Stratospheric versus pollution influences on ozone at Bermuda: Reconciling past analyses

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Received 27 January 2002; revised 3 June 2002; accepted 18 June 2002; published 16 November 2002.

[1] Conflicting interpretations of the spring ozone maximum observed at Bermuda (32°N, 65°W) have fueled the debate on stratospheric influence versus tropospheric production as sources of tropospheric ozone. We use a global three-dimensional (3-D) model of tropospheric ozone-NO_x-hydrocarbon chemistry driven by assimilated meteorological observations to reconcile these past interpretations. The model reproduces the observed seasonal cycle of surface ozone at Bermuda and captures the springtime day-to-day variability ($r = 0.82$, $n = 122$, $p < 0.001$) driven by high-ozone events. We find that transport of North American pollution behind cold fronts is the principal contributor to springtime surface ozone at Bermuda and is responsible for all the high-ozone events. The model reproduces the observed positive correlations of surface ozone with ^{7}Be and ^{210}Pb at Bermuda; the correlation with ^{7}Be reflects the strong subsidence behind cold fronts, resulting in the mixing of middle-tropospheric air with continental outflow in the air arriving at Bermuda, as indicated by the positive ^{7}Be-^{210}Pb correlation. This mixing appears to have been an obfuscating factor in past interpretations of subsiding back-trajectories at Bermuda as evidence for a stratospheric or upper tropospheric origin for ozone. Isentropic back-trajectories computed in our model reproduce the previously reported subsidence associated with high-ozone events. Even in the free troposphere, we find that the stratosphere contributes less than 5 ppbv (<10%) to spring ozone over Bermuda. Positive O_3-^{7}Be and negative O_3-^{210}Pb correlations observed at Tenerife (28°N, 16°W, 2.4 km) in summer are reproduced by the model and are consistent with a middle-tropospheric source of ozone, not an upper tropospheric or stratospheric source as previously suggested. A regional budget for the North Atlantic in spring indicates that the stratosphere contributes less than 10 ppbv ozone (<5%) below 500 hPa, while the lower troposphere contributes 20–40 ppbv ozone throughout the troposphere. *INDEX TERMS:* 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 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

Citation: Li, Q., D. J. Jacob, T. D. Fairlie, H. Liu, R. V. Martin, and R. M. Yantosca, Stratospheric versus pollution influences on ozone at Bermuda: Reconciling past analyses, *J. Geophys. Res.*, *107*(D22), 4611, doi:10.1029/2002JD002138, 2002.

1. Introduction

[2] There is a continuing debate surrounding the relative importance of tropospheric production versus stratospheric influx as sources of tropospheric ozone. A focal point of the debate is the spring ozone maximum observed at remote sites in northern midlatitudes [*Oltmans*, 1981; *Logan*, 1985; *Oltmans and Levy*, 1992, 1994; *Monks*, 2000]. A number of hypotheses have been proposed to explain this spring maximum, including stratospheric injection [*Logan*, 1985; *Levy et al.*, 1985], intensifying photochemistry in spring [*Penkett and Brice*, 1986], wintertime accumulation of ozone and its precursors at high latitudes [*Liu et al.*, 1987; *Honrath et al.*, 1996], and phase overlap between transport from the stratosphere and production in the troposphere [*Wang et al.*, 1998b; *Yienger et al.*, 1999]. Recent observations support photochemical production as the cause of the spring ozone maximum [*Kajii et al.*, 1998; *Pochanart et al.*, 1999; *Zanis et al.*, 2000]. In particular, O_3-^{7}Be correlations measured from aircraft over North America argue against a stratospheric cause (D. J. Allen et al., An estimate of the stratospheric input to the troposphere during TOPSE using ^{7}Be measurements and model simulations,

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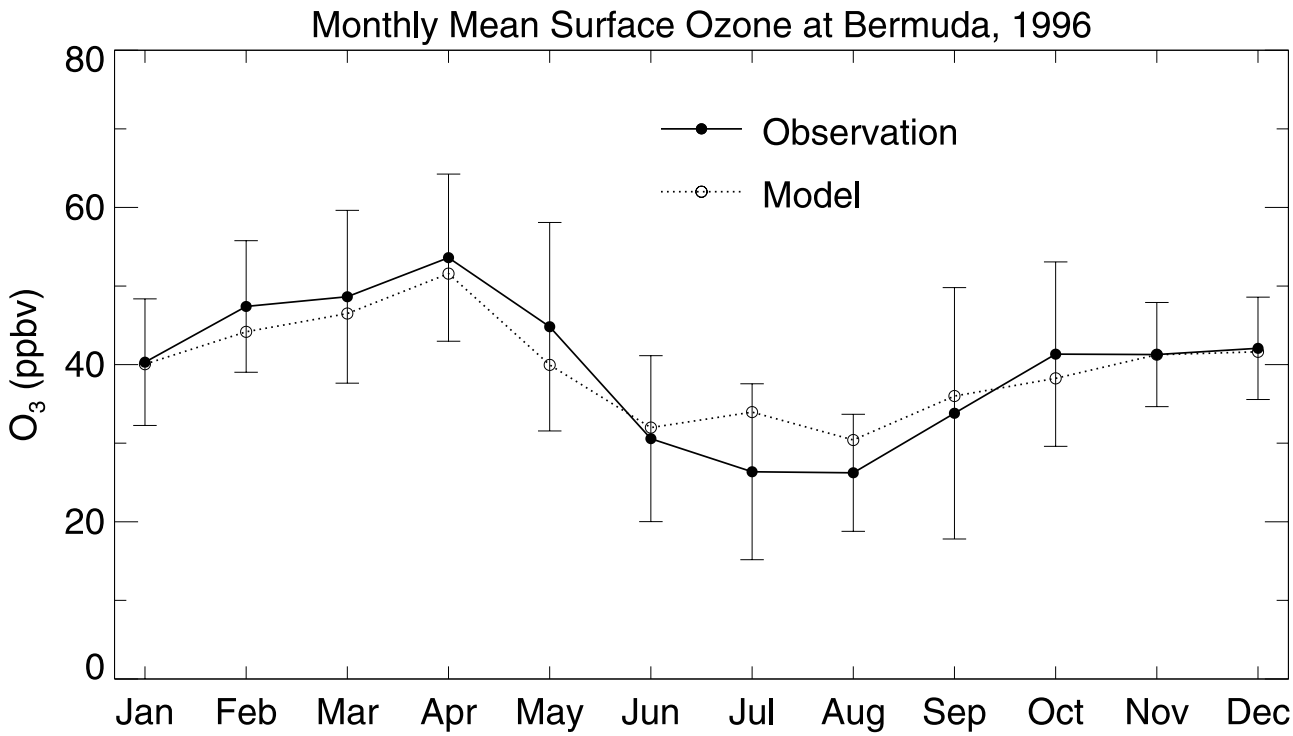

Figure 1. Observed and simulated monthly mean surface ozone concentrations at Bermuda for 1996. The vertical lines show the standard deviations for the observations. The observations are from the Climate Monitoring and Diagnostics Laboratory (CMDL) network [*Oltmans and Levy*, 1992, 1994] and were provided by Samuel J. Oltmans.

submitted to *Journal of Geophysical Research*, 2002; J. E. Dibb et al., Stratospheric influence on the northern North American free troposphere during TOPSE: ^{7}Be as a stratospheric tracer, submitted to *Journal of Geophysical Research*, 2002).

[3] Resolving stratospheric and anthropogenic influences on tropospheric ozone over the North Atlantic has been a central objective of the North Atlantic Regional Experiment (NARE) [*Fehsenfeld et al.*, 1996a, 1996b]. Positive correlation between ozone and CO over the region in summer implies a major anthropogenic influence [*Parrish et al.*, 1993, 1998]. In spring, however, ozonesonde measurements and isentropic back-trajectories have been used to suggest a dominant stratospheric influence [*Oltmans et al.*, 1996]. Summer observations of ozone at Tenerife (28°N, 16°W, 2.4 km altitude) show a positive correlation with cosmogenic ^{7}Be, and a negative correlation with terrigenic ^{210}Pb, which have been interpreted as implying a stratospheric or at least a high-altitude ozone source [*Prospero et al.*, 1995].

[4] Ozone observations at Bermuda (32°N, 66°W) have received particular attention. Surface ozone at that site shows a strong spring maximum and summer minimum [*Oltmans and Levy*, 1992, 1994; *Logan*, 1999]. The summer minimum is due to a combination of photochemical loss and inflow of tropical marine air around the Bermuda-Azores high [*National Research Council* (*NRC*), 1991; *Oltmans and Levy*, 1992, 1994; *Moody et al.*, 1995]. The spring maximum has been attributed by *Oltmans and Levy* [1992, 1994] and *Moody et al.* [1995] to a stratospheric influence, on the basis of isentropic back-trajectories indicating strong subsidence. However, *Dickerson et al.* [1995] argued that half or more of the excess ozone at Bermuda in spring represents North American pollution transported behind cold fronts. Chemical observations show that transport of North American pollution to Bermuda peaks in spring [*Van Valin and Luria*, 1988; *Huang et al.*, 1999; *Milne et al.*, 2000], reflecting the frequency of frontal passages. However, *Moody et al.* [1995] found a positive correlation between ozone and ^{7}Be in spring, supporting a high-altitude origin for ozone. *Arimoto et al.* [1999] and *Huang et al.* [1999] reported correlated maxima of ^{210}Pb, ^{7}Be and ozone at Bermuda when airflow is from the northwest, further complicating the interpretation.

[5] We use here the GEOS-CHEM global three-dimensional (3-D) model of tropospheric ozone-NO_x-hydrocarbon chemistry driven by assimilated meteorological observations to determine the relative influences of transport from the stratosphere and photochemical production on ozone at Bermuda in particular and over the North Atlantic in general. Through analysis of simulated and observed fields of ozone, CO, and radionuclides, as well as through Lagrangian examination of isentropic back-trajectories. We show that we can resolve the conflict in the past interpretations of the spring maximum of ozone at Bermuda. Our results demonstrate conclusively that this maximum is due to North American pollution.

2. Model Description

[6] The original description of the GEOS-CHEM model is given by *Bey et al.* [2001a]. We use here GEOS-CHEM version 4.16 (see http://www-as.harvard.edu/chemistry/trop/

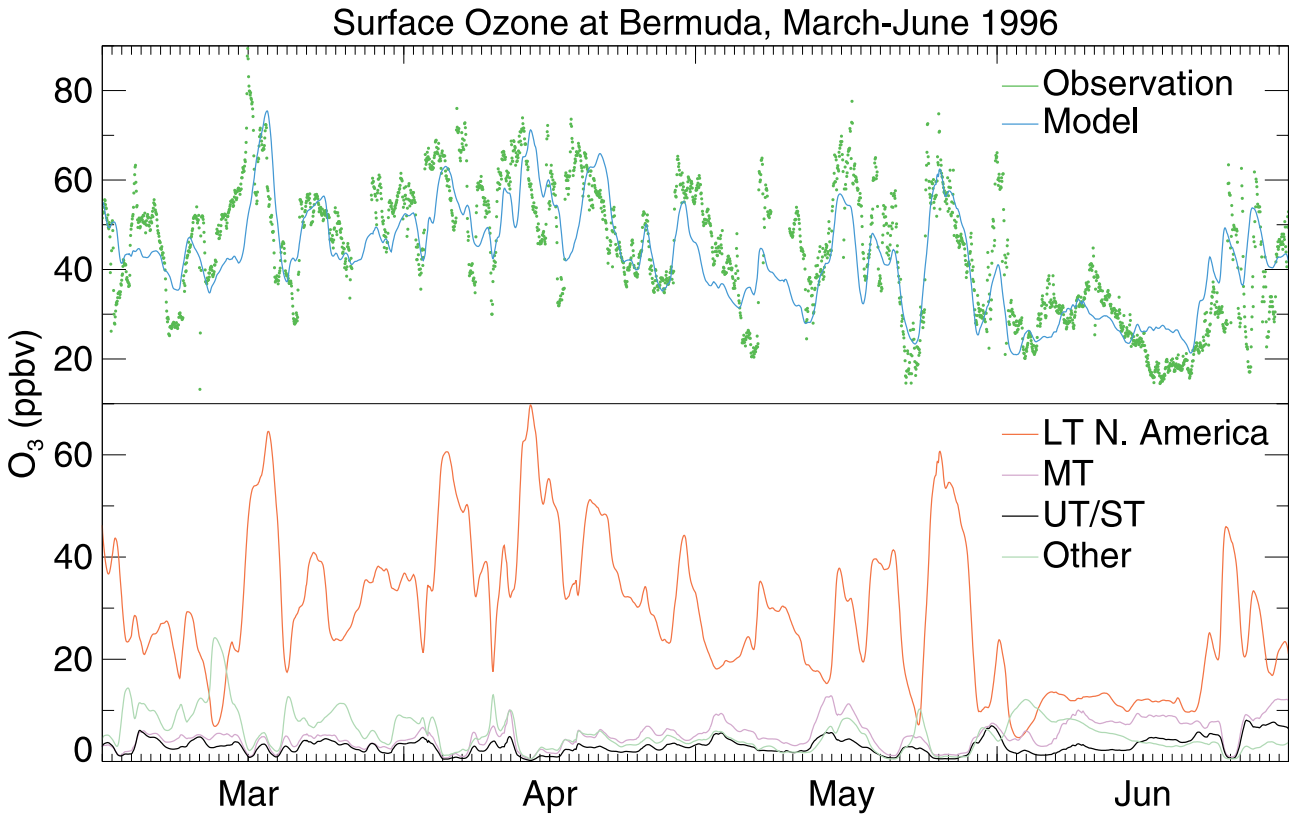

Figure 2. Daily mean surface ozone concentrations at Bermuda in March–June 1996. The contributions from different source regions are shown using the tagged ozone tracers. "LT N. America" refers to ozone produced in the lower troposphere (700 hPa-surface) over North America and the western North Atlantic (25–75°N, 50–160°W). "MT" refers to ozone produced in the middle troposphere (400–700 hPa). "UT/ST" refers to ozone produced in the upper troposphere (400 hPa-tropopause) and the stratosphere. "Other" refers to ozone produced in the lower troposphere outside of 25–75°N and 50–160°W.

geos). The model is driven by assimilated meteorological fields from the Goddard Earth Observing System (GEOS) of the NASA Data Assimilation Office (DAO) [*Schubert et al.*, 1993]. We use meteorological fields for 1996 (GEOS-STRAT) which are provided with 6-hour temporal resolution (3-hour for surface variables), 2° × 2.5° horizontal resolution, and 46 vertical sigma levels with the lowest three levels centered at 50 m, 300 m, and 500 m above the surface for a column based at sea level. For the work presented here, we regrid the meteorological fields to 4° × 5° horizontal resolution for computational expediency and merge the vertical levels above the lower stratosphere. A 1-year simulation with the 1995 (GEOS-1) meteorological fields is conducted to provide proper initialization for the 1996 simulation.

[7] The model includes 80 chemical species and transports 24 tracers to describe tropospheric ozone-NO_x-hydrocarbon chemistry. Anthropogenic emissions in the model are specified using a base emission inventory for 1985 described by *Wang et al.* [1998a], scaled to 1996 using national emission inventories and economic data [*Bey et al.*, 2001a]. The current model version includes updated CO emissions from *Duncan and Logan* [2001], and an improved emission inventory for biomass burning that includes interannual variability determined from satellite observations (B. N. Duncan et al., Interannual and seasonal variability of biomass burning emissions constrained by satellite observations, submitted to *Journal of Geophysical Research*, 2002).

[8] Transport of ozone from the stratosphere is simulated with the Synoz (synthetic ozone) method of *McLinden et al.* [2000]. In this method, stratospheric ozone is represented by a passive tracer that is released uniformly in the tropical lower troposphere (between 30°S to 30°N and 70 to 10 hPa) at a rate constrained to match a prescribed global mean cross-tropopause ozone flux. Cross-tropopause fluxes used in recent modeling studies range from 400 to 850 Tg O_3 yr^{-1} [*Lelieveld et al.*, 1999] and satellite observations imply a narrower range of 450–590 Tg O_3 yr^{-1} [*Gettelman et al.*, 1997]. We adopt a global cross-tropopause flux of 475 Tg O_3 yr^{-1} recommended by *McLinden et al.* [2000], which results in a satisfactory simulation of vertical ozone profiles at northern middle and high latitudes [*Bey et al.*, 2001a, 2001b; *Liu et al.*, 2002]. Global tropospheric production and loss rates of ozone (actually odd oxygen $O_x = O_3 + NO_2 + 2 \times NO_3 + HNO_3$ + peroxyacyl nitrates + $HNO_4 + 3 \times N_2O_5$) in the model are 4900 Tg O_3 yr^{-1} and 4300 Tg O_3 yr^{-1}, respectively. Previous global 3-D models indicate photochemical production ranging from 3425 to 4550 Tg O_3 yr^{-1} and photochemical loss from 3350 to 4065 Tg O_3

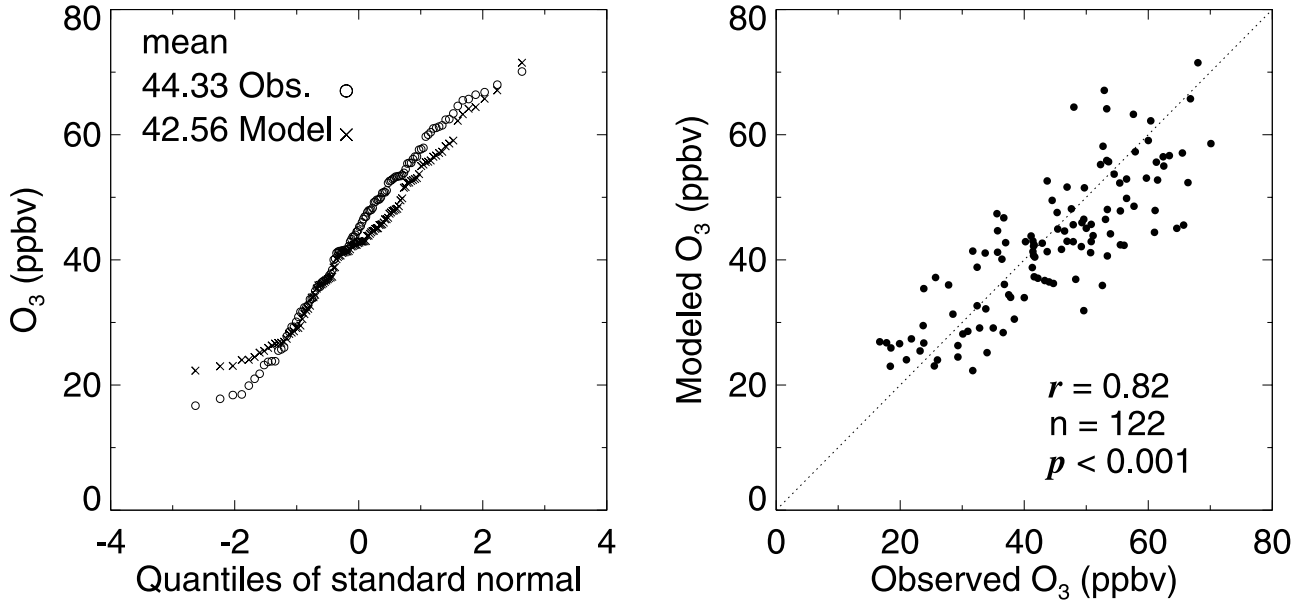

Figure 3. Statistics of comparison between simulated and observed time series of surface ozone at Bermuda in March–June 1996: cumulative probability distributions (left panel) and scatterplot of simulated versus measured values (right panel). Values are daily averages for both the observations and the model. Also shown in the scatterplot are the correlation coefficient (r), the number of data points (n), and the p-value indicating the significance level of the correlation.

yr^{-1} [*Lelieveld et al.*, 1999]. As discussed by *Bey et al.* [2001a], we believe that the higher values in our model reflect an improved treatment of radiative transfer through clouds with the Fast-J algorithm of *Wild et al.* [2000].

[9] A global evaluation of the model for tropospheric ozone and its precursors is presented by *Bey et al.* [2001a] using the 1994 GEOS-1 meteorological fields. More focused evaluations of the GEOS-CHEM simulation of tropospheric ozone chemistry for different regions of the world and for different years have been presented in a number of papers [*Bey et al.*, 2001b; *Li et al.*, 2001a, 2001b, 2002; *Chandra et al.*, 2002; *Fiore et al.*, 2002; *Martin et al.*, 2002a, 2002b; *Liu et al.*, 2002]. Of particular relevance here, *Fiore et al.* [2002] showed detailed comparisons with observational statistics for ozone and its precursors in the United States, and *Li et al.* [2002] evaluated transatlantic transport in the model with long-term ozone and CO measurements at coastal sites on both sides of the North Atlantic. The later study showed that the model reproduces well the day-to-day variabilities of surface ozone and CO at Sable Island (Canada), Westman Island (Iceland), and Mace Head (Ireland), including the magnitudes and frequencies of pollution episodes. *Allen et al.* [1996a, 1996b] previously showed in a 3-D model similarly driven by GEOS meteorological data that the transport of North American ^{222}Rn and CO to Bermuda behind cold fronts is well simulated throughout the year.

[10] To investigate the contributions to tropospheric ozone concentrations over the North Atlantic from different source regions, we include tagged ozone tracers [*Wang et al.*, 1998b; *Li et al.*, 2001b, 2002] in our simulation. The tagged ozone tracer simulation uses archived daily 3-D fields of O_x production rates and loss frequencies from the standard full-chemistry simulation to transport eight separate O_x tracers originating from different regions: the stratosphere (ST), the upper troposphere (UT: 400 hPa-tropopause), the middle troposphere (MT: 400–700 hPa), the continental lower troposphere (LT: 700 hPa-surface; separately North America, Europe, Asia, and other continents), and the marine lower troposphere. Here we define

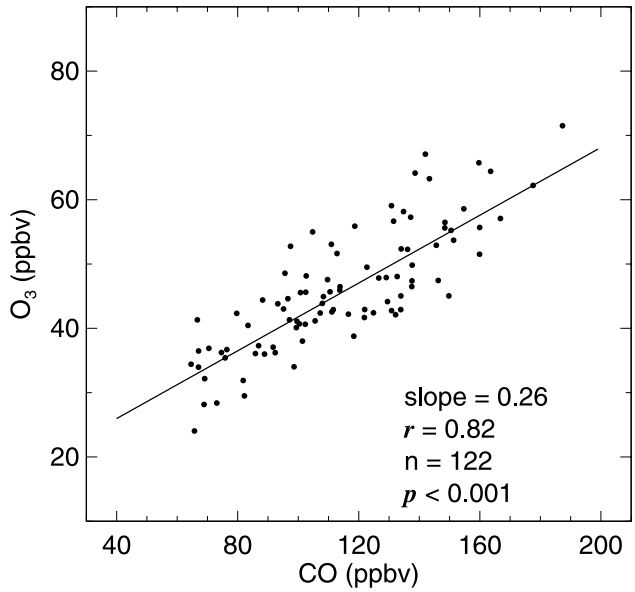

Figure 4. Scatterplot of simulated ozone versus CO at Bermuda for March–June 1996. Values are daily averages. Also shown are the correlation coefficient (r), the number of data points (n), and the p-value indicating the significance level of the correlation.

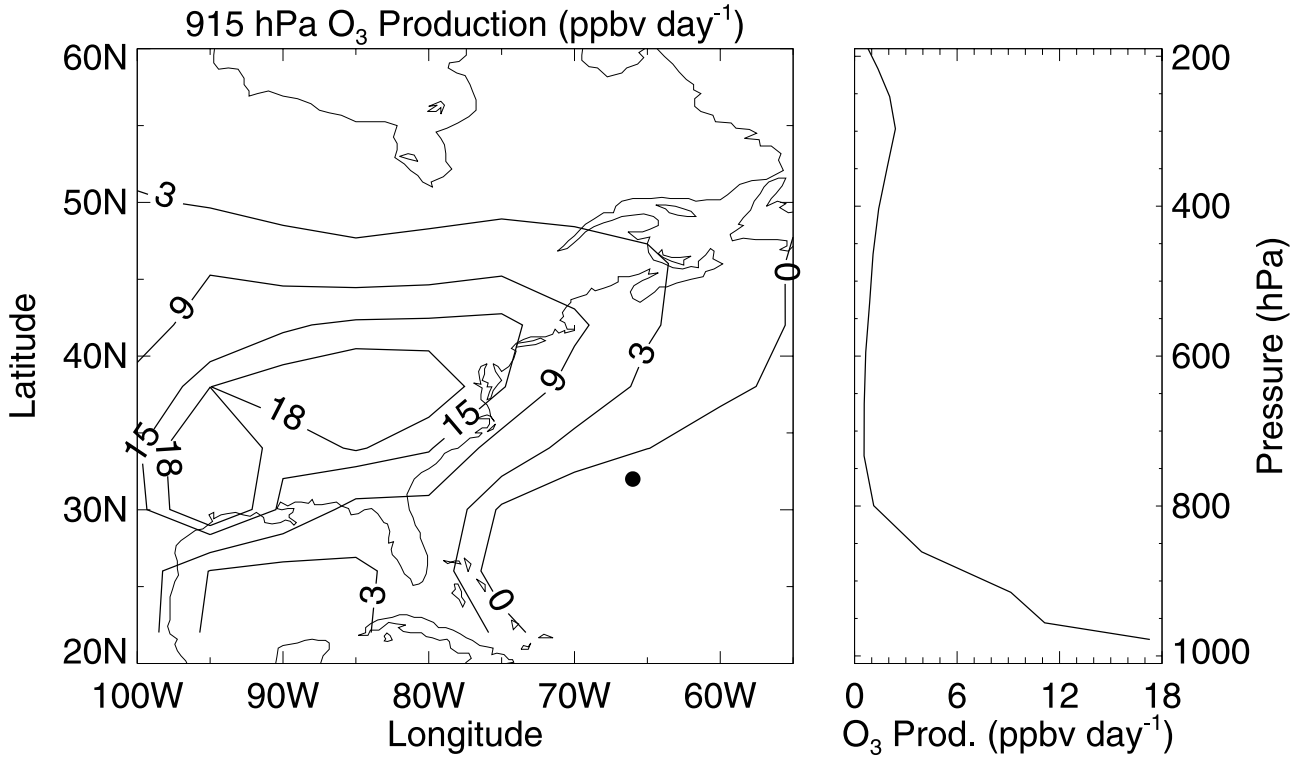

Figure 5. GEOS-CHEM monthly mean net ozone production (ppbv d^{-1}) at 915 hPa (left panel) and as a function of altitude over the eastern U.S. (30–50°N, 70–90°W) (right panel) for April 1996. The solid circle indicates the location of Bermuda.

North America as the domain (25–75°N, 50–160°W), including part of the western North Atlantic. The tracers are removed by chemical loss and dry deposition at the same frequencies as those for total O_x in the standard simulation. By summing the concentrations of all eight tracers, we reproduce closely the total O_x concentrations in the standard full-chemistry simulation. Since ozone typically accounts for over 95% of O_x, we will refer to the tagged O_x as tagged ozone in what follows.

3. Ozone Over Bermuda

3.1. Seasonal Variation of Surface Ozone

[11] The observed and simulated monthly mean surface ozone concentrations at Bermuda for 1996 show a distinct spring maximum and a summer minimum (Figure 1). The observed and simulated ozone concentrations agree within 2–5 ppbv except for July, when the model is too high by 7 ppbv. The observations show a maximum of 52 ppbv in April and a minimum of 26 ppbv in July–August, while the corresponding model results are 50 ppbv and 32 ppbv.

[12] The model overestimate in summer is caused by excessive deep convection in the GEOS-STRAT data over the Caribbean and western North Atlantic during that season, resulting in excessive ozone being entrained from aloft. *Allen et al.* [1997] previously identified this problem in the 1990–1992 GEOS-1 data by comparison with satellite observations of deep convective clouds [*Schiffer and Rossow*, 1983; *Rossow et al.*, 1996]. We find the same problem in the July 1996 data. Observed surface ozone at Bermuda in summer shows a diurnal variation with a maximum in early morning and a minimum in the afternoon with an amplitude of about 1.5 ppbv [*Oltmans and Levy*, 1994], reflecting photochemical ozone destruction during daylight hours in a regime with very low NO_x concentrations [*Oltmans*, 1981; *Oltmans and Levy*, 1992, 1994]. The model shows a similar diurnal cycle with an amplitude of about 1.2 ppbv and net photochemical loss of surface ozone at Bermuda in summer (not shown), indicating that it is not photochemistry but rather transport that causes the overestimate.

3.2. Day-to-Day Variations of Surface Ozone

[13] The March–June 1996 observations (Figure 2) show large day-to-day variations typical of springtime surface ozone at Bermuda [*Oltmans and Levy*, 1992, 1994]. The model results are superimposed on Figure 2. The simulated contributions from different source regions are also shown using tagged ozone tracers.

[14] Both the observations and model results in Figure 2 show an ozone background of 30–40 ppbv, with events in excess of 60 ppbv. The high-ozone events, for example on 15–16 March, 13 April, and 26 May, are associated with the passage of cold fronts, as diagnosed by abrupt increases in pressure and decreases in temperature. The simulated ozone closely matches the observations during periods of frontal passage. Figure 3 shows statistics of comparison between the observed and simulated time series. The model captures the background concentrations, the probability distribution, the frequencies and magnitudes of the pollution events, and the day-to-day variations (r = 0.82, n = 122, p < 0.001). The model evidently has a good predictive

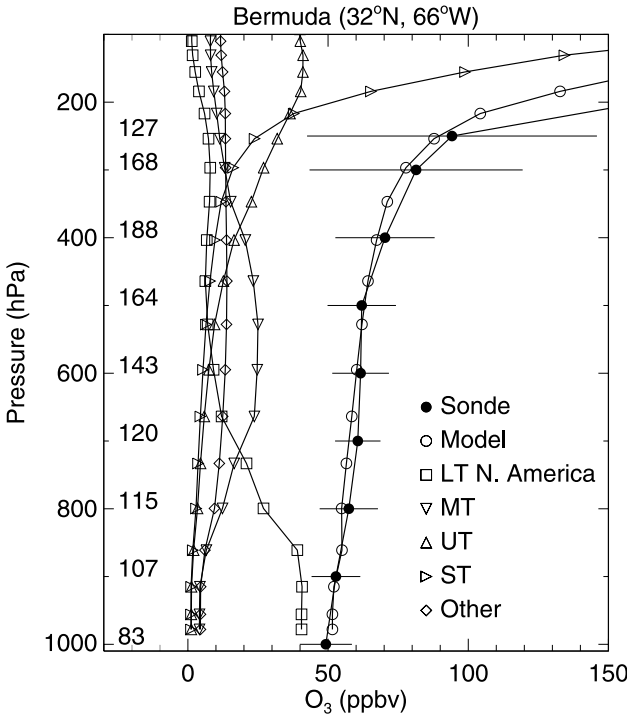

Figure 6. Monthly mean vertical profile of ozone at Bermuda in April 1996. The solid circles are averages of 28 ozonesonde soundings during the month, provided by Samuel J. Oltmans. The horizontal lines show the standard deviations for the observations. The open circles show the model results. The contributions from different source regions in the model are shown using the tagged ozone tracers. "LT N. America" refers to ozone produced in the lower troposphere (700 hPa-surface) over North America and the western North Atlantic (25–75°N, 50–160°W). "MT", "UT", and "ST" refer to ozone produced in the middle troposphere (400–700 hPa), the upper troposphere (400 hPa-tropopause), and the stratosphere, respectively. "Other" refers to ozone produced in the lower troposphere over regions outside of 25–75°N and 50–160°W.

capability for surface ozone at Bermuda. The simulated ozone and CO concentrations at Bermuda for March–June are positively correlated with a slope of 0.26 mol/mol and a correlation coefficient of 0.82 (n = 122, p < 0.001) (Figure 4), consistent with observations where the corresponding values are 0.27 mol/mol and 0.81 [*Dickerson et al.*, 1995]. The positive correlations are a clear indication of anthropogenic influence [*Parrish et al.*, 1993, 1998].

[15] Decomposition of the model time series into tagged ozone tracers (Figure 2) shows that transport of ozone produced in the lower troposphere (below 700 hPa) over North America and the western North Atlantic accounts for on average 70% of surface ozone at Bermuda, and singly determines the occurrence of the high-ozone events. Ozone produced in the upper troposphere and the stratosphere contributes only about 5 ppbv, and production in the middle troposphere contributes 5–10 ppbv. Our model results agree with the previous estimate by *Dickerson et al.* [1995] that half or more of the excess surface ozone in Bermuda in spring originates from pollution over eastern North America. They do not support a stratospheric or upper tropospheric origin for this excess ozone [*Oltmans and Levy*, 1992, 1994; *Moody et al.*, 1995]. We find in the model mean net ozone production below 800 hPa from the eastern U.S. all the way to Bermuda (Figure 5).

3.3. Vertical Distribution

[16] Figure 6 shows simulated and observed monthly mean vertical profiles of ozone over Bermuda for April 1996 from 28 ozonesonde soundings [*Oltmans et al.*, 1996]. The simulated monthly mean vertical profile for April 1996 is superimposed, along with contributions from different source regions. The observed and simulated ozone concentrations agree within 5 ppbv throughout the troposphere. We find that ozone produced in the lower troposphere over North America and the western North Atlantic contributes 40 ppbv (70–80%) to the total ozone below the 800 hPa pressure level but drops rapidly above. Transport of ozone from the stratosphere contributes less than 5 ppbv (<10%) to ozone below 400 hPa. The remainder of ozone produced in the middle and upper troposphere.

[17] Arguments for a stratospheric or upper tropospheric origin of ozone at Bermuda in spring, both at the surface and in the free troposphere, have largely been founded on correlation with subsiding back-trajectories originating over North America [*Oltmans and Levy*, 1992, 1994; *Moody et al.*, 1995]. Back-trajectories generated from our model reproduce these previous analyses and are still consistent with a North American pollution source for ozone at Bermuda, as discussed in section 5. To further evaluate our model results we compared the simulated vertical ozone distributions in spring over North America with ozonesonde measurements obtained from the World Ozone and Ultraviolet Data Center (WOUDC), Environment Canada, Ontario (http://www.msc-smc.ec.gc.ca/woudc) [*Logan*, 1999]. The results are shown in Figure 7. The simulated and observed ozone concentrations agree within 5 ppbv (<10%) throughout the troposphere below 400 hPa. The model underestimates ozone concentrations above 400 hPa, a problem that we attribute to the coarse vertical resolution near the tropopause, which makes it difficult to diagnose accurately the location of the tropopause. This underestimate does not affect the overall cross-tropopause flux of ozone in the model, which is prescribed as a boundary condition using the Synoz algorithm (see section 2).

4. Ozone Correlations With ^{7}Be and ^{210}Pb

[18] Observations at Bermuda in spring indicate positive correlations of ozone with both ^{7}Be and ^{210}Pb [*Moody et al.*, 1995; *Arimoto et al.*, 1999; *Huang et al.*, 1999], while observations at the Tenerife free-tropospheric site (28°N, 16°W, 2.4 km altitude) in the eastern North Atlantic in summer show that ozone is positively correlated with ^{7}Be but negatively correlated with ^{210}Pb [*Prospero et al.*, 1995]. The combination of ^{7}Be and ^{210}Pb provides a sensitive test of vertical transport in global 3-D models [*Koch et al.*, 1996; *Liu et al.*, 2001]. We examine in this section the ability of our model to reproduce these correlations using the ^{210}Pb and ^{7}Be GEOS-CHEM simulation for 1996 previously reported by *Liu et al.* [2001]. Comparisons presented in that paper with worldwide observations of

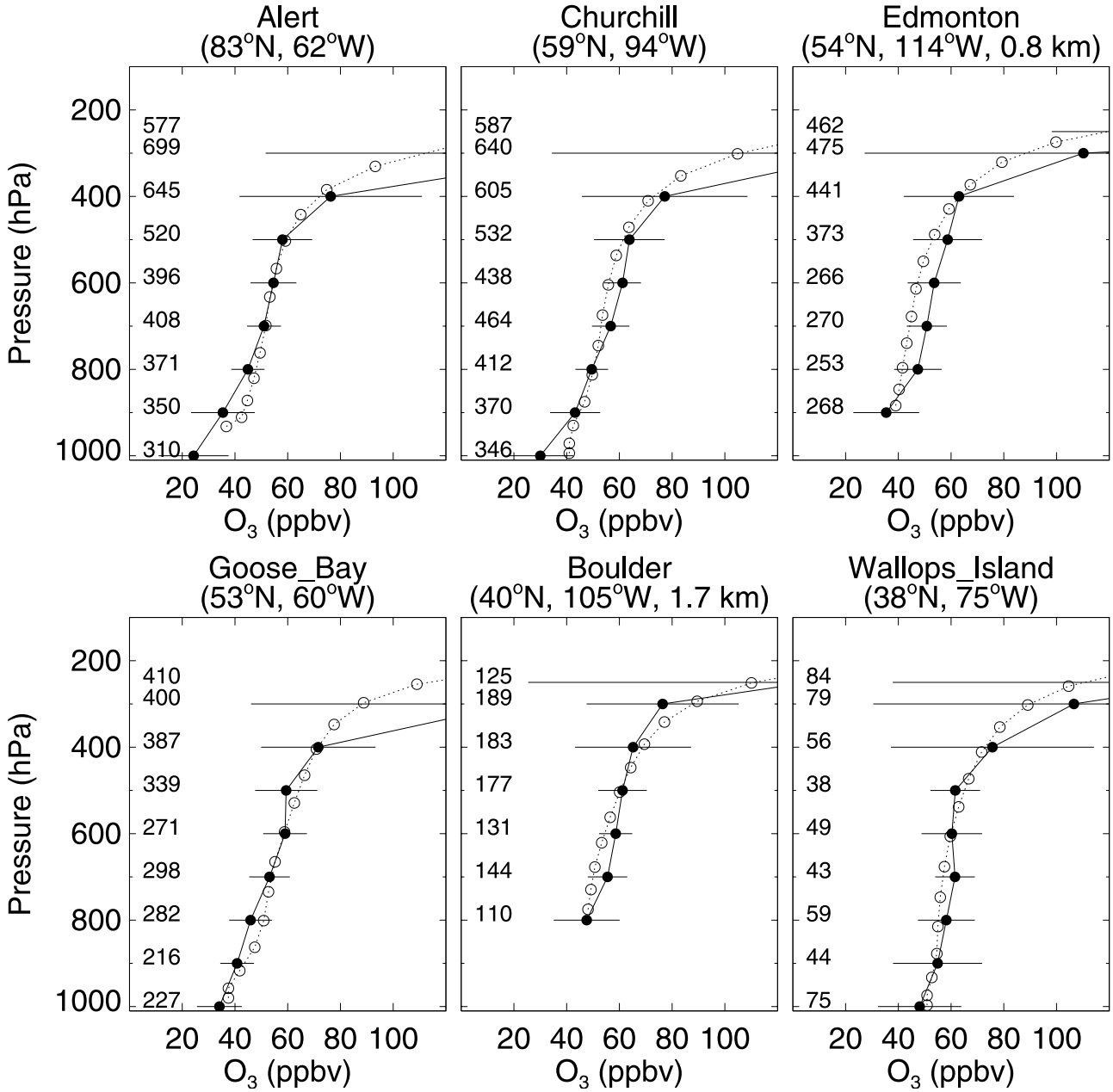

Figure 7. Observed (solid lines, solid circles) and simulated (dashed lines, open circles) monthly mean vertical profiles of ozone at Alert, Churchill, Edmonton, Boulder, Goose Bay, and Wallops Island for April. The measurements are averages of ozonesonde soundings for 1988–2001, obtained from the World Ozone and Ultraviolet Data Center (WOUDC) at http://www.msc-smc.ec.gc.ca/woudc. The horizontal lines show the standard deviations for the observations (the number of observations is given as inset on each panel). The model results are monthly averages for April 1996.

^{210}Pb and ^{7}Be concentrations and deposition fluxes indicate no significant global bias, and significant success in reproducing the observed latitudinal and seasonal distributions.

[19] Our model results show positive ozone correlations with ^{210}Pb ($r = 0.71$, $n = 92$, $p < 0.001$) and with ^{7}Be ($r = 0.36$, $n = 92$, $p < 0.001$) for March–May 1996 at Bermuda (upper panels, Figure 8), consistent with observations [*Moody et al.*, 1995; *Arimoto et al.*, 1999; *Huang et al.*, 1999]. Our simulated correlation coefficient of 0.36 between ozone and ^{7}Be is consistent with that observed by *Moody et al.* [1995] ($r = 0.34$). At Tenerife in summer, we find a positive correlation between ozone and ^{7}Be ($r = 0.52$, $n = 92$, $p < 0.001$) and a negative correlation between ozone and ^{210}Pb ($r = -0.59$, $n = 92$, $p < 0.001$) (bottom panels, Figure 8), consistent with the observations of *Prospero et al.* [1995]. The simulated ^{7}Be and ^{210}Pb concentrations at Tenerife are higher than those at Bermuda, consistent with observations [*Arimoto et al.*, 1999] and reflecting both higher altitude (for ^{7}Be) and greater aridity (less aerosol scavenging).

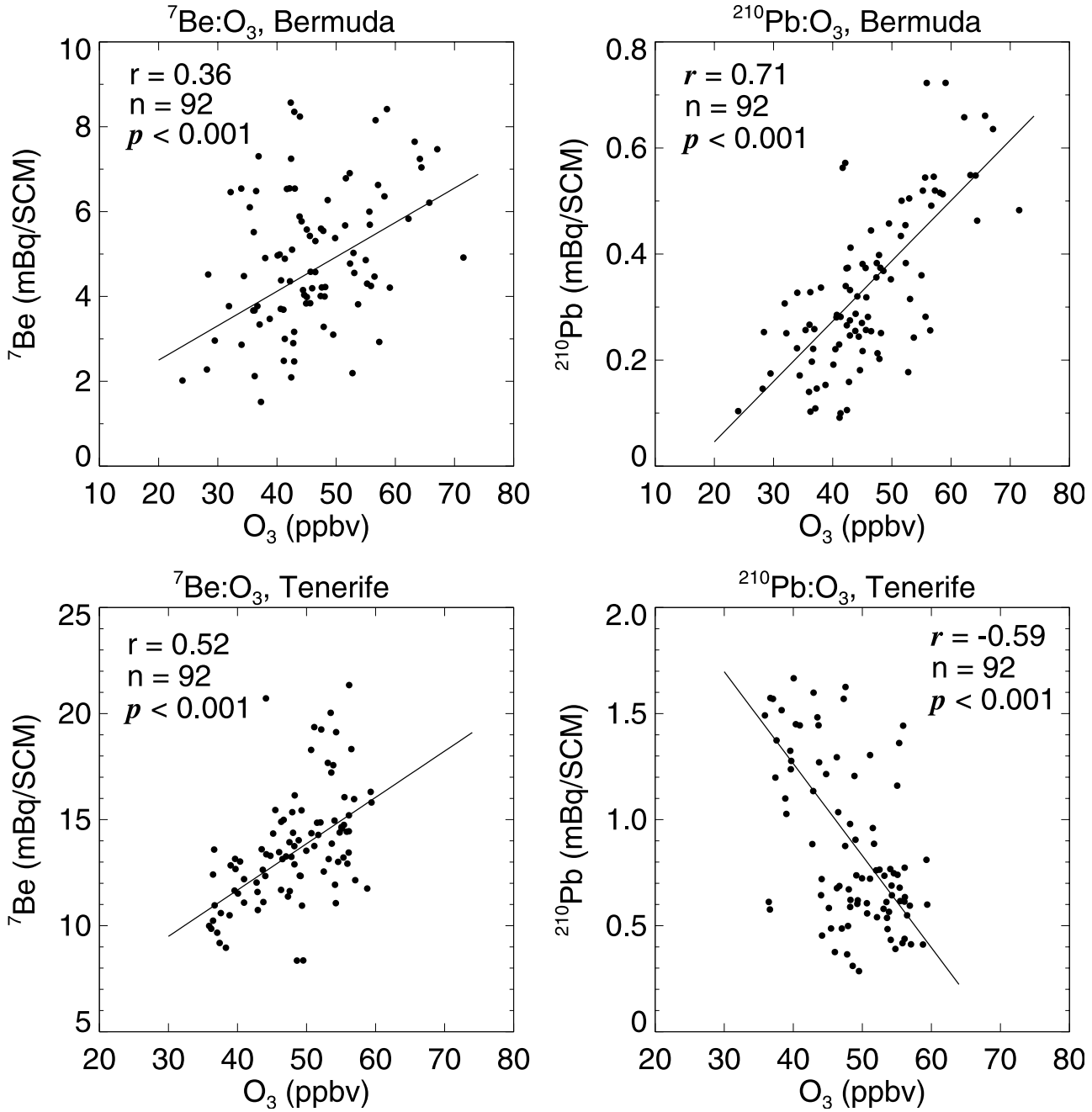

Figure 8. Scatterplots of simulated ozone versus ^{7}Be and ^{210}Pb at Bermuda for March–May 1996 (upper panels) and at Tenerife (28°N, 16°W, 2.4 km altitude) for June–August 1996 (bottom panels). Values are daily averages. Also shown in each scatterplot are the correlation coefficient (r), the number of data points (n), and the p-value indicating the significance level of the correlation.

[20] The simulated time series of ^{7}Be, ^{210}Pb, and ozone at Bermuda for March–May 1996 are shown in Figure 9. High ^{210}Pb and ^{7}Be are associated with high-ozone events originating from the lower troposphere over North America, as previously discussed. Since there is no significant latitudinal gradient in ^{7}Be in the lower troposphere at northern mid-latitudes [*Liu et al.*, 2001], the positive ozone correlation with ^{7}Be at Bermuda must reflect subsidence. This point will be discussed further in section 5. The positive ozone correlation with ^{210}Pb at Bermuda is consistent with the lower-tropospheric source for ozone. We find in the model a positive correlation (r = 0.52, n = 92, p < 0.001) between ^{7}Be and ^{210}Pb at Bermuda in spring (Figure 10), consistent with observations [*Arimoto et al.*, 1999; *Huang et al.*, 1999] and reflecting the mixing of subsiding air and continental outflow behind cold fronts.

[21] The simulated time series of ozone, ^{210}Pb, and ^{7}Be at Tenerife for June–August 1996 are shown in Figure 11. *Prospero et al.* [1995] suggested that the positive ozone correlation with ^{7}Be and the negative ozone correlation with ^{210}Pb observed at Tenerife are evidence for a high-altitude source of ozone, possibly from the stratosphere, but we find

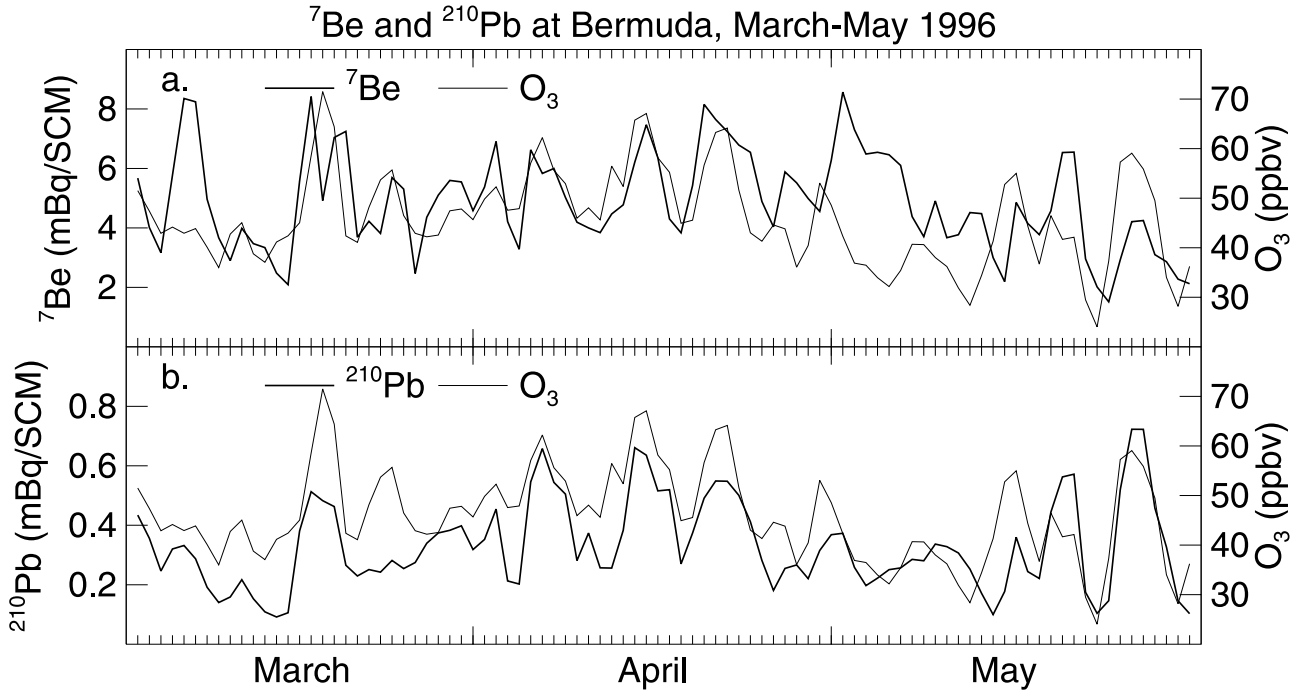

Figure 9. Time series of simulated (a) ^{7}Be and ozone and (b) ^{210}Pb and ozone at Bermuda for March–May 1996. Values are daily averages.

that they simply reflect the common vertical trends of ^{7}Be and ozone, and the opposite vertical trend of ^{210}Pb. We see from Figure 11 that the positive ozone correlation with ^{7}Be and the negative ozone correlation with ^{210}Pb are mostly driven by ozone produced in the middle troposphere (400–700 hPa). Sources of ozone in the lower, middle, and upper troposphere contribute on average 15 ppbv (32%), 24 ppbv (49%), and 7 ppbv (14%), respectively, to the total ozone at Tenerife, while ozone transported from the stratosphere contributes 2 ppbv (5%) (bottom panel, Figure 11). Our model results are consistent with the analysis by *Graustein and Turekian* [1996], who found that a stratospheric source could not explain the observed ozone correlation with ^{7}Be at Tenerife once correlation is made for ^{7}Be scavenging using concurrent observations of ^{210}Pb. They suggested that the elevated ozone observed at Tenerife is due to the lifting of continental boundary layer air to the middle and upper troposphere followed by net ozone production. Even though episodic stratosphere-troposphere-exchange events may make a large occasional contribution to ozone at Tenerife [*Kentarchos et al.*, 2000], our model results suggest that the overall ozone levels are controlled by photochemical formation in the middle and lower troposphere.

5. Back-Trajectory Analyses

[22] In this section we compare our results with past inferences of a high-altitude source of ozone at Bermuda based on isentropic back-trajectory analyses and correlation with ^{7}Be [*Oltmans and Levy*, 1992, 1994; *Moody et al.*, 1995]. We compute isentropic back-trajectories for the spring of 1996 with the GEOS meteorological fields interpolated from the native sigma grid to potential temperature (θ) surfaces. We apply for this purpose the NASA Langley 3-D trajectory model [*Pierce and Fairlie*, 1993; *Pierce et al.*, 1994], which uses fourth-order Runge-Kutta time stepping and a 20-min time step. Air parcels are initialized at a 1° × 1° horizontal resolution; the winds are interpolated to the position of each parcel.

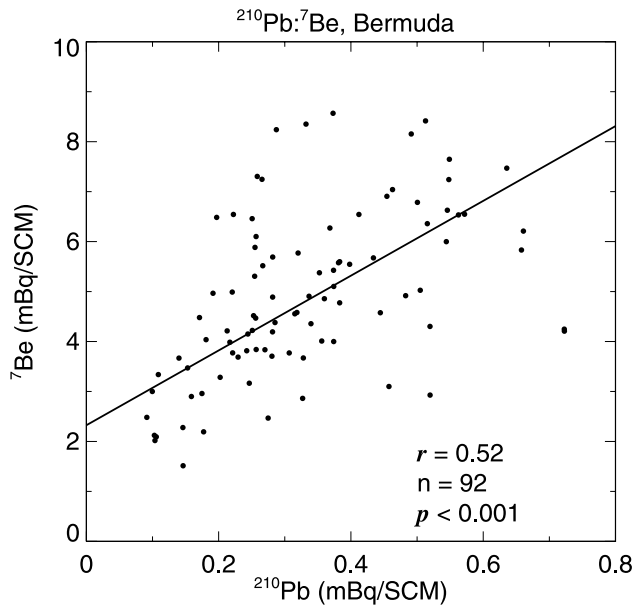

Figure 10. Scatterplot of simulated ^{7}Be versus ^{210}Pb at Bermuda for March–May 1996. Values are daily averages. Also shown are the correlation coefficient (r), the number of data points (n), and the p-value indicating the significance level of the correlation.

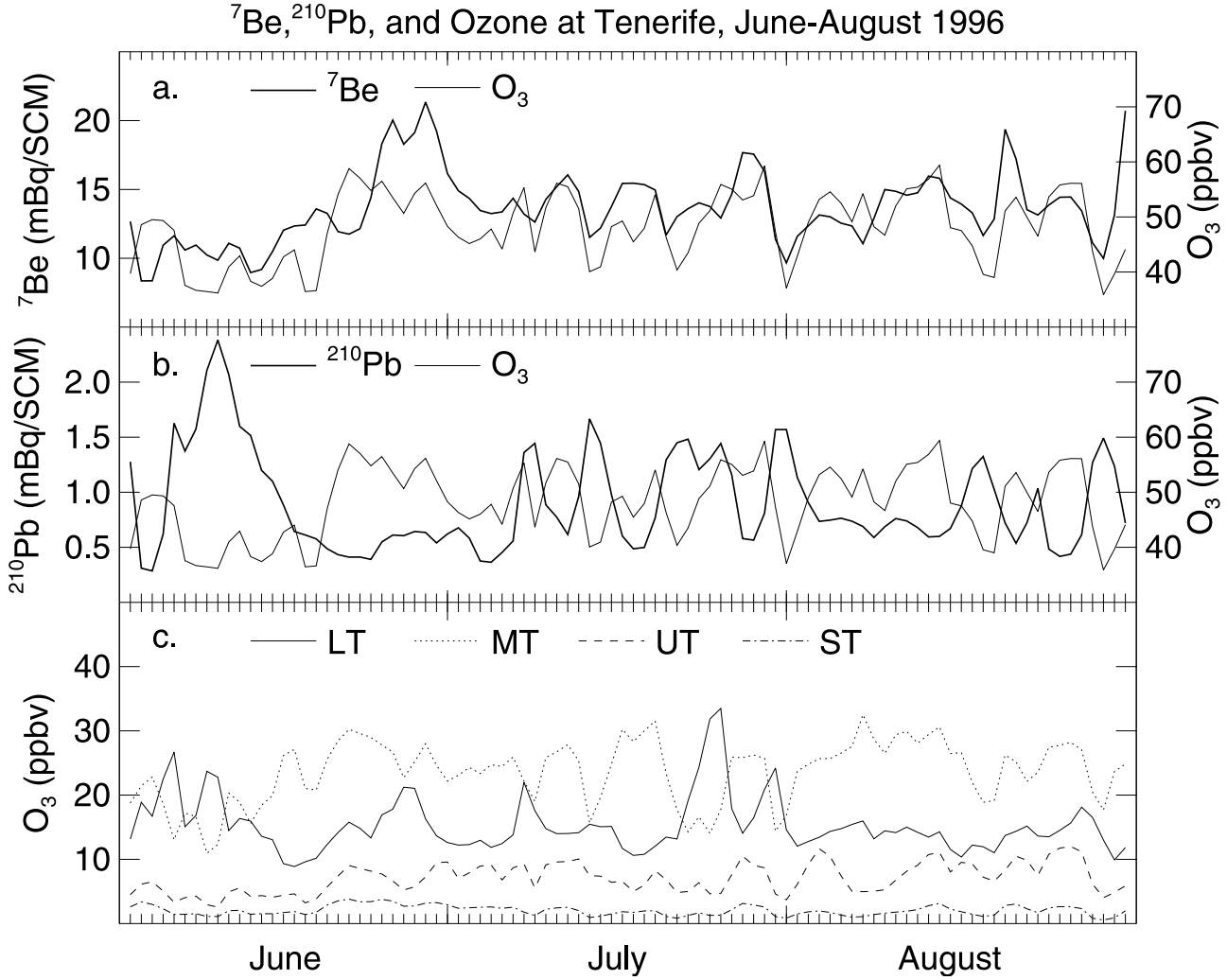

Figure 11. Time series of simulated (a) ^{7}Be and ozone, (b) ^{210}Pb and ozone, and (c) tagged ozone tracers at Tenerife (28°N, 16°W, 2.4 km altitude) in the Canary Islands for June–August 1996. Values are daily averages. "LT", "MT", "UT", and "ST" refer to ozone produced in the lower troposphere (surface-700 hPa), the middle troposphere (400–700 hPa), the upper troposphere (400 hPa-tropopause), and the stratosphere, respectively.

[23] The most thorough trajectory analysis of transport patterns for Bermuda was given by *Moody et al.* [1995], who examined the major transport patterns for Bermuda by applying cluster analysis to isentropic trajectories for a 2-year period (1988–1991). They found that the back-trajectories associated with springtime high-ozone events originate from an average altitude of 700 hPa over northwest North America (see their Plate 2). *Oltmans and Levy* [1994] also showed that trajectories associated with springtime high-ozone events all come from north of 50°N and altitudes near 600 hPa (see their section 5).

[24] We computed 10-day isentropic back-trajectories using the GEOS fields for each high-ozone event at Bermuda during the spring of 1996. All show strong subsidence from around the 600–700 hPa pressure level to the surface, consistent with the results of *Moody et al.* [1995] and *Oltmans and Levy* [1994]. We examined further the particularly strong episodes on 16 March, 13 April, and 26 May (see Figure 2). Figure 12 shows a mean isentropic back-trajectory at $\theta = 290$ K for a cluster of air parcels arriving at Bermuda on 16 March 1996. The mean back-trajectory originates from northwest North America, and exhibits strong subsidence from 600 to 700 hPa to the surface during the final 5 days of approach to Bermuda. Also shown in Figure 12 are the GEOS-CHEM daily mean net ozone production rates sampled every 6 hours along the back-trajectory. The model indicates net ozone production of 4–8 ppbv d^{-1} along the back-trajectory during the final 2 days of approach to Bermuda. The 16 March high-ozone event is associated with high ^{7}Be (Figure 9), clearly reflecting the subsidence suggested by the back-trajectory shown in Figure 12. Nevertheless, the dominant contribution to ozone at Bermuda is from production below 700 hPa over North America and the western North Atlantic during transit, not transport from the stratosphere (Figure 2). The concurrent positive ozone correlation with ^{210}Pb during this event and more generally in the Bermuda data (Figure 10) implies mixing between the subsiding air mass and the outflow

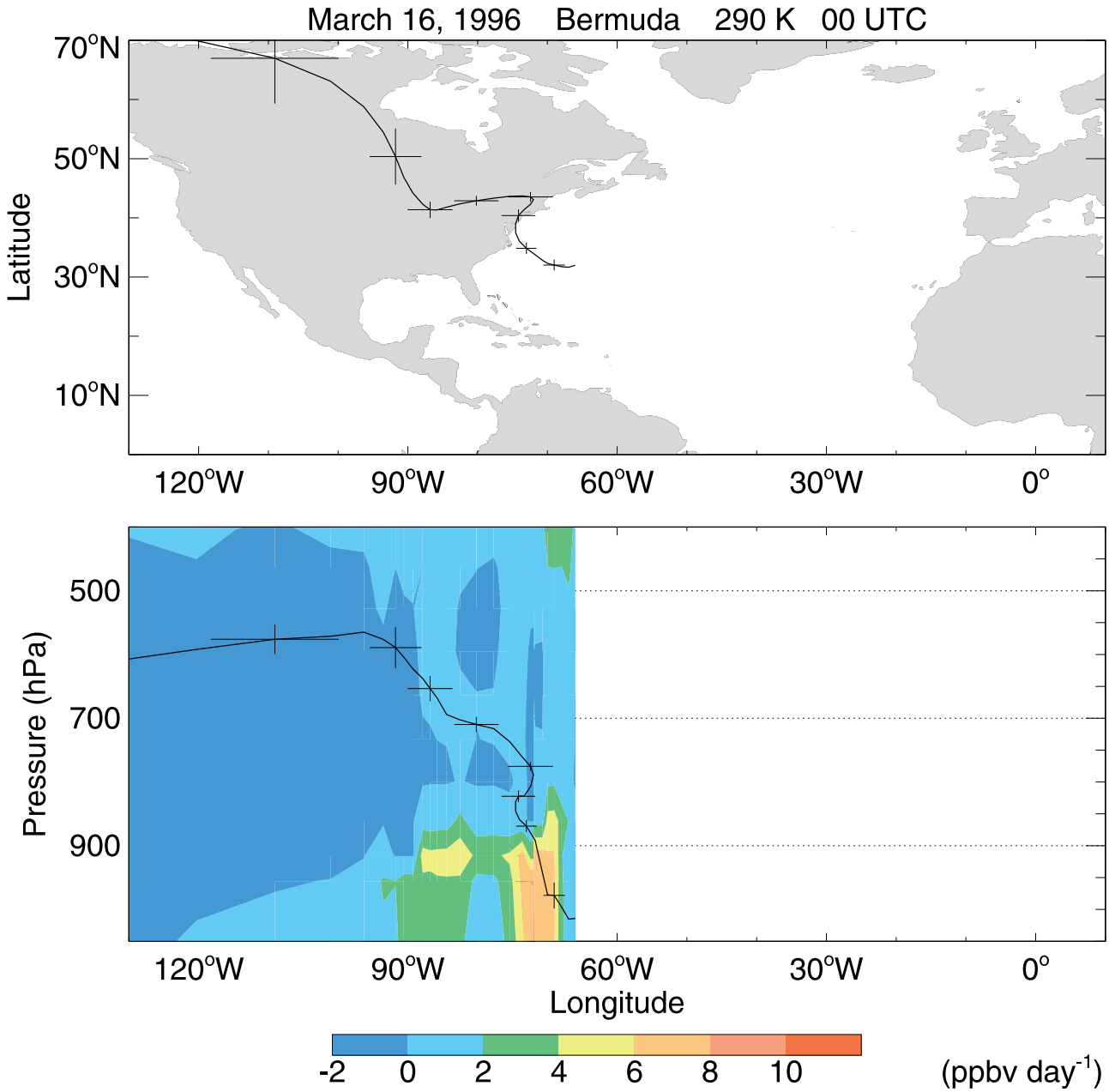

Figure 12. Isentropic back-trajectory computed from the GEOS meteorological fields at θ = 290 K for air arriving at Bermuda at 0000 UTC, 16 March 1996. Shown is the average trajectory for 25 parcels ending within the area of 30–34°N and 64–68°W. The parcels are initialized at a horizontal resolution of 1° longitude by 1° latitude. The error bars show the standard deviations for longitude, latitude, and pressure at each 24-hour interval. The color contours show the GEOS-CHEM daily mean net ozone production (ppbv d^{-1}) sampled every 6 hours along the trajectory.

from continental boundary layer behind the cold fronts delivering high ozone to the site.

[25] Figure 13 shows the mean isentropic back-trajectory at θ = 295 K for a cluster of air parcels arriving at Bermuda on 13 April 1996. Again, it indicates subsiding flow from 700 hPa over northwest North America. We find daily mean net ozone production of 4–10 ppbv d^{-1} along the trajectory during the final 2 days of approach to Bermuda, larger than for the 16 March event because of stronger solar radiation. However, despite the higher net ozone production, the ozone peak for the 13 April event is less than that for the 16 March event (Figure 2). This can be explained by the shorter transport time from the east coast to Bermuda.

[26] For the 26 May high-ozone event (not shown), we find that the mean isentropic back-trajectory at θ = 295 K shows direct boundary layer transport off the eastern U.S., while that at θ = 300 K shows strong subsidence, illustrating the concurrence of the two patterns during high-ozone episodes. One might expect higher ozone levels during

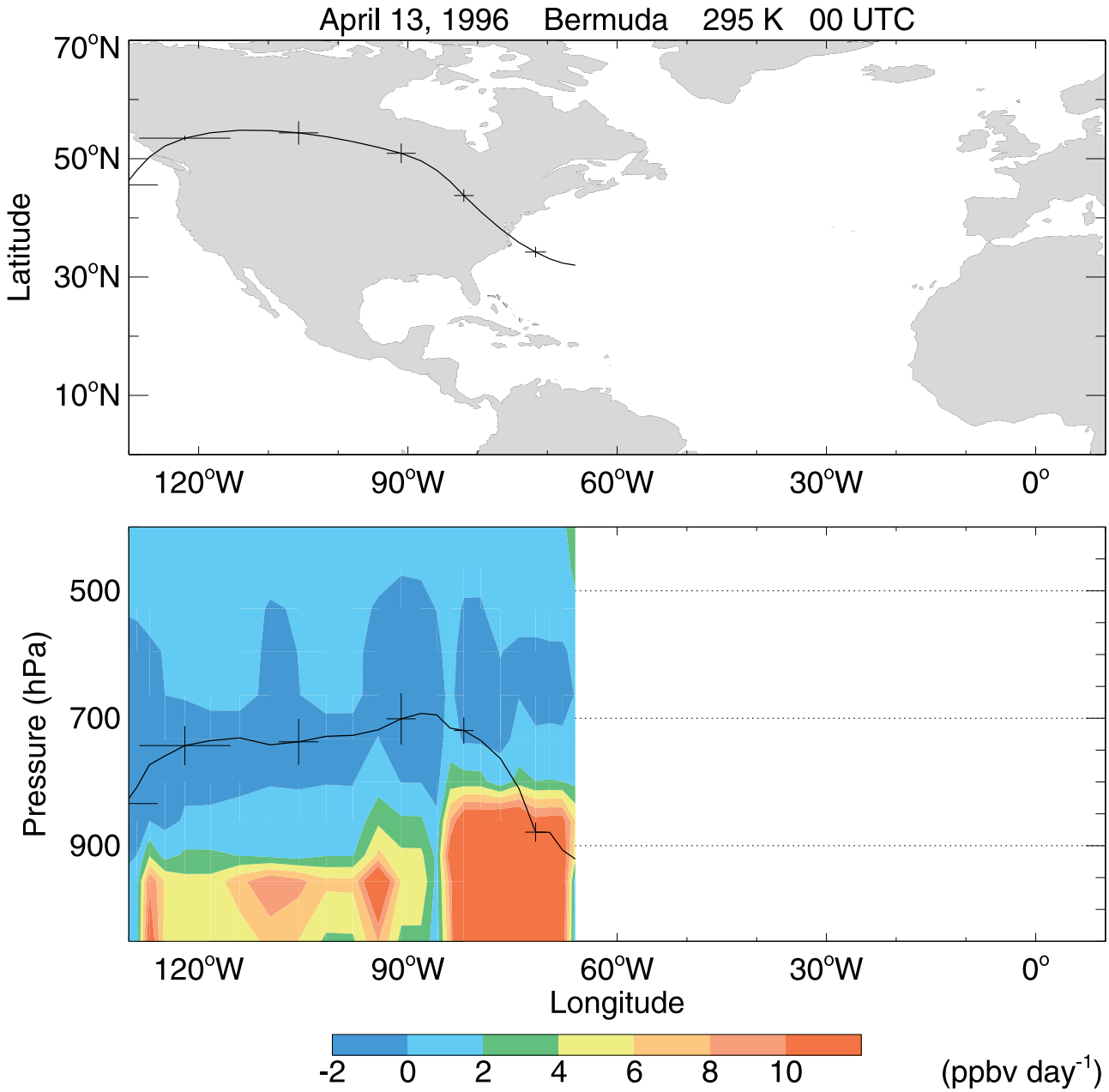

Figure 13. Same as Figure 12, except for 13 April 1996 and θ = 295 K.

the 26 May events than the earlier events because of higher ozone production. However, in addition to a shorter lifetime of ozone in May, the core of the North American outflow shifts northward from beginning to late spring, and Bermuda then receives only the southern edge of the continental plume [*Li et al.*, 2002]. The 26 May event is also associated with high ^{210}Pb and ^{7}Be, but ^{7}Be is much lower than during 16 March and 13 April (Figure 9), reflecting the seasonal weakening of subsidence.

[27] We find that back-trajectories during periods of low ozone at Bermuda originate from the marine boundary layer over the tropical North Atlantic, also consistent with previous back-trajectory analyses [*Oltmans and Levy*, 1992, 1994; *Moody et al.*, 1995]. For example, Figure 14 shows a typical case for 23 May, when surface ozone dipped to below 20 ppbv (Figure 2). Net ozone destruction of 2–6 ppbv d^{-1} takes place during the transport to Bermuda.

6. Sources of Tropospheric Ozone Over the North Atlantic in Spring

[28] Our source attribution for ozone over Bermuda can be generalized to the North Atlantic troposphere. Figure 15 shows the contributions from each source region (see section 2) to simulated ozone concentrations between 70°W and 10°W over the North Atlantic for April 1996. Transport from the stratosphere and production in the upper troposphere both contribute on average less than 5 ppbv (5%) to ozone in the lower troposphere. Examination of other seasons (not shown) indicates that stratospheric influ-

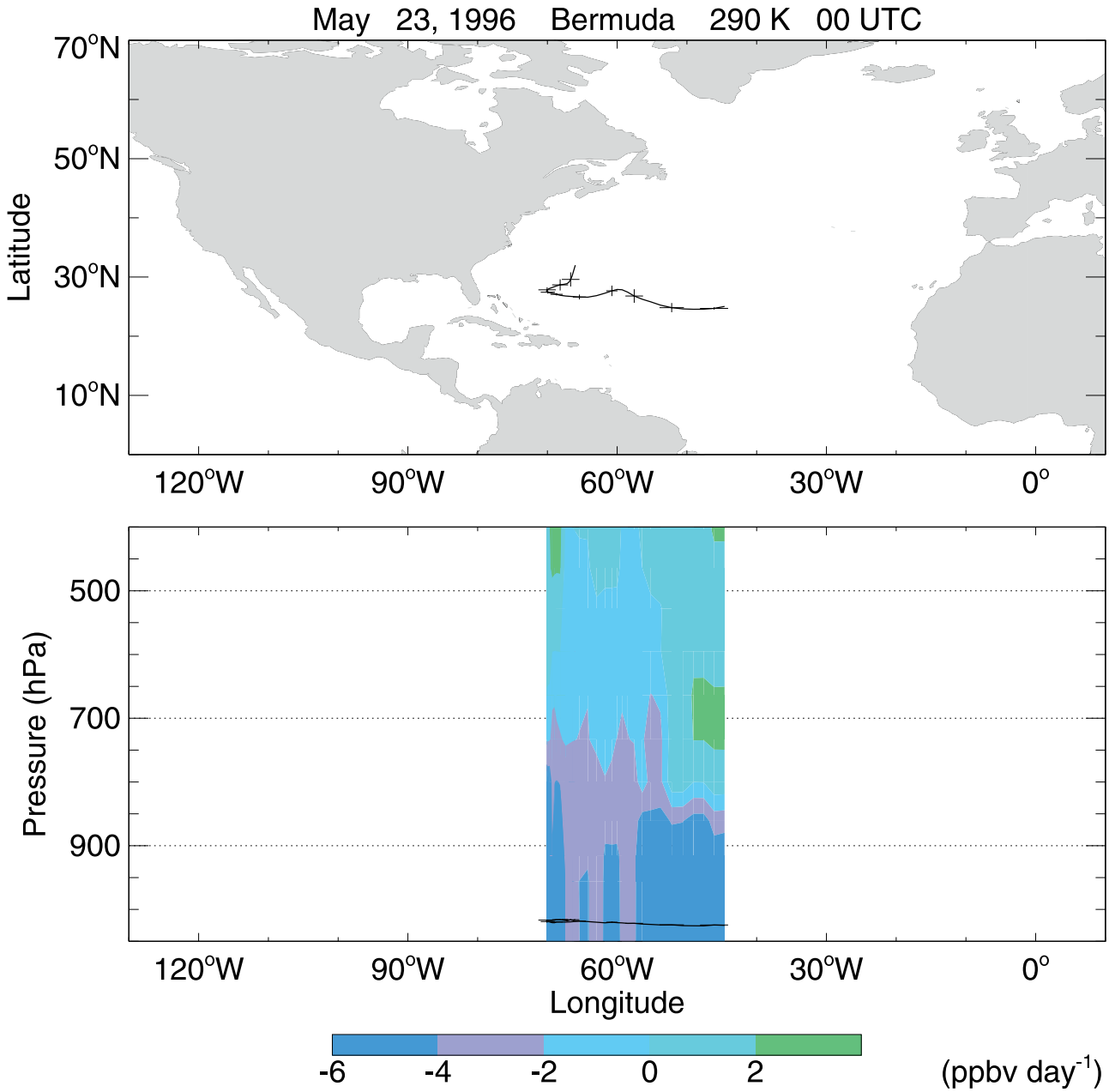

Figure 14. Same as Figure 12, except for 23 May 1996 and θ = 290 K. The color scale is different from that in Figures 12 and 13.

ence on the lower troposphere peaks in winter but is then only 10–15%. In comparison, *Follows and Austin* [1992] obtained in a two-dimensional model study a stratospheric contribution of less than 5% to surface ozone in all seasons, while *Wang et al.* [1998b] obtained in a 3-D model study a zonal mean stratospheric influence of 5% in summer and 10–20% in winter at northern midlatitudes. The stratospheric contribution increases above 500 hPa to reach about 40 ppbv (50%) just below the tropopause (Figure 15; also see Figure 6). Our results are not inconsistent with those of *Oltmans et al.* [1996], who suggested based on ozonesonde measurements and back-trajectories that stratospheric ozone plays an important role in loading the middle and upper troposphere over the North Atlantic with ozone in spring. However, we find that most of the ozone in the middle and upper troposphere in spring originates from the troposphere, with all altitudes contributing (Figure 15).

[29] A remarkable result from Figure 15 is the pervasive influence of lower-tropospheric production on ozone concentrations at all levels in the troposphere. This result reflects the rapid production of ozone in the continental boundary layer and the long lifetime of ozone in spring, particularly at higher latitudes.

7. Summary and Conclusions

[30] Conflicting interpretations in the literature of stratospheric versus anthropogenic influences on the springtime

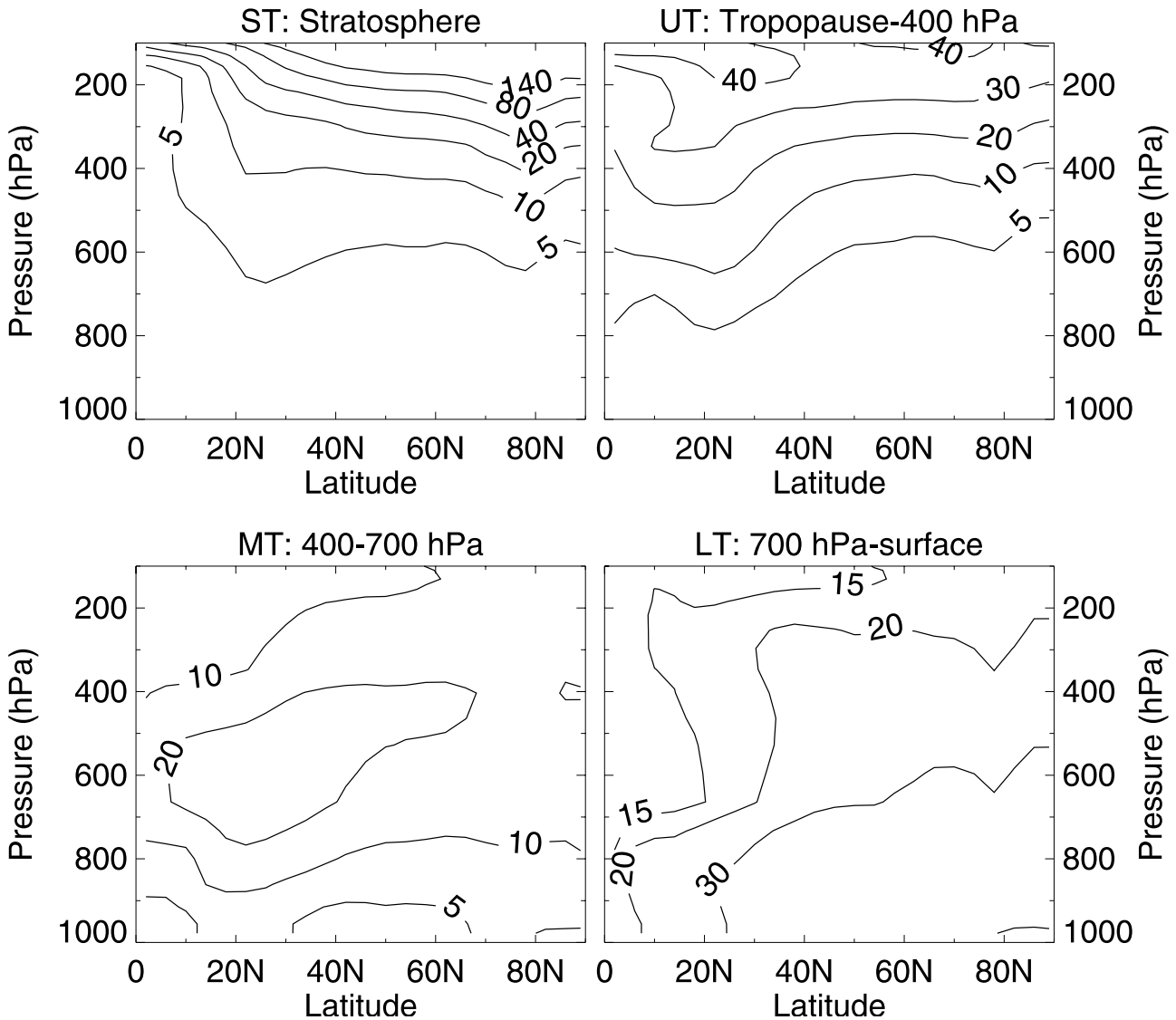

Figure 15. Contributions (in ppbv) from sources at different altitudes to simulated ozone concentrations averaged between 70°W and 10°W over the North Atlantic for April 1996.

ozone maximum at Bermuda have led to ambiguity in the assessments of the sources of tropospheric ozone over the North Atlantic and more generally have fueled the debate on the stratospheric contribution to the tropospheric ozone budget. We have used here the GEOS-CHEM global 3-D model of tropospheric ozone-NO_x-hydrocarbon chemistry driven by assimilated meteorological observations for 1996 to examine the relative importance of stratospheric versus anthropogenic influences on the springtime ozone maximum at Bermuda. The model reproduces the observed seasonal cycle of surface ozone at Bermuda to within 2–5 ppbv. It captures the day-to-day variation of springtime ozone at the site (r = 0.82), including the occurrence of events with concentrations in excess of 60 ppbv. We find that this variability is singly driven by ozone produced in the lower troposphere over North America and advected to Bermuda behind cold fronts. This result agrees with some previous analyses of observations [*Van Valin and Luria*, 1988; *Dickerson et al.*, 1995; *Huang et al.*, 1999; *Milne et al.*, 2000]. Ozone in the model correlates with CO and ^{210}Pb similarly to the observations, further supporting this interpretation.

[31] Other past analyses based on isentropic back-trajectories pointed out that high ozone at Bermuda occurs when airflow is from the middle troposphere over North America, and argued that the associated strong subsidence and observed correlation with ^{7}Be imply a stratospheric or upper tropospheric origin for ozone [*Oltmans and Levy*, 1992, 1994; *Moody et al.*, 1995]. We computed isentropic back-trajectories with the GEOS meteorological fields and find that they are consistent with these past analyses, i.e., back-trajectories associated with high-ozone events originate typically from 600 to 700 hPa over northwest North America. Ozone and ^{7}Be are correlated in the model similarly to observations. However, we demonstrate that the subsidence does not imply a dominant transport of ozone from the stratosphere or even the free troposphere to Bermuda. Instead, ozone originates from continental boundary layer outflow and mixes with the subsiding air during the transport

to Bermuda behind cold fronts. Positive correlation between ^{7}Be and ^{210}Pb during the high-ozone events provides evidence for this mixing, which was not accounted for in the past isentropic back-trajectory analyses, but is readily apparent in our Eulerian model.

[32] The model also reproduces the observed positive and negative correlations of summertime ozone at Tenerife (Canary Islands, 2.4 km altitude) with ^{7}Be and ^{210}Pb, respectively. We find that the positive correlation with ^{7}Be is driven by ozone produced in the middle troposphere (400–700 hPa), rather than from the stratosphere or even upper troposphere as previously proposed on the basis of this correlation [*Prospero et al.*, 1995]. The average stratospheric contribution at the site is less than 10 ppbv.

[33] We examined the sources of ozone at Bermuda at different altitudes in the troposphere. The model reproduces the observed vertical ozone distributions there and over North America to within 5 ppbv throughout the troposphere. We find that the stratospheric contribution to ozone in the free troposphere over Bermuda is less than 5 ppbv (10%) below the 400 hPa pressure level and increases to 50% just below the tropopause. Generalization to the North Atlantic troposphere shows significant lower tropospheric influence on ozone at all altitudes.

[34] **Acknowledgments.** We thank Samuel J. Oltmans for providing the surface ozone and ozonesonde measurements at Bermuda. Discussions with Clarissa Spivakovsky and Mathew Evans were very helpful. This work was supported by the NOAA Office of Global Programs and by the NASA Atmospheric Chemistry Modeling and Analysis Program.

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