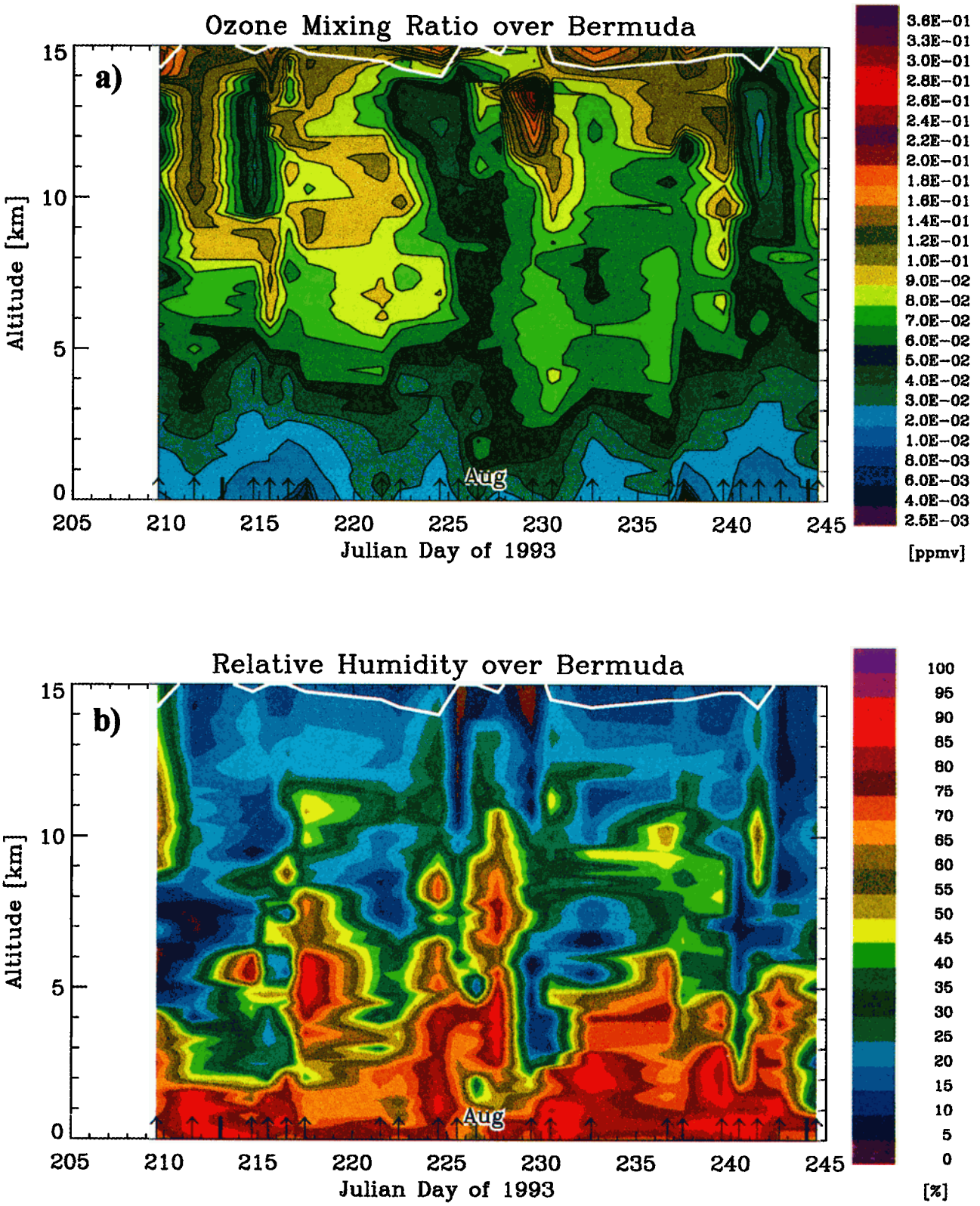

Plate 3. As Plate 1 but for Bermuda Naval Air Station in August 1993.

midtroposphere. Equally apparent at both these locations is the presence of regions of relatively small mixing ratios (30-40 ppb) near the tropopause. In some cases these features extend from near the surface to near the tropopause (e.g., around Julian day 227 (August 15) at both Bermuda and the Azores). The regions of smaller ozone mixing ratios are always associated with higher humidity (Plates 2b and 3b). The very strong correspondence between high humidity and smaller ozone amounts is consistent through the month and through the entire depth of the troposphere. At both

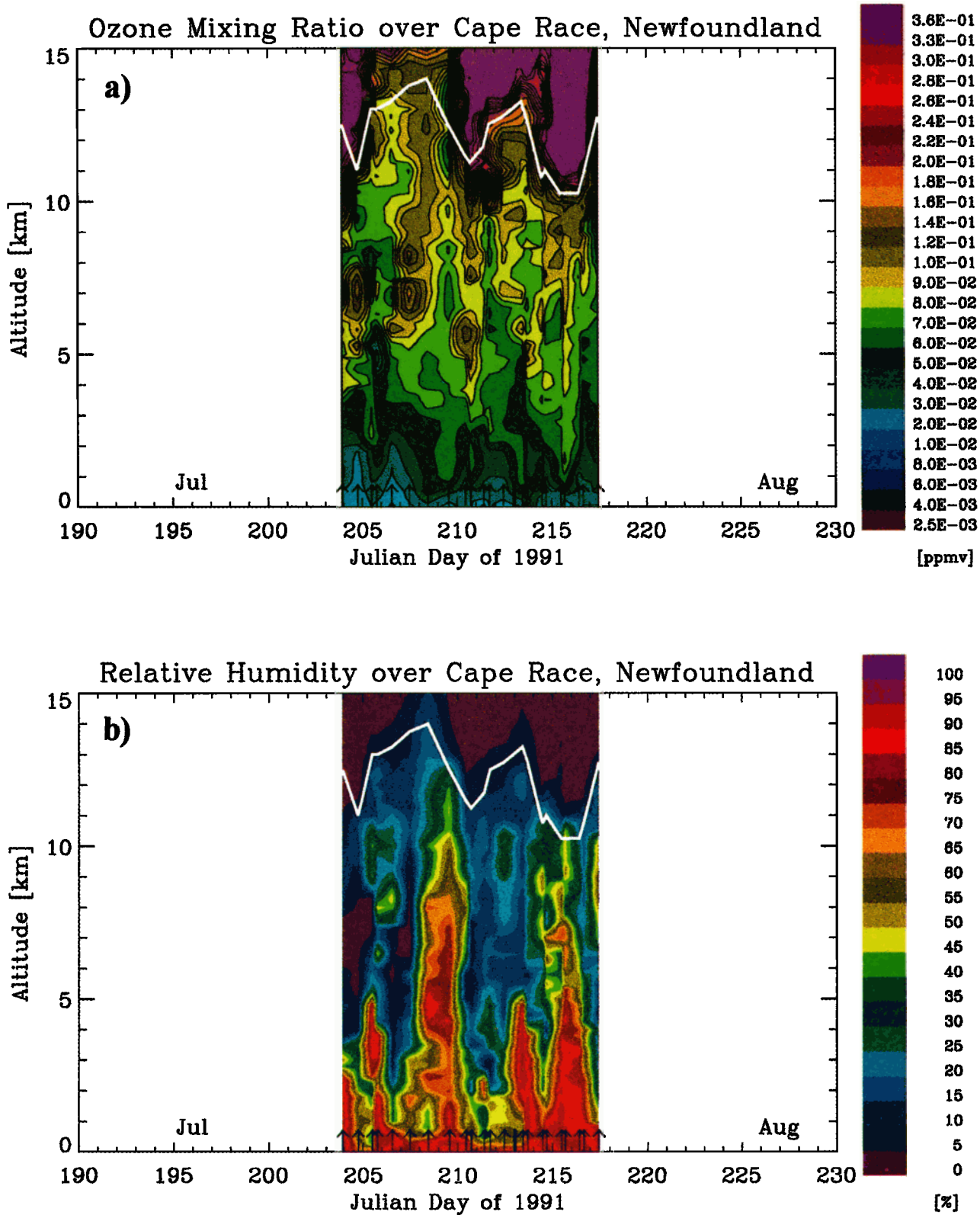

Plate 4. As Plate 1 but for Cape Race, Newfoundland, in July and August 1991.

Bermuda and the Azores the two periods, which show this pattern most dramatically, occur very near the same times (Julian days 227 and 242 (August 15 and 30)) of the month.

Abundant moisture in the lower troposphere (<2 km) during the summer sets the stage for significant ozone photochemistry. The local levels of NO_x determine whether this results in net destruction or production [*Crutzen*, 1988]. The background ozone values at Bermuda are smallest in the summer and the vertical depth of this layer reaches 2 km much more consistently than at the other two locations. At the surface, ozone displays a diurnal signal with an afternoon minimum, just as has been observed at the tropical remote

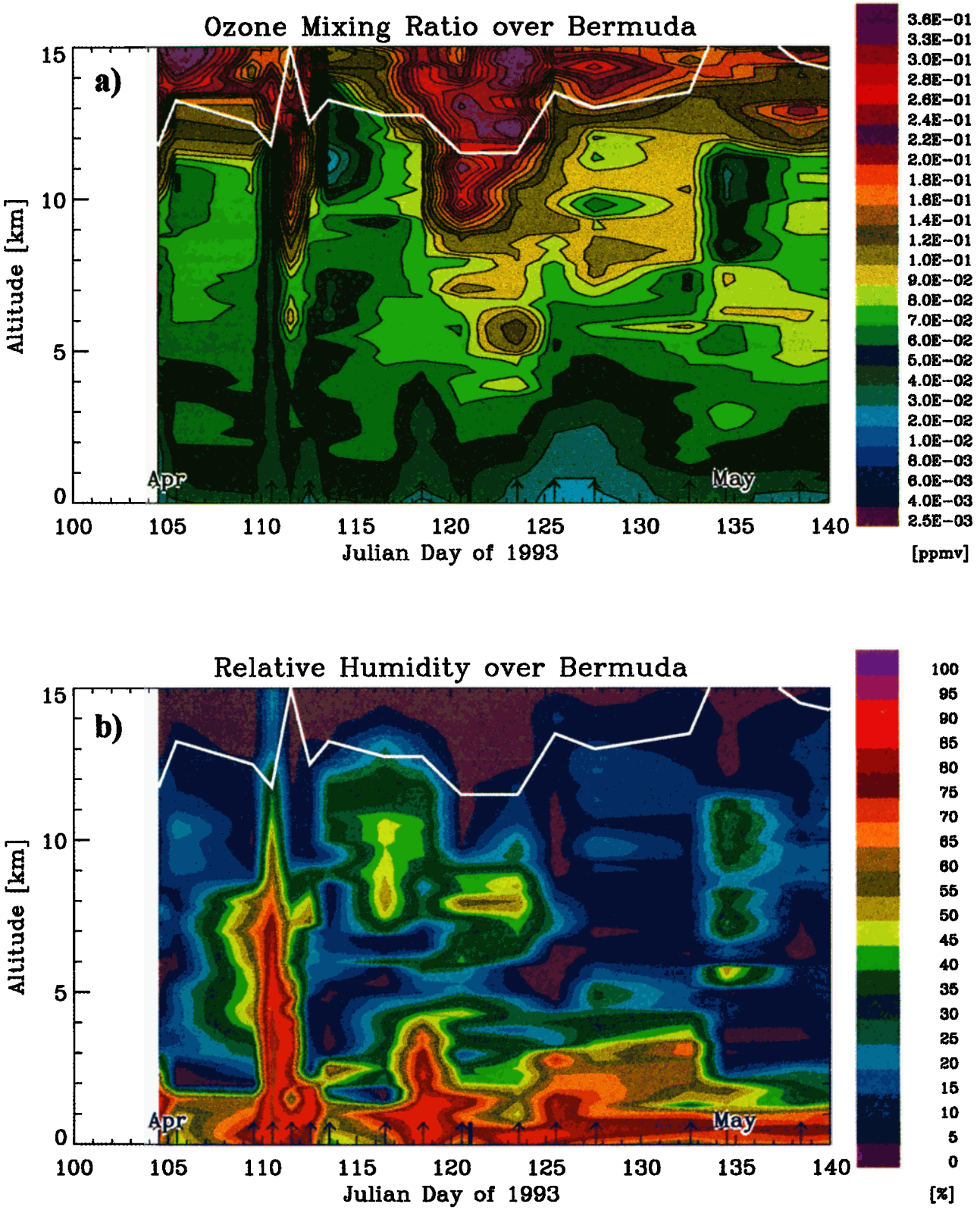

Plate 5. As Plate 1 but for Bermuda in April and May 1993.

locations of Barbados and Samoa [*Oltmans and Levy II*, 1992; *Oltmans*, 1981]. This behavior combined with the low background levels of surface NO_x reported by *Dickerson et al.* [1995] and the simulations of ozone chemistry reported by *Kasibhatla et al.* [this issue], strongly suggests that net destruction dominates. Definitive proof of this hypothesis awaits the simultaneous measurement of ozone, water, CO, and NO_x in this layer at a location like Bermuda.

For Cape Race (Plate 4) the intensive observations cover 2 weeks at the end of July and early August 1991. The upper troposphere shows that the strong influence of the very large ozone amounts in the overlaying stratosphere and ozone

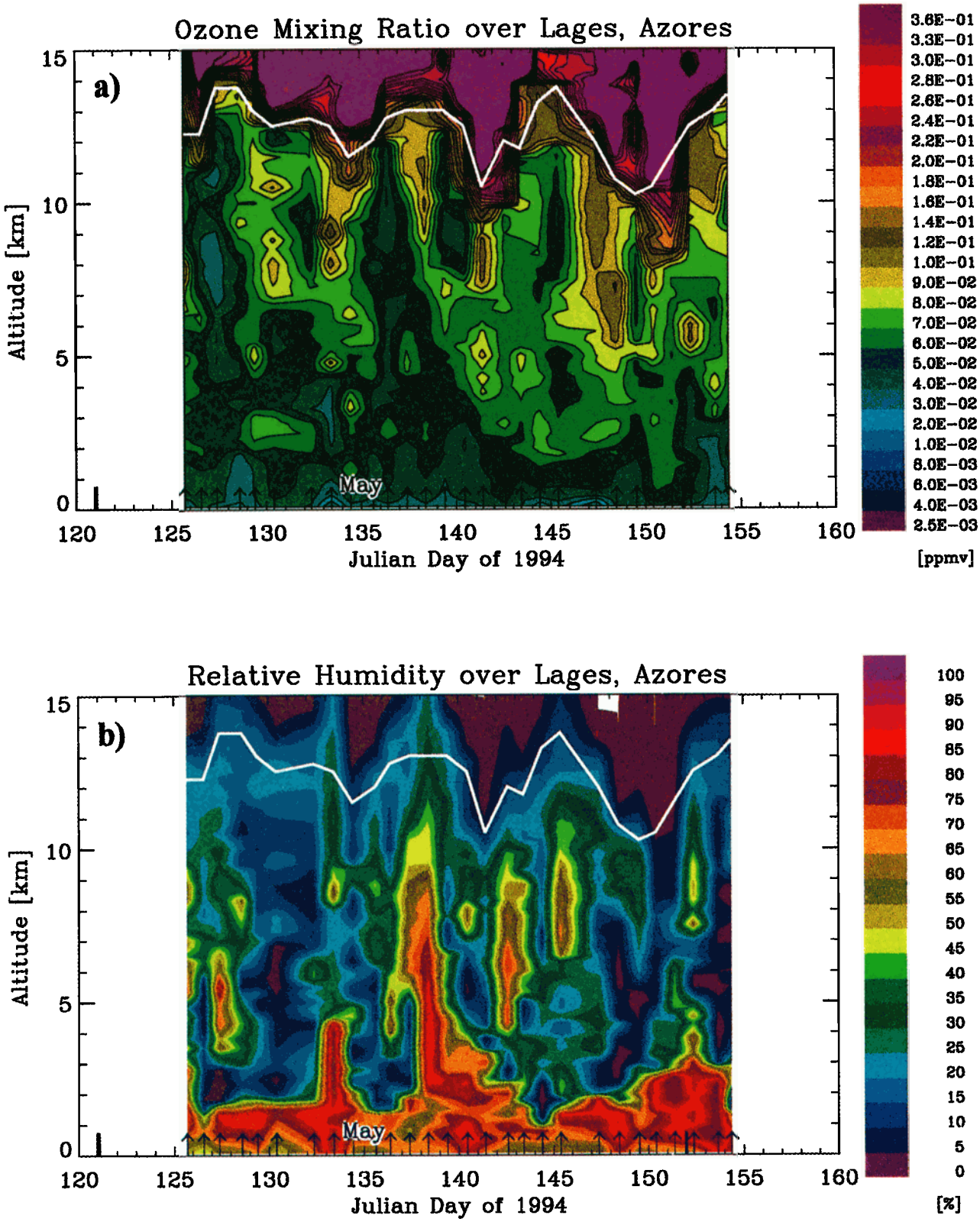

Plate 6. As Plate 1 but for the Azores in May 1994.

amounts of ~100 ppb reach into the midtroposphere (Plate 4a). The extension of the large ozone amounts into the midtroposphere is associated with both high and low tropopauses. Several periods when smaller ozone mixing ratios extend from the surface into the upper troposphere can also be seen. As at other locations, these are associated with higher relative humidity (Plate 4b).

Spring profile measurements were done in Bermuda in April/May 1993 (Plate 5) and the Azores in May 1994 (Plate 6). At Bermuda during the second half of May, the soundings are less frequent, so that some of the features look more persistent than they probably are. In the Azores there are significantly larger variations in the tropopause height than during the summer. The regions of very large ozone

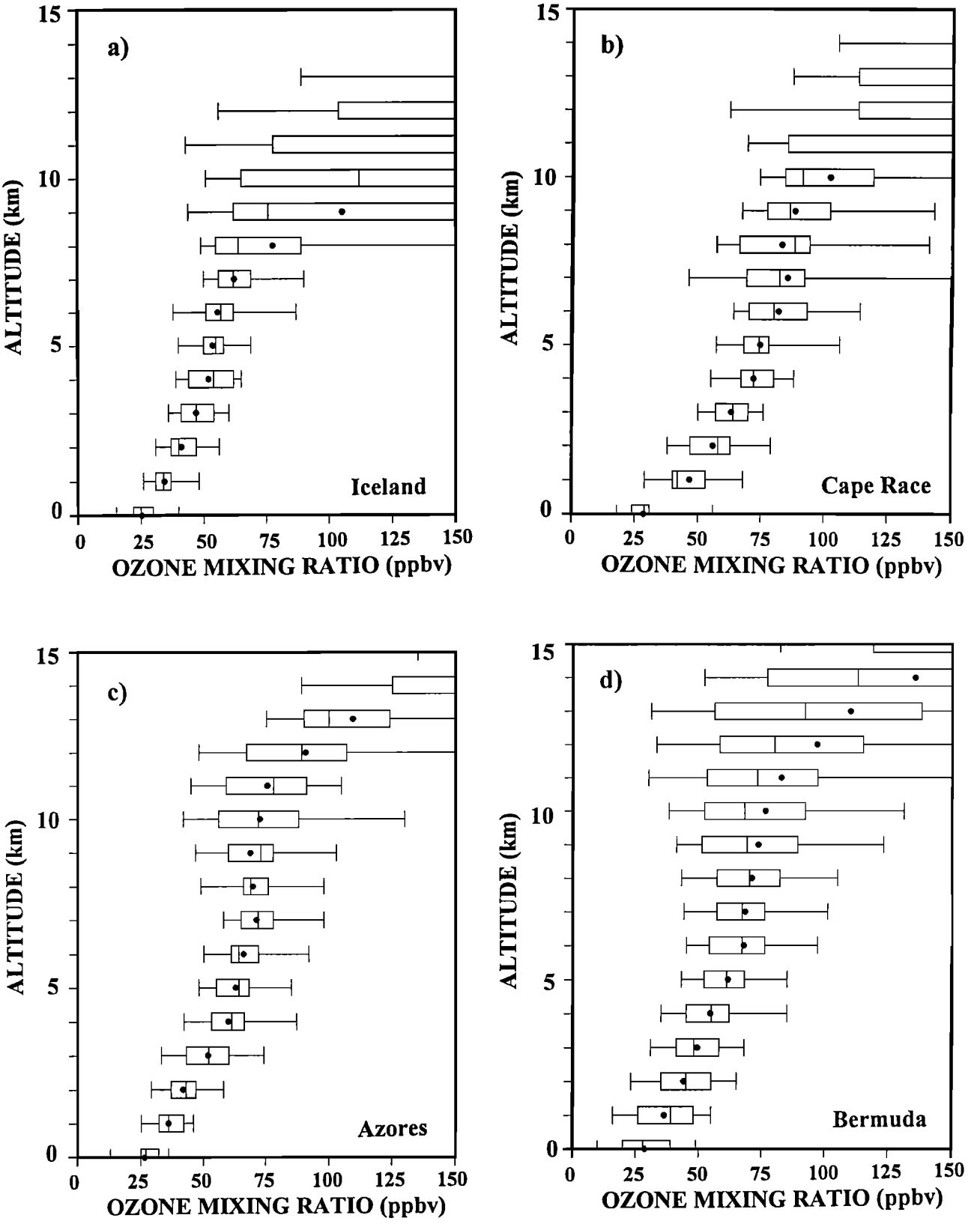

Figure 2. Tropospheric ozone mixing ratios at 1-km intervals for (a) Iceland, August 1993; (b) Cape Race, July/August 1991; (c) Azores, August 1993; (d) Bermuda, August 1993; and (e) Tenerife, August 1993. The solid dot is the mean; the bar is the median; the box is the inner 50th percentile; and the whiskers are the inner 90th percentile.

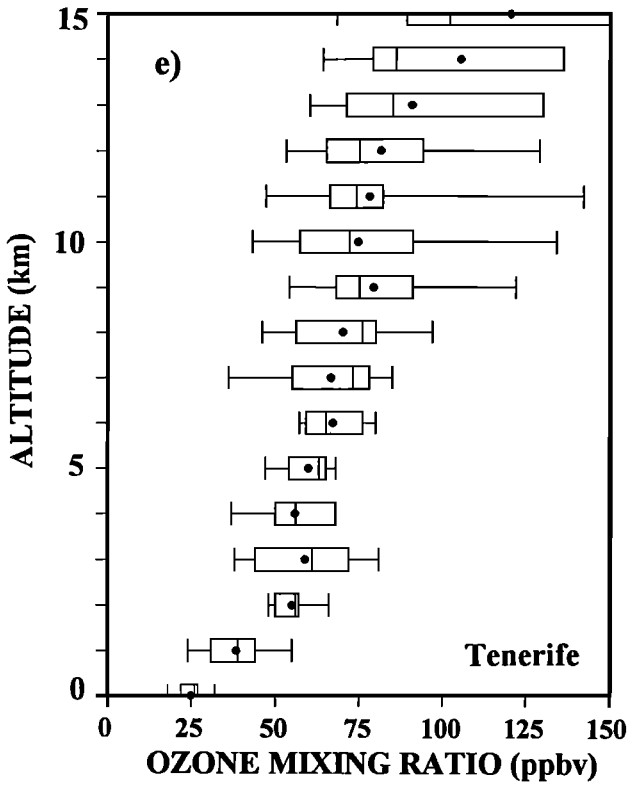

Figure 2. (continued)

amounts (>150 ppb) that dip below ~10 km are generally in the stratosphere. At Bermuda (Plate 5a) the regions of large ozone mixing ratios below 14 km are all within the troposphere.

In the Azores, because there are profiles almost every day during the observing period, a clear picture of the frequency of the variations at different levels is seen. At most levels, significant maxima or minima are seen every 3-6 days, which is consistent with synoptic scale meteorological influence on the changes in ozone concentration. Regions of larger ozone amounts (>80 ppb) tend to extend downward from the tropopause to about 5-7 km. Below 5 km, down to about 2 km, there are still significant periods and regions with ozone mixing ratios >60 ppb. This is the case especially during the latter half of May. The regions with ozone >60 ppb all have low humidity (Plate 6b) of <20%. Both the dryness of the air and the vertical connection of the large ozone mixing ratio region with the tropopause suggest that the stratosphere plays a major role during this time in loading the middle and upper troposphere with ozone. During May there are fewer events in which smaller ozone mixing ratios are found in the middle and upper troposphere compared to the summer. On Julian days 126, 127, and 137 (May 6, 7, and 17), columns of smaller ozone mixing ratio and high humidity are present. The event of Julian day 137 (May 17) is one which extends upward all the way from the surface. After this the troposphere is dominated almost exclusively by air with ozone mixing ratios exceeding 60 ppb from the tropopause to 2 km. The troposphere appears to be gradually filling with ozone from above during the latter half of the month. During this time there are none of the events in which small ozone amounts and high humidity extend upward from the surface into the troposphere.

At Bermuda the less frequent profiles limit any generalization that can be made from Plate 5 on the frequency and timing of the events. Two events in mid-April and the beginning of May appear to bring stratospheric air into midtropospheric levels. Just prior to the mid-April event, strong convection mixes surface air to the tropopause. This particular case is be discussed later. As at the Azores, surface amounts are significantly higher in spring than during the summer [*Oltmans and Levy*, 1992].

The picture that emerges from the cross-sectional representation of the intensive ozone profile data in both the spring and the summer is the connection between large ozone mixing ratios and dry air in the middle and upper troposphere with the large ozone values in the tropopause region. On the other hand, smaller ozone amounts at these altitudes are associated with high humidity and are often connected vertically with the surface. The timescale of changes from large to small ozone mixing ratios or water vapor amounts is of the order of a few days (somewhat longer in the summer), which is similar to synoptic scale variations.

Average Behavior

To look at differences between seasons and locations, we use the box and whisker representation of the median, inner 50th, and inner 90th percentiles to show average behavior and dispersion at 1-km increments for each of the periods of observations (Figures 2a-2e). In addition to the four sites discussed in the previous section, profile data from Tenerife, Canary Islands, for August 1993 and May 1994 will be used to broaden the scope of the results. One of the most striking features of the summer average profiles (Figure 3) is the

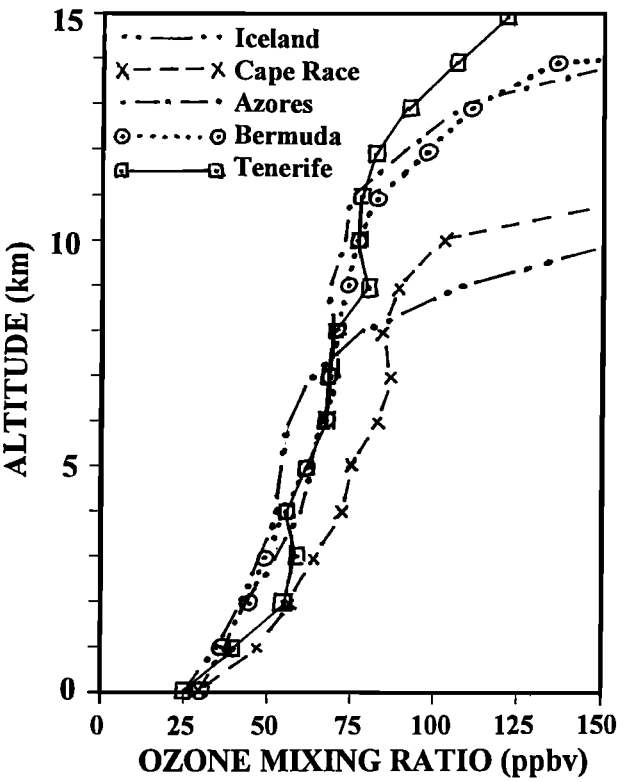

Figure 3. Average ozone profiles for each of the places and times shown in Figure 2.

larger mixing ratios at all levels in the troposphere at Cape Race. At the surface the mean (the solid dot) at all locations (Figure 2) is between 25 and 30 ppb except at Bermuda where it is slightly smaller (Figure 2d). At Cape Race there are surface events exceeding 50 ppb not seen at the other sites (Figure 2b). There is also a larger discontinuity seen at Cape Race between ozone amounts in the boundary layer and the next higher layer. On average there is about twice as much ozone in this layer at 1 km then at the surface (Figure 2b). This is consistent with the effect on air flowing over the North American continent found by *Berkowitz et al.* [1995]. Tenerife shows a similar feature (Figure 2e) which may result from the influence of the nearby African continent on air flowing to the Canary Islands.

During August the ozone mixing ratios above 4 km at the Azores, Bermuda, and Tenerife (Figure 3) are very similar up to the tropopause differing by 5 ppb or less at each level. Given the high degree of variability seen at each site, this difference of less than 10% in the mean concentration at each level is somewhat unexpected. This may suggest that at these mid-North Atlantic Ocean sites during the summer, the broad influence of the dominant subtropical high-pressure regime also shapes the ozone distribution over much of the region. It should be noted, however, that each of the sites is located quite differently relative to the center of this high-pressure system. In the 3 to 7-km region in Iceland (up to near the tropopause), mixing ratios are generally at least 10% smaller than the other island locations. At all locations there is a rapid drop of at least 50% in ozone concentration between 4 km and the surface. At Tenerife (Figure 2e), however, this drop in mixing ratio takes place primarily below 2 km. This is consistent with the results of *Schmitt et al.* [1988] and *Prospero et al.* [1995], which show elevated ozone values persisting through the summer months at the mountain station at Izaña located on the island of Tenerife. *Schmitt et al.* [1988] suggest that these enhanced summer ozone amounts could be from the transport of ozone resulting from anthropogenically produced emissions in Europe. This was based on the similarity of the annual ozone cycle at Izaña with that at anthropogenically influenced sites in Europe and in contrast to the distinct spring maximum found at Mauna Loa, Hawaii. *Prospero et al.* [1995], however, showed that the large summer concentrations were more closely related to tracers of upper tropospheric air which did not have a signature of recent continental origin. A very recent set of intensive ozone profiles obtained during June and July 1995 (E. Cuevas, private communication, 1996) shows that high ozone mixing ratios dominate the entire troposphere during the early summer and the large values at Izaña at 2.5 km are really an extension of this.

The average behavior in spring (for these averages this is primarily May data with a few profiles in late April and early June) at the subtropical island sites is roughly similar (Figure 4). Tropopause heights are several kilometers lower in the spring than in the summer. At the Azores and Bermuda, there is more ozone in the boundary layer in the spring than the summer, which is consistent with enhanced photochemical ozone loss in the summer. At Tenerife, on the other hand, May has less ozone in the 1 to 4-km region than August, reflecting the summer enhancement at this altitude. At each site there is a region of near constant or slightly increasing mixing ratio from 5 km to near the tropopause. Below 5 km, mixing ratios decline with an even sharper decline in the lowest kilometer. During May the

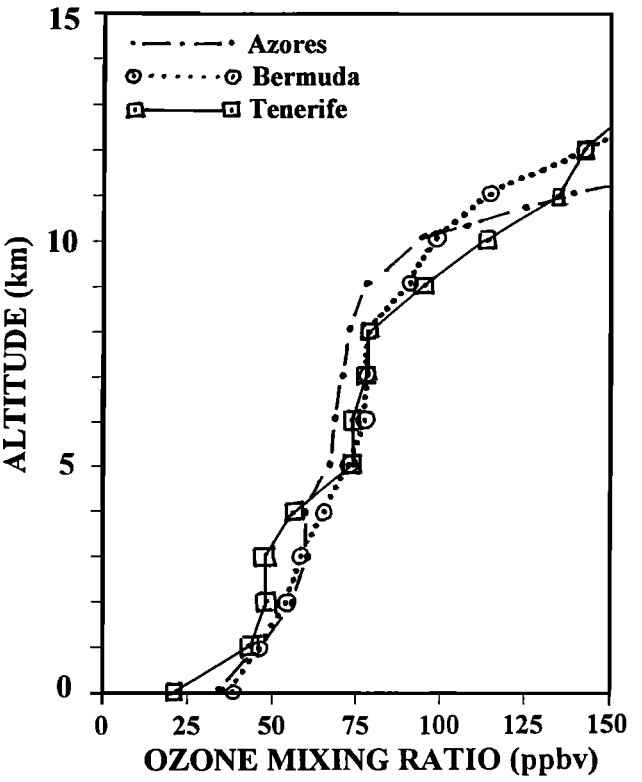

Figure 4. Average ozone profiles for May at the Azores (1994), Bermuda (1993), and Tenerife (1994).

Azores clearly has less ozone than Bermuda above 3 km, while during the summer, they were nearly identical. Of the three island sites at subtropical latitudes, the Azores has the smallest difference between spring and summer, while Bermuda has significantly more ozone in the spring. Because the tropopause is higher in the summer, this means that at Bermuda the spring and summer tropospheric column amounts are quite similar, but at the Azores there is about 50% more ozone in the summer column.

Case Studies

A number of individual ozone profiles from both the summer and the spring periods are presented in this section in order to use the transport characteristics, and in some cases other meteorological information, to help understand the features in the profile.

Summer events. In the period August 3-4, 1993, there are profiles from each of the three subtropical sites: Bermuda, the Azores, and Tenerife. This early August event at Bermuda is discussed in some detail by *Merrill et al.* [this issue]. At each location there is an enhanced ozone layer (>100 ppb) in the middle or upper troposphere (Figures 5a, 6a, 7a). For each location a back trajectory is shown for an end point that arrives in the boundary layer (Figures 5b, 6b, 7b) and one that arrives in the enhanced ozone layer (Figures 5c, 6c, 7c).

At Bermuda the trajectory near the time of the profile (1200 UT) shows strong cyclonic curvature and descent as the air parcel approaches Bermuda at the 8-km level (Figure 5c). The parcel passes through a region of enhanced potential vorticity over the northeast coast of the United States 2 days prior to reaching Bermuda [*Merrill et al.*, this

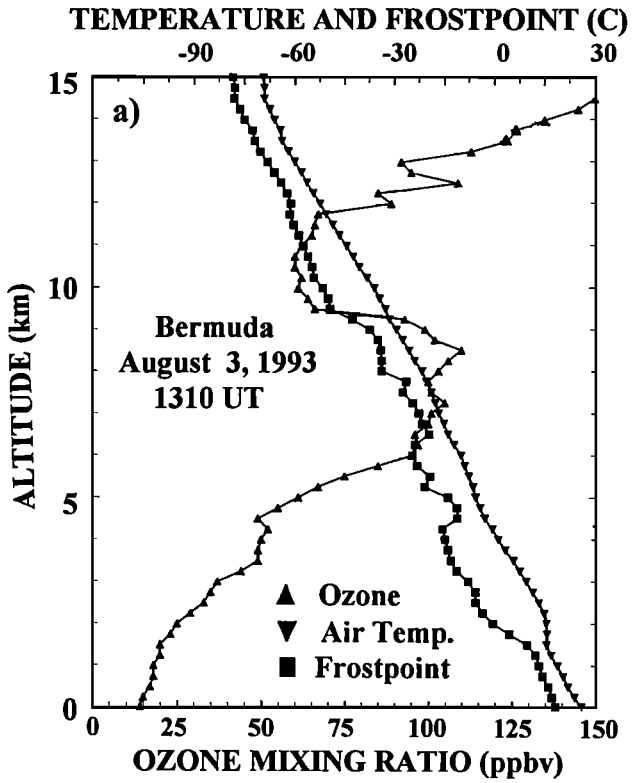

Figure 5. (a) Ozone mixing ratio, temperature, and frostpoint temperature profiles at Bermuda on August 3, 1993. (b) Trajectories for Bermuda on August 3 arriving at 1 km (a level in the boundary layer). (c) Same as Figure 5b but arriving at 8 km (a level near the center of the enhanced ozone layer).

issue]. In contrast, the low-level flow (Figure 5b) has remained south of 20°N for most of its transit over the ocean. Ozone amounts are about 20 ppb near 1 km in the profile, and the strong gradient below 3 km suggests that significant ozone is lost in the low levels.

On August 3 in the Azores (Figure 6a) a peak is seen at 7.5 km and a somewhat stronger one at 10 km. The trajectory reaching the Azores at 8 km (Figure 6c) shows strong descent 6 days earlier over the East Coast of the United States and passes near Bermuda about 4 days prior. This path indicates that the same event that brought the high ozone seen at Bermuda at the end of July (Plate 3a) also reached the Azores. The low-level flow (Figure 6b) on this day appears to come around the northern edge of the high-pressure system after being over the ocean for at least 10 days. The low-altitude amounts are not as low as Bermuda, however, where the trajectory stays much farther to the south. At Tenerife the ozone peak on August 4 is near 9 km (Figure 7a), which is well within the troposphere. The trajectory near the time of the sounding passes a bit east of the Azores (Figure 7c) about 2 days before reaching Tenerife. The peak at Tenerife may be part of the same event and flow that were responsible for the 10-km peaks in the Azores earlier. At 1 km over Tenerife the airflow (Figure 7b) also appears to bring air that reaches back to the North American continent but with a much different path than at higher levels. This air parcel path from higher latitude likely contributes to the 20 ppb larger amounts at 1 km at Tenerife compared to the other two sites.

At each of these locations the middle to high-elevation ozone peaks are related to flow back toward the North American continent. Limitations in this type of trajectory

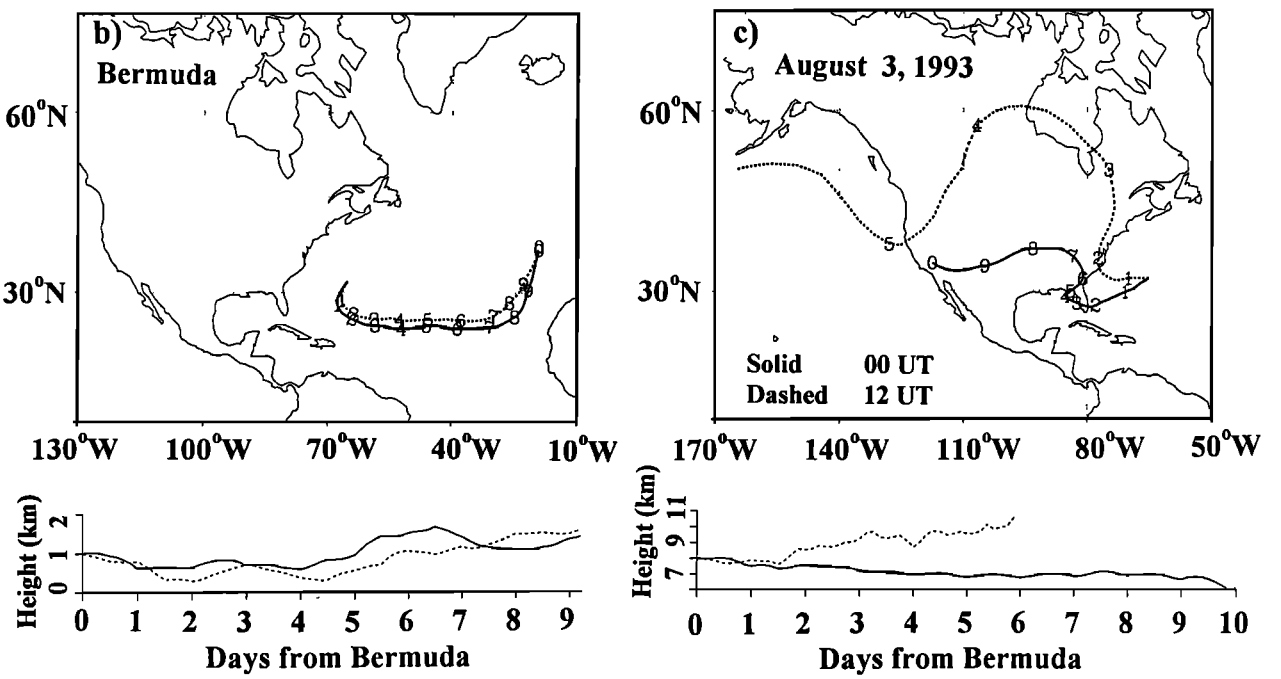

Figure 5. (continued)

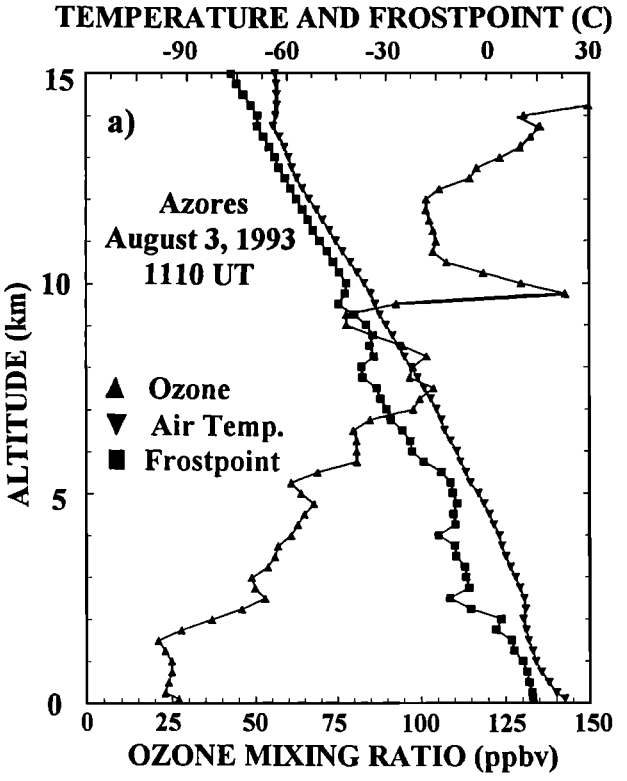

Figure 6. (a) Similar to Figure 5 but for the Azores on August 3, 1993, and with trajectory arrival at (b) 1 km and (c) 7 km.

analysis do not let us unequivocally tie features at one station with measurements at sites upwind, but they do suggest that high ozone seen over Bermuda may be related to similar features seen a few days later in the eastern subtropical Atlantic.

The higher average tropospheric ozone amounts at Cape Race were noted in a previous section. One type of event that contributes to this in the midtroposphere is shown in Figure 8. At 7 km on July 23, 1991, the ozone mixing ratio exceeds 150 ppb (Figure 8a). The previous day a layer was centered 2 km lower with a peak value of ~95 ppb (see Plate 4a). By July 24 the profile (Figure 8c) has relaxed back to about 75 ppb from 2 to 12 km with a couple of narrow layers with lower ozone content. The trajectories for July 23 and 24 (Figures 8b and 8d) show that flow by midday on July 23 is coming from the north and is associated with a large low-pressure system north of Baffin Island. The air parcels descend over 2 km in the 2 days before arriving at Cape Race. By July 24 the flow reaching Cape Race has become much more zonal, passing over the Pacific Ocean 3 days back. The high ozone peak on July 23 is also very dry (Figure 8a) with the relative humidity at all levels between 5 and 8 km on July 23 at less than 5%. Strong cyclonic activity is not located directly over Cape Race but well upstream in northern Canada. Although we do not have an ozone sounding from the location where the transfer of ozone from the stratosphere into the troposphere could actually occur, the pattern is similar to the August 3 case for Bermuda (also discussed by *Merrill et al.*, [this issue]). The rapidity with which changes can occur in the ozone profile over a station is demonstrated in this example. The soundings are only 18 hours apart, but in this time the ozone mixing ratio goes from over 150 ppb to under 50 ppb at 7 km. This is consistent with the rapid change in the air parcel path as represented by the trajectories.

From each of these summer cases from four different locations it is clear that events which bring ozone from the upper troposphere and stratosphere are relatively common, and that these events have peak ozone amounts as large as those seen in the spring. These events contribute substantially to the ozone budget of the troposphere during this season. At Cape Race where these events are the most frequent the tropospheric ozone mixing ratios are also the highest.

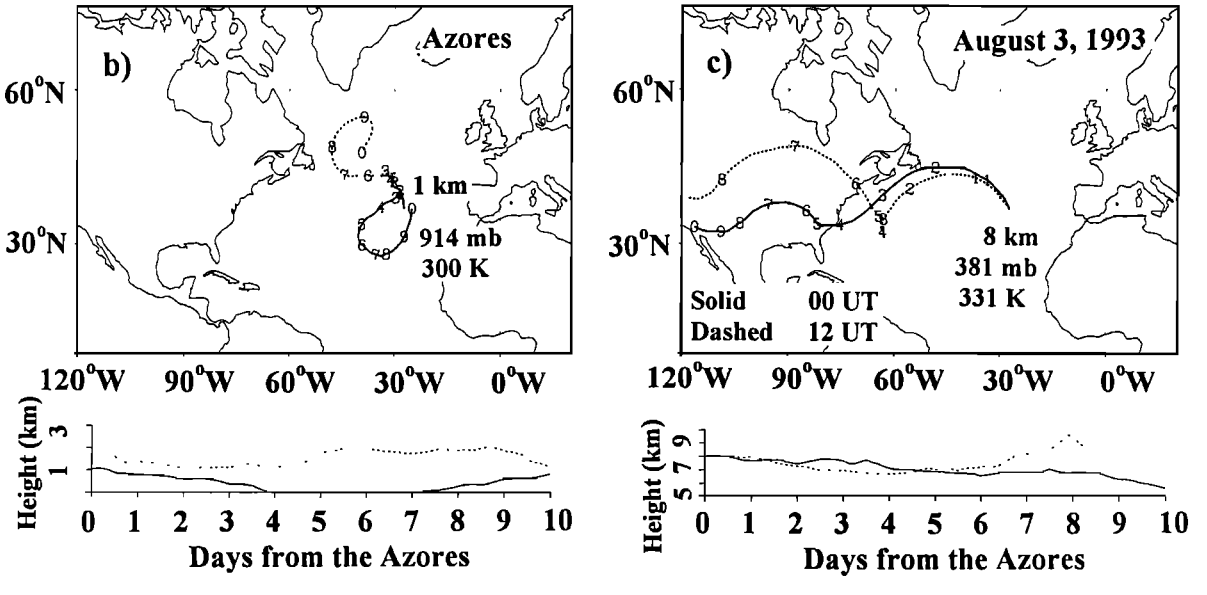

Figure 6. (continued)

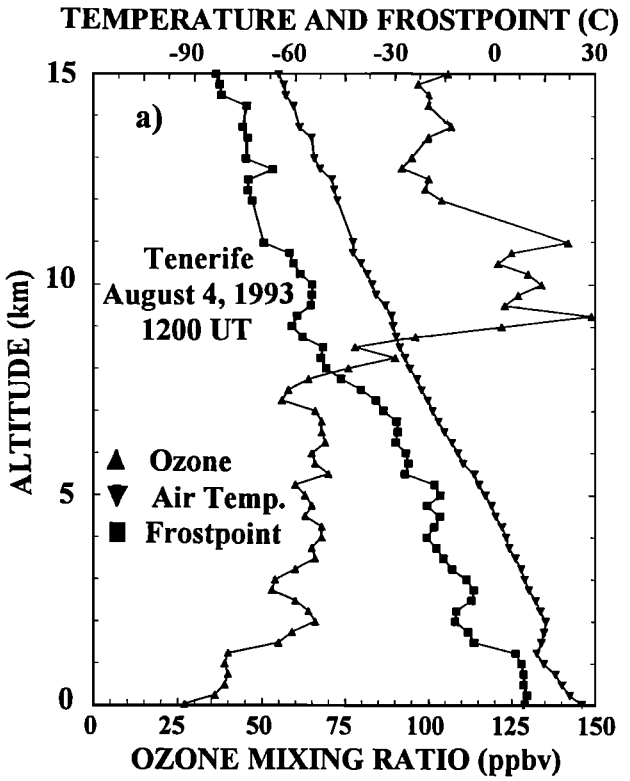

Figure 7. (a) Similar to Figure 5 but for Tenerife on August 4, 1993, and with trajectory arrival at (b) 1 km and (c) 9 km.

Spring Events. During the late spring (May) ozone mixing ratios in the middle and lower troposphere are somewhat higher than during the summer (compare Figures 4 and 5). The upper troposphere often has mixing ratios greater than 100 ppb. Prominent layers are common in the midtroposphere and lower tropospheric amounts of 50 ppb are relatively common. Examples from April, May, and June at each of the three subtropical island locations are used to illustrate the flow patterns associated with these profile characteristics.

The ozone profile of June 1, 1994, in the Azores shows a maximum of over 100 ppb between 5.5 and 6 km (Figure 9a). The humidity in this layer is under 10%, and in the cross section (Plate 6a), the ozone maximum shows up as a "bull's-eye" which is a common feature of this representation of the data. The trajectories for this layer (Figure 9c) and the surrounding levels at 2.5 km and 7.5 km (Figures 9b, 9d) show that the flow is dramatically different in each layer. For the trajectory ending within the enhanced ozone layer at 5.5 km, air travels from northern Canada and descends more than 2 km. This is quite similar to the trajectory seen at Cape Race for the summer case discussed earlier and follows much the same path (Figure 8b). At 2.5 km (Figure 9b) the air parcel remains over the Atlantic Ocean for most of the 10 days represented by the trajectory. At 7.5 km (Figure 9c) and 9.5 km (not shown) the flow represented by the trajectories is basically zonal, extending back over the Pacific Ocean. This example, and many more like it which we have examined, shows that the layered structure of ozone (and water vapor) results from varying transport at different levels from different source (and sink) regions. The air parcels with enhanced ozone (~100 ppb or greater) almost always have very low humidity, come from higher latitudes and altitudes, and descend significantly in altitude. In addition, the generally low tropopause heights in the region north of 60°N, through which many of the trajectories pass, contribute to the potential for significant transfer of ozone rich stratospheric air into the troposphere as observed in these layers.

A series of five profiles at Bermuda during April 19-23, 1993 (Plate 3a), demonstrate the dramatic day-to-day changes that occur in the troposphere and how various meteorological factors influence the ozone distribution over a particular site. On April 19 the ozone mixing ratio smoothly

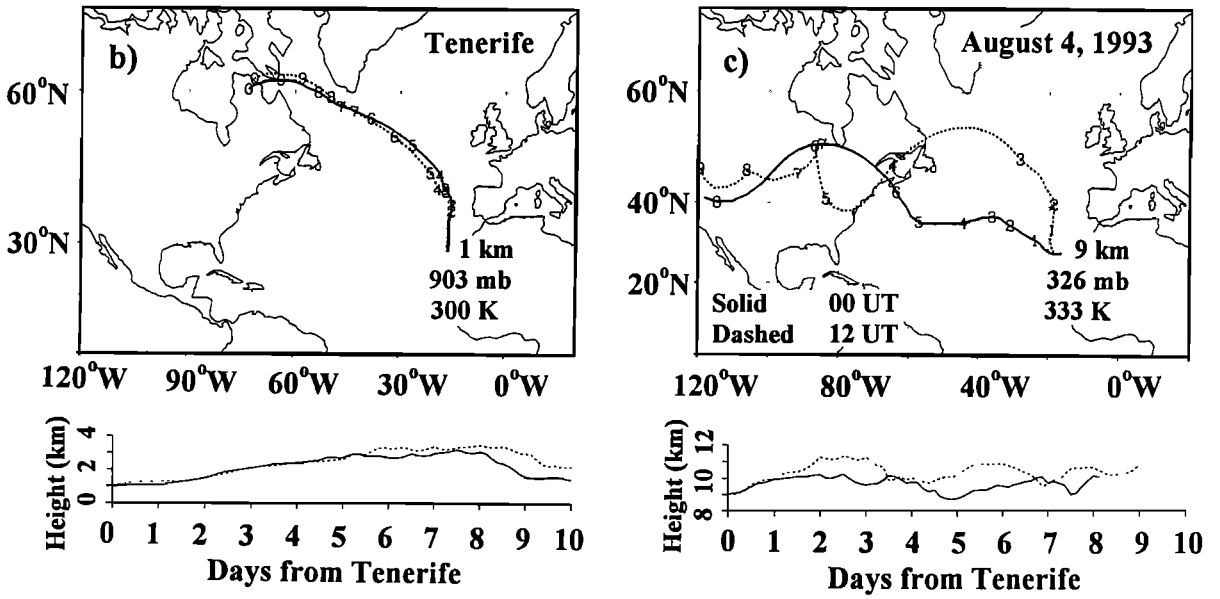

Figure 7. (continued)

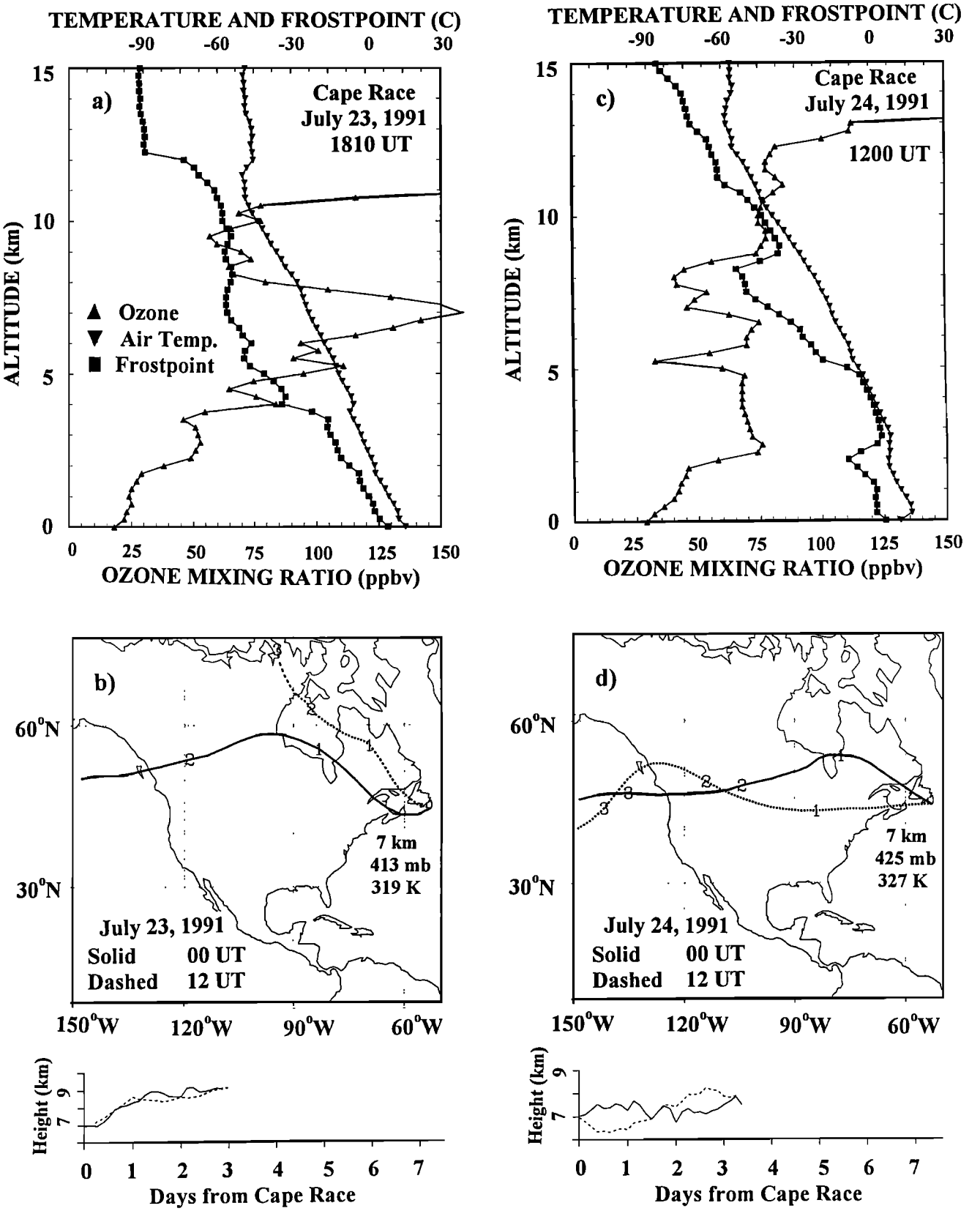

Figure 8. (a) Similar to Figure 5 but for Cape Race on July 23, 1991 and (c) for Cape Race on July 24, 1991, with trajectory arrival at 7 km for (b) July 23, and (d) July 24.

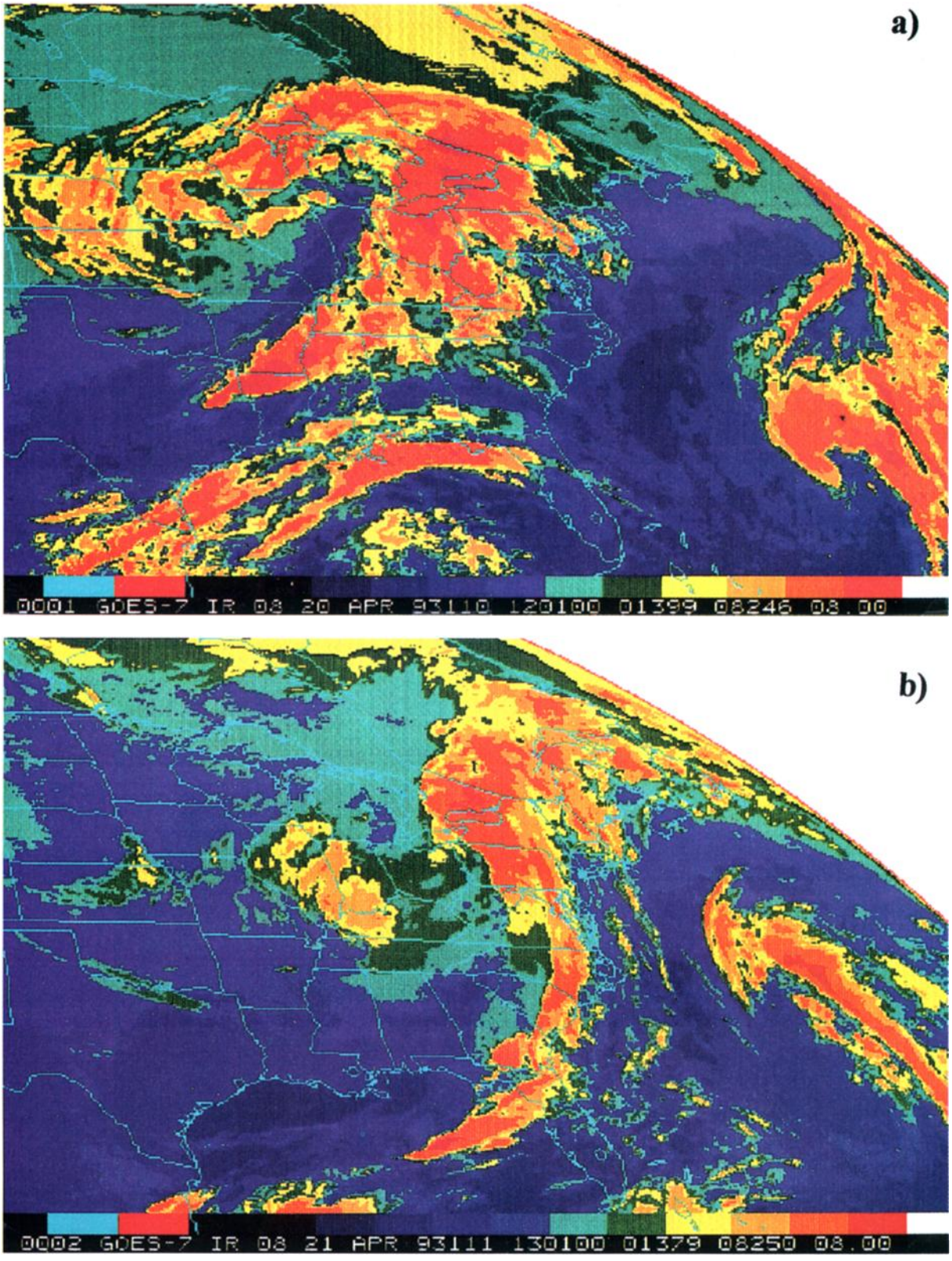

Plate 7. GOES 7 infrared satellite images for (a) April 20, 1993, and (b) April 21, 1993. The redder colors indicate the colder temperatures and thus the higher cloud tops.

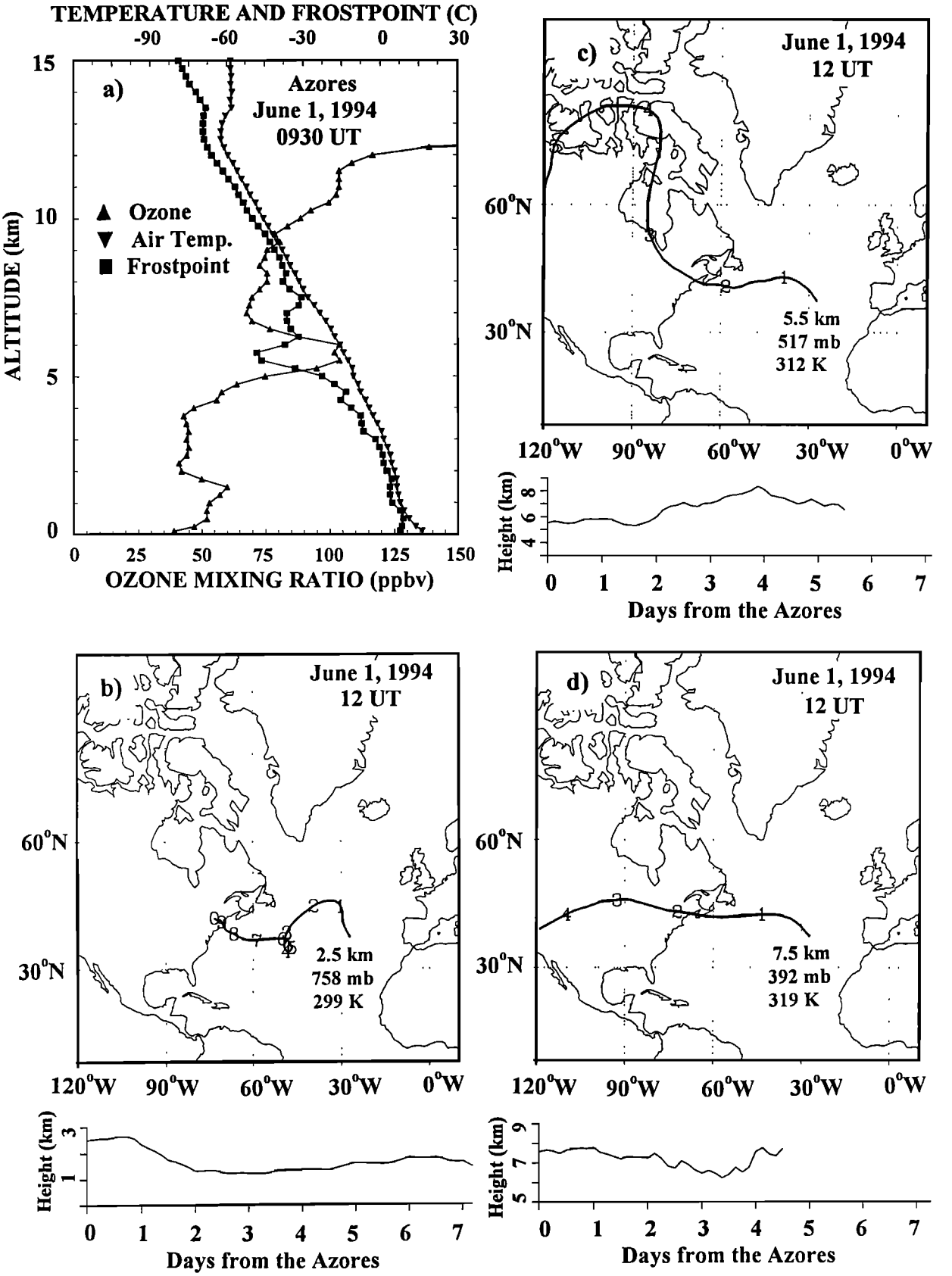

Figure 9. (a) Similar to Figure 5 but for the Azores on June 1, 1994, and with trajectory arrival at (b) 2.5 km, (c) 5.5 km, and (d) 7.5 km.

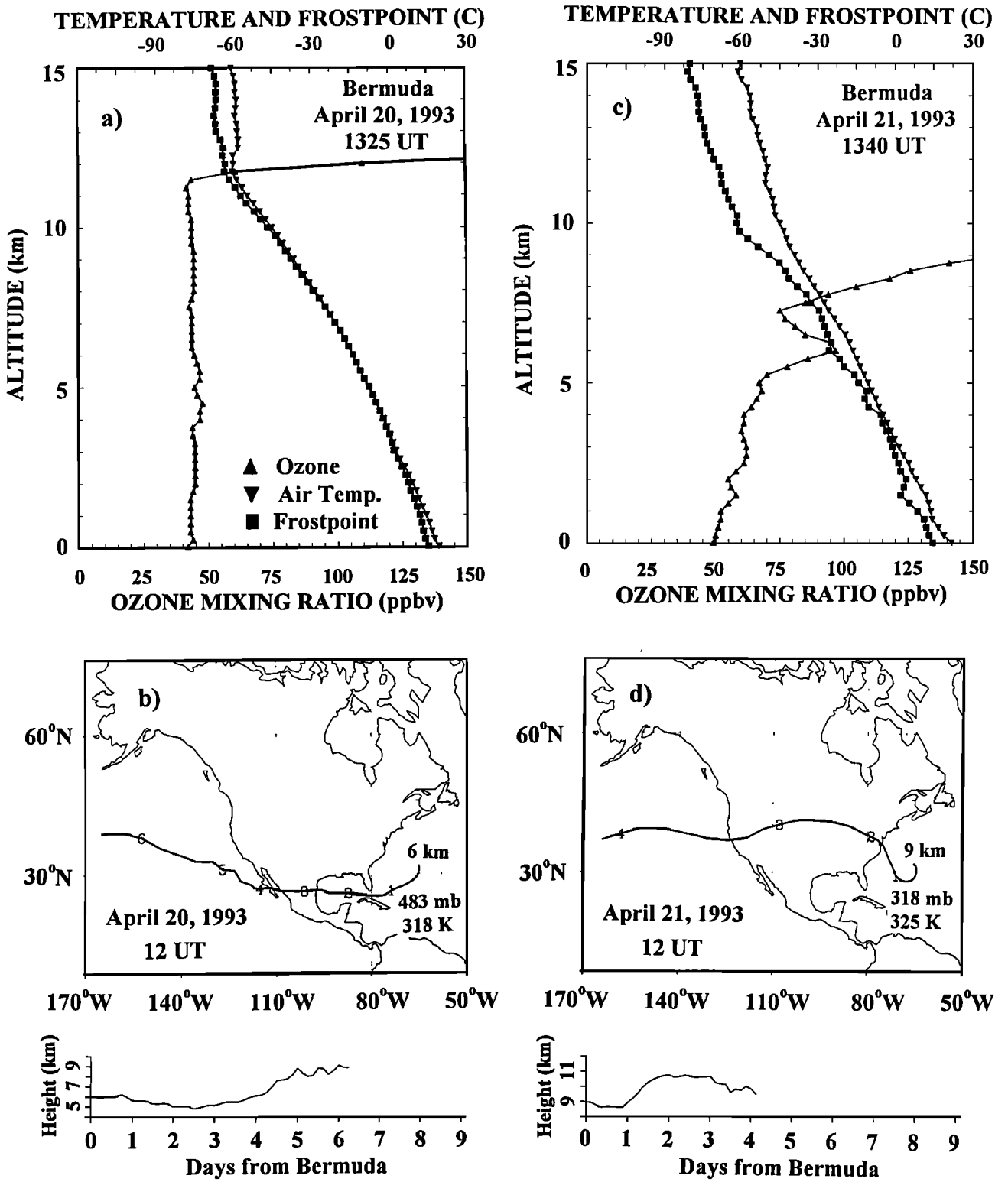

Figure 10. (a) Similar to Figure 5 but for Bermuda on April 20, 1993 and (c) April 21, 1993, with trajectory arrival at (b) 6 km for April 20 and (d) 9 km for April 21.

increases from 50 ppb at the surface to about 80 ppb near the tropopause. This relatively "unperturbed" profile looks similar to the average profile for this season at Bermuda (Figure 4). On April 20, Bermuda is located in a region of intense local convection in association with a deepening low-pressure center at the surface. A GOES7 enhanced infrared satellite image (Plate 7a) shows a mesoscale convective complex over Bermuda and the surrounding waters with cloud top temperatures of about -60°C which are equivalent to the temperatures at the height of the tropopause (Figure 10a). The ozone mixing ratio is extremely constant at 45 ppb from the surface to the tropopause and the atmosphere is nearly saturated over much of the same altitude range (Figure 10a). In the midtroposphere (6 km) the trajectory

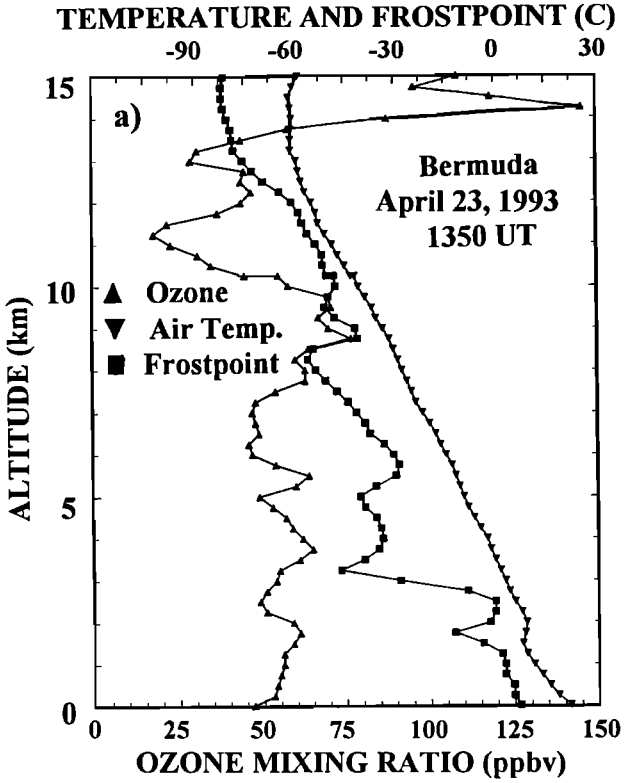

Figure 11. (a) Similar to Figure 5 but for Bermuda on April 23, 1993, with trajectory arrival at 11km for (b) April 22 and (c) April 23.

approaches Bermuda from the south after passing over the Caribbean and northern Mexico (Figure 10b) a few days earlier. The sounding was made in a fairly heavy rain shower, which is another indication that active convection was present.

By the following day (April 21) the low center over Bermuda had developed and moved in retrograde to the north and west of Bermuda, in conjunction with an upper level low which was almost cut off at 500 hPa. The satellite image for April 21 (Plate 7b) shows Bermuda was in a cloud free region. At Bermuda there is a 3-km-thick layer in the upper troposphere with ozone mixing ratios of ~250 ppb (Figure 10c) and the mixing ratio is over 100 ppb down to 8 km giving a 7-km-thick layer of enhanced ozone. The trajectory arriving at 9 km over Bermuda shows strong cyclonic curvature and a drop of over 2 km between the East Coast of the United States and Bermuda (Figure 10d) in the region where the upper level trough deepened. The region of subsidence associated with this upper level feature was upwind (to the north and west) of the mesoscale convection present on April 20. On April 22 the layer of large ozone mixing ratio was only 3 km thick and peak values are ~140 ppb (see Plate 3a). By April 23, tropospheric mixing ratios (Figure 11a) are mostly less than 60 ppb and values under 25 ppb are present near 11km. This region of small ozone amounts is relatively moist (RH>30% compared to <20% below and <10% above this layer). There is an important change in the trajectory at 11 km between April 22 and 23 that provides evidence for the source of the small ozone amounts at 11 km. On April 22 the trajectory to Bermuda at 1200 UT (Figure 11b) stays north of about 25°N. On April 23, however, the air parcel comes from south of 20°N to Bermuda (Figure 11c) in just 1 day. Equally important, there is a bank of convective clouds across southern Mexico (the northern edge of this band can be seen in Plate 7) in close proximity to the air parcel path as defined by the trajectory. The air parcel also passes over southern Florida where another area of convective activity is present on April 22. The small ozone mixing ratio (~20 ppb) at 11 km suggests that the air would have to come from the subtropical or tropical marine boundary layer especially since some

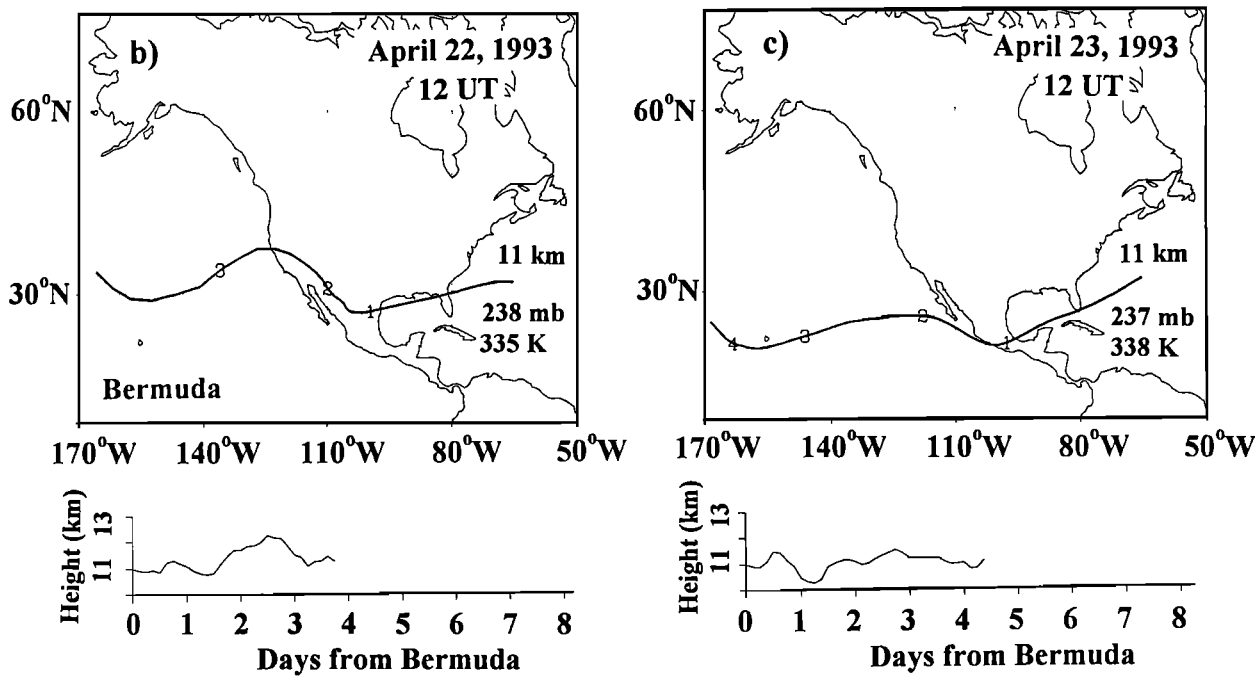

Figure 11. (continued)

entrainment of air with larger mixing ratios is likely. For example, at Barbados, which is at 13°N, the average surface ozone during the last half of April 1993 was about 18 ppb with amounts varying between 16 and 20 ppb. We hypothesize that the small ozone mixing ratio at 11 km over Bermuda is a remnant of air mixed from low in the troposphere, likely from a convective event earlier in the air parcel history. Thus it appears that both peaks (as seen in the June Azores profile) and relative minima, as seen here, can be caused by abrupt changes of air parcel source with altitude. This sequence of profiles over a 4-day period shows the strong modulating effect that meteorological changes play in determining the ozone distribution in the troposphere.

At Tenerife a profile on May 25, 1994 (Figure 12a), has ozone mixing ratios over 100 ppb from 7 km to the tropopause at ~13 km. Below 5 km, ozone drops markedly from ~75 ppb to <20 ppb at the surface. A series of trajectories on May 25 from 11 km to 1 km, in 2 km increments (Figure 12b-12g), demonstrates the consistency in the behavior with altitude of the flow regimes in explaining the structure of the ozone profile. At the lowest two levels (Figures 12f and 12g), air parcels reaching Tenerife have spent the entire previous 10 days over open ocean (keeping in mind the limitations of trajectories out to this length of time) and have likely experienced significant photochemical ozone destruction as discussed earlier. At the 5 to 11-km levels there is a coherent pattern where flow around a deep trough over the eastern United States reaches Tenerife in 3-5 days. As with the other cases presented here and two other more detailed studies [*Moody et al.*, this issue; *Merrill et al.*, this issue], the dramatically elevated ozone amounts in the middle and upper troposphere are associated with strong cyclonic activity that likely produces exchange between the stratosphere and the troposphere.

Discussion and Conclusions

From an examination of several sets of intensive ozone profiles obtained over the past several years and the application of air parcel trajectory information, we have developed a basic picture of the way in which meteorological conditions (systems) influence the tropospheric ozone distribution over the North Atlantic Ocean. Several of the important patterns derived for surface ozone behavior, primarily at Bermuda [*Oltmans and Levy*, 1992; *Moody et al.*, 1995], can be extended to other parts of the troposphere. As was seen in the surface observations, larger ozone amounts (in most cases in several kilometer-thick layers) in the middle and upper troposphere were associated with dry air moving from higher latitudes and altitudes to the observing site. Although none of the trajectories we examined show air coming all the way from the tropopause to the lower troposphere, the example from May 25, 1994, at Tenerife (Figure 12b-12e) shows that air parcels at progressively lower levels have come from layers several kilometers above which in turn have received air from layers even higher in elevation. At the time of an individual ozone profile the transport above the station is often not so coherent as in the May 25 example at Tenerife. Under the circumstances of a less coherent flow pattern over the station, only the flow in a restricted layer may be arriving from a region where active exchange with layers above has taken place. There are also some significant differences between lower and upper tropospheric behavior. At the lowest levels in the troposphere (<2 km) during the summer, ozone amounts are generally low (<30 ppb) and the strong gradient below ~4 km is evidence that ozone is being destroyed, probably photochemically. At middle and upper tropospheric altitudes, on the other hand, summer ozone amounts are similar or only slightly less than those in spring.

In a rare instance in which an ozone profile was obtained within a precipitating convective cell, we saw the mixing of air with relatively smaller, near-surface ozone concentrations all the way to the tropopause. At each location studied, both in the summer and in the spring, the time-height cross sections show features that appear to extend vertically from the surface to near the tropopause in which ozone amounts are small and the humidity high (see, for example, Julian day 241 in both Plate 2 and Plate 3). These events last 2-3 days and seem to be more coherent in their vertical structure than the larger ozone concentration events that extend downward from above. Such features (small ozone mixing ratios and high humidity through much of the troposphere) could occur not only by mixing immediately above the station but also by transport of air that had been mixed earlier by convective activity.

For all of the sites studied here, except Iceland, the summer also has numerous events where ozone mixing ratios attain 75 ppb deep into the troposphere and mixing ratios >100 ppb are seen fairly often between 7 km and the tropopause. These high ozone events usually extend downward from the tropopause region. There are also numerous local maxima of high ozone in the cross section

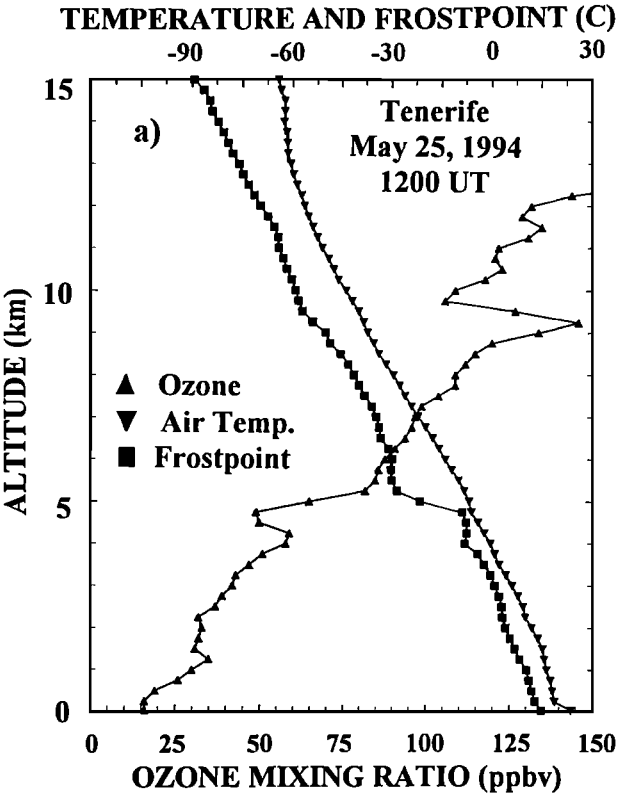

Figure 12. (a) Similar to Figure 5 but for Tenerife on May 25, 1994, and with trajectory arrival at (b) 11 km, (c) 9 km, (d) 7 km, (e) 5 km, (f) 3 km, and (g) 1 km.

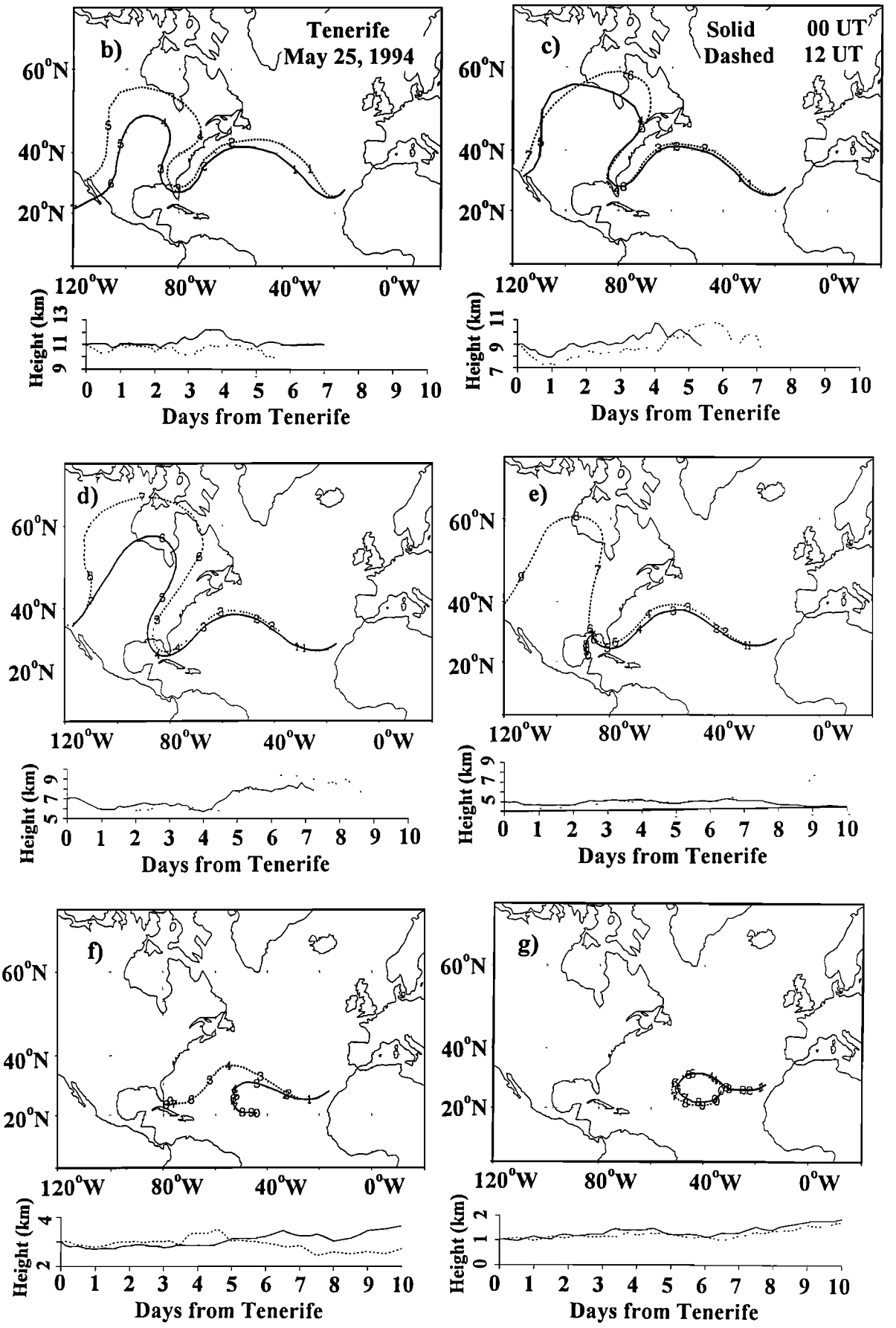

Figure 12. (continued)

that appear to be a result of varying air parcel origin with altitude that gives a layered structure to individual profiles. These layers of high ozone are also regions of lower relative humidity in the profile. Trajectories calculated to arrive at the elevation of the peak ozone concentration show distinctive characteristics in the transport path that strongly implicate the upper troposphere and stratosphere as the source of the elevated ozone concentration layer. These characteristics are strong descent of air parcels prior to arrival at the altitude of the elevated concentration layer, a trajectory path that extends back to the region of an upper level trough or cutoff low (typically associated with regions of high isentropic potential vorticity [see *Moody et al.* this issue; *Merrill et al.*, this issue]), and trajectories that often come from higher latitudes, often north of 60°N, where tropopause height is generally lower.

There are many profiles or portions of a profile when ozone is not greatly elevated above the median value. We have not systematically looked at the trajectories for every ozone profile throughout the tropospheric height range. We have looked at some of these cases, however, and find that the flow is more zonal, the altitude changes of the air parcel are not so marked, nor do they show strong descent. Ozone amounts of 50-75 ppb are often associated with these conditions through much of the troposphere above 3 km. The source of this "background" concentration cannot be so readily assessed from the analysis carried out here, but several points can be made. First, cases of elevated ozone layers are common both in the spring and in the summer. Such layers make a significant contribution to the "average" profile ozone levels. It is likely that as these 2 to 4 km-thick layers are mixed horizontally and vertically as the air is transported over time and space that they are an important contribution to the "background" condition [*Browell et al.*, 1992, 1994]. Events in which higher ozone from the boundary layer (<2 km) could be traced to higher levels were not found. There were, however, events where lower ozone amounts in the middle and upper troposphere appeared to be linked to the lower boundary layer amounts, probably through convective mixing. We plan to carry out additional intensive sounding campaigns at Bermuda, the Azores, Tenerife, and Newfoundland. The focus in these intensives will be to make profile measurements at near daily frequency at all of the sites simultaneously. In addition, aircraft campaigns, in which several tracers and key ozone precursors are to be measured, will be carried out between the eastern United States and Bermuda in the spring 1996. The strong constraints placed on the ozone distribution by the profile measurements and the additional planned chemical constituent measurements should lead to further progress in understanding the controlling mechanisms in the ozone budget over the North Atlantic.

References

Berkowitz, C. M., K. M. Busness, E. G. Chapman, J. M. Thorp, and R. D. Saylor, Observations of depleted ozone within the boundary layer of the western North Atlantic, *J. Geophys. Res.*, *100*, 11,483-11,496, 1995.

Browell, E. V., C. F. Butler, S. A. Kooi, M. A. Fenn, R. C. Harriss, and G. L. Gregory, Large-scale variability of ozone and aerosols in the summertime Arctic and subarctic troposphere, *J. Geophys. Res.*, *97*, 16,433-16,450, 1992.

Browell, E. V., M. A. Fenn, C. F. Butler, W. B. Grant, R. C. Harriss, and M. C. Shipham, Ozone and aerosol distributions in the summertime troposphere over Canada, *J. Geophys. Res.*, *99*, 1739-1755, 1994.

Crutzen, P. J., Tropospheric ozone: An overview, in *Tropospheric Ozone*, edited by I.S.A. Isaksen, pp. 3-32, D. Reidel, Norwell, Mass., 1988.

Dickerson, R. R., B. G. Doddridge, P. Kelley, and K. P. Rhoads, Large-scale pollution of the atmosphere over the remote Atlantic Ocean: Evidence from Bermuda, *J. Geophys. Res.*, *100*, 8945-8952, 1995.

Fehsenfeld, F. C., A. Volz-Thomas, S. Penkett, M. Trainer, and D. D. Parish, North Atlantic Regional Experiment (NARE) 1993 summer intensive: Foreword, *J. Geophys. Res.*, this issue.

Harris, J. M., and J. D. W. Kahl, Analysis of 10-day isentropic flow patterns for Barrow, Alaska: 1985-1992, *J. Geophys. Res.*, *99*, 25,845-25,855, 1994.

Kasibhatla, P. S., H. Levy II, A. Klonecki, and W. L. Chameides, A three-dimensional view of the large-scale tropospheric ozone distribution over the North Atlantic Ocean during summer, *J. Geophys. Res.*, this issue.

Komhyr, W. D., Electrochemical cells for gas analysis, *Ann. Geophys.*, *25*, 203-210, 1969.

Komhyr, W. D., R. A. Barnes, G. B. Brothers, J. A. Lathrop, and D. P. Opperman, Electrochemical concentration cell ozonesonde performance evaluation during STOIC 1989, *J. Geophys. Res.*, *100*, 9231-9244, 1995.

Merrill, J. T., J. L. Moody, S. J. Oltmans, and H. Levy II, Meteorological analysis of tropospheric ozone profiles at Bermuda, *J. Geophys. Res.*, this issue.

Moody, J. L., S. J. Oltmans, H. Levy II, and J. T. Merrill, Transport climatology of tropospheric ozone: Bermuda, 1988-1991, *J. Geophys. Res.*, *100*, 7179-7194, 1995.

Moody, J. L., J. C. Davenport, J. T. Merrill, S. J. Oltmans, D. D. Parish, J. S. Holloway, H. Levy II, G. L. Forbes, M. Trainer, and M. Buhr, Mechanism for transporting O_3 over the western North Atlantic: A case study for August 24-29, 1993, *J. Geophys. Res.*, this issue.

Oltmans, S. J., Surface ozone measurements in clean air, *J. Geophys. Res.*, *86*, 1174-1180, 1981.

Oltmans, S. J., and H. Levy II, Seasonal cycle of surface ozone over the western North Atlantic, *Nature*, *358*, 382-384, 1992.

Oltmans, S. J., and H. Levy II, Surface ozone measurements from a global network, *Atmos. Environ.*, *28*, 9-24, 1994.

Prospero, J. M., R. Schmitt, E. Cuevas, D. L. Savoie, W. C. Graustein, K. K. Turekian, A. Volz-Thomas, A. Diaz, S. J. Oltmans, and H. Levy II, Temporal variability of summertime ozone and aerosols in the free troposphere over the eastern North Atlantic, *Geophys. Res. Lett.*, *22*, 2925-2928, 1995.

Schmitt, R., B. Schreiber, and I. Levin, Effects of long-range transport on atmospheric trace constituents at the Baseline Station Tenerife (Canary Islands), *J. Atmos. Chem.*, *1*, 335-351, 1988.

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