Vertical distribution of ozone at four sites in the United States

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[1] We report ozonesonde observations from the following four locations across the United States: Trinidad Head, California; Boulder, Colorado; Huntsville, Alabama; and Wallops Island, Virginia. These ozone profiles clearly indicate evidence of stratosphere-troposphere exchange, boundary layer pollution, and strong seasonal variations. Significant variation at the shortest interlaunch frequencies (typically weekly) appears in all seasons, at all stations throughout the troposphere. Activity near the tropopause dominates in the winter and spring, while boundary layer ozone maximizes in the summer. The vertical extent and maximum values of boundary layer ozone are larger at the eastern stations. Comparisons to the TOMS overpasses indicate agreement to within 2% for the total-column ozone at all stations, with station-to-station mean biases less than 2%. The seasonal variation of the total ozone column is essentially identical at Trinidad Head and Wallops Island, while the summertime values at Boulder are significantly smaller by comparison, and the amplitude of the annual cycle at Huntsville is smaller than the amplitude of the other three stations. The longitudinal character of upper tropospheric ozone shows amounts generally increasing westward from Huntsville, and in the lower troposphere, ozone decreases westward from Huntsville in all seasons. Values to the east of Huntsville increase at all altitudes and seasons, with the possible exception of August when Huntsville's boundary layer and free-tropospheric ozone dominate. *INDEX TERMS:* 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 3362 Meteorology and Atmospheric Dynamics: Stratosphere/troposphere interactions; *KEYWORDS:* ozonesonde, climatology, STE, tropospheric ozone profiles, stratosphere-troposphere exchange, boundary layer ozone

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1. Introduction

[2] The vertical distribution of ozone throughout the troposphere is highly variable in space and time. Dynamical and photochemical considerations such as long- and short-range transport of high or low ozone-laden air [*Oltmans et al.*, 1996], stratosphere-troposphere exchange (STE) [*Holton et al.*, 1995], and photochemical production/loss of ozone [*Frost et al.*, 1998; *Roberts et al.*, 1998] are responsible for the extent of this variability. Generally, tropospheric ozone concentrations increase during the summer months when photochemical production and oxidation of Volatile Organic Compounds (VOCs) in the presence of NOx are a maximum [*Chameides et al.*, 1992; *Montzka et al.*, 1993]. As a consequence, local natural and anthropogenic emissions of NOx and VOCs and their transport are crucial indicators of ozone concentrations.

[3] The spatial and temporal distribution of observation stations that measure the vertical profile of ozone [*Logan*, 1985, 1999a] is very much more sparse than the meteorological radiosonde network of temperature/humidity balloon sensors [*Kalnay et al.*, 1996]. In general, only weekly flights are available from most stations and the entire Unites States network comprises only four stations. However, these weekly observations are adequate to develop a climatology [*Logan*, 1999b] and, at locations with long records, trends in ozone amounts [*Logan*, 1999a]. We focus on observations from four United States ozonesonde stations: Trinidad Head, California; Boulder, Colorado; Huntsville, Alabama; and Wallops Island, Virginia, in the context of global tropospheric ozone morphology [*Logan*, 1999b]. Two of these stations (Trinidad Head and Huntsville) are published here for the first time, while the records from Boulder and Wallops Island are extended in this article.

[4] We compare and contrast the vertical profiles, seasonal variations, evidence of physical processes (e.g., stratosphere/troposphere exchange and local pollution) in the context of boundary layer, free troposphere, and tropopause regimes. Although the scope of this paper cannot include detailed case studies of these observations, clearly such

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studies are warranted from this initial description of the ozone vertical morphology.

2. Measurements

[5] Vertical profiles of ozone partial pressure, ambient pressure, temperature, and dew point are measured by balloon-borne ozonesondes employing an Electrochemical Concentration Cell (ECC) sensor [*Komhyr*, 1969] and an RS-80 Vaisala or Sippican Inc. MK-2 radiosonde. The balloons ascend, on average, to altitudes of 30–35 km (6 hPa), providing accurate in situ measurements of 95% of the entire atmospheric ozone column. Although high temporal- and spatial-resolution launches are currently unavailable, long-term data at select locations around the world provide an essential source for accurate characterization of climatological patterns at all atmospheric levels [*Beekmann et al.*, 1994; *Fortuin and Kelder*, 1998; *Logan*, 1999b; *McPeters et al.*, 1997; *Thompson et al.*, 2001] and provide validation tools for a number of ozone-measuring satellites [*Attmannspacher et al.*, 1989; *Brinksma et al.*, 2000; *Cunnold et al.*, 1989; *Hoogen et al.*, 1999; *Kim et al.*, 2001; *Lucke et al.*, 1999; *Margitan et al.*, 1995; *Newchurch et al.*, 2001a, 2001b; *Sasano et al.*, 1999].

[6] The electrochemical concentration cell (ECC) sensor used at all these stations has been extensively tested and compared to other instruments and is in wide use [*Johnson et al.*, 2002; *Komhyr et al.*, 1995; *Reid et al.*, 1996; *Tarasick et al.*, 1996]. The three NOAA/CMDL stations, Trinidad Head, Boulder, and Huntsville, use the EN-SCI model 2Z ozonesondes, with 2% unbuffered potassium iodide (KI) cathode solution. Since 1996, the NASA Wallops Flight Facility has used both EN-SCI model Z ECCs and Science Pump Corporation models 5a and 6a ECCs. Both types of ECCs are compatible with Sippican MK-2 radiosondes with both Loran-C wind finding capability and GPS (LOS) [(-y-z positions). Since late 1994, Wallops Flight Facility has been using 1% buffered KI solution.

[7] ECC sonde accuracies are about 10% for tropospheric mixing ratios, except in the case of very low mixing ratios (<10 ppb) when the accuracy may be degraded to 15%. Although the reaction with potassium iodide is not specific to ozone, concentrations of interfering species such as NO_2 and SO_2 are usually in the sub-ppb ranges and, hence, do not constitute a significant interferent [*Oltmans et al.*, 1996].

[8] Vertical profiles are obtained from weekly balloon launches and occasional more frequent launches at all four of the ozonesonde locations. The Wallops Island measurements began in 1970, and the Boulder soundings started in 1979. Programs at both of these sites have had some interruptions over this period but represent relatively long time series. The station at Trinidad Head was initiated in August 1997, and the Huntsville ozonesonde station commenced operation in April 1999. The station at Wallops Island is operated by the Upper Air Instrumentation Research Project, Observational Science Branch of the Laboratory for Hydrospheric Processes at the Wallops Flight Facility of NASA. The NOAA Climate Monitoring and Diagnostics Laboratory (CMDL) launch the soundings at Boulder. At Trinidad Head the soundings are a cooperative effort between CMDL and the Humboldt State University Marine Sciences Laboratory. The Huntsville ozonesonde station is a joint effort between the Earth System Science Center of the University of Alabama at Huntsville and CMDL. Data are available from the World Ozone and Ultraviolet Radiation Data Centre (WOUDC) for Wallops Island (Station Number 107), Boulder (067), and Huntsville (418) at http://www.msc-smc.ec.gc.ca/woudc. In addition, plots and/or data are available for Wallops Island at http://uairp.wff.nasa.gov; for Huntsville at http://www.nsstc.uah.edu/atmchem; and for Boulder, Trinidad Head, and Huntsville at http://www.cmdl.noaa.gov/info/ftpdata.html.

[9] Trinidad Head lies on the northwest coast of California and experiences predominantly air characteristic of the Pacific basin. Boulder is a high-altitude midsize city that is downwind of the Denver metropolitan area under southeasterly wind conditions. Huntsville lies in the southeastern united states, a region with abundant deciduous trees. Nearby cities include Birmingham, AL (130 km due South,) Nashville, TN (180 km due North,) and Atlanta, GA (370 km due southeast.) Wallops Island lies on the northeast coast of the United States and often experiences polluted continental air.

3. Results and Discussion

[10] The data used in this study represents ozonesondes launched between 1300 and 2300 GMT covering the period between April 1995 and March 2002, as indicated in Table 1. The Huntsville data also include daily ozonesondes launched as part of the Southern Oxidants Study 1999 (SOS99) Nashville field campaign (about 150-km north of Huntsville) from June 15 through July 15, 1999. Also included in the Huntsville data are two soundings launched during a Stratosphere-Troposphere Exchange experiment April 9–11, 2000.

[11] Figure 1 shows time-height cross-sections of ozone mixing ratios (ppbv) in the troposphere and lower stratosphere, observed from 1995 through 2002 over (Figure 1a) Trinidad Head, (Figure 1b) Boulder, (Figure 1c) Huntsville, and (Figure 1d) Wallops Island. The solid black line indicates the height of the thermal tropopause calculated from the radiosonde vertical temperature profile that accompanies the ozonesonde. Ozone concentrations generally exhibit a steep gradient near the tropopause; hence accurate characterization of the tropopause height is essential in differentiating tropospheric and stratospheric ozone [*Bethan et al.*, 1996; *Bodecker et al.*, 1998].

[12] The WMO defines the tropopause operationally as the lower boundary of a layer in which the temperature lapse rate is less than 2°C km^{-1} for a depth of at least 2 km [*Reiter et al.*, 1969]. In calculating the thermal tropopause, we have found that the midpoint of a 2-km layer whose average lapse rate is less than 2°C km^{-1}, better represents the observed tropopause. Although this definition pinpoints a well defined tropopause very accurately, it does not eliminate ambiguities in tropopause height that result in the vicinity of jets and upper level fronts due to the presence of multiple stable layers, [*Danielsen*, 1959, 1968; *Reiter et al.*, 1975]. When multiple tropopauses occur, the lowest altitude tropopause is taken as the correct one. No attempt was made to define the tropopause in terms of potential vorticity.

[13] Because the average time between launches is one week, and synoptic scale events are on the order of 3–6 days, the temporal extent of certain synoptic scale features,

Table 1. Summary of Data From the Four Ozonesonde Stations Used in This Study

Station Name	Affiliation	Lat, Lon, and Elev	Instrument Type	Solutions Used	Launch Frequency	Date Range	Number of Sondes
Trinidad Head, California	NOAA/CMDL	41.07°N 124.15° W 20 m asl	ECC EN-SCI model 2Z	2% KI, unbuffered	weekly	08/97 through 03/02	207
Boulder, Colorado	NOAA/CMDL	40.02°N 105.27°W 1743 m asl	ECC EN-SCI model 2Z	2% KI, unbuffered	weekly, with occasional HFLE[a]	01/95 through 03/02	352
Huntsville, Alabama	UAH/ESSC and NOAA/CMDL	34.73°N 86.58°W 196 m asl	ECC EN-SCI model 2Z	2% KI, unbuffered	weekly, with occasional HFLE[a]	04/99 through 03/02	153
Wallops Island, Virginia	NASA/WFF	37.90°N 75.50°W 13 m asl	ECC EN-SCI model Z, Science Pump Corp. models 5a and 6a	1% KI, buffered	weekly, with occasional HFLE[a]	07/95 through 03/02	380

[a]High-frequency launch experiments.

as shown in the cross sections of Figure 1, will likely be overestimated. One such example is the enhanced ozone event in November 1999 at Huntsville. The high ozone levels in the middle and upper troposphere are associated with a tropopause fold and vertical exchange of high-ozone stratospheric air into the troposphere [*Holton et al.*, 1995] as the fold passed over Huntsville. The temporal extent of the fold, as seen in meteorological analyses, was on the order of a few hours, but from the time series of Figure 1; it appears to be on the order of 1–2 weeks. Two similar examples are the enhanced ozone events in May and June of 1999 over Trinidad Head.

[14] The June and July 1999 period of daily soundings at Nashville as part of SOS99 (Figure 1c inset) is indicative of the daily ozone variability apparent throughout the troposphere. The upper-tropospheric variability results from STE and/or larger scale meteorological/photochemical processes, and the boundary layer variability, especially in the summertime, results from local pollution modulated by the local weather.

[15] Figure 2 shows the monthly average vertical ozone profiles at the four stations. The averages are performed at 50 hPa increments between 1000–100 hPa, and at 10 hPa increments between 100–10 hPa. The same average profiles were used to produce the monthly averages for the four stations at the eight atmospheric pressure levels shown in Figure 3, as well as the annual cycle of the mean monthly ozone between 1000–100 hPa of Figure 4. Only profiles with bursts at or above 10 hPa were used in computing the mean monthly profiles. Figure 2 shows the number of profiles averaged for a given station per month and Table 1 provides a summary of the data from the four ozonesonde stations.

[16] The annual peak in stratospheric ozone occurs during the winter and early spring months (December through March), with peak values of 15 mPa between 30–40 hPa. Coincident with the peak values in ozone is a narrowing of the altitude region with the highest ozone in the stratosphere. From late winter through the summer, the decrease in the stratospheric ozone peak is accompanied by a broadening in the vertical stratospheric column, as shown in Figure 2.

[17] Differences in the average profiles at the four stations are largest between 40–300 hPa in the winter and spring months and between 600–1000 hPa in the late spring and summer months. The region around 500 hPa shows little variation among the four stations in the fall, winter, and early spring months.

[18] One could question the significance of records as short as 3 years, as at Huntsville, in a climatology presented here. Inspecting the atmospheric variance captured in the 3-year records corresponding to the Huntsville time period to the longer records available at other stations (4 years at Trinidad Head, 7 years at Boulder, 7 years at Wallops Island) reveals that the 3-year record captures essentially the same variance as the longer records.

3.1. Stratosphere

[19] At 10 hPa, ozone mixing ratios over Huntsville (35°N) are higher than at the other three stations (Trinidad Head, Boulder, and Wallops Island at 41°N, 40°N, and 38°N, respectively) with the exception of the winter months, sometimes by as much as 15%, as in February (Figures 2

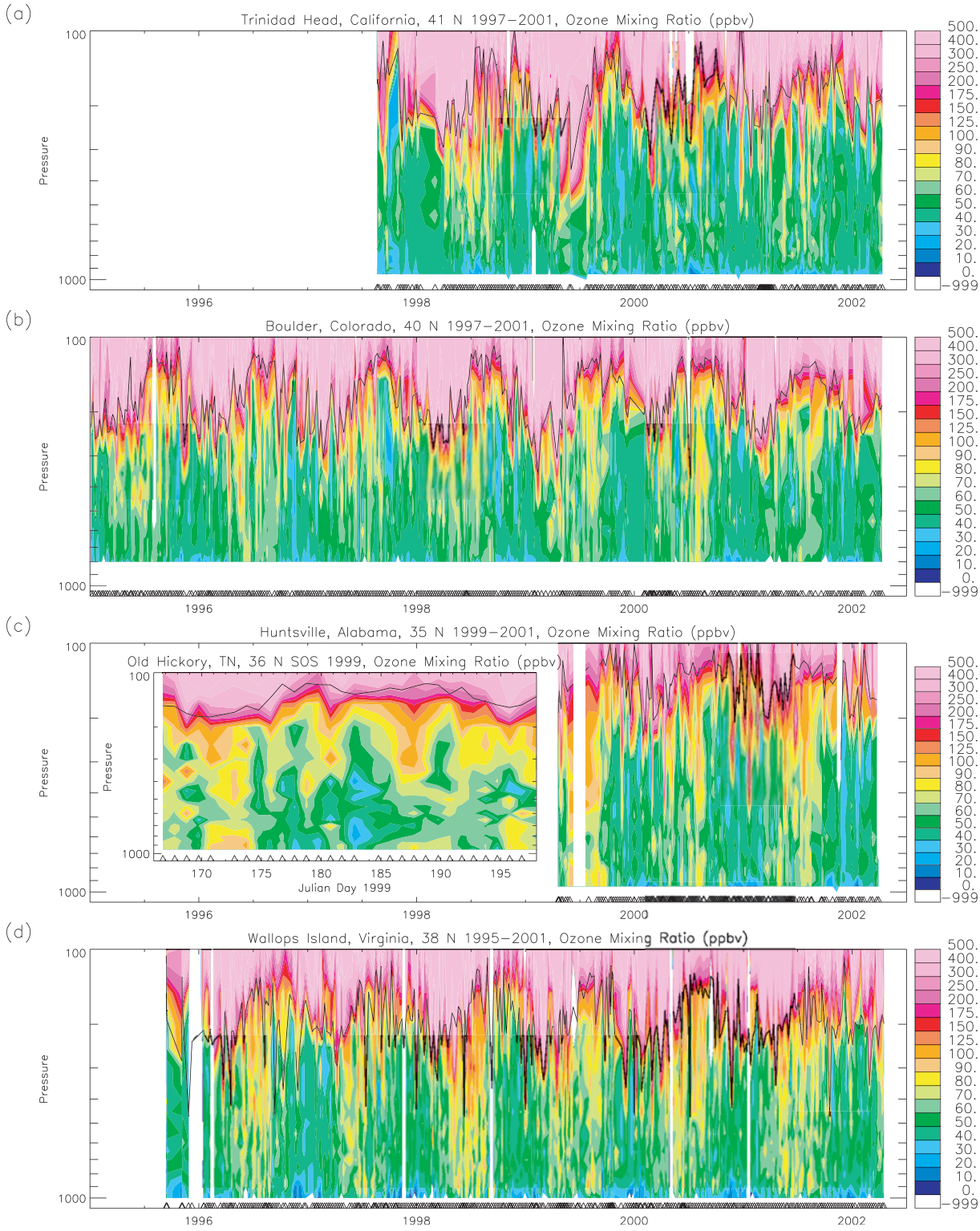


Figure 1. Time-height cross-sections of ozone mixing ratios (ppbv) from ozonesondes at (a) Trinidad Head, California; (b) Boulder, Colorado; (c) Huntsville, Alabama (inset: daily ozonesondes launched at Old Hickory, Tennessee, during SOS99, June 15 through July 15, 1999); and (d) Wallops Island, VA. The solid black line represents the thermal tropopause. The triangles at the base of the cross-sections indicate the time of each sounding.

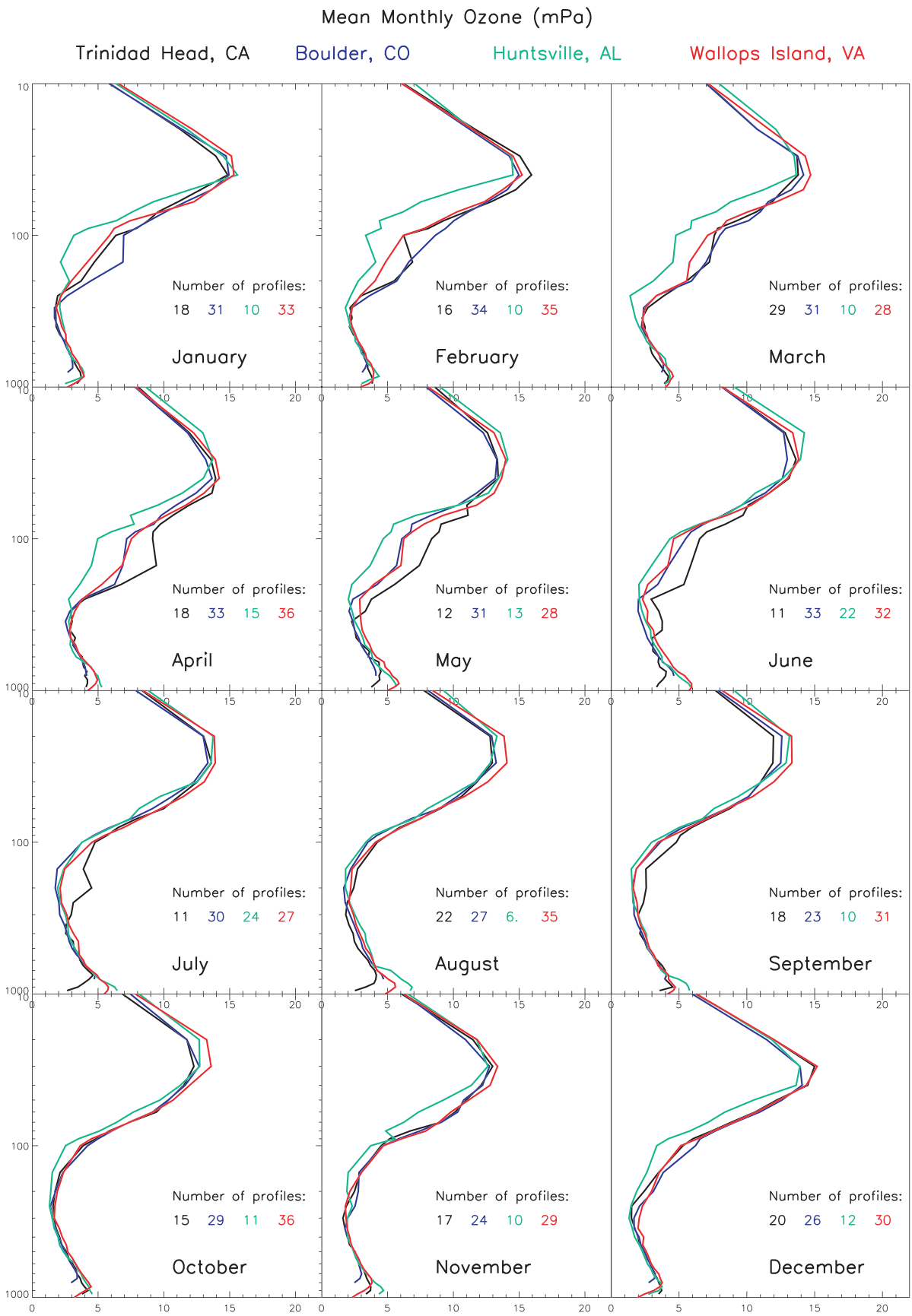
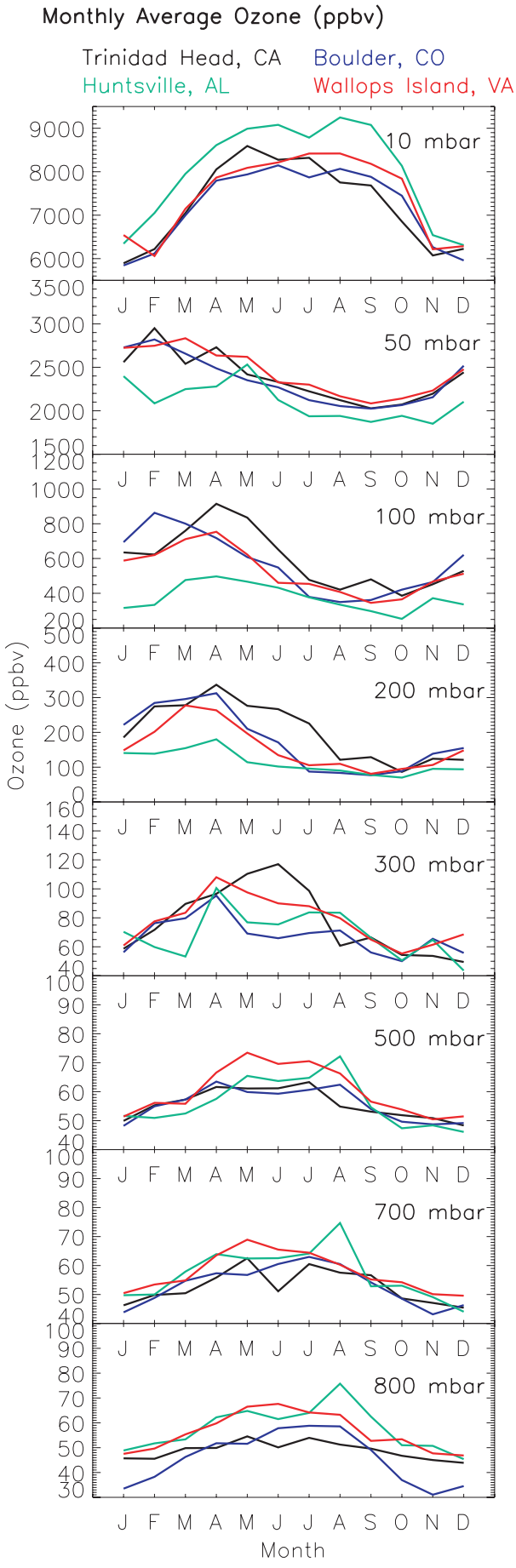


Figure 2. Monthly averaged vertical ozone profiles (partial pressure in mPa) for Trinidad Head, California (black); Boulder, Colorado (blue); Huntsville, Alabama (green); and Wallops Island, Virginia (red). The number of launches at each site for each month are indicated on the charts.



and 3). Below the ozone partial pressure peak, at 50 hPa, the pattern has completely reversed, and ozone concentrations over Huntsville are lower than at the other three stations throughout the year, with the exception of May. This pattern holds down to about 200 hPa.

[20] The midlatitudes is a region of strong ozone gradients in the stratosphere. The measured average profiles at the four stations are consistent with measured/modeled cross-sectional analyses of Northern-Hemispheric midlatitude stratospheric ozone [*Cunnold et al.*, 1975; *Logan*, 1999a] where a change in the sign of the ozone isopleth gradients occurs at around 20 hPa. In constructing an emerging ozone climatology across the United States with data from these four stations, which all lie within a 6° latitude band, to a first approximation, one might assume that they would belong to a similar latitudinally dependant regime. However, as shown in Figures 2 and 3, the latitudinal dependence of the altitude of the ozone peak at midlatitudes in the stratosphere can be strong enough to produce significant differences. The lower latitude at Huntsville further gives the mean vertical ozone profiles characteristics that are more subtropical relative to the other three stations.

[21] The seasonal cycle in the upper stratosphere (10 hPa) exhibits a broad maximum from early spring through the fall, peaking in June through August for Huntsville and Wallops Island, May and June for Boulder, and May for Trinidad Head. Between 50–200 hPa, the seasonal cycle in ozone peaks in early spring through early summer [*Logan*, 1999a].

[22] The lower stratosphere is a region of strong ozone variability [*Fortuin and Kelder*, 1998], on both a seasonal and interannual basis. Huntsville displays considerable differences in the mean monthly partial pressure ozone profiles compared to Trinidad Head, Boulder, and Wallops Island below 40 hPa. These differences first appear in October and intensify throughout the winter, with maximum differences in February. Recovering over the spring months, the mean profiles at Huntsville match those at the other three stations in the lower stratosphere throughout much of the summer (Figures 2 and 3.)

[23] Looking at the individual Huntsville profiles for the three winter periods included in the data set, one can clearly distinguish a sharp decrease in ozone between the winters of 1999/2000 and 2000/2001 between 100–200 hPa. This feature is further highlighted in Figure 4 by the large coefficient of variation of the monthly mean ozone over Huntsville between 100–200 hPa from November through March. Because the Huntsville data set is only for a 3-year period, the conclusions that can be drawn from the average profiles are limited. However, evidence from satellite total ozone analysis at the four stations, combined with average total ozone obtained from the ozonesondes addressed later in this paper, lends credence to the validity of these average profiles in characterizing an emerging ozone profile climatology at the four stations.

3.2. Stratosphere-Troposphere Interactions

[24] The annual cycle of the monthly mean ozone mixing ratios (ppbv) and the coefficient of variation for the tropo-

Figure 3. (opposite) Monthly average ozone mixing ratios (ppbv) for the four ozonesonde stations at pressure levels from 10 hPa to 800 hPa as indicated on the chart.

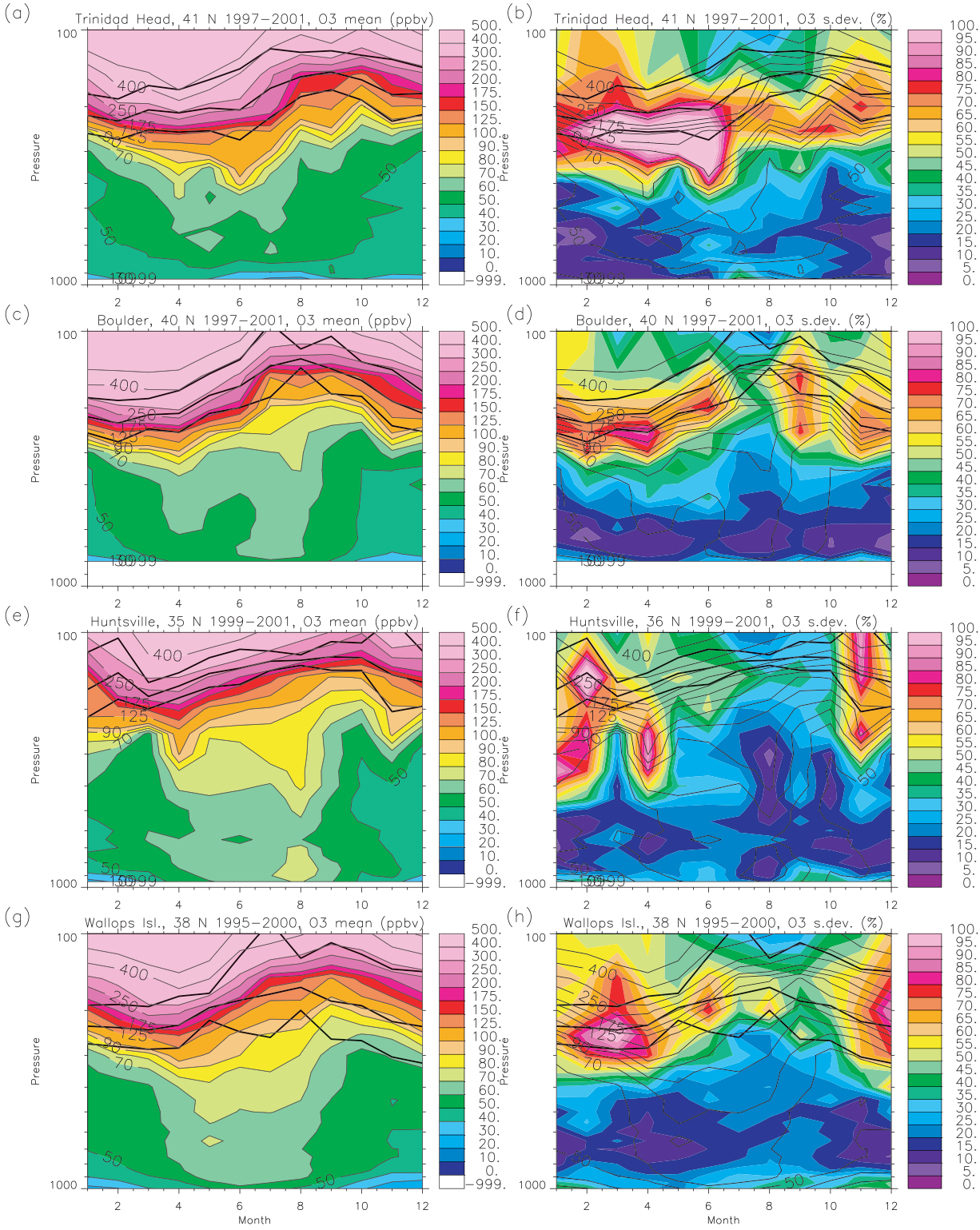


Figure 4. Vertical profiles of the annual cycle of monthly mean ozone mixing ratios (ppbv, left-hand panels) and coefficient of variation (right-hand panels) for (a, b) Trinidad Head, California; (c, d) Boulder, Colorado; (e, f) Huntsville, Alabama; and (g, h) Wallops Island, Virginia.

sphere and lower stratosphere appear in the time-height cross-sections of Figure 4. The three heavy solid lines represent the monthly averaged tropopause and tropopause ±1 standard deviation calculated from the individual soundings at each of the four stations.

[25] The winter, spring, and early summer broad and mostly continuous maximum in the coefficient of variation in the lower stratosphere and upper troposphere is the most dominant feature of Figure 4. This feature, combined with the strong ozone gradients about the location of the peak

coefficient of variation, is indicative of the strong ozone variability at those altitudes during these months. This variability is consistent with both the seasonal variation in the height of the tropopause, and the exchange of ozone-rich dry air from the stratosphere into the troposphere within tropopause folds associated with strong frontogenesis and cutoff-lows [*Cooper et al.*, 1998; *Danielsen*, 1968; *Holton et al.*, 1995; *Langford et al.*, 1996]. Further evidence of this process is in the vertical extent of these enhanced coefficients of variation across the mean tropopause.

[26] The coefficients of variation maxima are mostly below the mean tropopause, where ozone-mixing ratios in the upper troposphere are usually an order of magnitude smaller than in the lower stratosphere. The discontinuity in the high coefficient of variation over Huntsville in March is likely a consequence of the short duration of the data set, in which no stratosphere-troposphere exchange (STE) events were captured in that month.

[27] The Pacific coast station, Trinidad Head, exhibits the largest cross-tropopause coefficients of variation, along with the highest average ozone between 100–300 hPa. Trinidad Head also exhibits higher ozone at 300 hPa between January and July. This tendency is consistent with a higher frequency of occurrence of STE episodes within that time period and/or higher intensities of these events in terms of the amount of ozone exchanged within the folds relative to the other three stations. Mean ozone mixing ratios of 100 ppbv extend as far down as 400 hPa over Trinidad Head in June, compared to about 200–250 hPa over the other three stations for the same month.

[28] From the magnitude and vertical extent of the coefficient of variation peaks, a west-to-east gradient is evident in the frequency and/or relative magnitude of these STE events and upper free-tropospheric ozone mixing ratios. It should be noted at this point that it is very difficult to distinguish between high coefficients of variation caused by STE and the normal variations of the tropopause altitude in the winter and spring months from the monthly average profiles. However, for Trinidad Head the coefficient of variation maxima extends well below the average tropopause plus 1 standard deviation, as does the 125 ppbv ozone isopleth. This provides further evidence that the elevated upper tropospheric ozone levels over Trinidad Head are of stratospheric origin.

[29] There is significant interannual variability in ozone in the upper troposphere/lower stratosphere [*Logan*, 1994]. Comparison of data from the emerging climatology presented here with data from the climatology developed from aircraft observations [e.g., *Marenco et al.*, 1998; *Thouret et al.*, 1998a, 1998b] for Wallops Island shows good agreement with the ozonesonde and MOZAIC data with the exception of the 300 hPa level. There is a noticeable difference in the structure of the seasonal cycle between January and August at 300 hPa for the two ozonesonde data sets. The Wallops Island data set used by [*Thouret et al.*, 1998a] spanned a period from 1980 to 1993. Differences between the average ozone at Wallops Island at 300 hPa can be attributed to the strong interannual variability in both the height of the tropopause and the corresponding ozone concentrations at 300 hPa and possible changes in instrumentation/procedures associated with the ozonesonde launches at Wallops Island.

[30] Artificial variations in the height of the thermal tropopause can result from the definition used to identify the tropopause as outlined above. The two profiles of Figure 5 (Figures 5a and 5b) demonstrate the extremes in the temperature/ozone profiles that we have observed in this study. Figure 5a represents a profile that is within a tropopause fold where the height of the thermal tropopause is ambiguous by the definition outlined above. The resulting tropopause height gives tropospheric ozone values that are artificially large, which in turn affect the average tropospheric ozone calculations. On the other hand, Figure 5b shows the accuracy of the algorithm in pinpointing the exact height of the thermal tropopause when the latter is unambiguous.

[31] Figure 5c shows a spaghetti plot of the Trinidad Head ozonesonde profiles for the month of May. The average profile in red is the same as the average May profile shown in Figure 2, but in full resolution. This profile is strongly influenced by the four soundings in May of 1998 (shown in black) in which a high number of STE events occurred. Further evidence of this appears in the TOMS monthly mean total ozone for May 1998, Figure 5d. The average total ozone for May 1998 is over 45 DU (>13%) higher than the average total ozone for May 1997–2002 (see Figures 9a, 9b, and 9d). By virtue of its location in the northwestern United States, a region of strong frontogenesis in the spring months, Trinidad Head is expected to observe higher upper tropospheric and lower stratospheric ozone, as well as higher total ozone than the other three stations. However, May 1998 appears to be an especially active month and perhaps warrants further investigation.

[32] Analysis of individual soundings at the four stations reveals that the high coefficients of variation in the upper troposphere and lower stratosphere are due to a small number of soundings in which the relatively low height of the tropopause results in ozone mixing ratios in the "extended" lower stratosphere that are at least an order of magnitude higher than they normally are at that altitude (Figure 5c). In such cases, and when the tropopause is unambiguous, we observe low tropospheric ozone due to the decreased depth of the troposphere and a large increase in the total column ozone due to the elevated ozone in the lower stratosphere. On occasion there are soundings within a tropopause fold where the location of the actual tropopause is ambiguous, and as a result, the tropopause determined by the definition outlined above results in a tropopause height that is well into the stratosphere. These profiles contribute significantly to the enhanced coefficient of variation of the mean ozone in the upper troposphere as well as some of the increases in springtime tropospheric column ozone as shown in Figure 7 in section 3.4. Continuing analyses of these profiles may better quantify the question of irreversible stratospheric mixing into the troposphere.

3.3. Troposphere

[33] The seasonal cycle of ozone in the upper and middle troposphere peaks in the spring and early summer [*Chatfield and Harrison*, 1977; *Fishman et al.*, 1979] (Figures 3 and 4). In the summer, upper and middle tropospheric ozone mixing ratios over Trinidad Head actually decrease from their springtime high, while at the other three stations they increase toward the east. Seventy plus (ppbv) mixing ratios

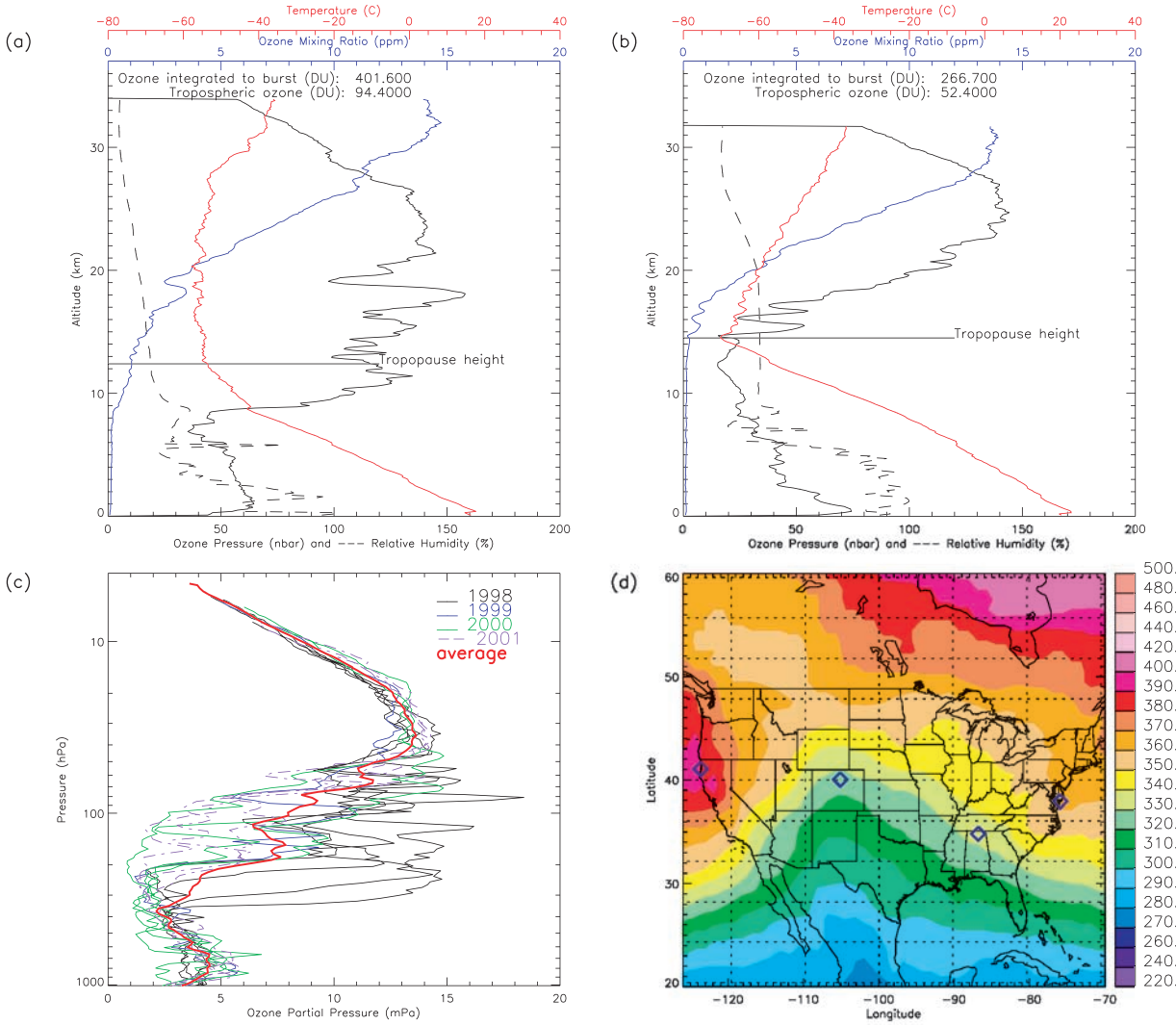


Figure 5. Individual soundings (a, b) from Wallops Island that demonstrate the extremes in lapse rate structure used to determine the height of the tropopause given the definition in the text and its effect on the computed tropospheric ozone. (c) Spaghetti plot of the nine Trinidad Head soundings in the month of May for the study period. The black profiles (4) are in 1998, the blue (1) is in 1999, the green (4) are in 2000, the magenta (3) are in 2001, and the red is the average profile. (d) Monthly mean total ozone from TOMS for May 1998. The blue diamonds mark the locations of the four ozonesonde stations.

extend as far down as 400 hPa over Boulder and 500–550 hPa over Huntsville and Wallops Island.

[34] Although they decrease substantially during the summer, the ozone coefficients of variation in the upper troposphere remain notable (40–70%). The summer coefficient of variation maximum is located almost entirely below the average tropopause, with a large gradient at the tropopause, highlighting the substantial week-to-week variability in the upper troposphere, as well as completely decoupling this variability from local stratospheric influences. Possible sources of this variability include transport of ozone previously exchanged into the upper troposphere at higher latitudes and/or en route photochemical production of ozone. [*Chatfield and Delany*, 1990] refer to a mechanism they call "mix-then-cook," in which vertical redistribution of ozone precursors by convection and subsequent transport can result in enhanced photochemical production of ozone and elevated middle and upper tropospheric ozone concentrations [*Dickerson et al.*, 1987; *Ellis et al.*, 1996; *Liu et al.*, 1987; *Pickering et al.*, 1989, 1992, 1990; *Thompson et al.*, 1994]. In a back-trajectory case study analysis of ozonesonde measurements, we also have observed evidence of this phenomenon during SOS99 in Nashville, TN (not shown).

[35] The amplitude of the seasonal cycle of ozone reaches a minimum in the middle troposphere at 500 hPa [*Logan*, 1985]. Coefficients of variation throughout the entire year and for all four stations show broad minima across the middle and lower free troposphere (about 500–800 hPa) (Figure 4). Of significance from the contour plot of mean ozone and standard deviations is the shape of the lower and middle-tropospheric mean ozone curves at the four stations. Boulder, Huntsville, and Wallops Island all show similar shapes of the annual cycle of the mean ozone,

differing only in the relative amplitudes of the cycle. Trinidad Head exhibits a rather different cycle in the annual mean ozone in the lower and middle troposphere, suggesting that the processes that govern ozone concentrations at Trinidad Head are different from those at the other three locations.

[36] In the lower troposphere, the seasonal cycle of ozone peaks in the summer months [*Logan*, 1985]. Little variation in the ozone cycle occurs in the lower troposphere over Trinidad Head; however, the seasonal signature is very strong over Huntsville and Wallops Island and is moderate over Boulder. Over Huntsville, ozone concentrations that exceed the mean of the other three stations by as much as 25–30% at 700 and 800 hPa in August, and 800 hPa in September (Figure 3) are clearly evident. However, the Huntsville August data is an average of only six profiles within a three year period, such a sparse record limits the conclusions that can be drawn from them. Within the planetary boundary layer, a steady increase in ozone mixing ratios during the summer months is evident at Boulder, Huntsville, and Wallops Island, but Trinidad Head exhibits a pronounced decrease in boundary layer ozone mixing ratios during the summer (Figure 6). At Huntsville, the summer peak in ozone extends from the surface to about 3 km (650 hPa) with a strong, well-mixed maximum in August of 70+ ppbv, and a notable gradient immediately above the convective boundary layer (CBL).

[37] Throughout the summer in the lower troposphere over Huntsville, ozone-mixing ratios are largest near the surface and decrease upward, suggesting a surface source for the elevated ozone. These surface sources could be accounted for by increased summertime natural emissions of isoprene from deciduous trees in the southeastern United States as well as other nonmethane hydrocarbons [*Andronache et al.*, 1994; *Doskey and Gao*, 1999; *Hagerman et al.*, 1997; *Liang et al.*, 1998; *Nouaime et al.*, 1998; *Sillman et al.*, 1995; *Starn et al.*, 1998]. Boundary layer ozone levels at the other three sites do not show maxima at the surface, especially at the two coastal sites, Trinidad Head and Wallops Island. There is a local minimum in ozone mixing ratios in a 1 km layer extending above the surface over Trinidad Head during July and August. This feature results in a summertime minimum in surface ozone at Trinidad Head, in contrast to the other three stations, further suggesting that the ozone source in that region is not from the surface and not local. The summer minimum could be accounted for by a shallow sea breeze coupled with the predominantly westerly flow that brings in clean air from the Pacific during the day and whose intensity is maximized in the summer when differential surface heating between land and water is greatest.

[38] Boundary layer ozone exhibits a larger diurnal signature than does ozone in the free troposphere, hence sensitivity to the average time at which the ozonesondes fly is higher in the boundary layer. Table 2 shows the mean, standard deviation, and mode of the launch times for the four stations in local standard time (LST). For Wallops Island, the large standard deviation of the mean launch time indicates that the sample represents an average over the entire day, which in turn would result in a lower average ozone profile for the boundary layer than would the mid-afternoon launches at Huntsville (standard deviation less than 1 hour,) and the other two stations as well.

3.4. Integrated Tropospheric Ozone

[39] Integrating the column ozone from the ground to the tropopause using data from the ozonesondes provides an accurate measure of the tropospheric ozone column. Figure 7 shows the tropospheric ozone columns for the four stations over the data period, along with the annual cycle of the monthly average tropospheric column ozone for each station. The figure shows a pronounced seasonal cycle in average tropospheric column ozone for Boulder, Huntsville, and Wallops Island, with increases in tropospheric ozone beginning early in the spring, and maxima well into the summer months. Trinidad Head, on the other hand, does not display the same structure apparent at the other three stations. There is an increase in tropospheric ozone in the early spring, but there is no such corresponding increase through the summer months. The magnitudes of the average tropospheric columns differ from station to station with peaks at or above 50 DU for Huntsville in July and August and for Wallops Island in May through July. The largest standard deviations of the monthly average tropospheric ozone column are in the spring and fall at all four stations.

[40] The increase in tropospheric column ozone in the summer is due to two main factors: an increase in the photochemical production of ozone, and a corresponding increase in the height of the average tropopause. Analysis of the seasonal variation in the height of the monthly averaged tropopause from Figure 4 shows the larger amplitudes over the two inland sites, Huntsville and Boulder, and smaller amplitudes for the seasonal cycle over the coastal stations, Trinidad Head and Wallops Island. The amplitude of the seasonal cycle in the height of the tropopause will tend to impose a dynamical, or nonphotochemical, effect on the increased tropospheric ozone columns observed during the summer months; however, a major contribution remains from the photochemistry.

[41] The dash-dotted lines in Figure 7 represent the height of the monthly averaged tropopause. The dashed lines represent the monthly average tropospheric ozone in (DU/km) $\times$ 10. Analysis of the annual cycle of integrated tropospheric ozone per km at all four stations shows an initial peak in April or May, reflecting the role of dynamical effects such as STE in modulating tropospheric ozone. At Trinidad Head, tropospheric ozone concentrations of over 3 DU/km are maintained through July, and they decrease with increases in tropopause height through the remainder of the summer and into fall and winter. Boulder and Wallops Island display similar slow decreases in tropospheric ozone concentrations through August; however, Wallops Island concentrations are about 40–50% higher than those at Boulder. Huntsville, on the other hand, displays a unique characteristic in its gradually increasing tropospheric ozone concentrations, which show a secondary peak of 3.5 DU/km in August. This difference from the other stations is due to the very high ozone mixing ratios observed in the boundary layer and upper troposphere over Huntsville (Figure 6).

[42] Boulder, Huntsville, and Wallops Island experience two periods of increasing tropospheric ozone. The first increase occurs in early spring as a result of stratosphere-troposphere exchange, and likely the initiation of photo-

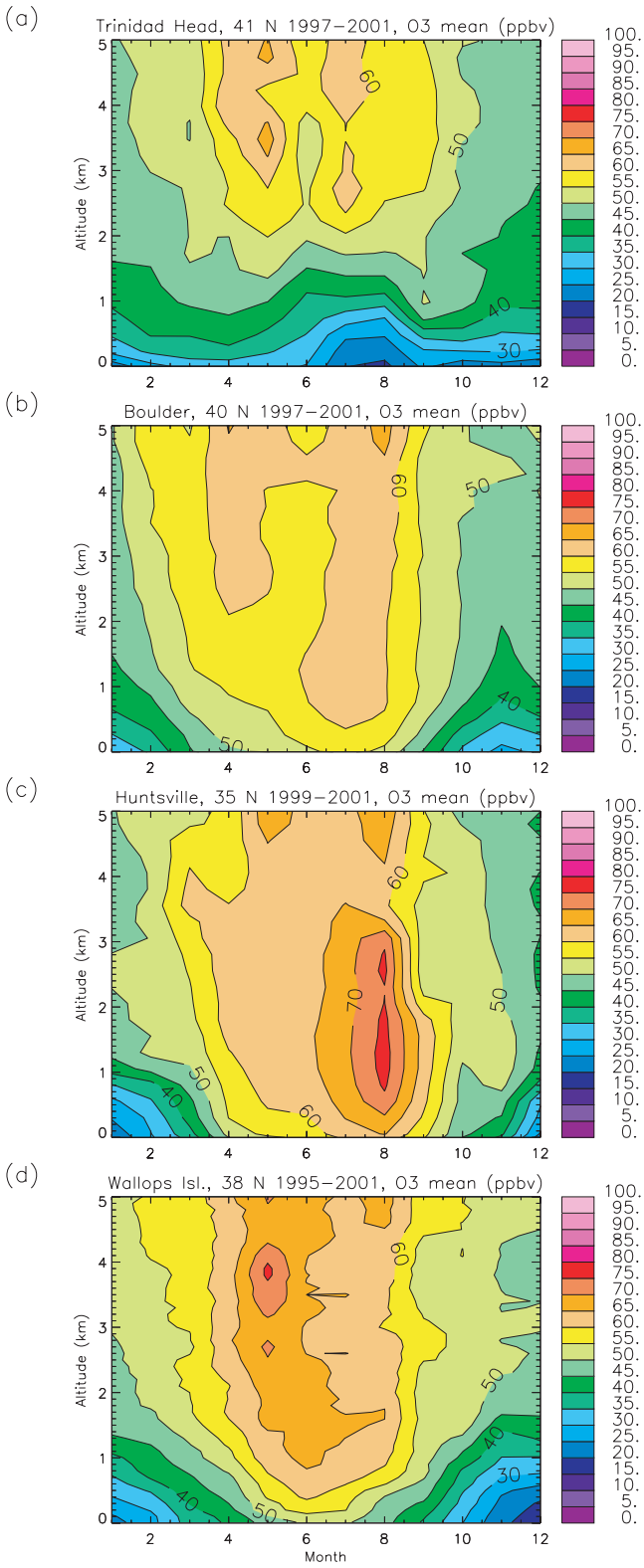


Figure 6. Vertical profiles of the annual variation in monthly mean ozone mixing ratios (ppbv) in the lower free troposphere and boundary layer relative to altitude above ground at (a) Trinidad Head, California; (b) Boulder, Colorado; (c) Huntsville, Alabama; and (d) Wallops Island, Virginia.

chemistry following the relative dormancy of winter (Figure 7). The second period commences in the summer with an annual peak in tropospheric ozone in July and August. This second increase corresponds to the strong influence of the natural and anthropogenic emissions of ozone precursors in the summer months [*Hagerman et al.*, 1997]. The monthly mean tropospheric column ranges from 22 DU in January to 38 DU in July at Boulder. The monthly mean exceeds 40 DU from April through September at Huntsville and Wallops Island. The highest monthly mean is 54 DU occurring in August at Huntsville.

[43] It must be noted that the data set used in this paper constitutes an emerging climatology of ozone across the United States. The statistical sample and the number of years of observation cannot classify the results as a true climatology. Interannual biases in the data can strongly affect the resulting average profiles. One such example is the Huntsville average August profile, which includes only six profiles within a 3-year sample. In the Huntsville area, 1999 and to an extent 2000 were dry years and could constitute such an interannual bias in the data. Because of a much wetter summer in Huntsville in 2001, observations through the early fall of 2001 show summertime boundary layer ozone profiles that are lower than those reported for 1999 and 2000. Hence there is evidence that the emerging true climatology lies somewhere between the extremes of 1999 and 2001.

3.5. Total Ozone Measurements From Ozonesondes and TOMS

[44] Total ozone from the Trinidad Head, Boulder, Huntsville, and Wallops Island measurements result from integrating the sonde column ozone to burst altitude and adding the SBUV climatological values for the remaining ozone above burst [*McPeters et al.*, 1997]. SBUV climatological values exist only for bursts at pressures greater than 30 hPa; therefore ozonesondes with burst pressures less than 30 hPa were not included in this comparison.

[45] Figure 8 shows the total ozone obtained from the sondes compared to ozone measured by the Total Ozone Mapping Spectrometer (TOMS) for coincident measurements within a six-hour period at the four stations. The average differences and standard errors of the mean between total ozone calculated from ozonesondes and TOMS at Trinidad Head, Boulder, Huntsville, and Wallops Island, computed as (sonde-TOMS)/TOMS, are $-2.1 \pm 0.3\%$, $-1.9 \pm 0.3\%$, $-1.5 \pm 0.4\%$, and $-1.0 \pm 0.3\%$, respectively. The sonde-TOMS differences exhibit signs of a temporal trend in the last 2–3 years of a few percent per year as seen in Figure 8; however, this period is too short to confirm a significant problem.

[46] CMDL changed its ECC cathode solution from 1% buffered to 2% unbuffered in July 1997 for all soundings at

Table 2. Mean, Standard Deviation, and Mode of Launch Times at the Four Ozonesonde Stations in Local Standard Time (LST)

Station Name	Mean Launch Time, LST	Standard Deviation, hours	Mode Launch Time, LST
Trinidad Head, California	1124	1.84	10
Boulder, Colorado	1121	2.30	11
Huntsville, Alabama	1234	0.83	12
Wallops Island, Virginia	1052	5.54	9

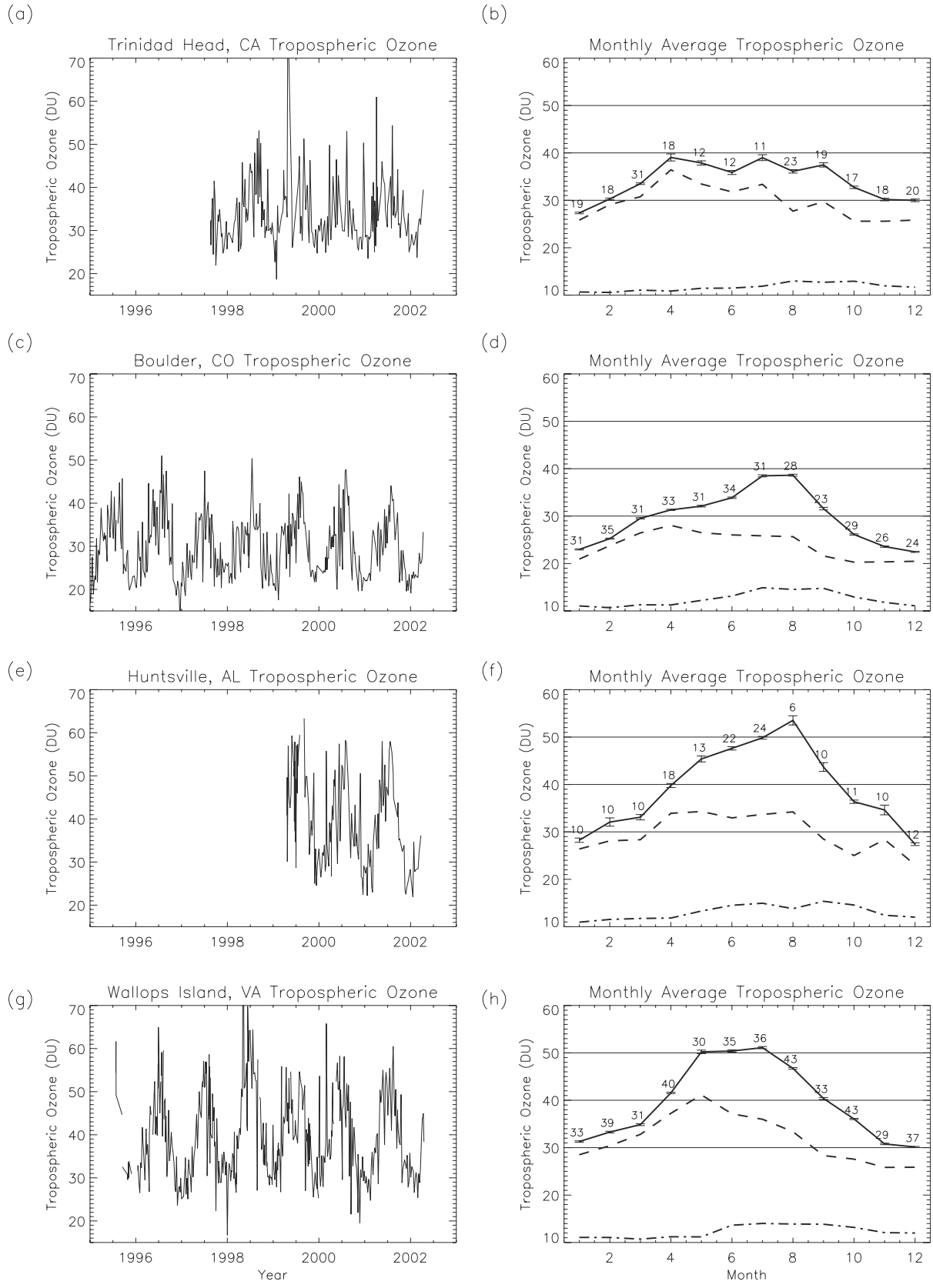


Figure 7. Time series of integrated tropospheric ozone (left-hand panels) and monthly averaged tropospheric ozone (right-hand panels) for (a, b) Trinidad Head, California; (c, d) Boulder, Colorado; (e, f) Huntsville, Alabama; and (g, h) Wallops Island, Virginia, respectively. In the average monthly tropospheric ozone plots, the dashed lines represent the average tropospheric DU/km $\times$ 10, and the dash-dotted lines represent the height of the average tropopause.

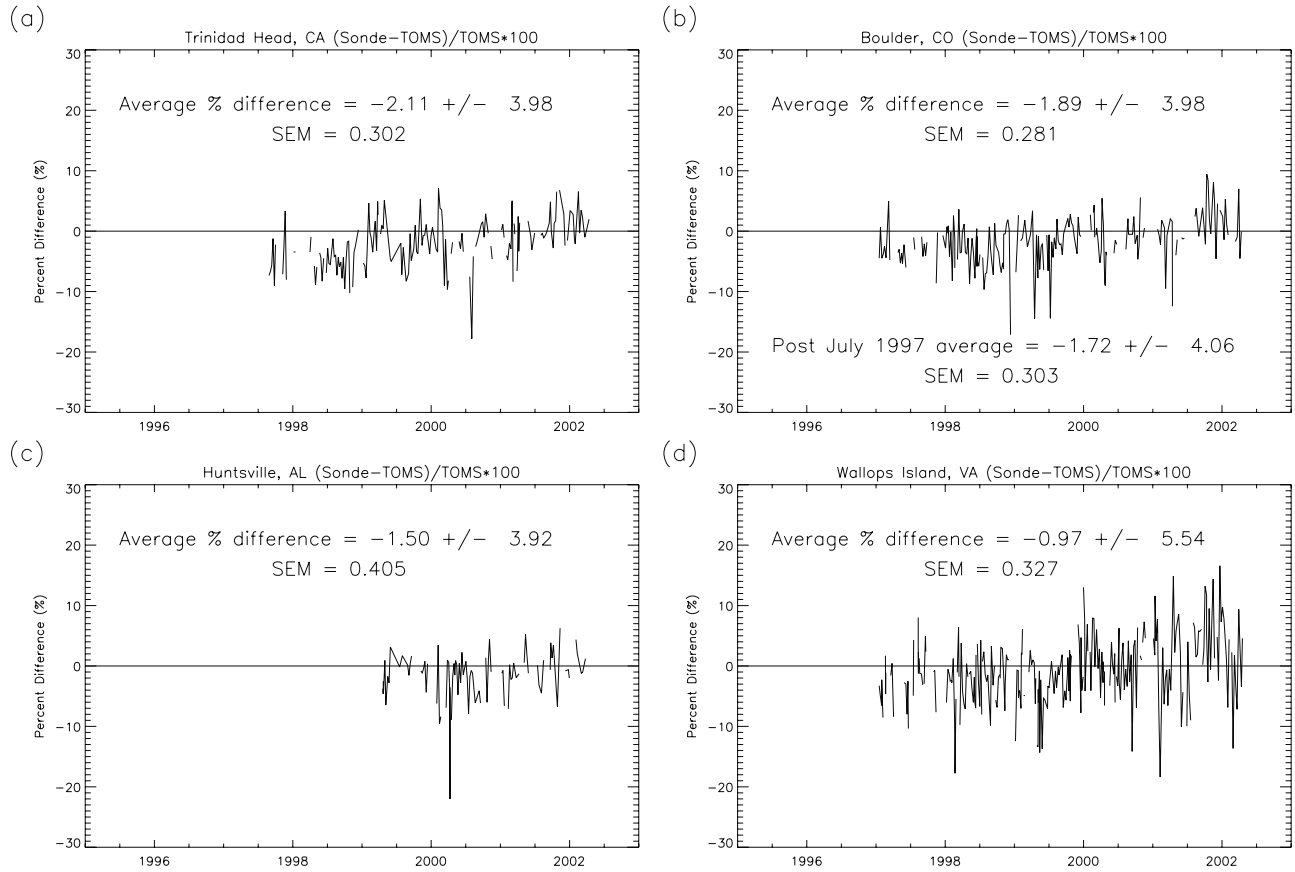


Figure 8. Percentage difference in total column ozone between TOMS and sondes calculated using *McPeters et al.* [1997] SBUV climatology above burst for (a) Trinidad Head, California; (b) Boulder, Colorado; (c) Huntsville, Alabama; and (d) Wallops Island, Virginia. One standard deviation and the standard error of the mean (SEM) are indicated on the chart.

Boulder. The buffered KI solution has been hypothesized to produce side reactions that may over-estimate the amount of ozone measured by the sonde [*Johnson et al.*, 2002]. Other stations, including Wallops Island, believe that a buffered solution is necessary in order to maintain a neutral pH during flight, which could be affected by pollution from ingested air. CMDL has applied a correction to the soundings from January 1995 through July 1997 in this study (132 soundings), and this correction accounts for the difference observed in dual flights between 1% buffered KI (standard cathode) and the 2% unbuffered KI cathode solutions. Removing the corrected 1% buffered sondes from the Boulder data set results in very little change in the percent differences as shown in Figure 8. The Trinidad Head and Huntsville stations use 2% unbuffered KI solution for all sondes in this study. The Wallops Island sondes using 1% buffered KI solution give an average percent difference that is comparable to those observed at the CMDL stations.

[47] The annual variations in the mean monthly total-column ozone from TOMS at a given location are on the order of 60–80 DU (Figures 9a and 9b) and are strongly dependant on the dynamical regimes of the stratosphere. The mean annual cycle of monthly averaged total ozone from ozonesondes plus SBUV climatology agrees well with those from TOMS (see Figure 9b in section 3.5). Therefore, one may conclude that the weekly frequency sonde flights produce a robust climatology with respect to the daily TOMS observations.

[48] From Figures 9a and 9b it is clear that wintertime total ozone values over Huntsville are consistently about 5–7% lower than at the other three stations. This difference can be reconciled by the lower monthly mean stratospheric ozone profiles over Huntsville relative to Trinidad Head, Boulder, and Wallops Island, observed in Figure 2. The higher standard deviation values for the monthly mean TOMS total ozone over the four stations during the winter and spring months are largely due to variations in lower-stratospheric ozone observed in the annual cycle of the monthly mean ozone of Figure 4.

[49] Trinidad Head and Wallops Island display consistent patterns in the monthly average total ozone and in the monthly average profiles of Figure 2. In the months when the lower stratospheric mean profile is considerably higher at Trinidad Head than at Wallops Island (April through July), the monthly average total ozone from TOMS reflects higher values at Trinidad Head relative to Wallops Island. During the summer months when the sonde average profiles are very similar, the TOMS monthly averages reflect similar values for the two locations.

[50] In a comparison of the annual cycle of the monthly mean TOMS total ozone with the annual cycle of tropospheric ozone from Figures 4 and 7, several consistent

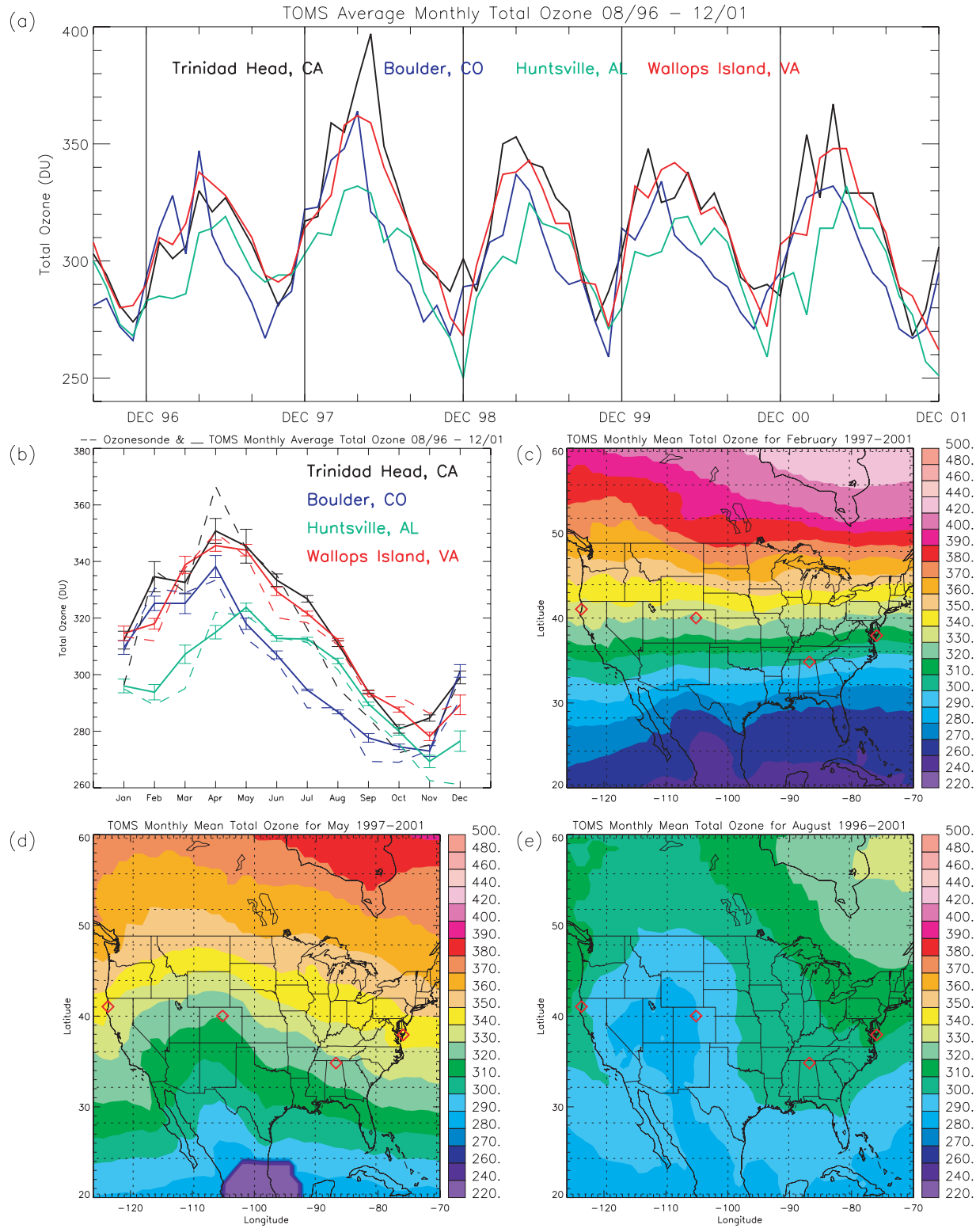
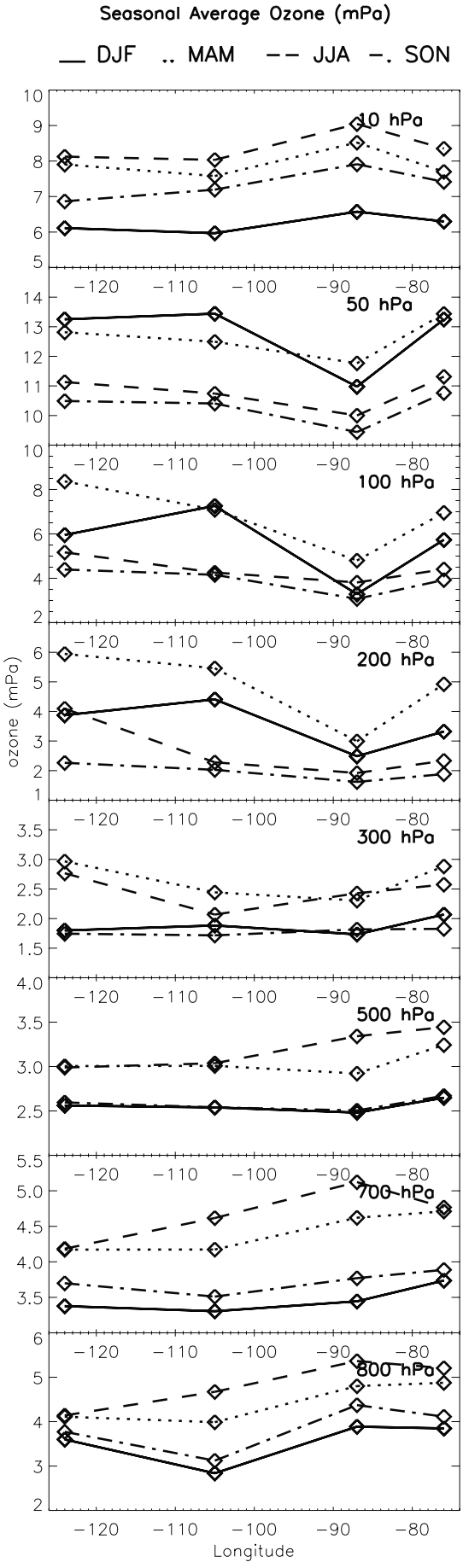


Figure 9. (a) Monthly averaged total column ozone from the Earth-Probe Total Ozone Mapping Spectrometer (EP-TOMS) from August 1996 through December 2001 for the four ozonesonde stations and (b) the average monthly total ozone for that period from ozonesondes and TOMS ± one standard deviation. (c, d, and e) Monthly mean total ozone from TOMS for February, May, and August, respectively, over the study period. The red diamonds mark the locations of the four ozonesonde stations.



features appear: (1) The peak in the monthly average TOMS total ozone over Trinidad Head between April and July (Figure 9) corresponds with the peak in lower-stratospheric/upper-tropospheric ozone over Trinidad Head relative to the other three stations (Figures 2, 3, and 4). (2) Although the annual variations of the total ozone column over Trinidad Head and Wallops Island are similar (Figure 9), the partitioning between tropospheric and stratospheric portions (Figures 4 and 6) changes over the year. (3) The Huntsville total column is the lowest of the four stations from December through April (Figures 9b and 9c) because of smaller ozone amounts in the lower stratosphere (Figure 2). (4) The decrease in total ozone at Boulder relative to Huntsville from May through October (Figures 9b and 9e) results from a combination of differences in altitude (about 5 DU) and a persistent planetary wave during the summer months in the stratosphere. This waveforms a feature of low ozone (about 15 DU) over the western plains of the United States (Figure 9).

3.6. Variations Across the Continental United States

[51] Figures 3, 4, and 5 suggest the presence of different mechanisms controlling ozone concentrations at different levels of the atmosphere, and especially in the troposphere, across the United States. A particular mechanism that couples latitudinal structure with longitudinal structure in the stratosphere is the presence of planetary waves with preferred seasonal phase. For example, Figures 9c, 9d, and 9e) shows the monthly average planetary wave structure in February, May, and August. This structure changes significantly during these months. As a result, the apparent longitudinal structure in February is actually a latitudinal difference between Huntsville and the other three stations in a zonal atmosphere. In August, however, because of the standing wave, the measurements show that Boulder has lower column ozone amounts compared to the other three stations, but this difference can be explained by the wave pattern.

[52] Figure 10 shows the seasonally averaged ozone partial pressures at eight atmospheric levels for the four stations. At 10 hPa, the seasonal averages show a maximum in June through August across the United States, with Huntsville showing the highest levels at all seasons. The relationship reverses in the middle stratosphere at 50 hPa, with a maximum in the winter and spring months, which is maintained down to 100 hPa. This feature is attributed to a latitudinal gradient in stratospheric ozone, as previously discussed in this paper. The continental variability is strongest in the lower stratosphere in all seasons, with the strongest variations in the winter and spring months. This relationship correlates directly with the seasons of maximum dynamic variability in the lower stratosphere.

[53] In the troposphere, the magnitudes of the station-to-station layer ozone partial pressures, as well as the seasonal variations, are much smaller than in the stratosphere, an indication of the different mechanisms involved in bringing about these variations. These variations are most apparent at 700 and 800 hPa. The local seasonal variation at 800 hPa

Figure 10. (opposite) Seasonally averaged longitudinal variation in ozone (partial pressure in mPa) for the four ozonesonde stations at 10 hPa to 800 hPa.

over Trinidad Head is the smallest of the four stations as well as the smallest for all atmospheric levels considered. Average ozone partial pressures for Trinidad Head from the surface to 500 hPa vary by less than 1 mPa over the entire year, with a minimum over the fall and winter months and a maximum over the spring and summer months. The magnitude of this seasonal variation at Trinidad Head provides further evidence that the ozone sources in the northwestern United States are primarily nonlocal. In the lower free troposphere (500–800 hPa in Figure 10), and within the planetary boundary layer a west-to-east increasing gradient in ozone is clearly discernable, however, particularly in the lower levels, we speculate that these increases are more likely attributable to local pollution effects than a longitudinal gradient across the United States.

4. Conclusions

[54] As a result of several years of ozonesonde measurements at four locations in the United States, a climatology of the vertical profile of continental U.S. ozone is beginning to emerge. This vertical distribution of ozone displays significant variation on timescales ranging from days to interannual in both intrastation and interstation observations. The records show strong evidence of stratosphere-troposphere exchange, especially in the winter and spring, and more so at the Pacific coast station, Trinidad Head. All stations show variability in the boundary layer pollution sources. The middle troposphere is the least variable region. The variability throughout the troposphere and lower stratosphere is quantified by coefficients of variation of the monthly means showing strong vertical and seasonal structure. Even with this strong variability, comparison to MOZAIC aircraft measurements shows good agreement, except at 300 hPa, which may be attributed to strong interannual variability between the data sets.

[55] In the lower troposphere, the two eastern stations, Huntsville, Alabama, and Wallops Island, Virginia, measure the highest ozone amounts compared to the two western stations, Trinidad Head, California, and Boulder, Colorado. The lower stratospheric ozone at Huntsville, Alabama, is noticeably lower on average than at the other three stations in the winter and springtime. All stations show very strong variability in this altitude region, especially in winter and springtime. During extreme events, stratospheric peak ozone partial pressures pervade the troposphere down to 500 hPa. Throughout the stratosphere, the Huntsville profiles display more tropical character than the other three stations, a distinction most noticeable during winter and spring.

[56] In comparing the seasonal signature of ozone across the United States, eastern stations exhibit higher tropospheric ozone concentrations as a result of local pollution effects. The seasonal cycle maximizes in the summer months at all stations except at Trinidad Head, which has the opposite phase. Huntsville experiences the highest ozone mixing ratios in the summertime convective boundary layer, reaching 75 ppbv on average in August. The other three sites experience significant vertical gradients in volume mixing ratio in the lowest ~1 km with surface minima.

[57] Boulder, Huntsville, and Wallops Island stations show a pronounced seasonal cycle in integrated tropospheric ozone maximizing in the summer; the amplitude at Trinidad Head is significantly smaller. Wintertime minima range from 25 DU at Boulder to 30 DU at Wallops Island. Huntsville and Wallops Island experience the largest tropospheric column ozone amounts (>50 DU); Trinidad Head and Boulder both peak at ~40 DU. These summertime maxima result from both higher mixing ratios and a higher tropopause. The signatures of stratosphere-troposphere exchange and photochemical production are both evident in the column effects.

[58] The sonde-TOMS average differences in total ozone column range from −1% to −2% with some indication of a positive secular change in that bias. The seasonal character of TOMS column ozone at the sonde locations is consistent with the sonde-plus-SBUV-climatology total columns. Therefore, inspecting the sonde variations within the spatial/temporal context of the TOMS-measured ozone morphology reveals preferred wave patterns in the ozone field that result in the observed ozone profiles and the coupling between latitude and longitude effects, which vary with altitude.

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