Analysis of the Summer 2004 ozone budget over the United States using Intercontinental Transport Experiment Ozonesonde Network Study (IONS) observations and Model of Ozone and Related Tracers (MOZART-4) simulations

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The origin of ozone over the summertime contiguous United States during summer 2004 was examined using the Intercontinental Transport Experiment (INTEX-A) Ozonesonde Network Study (IONS-04) over North America. We estimate the budget using the global chemistry transport Model of Ozone and Related Tracers version 4 (MOZART-4) with synthetic tracers that keep track of the ozone produced from selected NOx sources (stratosphere, lightning, anthropogenic, and biomass burning sources in Eurasia and the contiguous United States, and North American boreal fires). This “model budget” is analyzed in conjunction with results from a “laminar identification method” (LID), a more empirical approach to extracting information about contributions from ozone transported down from the stratosphere, advection, and convection. Both methods give comparable results for the contribution from stratospheric ozone, an average over all sites of 20 ± 7% for the LID budget and of 26 ± 6% for the model budget (the standard deviation gives the variability over the IONS sites). These results point toward the important contribution of downward transport of ozone from the stratosphere in assessing tropospheric ozone. The contributions for the other tracers are 25 ± 9% for U.S. sources, 13 ± 5% for Eurasian sources, 3 ± 2% for boreal fires and 10 ± 2% from lightning. In the boundary layer the dominant contribution generally comes from local (U.S.) sources. Eurasian sources can add up to 8% on average for some sites, lightning up to 4%, and North American boreal fires up to 10%. Variations in the tracer contributions across the different sites can be large, but the budget estimated by the model for the entire United States is similar to the budget averaged over the IONS-04 sites which lets us conclude that the sample of locations and launch days conveys a proper representation of the large-scale picture.


1. Introduction

Tropospheric ozone (O3) plays an important role in both atmospheric research and policy owing to its importance in atmospheric chemistry [e.g., Logan et al., 1981; Prather and Ehhalt, 2001] and climate change [Intergovernmental Panel on Climate Change, 2001; Ramaswamy et al., 2001], as well as its harmful effects on human health, agriculture and ecosystems [e.g., U.S. Environmental Protection Agency, 1999; Mauserall and Wang, 2001]. O3 is produced in the troposphere by photochemical reactions of carbon monoxide (CO) and volatile organic compounds (VOCs) in the presence of nitrogen oxides (NOx). Another source of tropospheric O3 is downward transport of stratospheric O3 into the troposphere. The latter is less important on an annual and global scale, but can account for large enhancements in regions of subsidence [Cooper et al., 2002].

Human-related activities have significantly altered the distribution and content of tropospheric O3. Understanding the current and future effects of changes in the O3 concentrations requires understanding the relative importance of their sources. In this study we examine the factors controlling O3 concentrations over the contiguous United States in summertime using a combination of observations, models, and data analysis tools. Modeling studies point toward a
major impact of North American emissions on net regional and global tropospheric O$_3$ production [Li et al., 2002], the important implications of increasing industrialization of the Asian continent for global tropospheric O$_3$ [Liang et al., 2007; Wild and Akimoto, 2001] and surface O$_3$ in the United States [Fiore et al., 2002] or the significant contribution of in situ O$_3$ production from lightning NO$_x$ sources in the upper troposphere over North America [Li et al., 2005; Cooper et al., 2006, 2007; Hudman et al., 2007]. However, verifying model estimates of the tropospheric budget is difficult because of the limited number of profiling sites across North America.

[4] In July and August 2004, a multinational and multi-platform set of experiments was conducted over North America, the northern Atlantic and Europe to investigate the transport and transformation of pollution in the midlatitudes during the most photochemically active part of the year. Under the umbrella of ICARTT (International Consortium of Atmospheric Research of Transport and Transformation) with its principal components the NASA INTEX-A (Intercontinental Transport Experiment-North America [Singh et al., 2006]), the NOAA NEQS-ITCT 2004 (New England Air Quality Study/Intercontinental Transport and Chemical Transformation [Fehsenfeld et al., 2006]), and the European program ITOP (Intercontinental Transport of Pollution), nine aircraft, five ground sites and an oceanographic ship coordinated operations to sample trace gases, aerosols and meteorological parameters. Further, coordination with satellite overpasses, predominantly the NASA EOS satellites, was established.

[5] The variety of measurement platforms combined in ICARTT complement each other and allow for studying a wide range of scales and processes. Satellites provide global coverage with a fixed schedule, but have little vertical information and relatively few constituents. Aircraft observations produce very detailed information, but not continuous in time and space. The latter can be accomplished with ground-based and balloon-based instruments. In particular, ozonesonde-radiosonde combinations offer consistent vertical resolution from the surface up to the midstratosphere (~35 km, 5 hPa) and provide concurrent O$_3$ and pressure-temperature-humidity (P-T-U) profiles.

[6] During INTEX-A, an ozonesonde network, IONS-04 (INTEX Ozonesonde Network Study) was assembled over North America to complement the set of aircraft and satellite observations. This data set has been used in various modeling studies [e.g., Cooper et al., 2006; Pierce et al., 2007; Tarasick et al., 2007], and the results showed that many models have difficulties in representing tropospheric O$_3$, especially in the mid and upper troposphere. Large uncertainties exist in regard to the contributions of downward transport of O$_3$ from the stratosphere and of O$_3$ produced in association with lightning NO$_x$.

[7] The IONS-04 data set forms the basis of the present study in which we examine the origin of O$_3$ over the summertime United States. We estimate the O$_3$ budget using the global chemistry transport model MOZART-4 (Model for Ozone and Related Chemical Tracers, version 4). While most models estimate budgets by varying the emissions strength of a particular source, we incorporate synthetic tracers into the model to track the exact amount of O$_3$ produced from selecte $x$ sources (section 2.2). The MOZART-4 derived budget is compared to a tropospheric O$_3$ budget determined from an O$_3$ laminar identification method (LID) [Thompson et al., 2007a, 2007b] that is a more empirical approach to computing contributions from stratospheric O$_3$, advection and convection (section 2.1).

[8] These two independent approaches allow us to determine the factors controlling O$_3$ concentrations over the summertime United States in greater detail and their representativeness can be evaluated by comparing the methods in several ways. In particular, the comparison of modeled stratospheric O$_3$ contributions with the LID results lets us evaluate the performance of the stratospheric-tropospheric exchange in a state-of-the-art tropospheric model. Further, the model can be used to break down the budget terms from the LID analysis into geographical source regions. The evaluation of modeled O$_3$ fields with sonde profiles also benefits from the source information because it helps to assess the most likely processes contributing to model-measurement biases.

[9] The structure of the paper is the following. In section 2 we introduce the observations, the LID analysis and the model simulations. The comparison of modeled and observed O$_3$ profiles at the IONS-04 sites is described in section 3, followed by a discussion of the modeled O$_3$ budget for the contiguous United States in section 4. In section 5 the O$_3$ budget terms from the LID analysis and the model tracers are analyzed together and the findings are summarized in section 6.

2. Observations and Model Simulation

2.1. IONS Ozonesonde Data and Laminar Identification Method

[10] O$_3$ sonde profiles collected by the IONS-04 network during 1 July through 15 August 2004 can be accessed from the public data archive (http://croc.gsfc.nasa.gov/intex/ions.html). The sondes network is described by Thompson et al. [2007a, 2007b]. Eight of the eleven IONS-04 sites were arranged from the south central United States toward New England and the maritimes in a pattern that includes much of the pollution formation and export eastward from North America. A northern site (Pellston, MI (Pe)) captures signals from the North American boreal fires and a west coast site (Trinidad Head, CA (Tr)) addressed the ICARTT objective of capturing air masses entering North America from the Pacific. In addition, a site in Boulder, CO (Bou), is included as a long-term reference [Olmiens et al., 2006]. Table 1 lists site specific information.

[11] Over 260 profiles went into the analysis. The number of profiles for each site ranges from 40 for Trinidad Head to 7 for Boulder. The low number of profiles at some sites (including Boulder, Beltsville and Yarmouth) adds uncertainty to the analysis, in particular in determining the mean and standard deviation O$_3$ profile. The balloon-borne ozonesondes carry electrochemical concentration cell sensors that have an accuracy of about 10% in the troposphere. The accuracy can degrade to 15% if O$_3$ is less than 10 ppbv [Newchurch et al., 2003].

[12] The LID of Thompson et al. [2007a, 2007b, 2008; Pierce and Grant, 1998; Teitelbaum et al., 1996] is based on the observations by Dobson [1973], Holton [1987] and Reid and Vaughan [1991] that most soundings show a relatively
constant O\textsubscript{3} profile within the troposphere or stratosphere except where localized perturbations lead to stable laminae that deviate significantly from the mean. The LID method uses vertical profiles of O\textsubscript{3} mixing ratios together with concurrent P-T-U radiosonde data and derives four budget terms from the analysis.

[13] The laminae are first isolated as a normalized O\textsubscript{3} layer computed from the running mean mixing ratio; a 10% deviation is the minimum criterion, typically more than 2–3 times the measurement precision. Potential temperature (T\textsubscript{pot}) deviations are also calculated as a measure of atmospheric instability. Whether an O\textsubscript{3} lamina is Rossby-wave or gravity wave influenced is determined by anticorrelation or positive correlation between deviations in O\textsubscript{3} and T\textsubscript{pot}. Each stable lamina that is associated with Rossby wave influence is further filtered using sondes measurements of humidity, back trajectories and potential vorticity tracers to isolate O\textsubscript{3} layers with stratospheric origin (ST O\textsubscript{3}). Laminae that are associated with gravity waves are classified as O\textsubscript{3} layers with stratospheric origin (ST O\textsubscript{3}).

[14] The LID budget as used here is based on slight modifications to work by Thompson et al. [2007b]. The boundary layer height (PBLH) is determined from measured temperature and pressure profiles from the radiosonde [Thompson et al., 2008; J. E. Yorks et al., The variability of free tropospheric ozone over Beltsville, Maryland (39N, 77W) in the summers 2004–2007, submitted to Atmospheric Environment, 2008] in contrast to a PBLH of 1 km from Thompson et al. [2007a, 2007b]. A thermal tropopause (TP) [World Meteorological Organization, 1957] was used for total O\textsubscript{3} integration inst… an ozonopause [Browell et al., 1996a, 1996b]. On average, the thermal TP and ozonopause agreed to within 2 km, but occasionally the ozonopause was 6–7 km lower than the thermal TP. These modifications do not affect the conclusions from Thompson et al. [2007a, 2007b] that stratospheric O\textsubscript{3} and lightning are significant contributors to tropospheric O\textsubscript{3}.

2.2. MOZART-4 Simulations

[15] Version 4 of the MOZART chemistry transport model (L. K. Emmons et al., Impact of Mexico City emissions on regional air quality from MOZART-4 simulations, manuscript in preparation, 2008) was used in this study. Modifications from Version 2 published by Horowitz et al. [2003] include, among others, a more complete description of anthropogenic hydrocarbon chemistry, the inclusion of tropospheric aerosols (extended from the work of Tie et al. [2001, 2005]), and online calculations of photolysis rates, dry deposition, H\textsubscript{2}O\textsubscript{2}, and biogenic emissions [Pfister et al., 2008].

[16] For this study the model was run at a horizontal resolution of ~2.8 degrees by 2.8 degrees. The meteorological fields for 2004 for driving MOZART were taken from NCEP-GFS-Analysis (National Center for Environmental Prediction, Global Forecasting System) and were regridded to our model resolution and interpolated from a 6-h time structure to the 20-min time steps of the simulations. The vertical resolution of the model consists of 42 hybrid levels between the surface and 2 hPa (~45 km). Of those, about 7 are within the first kilometer, and 25 between the surface and 10 km.

[17] Biofuel and fossil fuel emissions for the globe were taken from the European Union project POET (Precursors of Ozone and their Effects in the Troposphere) [Granier et al., 2004] and for Asia from Ohara et al. [2007]. Biomass burning emissions are from GFED-v2 [van der Werf et al., 2006]. For the Alaska and Canada region, the biomass burning emissions for CO for 2004 are based on an inverse modeling study [Pfister et al., 2005], and emissions for NO\textsubscript{x}, VOCs and aerosols were deduced from this inventory by applying emission factors based on work by Andreae and Merlet [2001]. MOZART does not consider stratospheric chemistry explicitly, but O\textsubscript{3} concentrations are relaxed to prescribed O\textsubscript{3} fields above the model tropopause. We adopt here a thermal definition of the tropopause as the lowest model level at which the temperature vertical gradient decreases below 2 K km\textsuperscript{-1} [World Meteorological Organization, 1957]. The stratospheric-tropospheric exchange of O\textsubscript{3} in the model is driven explicitly by the GFS meteorology and results in an annual flux of ~500 Tg O\textsubscript{3}/a. While many offline transport models driven by assimilated meteorology result in a too great downward transport of O\textsubscript{3} from the stratosphere and use synthetic O\textsubscript{3} tracers for constraints [e.g., McLinden et al., 2000], this does not seem a significant issue when MOZART is driven by the GFS analyses. One important point of the comparison with the LID budget is to evaluate the stratospheric contribution in the model without the constraints of synthetic O\textsubscript{3} tracers.

[18] The lightning parameterization in MOZART-4 differs slightly from that used in MOZART-2 [Horowitz et al., 2003] and is described in more detail by Emmons et al. (manuscript in preparation, 2008). The lightning strength

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**Table 1. IONS-04 Site Specifics**

<table>
<thead>
<tr>
<th>Site Name</th>
<th>Location, deg</th>
<th>Elevation, m</th>
<th>Launches</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trinidad Head, Calif. (Tri)</td>
<td>41.05N, 124.15W</td>
<td>107</td>
<td>40</td>
</tr>
<tr>
<td>Boulder, Colo. (Bou)</td>
<td>40.30N, 105.20W</td>
<td>1743</td>
<td>7</td>
</tr>
<tr>
<td>Houston, Tex. (Hou)</td>
<td>29.97N, 95.33W</td>
<td>19</td>
<td>24</td>
</tr>
<tr>
<td>Huntsville, Ala. (Hun)</td>
<td>34.73N, 86.58W</td>
<td>196</td>
<td>14</td>
</tr>
<tr>
<td>Pullston, Mich. (Pel)</td>
<td>45.57N, 84.68W</td>
<td>235</td>
<td>38</td>
</tr>
<tr>
<td>Bellsville, Md. (Bel)</td>
<td>76.52W, 39.04N</td>
<td>24</td>
<td>8</td>
</tr>
<tr>
<td>Wallops, Va. (Wal)</td>
<td>37.85N, 75.50W</td>
<td>13</td>
<td>18</td>
</tr>
<tr>
<td>Narrangansett, R.I. (Nar)</td>
<td>41.52N, 71.32W</td>
<td>21</td>
<td>35</td>
</tr>
<tr>
<td>Yarmouth, N.S. (Yar)</td>
<td>44.83N, 66.12W</td>
<td>9</td>
<td>12</td>
</tr>
<tr>
<td>Sable Island, N.S. (Sab)</td>
<td>44.95N, 59.92W</td>
<td>5</td>
<td>33</td>
</tr>
<tr>
<td>Ron Brown (RBB)</td>
<td>Research vessel operating in the Gulf of Maine</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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*aLocation, elevation and number of sonde launches during the ICARTT period.*
still depends on cloud top height, with a stronger dependence over land than ocean [Price et al., 1997], but ocean grid boxes have been redefined to include only boxes surrounded by ocean, so that the land parameterization is extended one grid box beyond the continents [Price and Rind, 1992]. Flash frequency is determined by area and the lightning production is calculated after clouds are updated and before the chemistry routine is called. The vertical distribution of lightning NO emissions has been modified from that given by Pickering et al. [1998]. We have a reduced proportion of the emissions emitted near the surface and the strength of intracloud lightning strikes is assumed to be equal to cloud-to-ground strikes, as recommended by Ridley et al. [2005]. The global lightning source is 5.6 Tg N a⁻¹, which is within the currently accepted range of 5 ± 3 Tg N a⁻¹ [Schumann and Huntrieser, 2007].

[19] Our model simulations cover the months June through August 2004. We use 3-h average model fields in the analysis and match the model time output window to the sondé launch time, which usually took place in the local afternoon to coincide with satellite overpasses. We included a tagging scheme in the model, which allows estimating the contributions of various source terms to atmospheric O₃ concentrations. The scheme tags the emitted NO and maintains the tag through all simulated odd nitrogen species (e.g., PAN, nitrates, HNO₃). We also tag the O₃ produced by the photolysis of tagged NO₂. This tagged O₃ is destroyed at the same rate as the full O₃. Except for a few minor reactions, tropospheric O₃ in the MOZART model is only produced through the photolysis of NO₂. Although there are some minor pathways to create O₃ without the presence of NOₓ, the accuracy of the tagging technique has been estimated as better than 95% on a monthly basis [Lamarque et al., 2005]. Comparable accuracy is expected for our statistical analysis. The scheme is conservative in a sense that the sum of a group of tagged subsources is equal to tagging the entire NO source. The scheme is described in greater detail by Lamarque et al. [2005], Pfister et al. [2006] and Hess and Lamarque [2007].

[20] We keep track of 5 source terms: stratosphere (O₃STRATO), lightning (O₃LIGHT), Alaskan/Canadian wildfires (O₃FIRE), anthropogenic and biomass burning sources in the contiguous United States (O₃ASIA) and Eurasian anthropogenic and biomass burning sources (O₃ASIA). To derive O₃STRATO we calculate the difference between the total O₃ concentrations and O₃ tagged from all tropospheric NOₓ sources (surface and aircraft emissions, soil, and lightning). The spin-up phase for the stratospheric tracer simulation was 2 years. However, GFS analysis fields are available to us only since April 2004, and therefore the model was spun up for April 2004 to April 2006 and this atmospheric state then used as initial conditions for the analysis simulations starting in April 2004. For all other tracer simulations we used the same initial conditions, but set all initial tracer precursor and O₃ concentrations to zero.

2.3. Model Evaluation With INTEX-A Aircraft Observations

[21] The model concentration fields and emission inventory have been evaluated in terms of CO and O₃ in previous studies by comparison with satellite, aircraft and ground-based measurements conducted during INTEX-A [Pfister et al., 2005, 2006]. Here, we extend the evaluation by comparing to observations of NOₓ (= NO + NO₂), PAN, HNO₃, CH₂O, OH and HO₂ from instrumentation onboard the DC-8 aircraft (Figure 1). The NASA DC-8 flights took place 29 June to 14 August over the Central and eastern United States. The measurements and observing techniques have been previously published and are summarized by Singh et al. [2006]. The model data are interpolated to the time and location of the aircraft. Following Ren et al. [2008], the OH and HO₂ measurements have been corrected by a factor of 1.64. In addition to total model concentrations, we also include mean contributions for model tracers for lightning, Asian, fire and U.S. sources where available to support the following analysis.

[22] CO is overestimated at the lowest altitudes as is NOₓ consistent with an overestimate in surface emission, found in other studies. CO and NOₓ emissions in the POET inventory are comparable in magnitude and spatial distribution to the NEI EPA 1999 emissions inventory (11.9 Tg CO versus 11.6 Tg CO and 0.8 Tg N versus 0.9 Tg N for the contiguous United States), which was found too high in CO and NOₓ when compared to 2004 measurements [Frost et al., 2006; Parrish, 2006; Hudman et al., 2007]. In auxiliary material Figure S1 we show a comparison of modeled CO with observations from the European MOZAIK program [Thouret et al., 1998; Nedelc, 2003] over the United States. Both model and observations show that on average the troposphere over the western part of the United States is generally less polluted than the eastern part of the country. The model overestimates surface concentrations and especially for the eastern United States also overestimates CO in the free troposphere. This likely is related to the high bias at the surface, but in addition might also be caused by too strong lofting of pollution in the model.

[23] NOₓ is well represented by the model up to about 5 km but is clearly underestimated in the upper troposphere. A low model bias in upper tropospheric NOₓ has also been found by Hudman et al. [2007], who used a comparable lightning source over the United States for the time period considered (0.07 Tg N versus 0.06 Tg N in our simulation) and increased lightning NOₓ emissions by a factor 4 to better match modeled NOₓ concentrations with upper tropospheric observations. A significant contribution of lightning NOₓ was also found in other studies [Cooper et al., 2006; Li et al., 2005; Zhang et al., 2003] while in our simulations the amount of NOₓ from lightning represents a relatively small term (Figure 1).

[24] The spatial distribution of the lightning NOₓ production in our model is evaluated by comparison to lightning flashes provided by the National Lightning Detection Network (NLDN) (auxiliary material Figure S2). The model represents well the overall distribution in the upper tropospheric NOₓ fields (spatial correlation r = 0.83) but shows less pronounced features in the midwest and southwest (auxiliary material Figure S3). While sensitivity simulations with altered lightning parameterizations are beyond the scope of this study, we look at observed and modeled spatial distributions and statistics of upper tropo-
spheric NO$_x$ concentrations to more closely examine this discrepancy (auxiliary material Figure S3).

Both observations and model show similar spatial characteristics in upper tropospheric NO$_x$ concentrations (correlation of 0.6) with largest values over the south and southeastern United States. The model values are overall lower, but there is no clear spatial signature in the relative model-measurement difference. Similar correlations coefficients are found between the absolute measurement-model bias and both the model NO$_x$ tracers for lightning (0.36) and U.S. sources (0.34).

We applied an optimal estimation technique [Rodgers, 2000] to the spatial averages shown in auxiliary material Figure S3 to determine how the tagged NO$_x$ contributions have to be adjusted to minimize the measurement-model differences (0.40 ± 0.29 ppb). This estimate does not consider feedbacks from the chemical system, but gives some insight into which sources are mostly likely contributing to the model-measurement differences. Similar correlations coefficients are found between the absolute measurement-model bias and both the model NO$_x$ tracers for lightning (0.36) and U.S. sources (0.34).

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These results do not let us unambiguously determine the reason for the low NO$_x$ bias, but suggest that the model-measurement discrepancy is not related to one single source. It is interesting to note that even after the fourfold increase in lightning NO$_x$, the modeled NO$_x$ field of Hudman et al. [2007] is biased low compared to the aircraft observations. Thus in addition to the models being likely too low in the magnitude of emitted lightning NO$_x$, other sources of error need to be considered.

The modeled O$_3$ production is further evaluated, as shown in auxiliary material Figure S4, by comparing observed and modeled relationships between O$_3$ (= O$_3$ + NO$_y$) and NO$_x$ (NO$_y$ – NO$_x$) concentrations [Kleinman et al., 2002]. NO$_x$ is estimated as the sum of NO$_x$, PAN and HNO$_3$ only, because data sets for the other NO$_y$ species are sparse and generally account for <10% of NO$_x$ [Hudman et al., 2007]. The results show that the model is simulating well the...
observed $O_3$ production efficiency for a range of different altitudes and types of air masses.

3. Comparison of Modeled and Observed Ozonesonde Profiles

[29] The comparison of observed and modeled $O_3$ profiles for the different IONS sites is shown in Figure 2 and in support of the analysis we also include the average model tracer concentrations for each site. MOZART represents the overall shape of the $O_3$ profiles throughout most of the troposphere but has less variability with its comparably coarse vertical and spatial resolution.

[30] At the lowest altitude levels, the model overestimates concentrations near the surface at most east coast IONS sites and this also influences the average bias calculated over all IONS sites, which is $+14 \text{ ppb}$. A high bias in the eastern United States has been found in previous MOZART simulations [Lin et al., 2008; Murasaki and Hess, 2006]. Multimodel estimates of surface $O_3$ for the year 2001 performed in the frame of HTAP (Hemispheric Transport of Air Pollution, www.htap.org) show a high bias over the eastern United States for the majority of models (A. M. Fiore et al., Multimodel estimates of intercontinental source-receptor relationships for ozone pollution, submitted to Journal of Geophysical Research, 2008). The results suggest that global models generally may have difficulties representing conditions leading to below average surface ozone because 2001 as well as 2004 [Thompson et al., 2007a] were low ozone years for the eastern United States.

[31] The analysis of the model tracers shows that at sites with a positive surface bias, $O_3$ from U.S. NO$_x$ sources is the dominating contributor and as mentioned above, part of this bias is likely due to an overestimate in surface emissions. Coarse resolution also impacts the comparison of large-scale models with in situ observations. For example, the model might have a surface source included within the grid box, while the sampling site is located far from sources. This is the case for the two sites with the highest surface bias: Wallops, which is collocated with a grid box with some of the highest model NO emissions at the east coast, and Narragansett. These two sites may also be influenced by onshore and offshore wind patterns, which are not well resolved by the coarse model resolution. Modeled surface concentrations for other parts of the United States are well represented in the model.

[32] Very good agreement is found in the free troposphere where the model reproduces observed $O_3$ concentrations to within a few parts per billion (ppb) (Figure 2). $O_3$ concentrations at this altitude are mostly impacted by large-scale transport and less sensitive to grid resolution. A high surface bias with a small low free tropospheric bias as seen for many of the east coast sites might indicate insufficient boundary layer ventilation in the model. However, free tropospheric altitudes also include significant contributions from other sources, for example, lightning and stratospheric $O_3$ or nontagged sources, and we cannot draw a consistent conclusion.

[33] The largest midtropospheric bias of all sites is found at Trinidad Head, $-14 \text{ ppb}$ at $5 \text{ km}$. Trinidad Head is strongly influenced by stratospheric $O_3$ as has been found in other studies [Cooper et al., 2006; Hudman et al., 2004; Oltmans et al., 2004] as reflected in the $O_3^{\text{STRAT}}$ tracer being higher over Trinidad compared to other sites. However, our simulated $O_3$ closely matches the observations in the upper troposphere where the stratospheric influence is strongest and thus it seems more likely that the contribution from $O_3^{\text{EURASIA}}$, which has a strong signal in the midtroposphere, is underestimated. An increase in $O_3^{\text{EURASIA}}$ would also impact other sites, but to a lesser extent.

[34] Absolute differences between the sondes and modeled profiles increase in the upper troposphere/stratosphere with model values generally biased high (Figures 1 and 2). This can be explained in that MOZART is designed as a tropospheric model that is constrained in the stratosphere by climatological values (see section 2.2), which is too high for the studied area and time period suggesting that the model transports too much stratospheric $O_3$ into the troposphere. However, the model correctly represents the transition from the tropospheric to the stratospheric regime supported by the model matching the general shape of the $O_3$ profiles and also supported by the comparison of CO-$O_3$ correlations in the model to the suite of observations provided by the MOZAIC program (auxiliary material Figure S5). Further evaluation of the modeled stratospheric contributions is given in section 5.2 by comparison to the LID budget.

[35] Figure 2b gives a measure of how the $O_3$ profile changes across the United States and shows well the model represents this spatial variation among the IONS-04 sites. We show for each site the deviation from the mean profile, calculated as average over all sites for both, the model and the observations. Throughout most of the troposphere we find a high correlation between the modeled and observed spatial variability confirming the model’s ability to simulate the spatial characteristics of the $O_3$ fields over the United States. The most pronounced outlier is the surface concentration over Narragansett where the model predicts highest concentrations while observations define it as an average location. As mentioned above, this might be explained by the coarse model resolution.

[36] Trinidad Head shows the lowest surface $O_3$ amounts because it is mostly impacted by clean maritime air masses. Stations in the southeast show highest $O_3$ from a combination of high emissions, humidity and solar radiation. The model also represents well the upper tropospheric variations with lowest $O_3$ values at $10-15 \text{ km}$ for the southernmost sites Houston and Huntsville due to a higher tropopause toward lower latitudes.

[37] In addition to the total $O_3$, we include in Figure 2b the modeled $O_3$ profile minus the stratospheric component representing the spatial variations from tropospheric sources only ($O_3^{\text{TROP}}$), which shows quite different spatial variations above $\sim 6 \text{ km}$ compared to total $O_3$. In agreement with findings from other studies [Cooper et al., 2006, 2007], $O_3^{\text{TROP}}$ values are larger at the east coast compared to the west coast and the largest positive anomalies at high altitudes are seen over Houston and Huntsville mostly due to the strong influence of lightning.

4. Model Ozone Budget and Representativeness of IONS Sites

[38] Figures 3 and 4 illustrate the modeled spatial distribution, as represented by the total column amount, and vertical distribution, as represented by zonal averages, of total and
Figure 2. (a) Observed (gray solid symbols) and modeled (black open symbols) ozone profiles for the different IONS stations. The contributions of the model tracers are illustrated by different colors. Mean model and observed ozone profile and mean bias over all sonde locations are illustrated in a separate graph together with mean difference between model and observation (red pluses). (b) Observed (solid symbols) and modeled (open symbols) average deviation from the mean profile for each location. Model profiles with the stratospheric component removed are shown by blue symbols.
tracer O$_3$ concentrations over North America averaged over the time period 1 July to 15 August 2004. For the total O$_3$ we show absolute values, while the tracers are shown in terms of relative contributions. The tropospheric column in the model is calculated as the column amount between the surface and the thermal TP. In Figure 5 we show, in addition, the surface concentrations of different tracers.

[39] The simulated contribution of O$_3$ STRATO to the tropospheric column (Figures 3b and 4b) is in the range of 10–40% with contributions generally increasing toward high latitudes. Large values for the contiguous United States are seen over the Rocky Mountains in the model, which may partly be a numerical artifact. The use of sigma coordinates in the model causes a more narrow vertical spacing in the tropopause region over high-elevation terrains, which can lead to an increased downward transport of stratospheric O$_3$. For example, over Boulder the vertical spacing is 20 hPa at 10 km compared to 30 hPa over low elevation sites. An increased stratospheric contribution not only shows up over the Rocky Mountain region, but is seen over other high-elevation regions like Greenland or the Tibetan Plateau as well. This issue needs to be considered in the analysis.

[40] Highest impact from stratospheric O$_3$ is, as expected, found in the upper troposphere and is by far the dominating factor near the tropopause (Figure 4b). In the midtroposphere, the stratospheric term accounts for about 10–20% (10–20 ppb) of the O$_3$ over the contiguous United States. The contributions of O$_3$ STRATO to surface concentrations (Figure 4) are negligible for the time period considered (<1 ppb). This has been also found by other modeling studies; for example, Hauglustaine and Brasseur [2001] state that the stratospheric contributions in the boundary layer during July is at a minimum (approximately a few percent) over the Northern Hemispheric continents and Fiore et al. [2002] found that stratospheric O$_3$ never exceeded 2 ppbv at the surface over the summertime continental United States.

[41] Figures 3c and 4c show the same analysis, but for the lightning tracer. The O$_3$ LIGHT tracer in the model is produced from global lightning sources, and considering that the O$_3$ lifetime in the upper troposphere can be on the order of weeks, the O$_3$ LIGHT loading over the United States is a combination of O$_3$ produced from lightning sources within and outside the United States. The transport of O$_3$ LIGHT is evident from Figure 3c, where we see the outflow of O$_3$ LIGHT from the south and southeastern United States, which is the region within the United States that shows the strongest NO lightning production. Average tropospheric columns of O$_3$ LIGHT over the ocean off the U.S. West Coast are on the order of 4 ± 0.5 DU, which is approximately the amount of O$_3$ LIGHT transported into the United States. Over the United States region, where the local NO production from lightning is more than a factor of 100 higher compared to the oceanic regions, the lightning contribution increases to 5 ± 2 DU owing to local production, with maximum values up to 10 DU found in the southern United States. For the U.S. outflow region over the Atlantic we also find higher column amounts, 6 ± 1DU. The average amount of O$_3$ ASIA decreases by about a factor of 2–3 between the western and the eastern region (13 DU compared to 5 DU), and provides an estimate of the photochemical destruction and dilution of ozone during its transport across the continent. The extent of the regions we refer to for these averages are indicated in Figure 3c.

Figure 3. (a) Total tropospheric ozone column and total columns of (b) O$_3$ STRATO, (c) O$_3$ LIGHT, (d) O$_3$ U.S., (e) O$_3$ FIRE, and (f) O$_3$ EURASIA over North America. Averages for 1 July to 15 August 2004. Two letter codes represent the sonde locations. The regions indicated in Figure 3c are referred to in the text.
shows a pronounced N-S gradient and the column contributions range from 8 to 20% (4–10 DU) of total tropospheric O$_3$ over the continental United States (Figure 3c). Our estimate is similar to that of Zhang et al. [2003] who conclude that about 20% of the tropospheric O$_3$ content over the contiguous United States in July is due to lightning. We find the maximum impact in the middle to upper troposphere with values ranging from 15% (20 ppb) at the northern latitudes up to 30% (20 ppb) in the southernmost parts of our region. In the analysis Cooper et al. [2006] applied to the IONS-04 data, they found that the upper troposphere over eastern North America (>6 km) contained an additional 16 ppbv O$_3$ compared to the West Coast and attributed 11–13 ppb of this to in situ production from lightning NO$_x$. Over Houston the lightning contribution was estimated as about 20 ppbv. Our lightning contributions are of similar order (15–20 ppbv for east coast sites, 18 ppbv for Houston), but the results are not directly comparable because we tag the global lightning source thus including contributions due to transport. The contribution of O$_3^{\text{LIGHT}}$ at Trinidad Head is ~10 ppb and considering a factor 2 decay discussed earlier, about half this may be representative of O$_3^{\text{LIGHT}}$ transported across the Pacific into the United States. This implies that the lightning contribution in our model is ~5 ppbv compared to Cooper et al. [2006]. Hudman et al. [2007] estimate an increase in upper tropospheric O$_3$ of 10 ppb when increasing in the lightning source by a factor of 4. An increase in the lightning source in our model would benefit, but not optimize, the comparison of modeled to observed NO$_x$ fields in the upper troposphere (section 2.3). Assuming a similar response in our simulated O$_3$ as derived by Hudman et al. [2007], this degrades the agreement with O$_3$ measurements. However, as discussed earlier (section 3), it is likely we overestimate the amount of stratospheric O$_3$.

The O$_3$ produced from U.S. anthropogenic NO$_x$ sources (Figures 3d and Figure 4d) accounts for up to 40 ppb (over half of the O$_3$ concentrations) near the surface on a zonal average and for up to 30% (20 ppb) of the O$_3$ in the midtroposphere over the contiguous United States. The highest signal is found over the eastern part of the United States. O$_3^{\text{U.S.}}$ in this region accounts for up to 30% (20 DU) of the tropospheric O$_3$ column, while contributions in the western part of the country are 10–20% (5–10 DU).

Surface contributions from non-U.S. sources (defined as O$_3$ from sources other than United States anthropogenic sources) are shown in Figure 5. The lowest values, 5 ppbv or less, are found over the highly polluted regions, away from these regions the values can be as high as 30 ppbv. The average contributions are 14 ± 6 ppbv for the western United States.
States, and 12 ± 6 ppb for the eastern United States. While Eurasian sources and lightning sources are able to explain some part of the non-U.S. emission concentrations (up to 7 ppb and 5 ppb, respectively), none of the sources tagged in the model contribute a significant amount to the non-U.S. surface concentrations (less 1–2 ppb). The missing part is due to sources not tracked in our simulations. For example, in the most southern part of the United States, \( \text{O}_3 \) from \( \text{NO}_x \) sources in Mexico and Central America contribute to the nonlocal budget term. In Florida, the non-U.S. \( \text{O}_3 \) concentrations reach up to 40 ppb.

[45] Non-U.S. contributions to afternoon \( \text{O}_3 \) concentrations over the United States estimated by Fiore et al. [2002] are 15–20 ppb for the eastern United States and 25–35 ppb for the western United States, respectively. If we restrict our analysis to afternoon values only (average for 2100–2400 UTC), the nonlocal term increases to 14 ± 6 ppb for the eastern United States and 18 ± 8 ppb for the western United States, respectively. Differences can be explained by the use of different models and emission inventories, but also by the different methods used to determine non-U.S. contributions. While our approach tracks the \( \text{O}_3 \) production from selected sources independent of where the actual \( \text{O}_3 \) production from these emissions takes place, the approach by Fiore et al. [2002] tracks the in situ \( \text{O}_3 \) production within the U.S. boundary layer.

[46] \( \text{NO}_x \) emissions from the wildfires in Alaska and Canada are estimated as 0.5 Tg N for 1 July to 15 August. The signal of the \( \text{O}_3 \) produced from this source (Figures 3e and 4e) is most dominant in the northern latitudes, but we see significant amounts of \( \text{O}_3 \)^{\text{FIRE}} as far south as Narragansett. In addition to the main westerly transport pathway, we also see enhanced transport across the south toward the West Coast. In the northern contiguous United States, the average contributions to tropospheric \( \text{O}_3 \) are up to 15% (10 DU) and to surface concentrations up to 5 ppb.

[47] Modeled Eurasian \( \text{NO}_x \) sources (anthropogenic and biomass burning) are 2. for 1 July to 15 August. The largest \( \text{O}_3^{\text{EURASIA}} \) contributions over North America are seen in the midtroposphere with a maximum contribution of 25% (20 ppb) found at the northern latitudes of our region (Figures 3f and 4f). In the lower troposphere the contributions are 15% and below. The strongest impact is evident at the West Coast, where up to 25% (10 DU) of the tropospheric \( \text{O}_3 \) column and 5 ppb of surface \( \text{O}_3 \) is attributed to Eurasian sources.

[48] The modeled budget analysis for the different IONS sites in terms of the tropospheric column amount, the average over all sites (referred to as “IONS budget”) and the budget for the entire summertime contiguous United States (continental areas between 30°N and 50°N; referred to as “regional budget”) are summarized in Figure 6. Figure 6 also includes results from the LID budget that will be discussed in section 5. In order to conform to the LID budget (section 2.1), the individual tracer contributions are not integrated over the entire troposphere, but only from the top of the boundary layer to the tropopause. \( \text{O}_3 \) integrated over the boundary layer is treated as a separate term. For the IONS budget, only days with launches are included, and each site is weighted independently of the number of measured profiles. As can be seen from Figure 6, the model \( \text{O}_3 \) tracers included in this study can explain at least 80% of the tropospheric \( \text{O}_3 \) at all the IONS sites and over the contiguous United States.

[49] The contributions of \( \text{O}_3 \) within the boundary layer to the total tropospheric column range from a few percent at Sable Island or Trinidad Head to nearly 15% for Houston and Huntsville. On average we estimate 6 ± 4% for the IONS budget and 6 ± 6% for the regional budget. The specified standard deviation represents the spatial variability over the IONS location and the contiguous United States, respectively. A more detailed analysis of the boundary layer contributions is given in section 5.3. Contributions from \( \text{O}_3^{\text{U.S.}} \) in the free troposphere range from 6% at Trinidad Head, strongly impacted by inflow of \( \text{O}_3 \) and precursors, to 30–35% at the eastern locations, which are well within the

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Figure 5. Surface concentrations (ppb) averaged for 1 July to 15 August for the different ozone tracers and for nonlocal sources (calculated as \( \text{O}_3^{\text{U.S.}} \)).
North American outflow region. On average we calculate 25 ± 9% in the IONS budget and 20 ± 12% in the regional budget. The stratospheric contribution in the IONS budget is 26 ± 6% compared to 32 ± 11% for the regional budget. Contributions for lightning, fire and Eurasian sources in the IONS budget are 10 ± 2%, 3 ± 2%, and 13 ± 5%, respectively with similar contributions in the regional budget. Omitting Boulder in the IONS budget and high-elevation areas (>1 km) in the regional budget does not alter the statistics significantly, the largest changes occur in the stratospheric term of the regional budget which decreases to 29 ± 10%.

The analysis of the individual IONS sites reflects the spatial variability in the O$_3$ budget. Houston shows the largest contribution of O$_3^{\text{LIGHT}}$ with 15% (8.5 DU) of the total tropospheric column due to lightning NO$_x$. Pellston experiences the highest impact from O$_3^{\text{FIRE}}$ with 8%. The largest fraction of O$_3^{\text{EURASIA}}$ is at Trinidad Head accounting for 28% of the O$_3$ column. At this site we find the smallest influence from U.S. sources (6%), while for the IONS sites located in the eastern part of the United States up to ~35% of the total tropospheric O$_3$ is due to local anthropogenic sources. The O$_3$ budget terms have a clear spatial variability across the contiguous United States, but this analysis shows that an average over all sonde locations gives a very good representation of the regional budget. Thus we can conclude that the sample of IONS stations and launch days conveys a proper representation of the large-scale picture.

5. Comparison of LID and Model Budgets

The O$_3$ budget terms derived from the LID analysis (section 2.1) are now directly compared with the modeled budget analysis (section 3). A direct match between the LID budgets and the model O$_3$ tracers is only possible for the terms O$_3^{\text{STRATO}}$ and BL O$_3$, while for the other terms we use sonde and model budgets in a complementary analysis. O$_3^{\text{LIGHT}}$ and O$_3^{\text{U.S.}}$ might add to the RCL as well as the ADV terms because they are global and continental markers, respectively. O$_3^{\text{FIRE}}$ and O$_3^{\text{EURASIA}}$ can be mostly attributed to the ADV terms as the sonde stations are within a few days transport time. The LID and modeled budget terms are derived such that the BL term is integrated between the surface and the boundary layer top, while all other terms are integrated between the top of the boundary layer and the thermal TP.

5.1. Tropopause Level and Tropospheric Column

In Figure 7 we show a comparison of the tropospheric O$_3$ column derived from the LID budget analysis and that derived from the model. Because of the close connection...
between TP height and tropospheric O₃ column amount; that is, generally a higher TP leads to a higher column amount, we also include modeled and observed TP in this comparison. Statistics are given including the Boulder site, but similar results are derived when Boulder is omitted. Average columns and TP agree very well. The mean tropospheric O₃ column over all profiles is 47 ± 6 DU for the LID budget compared to 51 ± 4 DU for the model. Accordingly, for TP we retrieve 13.6 ± 1 km and 14.2 ± 1 km, respectively. At most sites we find a good agreement between the model and sondes column and the model represents the spatial variability in the IONS locations fairly well. Correlation coefficients for variations in TP and total O₃ column are 0.51 and 0.56, respectively. Yarmouth, Wallops, Beltsville and Houston show up as sites with the highest column amounts in the LID budget and also some of the highest amounts in the model budget.

The differences in the total column are linked to the differences in TP; to investigate the impacts of differences in tropopause height and in O₃ mixing ratios separately, we calculate O₃ column amounts using a fixed altitude range instead of the height of the TP. Setting an upper limit of 20, 15 or 8 km assures that the calculations consider those parts of the profile that are generally above, partly above and partly below TP, increases the correlation to 0.89, 0.87, and 0.90, respectively. Another way to look at this sensitivity is to calculate correlations between differences in modeled and observed TP height and differences in modeled and observed tropospheric column amounts. For most of the sites the correlation coefficients are in the range of 0.5 (0.64 at Beltsville, 0.57 at Huntsville, 0.57 at Narragansett, 0.44 at Pellston, 0.62 for Ron Brown, 0.51 at Trinidad Head, 0.55 for Houston). These statistics indicate that differences in modeled and observed TP might explain approximately one fourth of the differences between modeled and observed tropospheric O₃ columns.

5.2. Stratospheric Contribution

As mentioned earlier, one term that can be compared directly between the LID and the model budget is the contribution of stratospheric O₃. However, a small disparity between modeled and LID term is that the latter identifies “recent” stratospheric O₃, i.e., O₃ from the stratosphere that has not yet been mixed into the background, while the model also identifies stratospheric O₃ after it has been mixed into the background air. Thus the LID budget is expected to give a lower limit to the model estimate. Figure 8 shows the mean and standard deviation of absolute and relative stratospheric terms for the individual IONS sites. The average contributions over all sites are 10 ± 4 DU or 20 ± 7% of the total column for the LID budget and 13 ± 3 DU or 26 ± 6% for the model. Excluding the Boulder site from the statistics brings the two budgets closer together by reducing the relative model contribution to 25 ± 6% and increasing the LID budget to 22 ± 4%.

Aside from Boulder, the largest stratospheric impacts in the MOZART analysis are found at Trinidad Head with smaller impacts found for the east coast sites. This agrees with Cooper et al. [2006], who, using a potential vorticity based FLEXPART retroplume technique, estimate the proportion of stratospheric O₃ in the upper troposphere at the IONS-04 sites as ranging from an average of 27% at Trinidad Head-on the West Coast to 13% at Sable Island on the east coast. Boulder was not considered in their work. The LID analysis does not show a significant difference between Trinidad Head and the east coast sites.

This analysis gives an estimate of uncertainties in stratospheric contributions based on two independent methods: the average difference between the LID and the budget term is 4 ± 6 DU or 7 ± 12% of the O₃ column amount (2 ± 3 DU or 3 ± 5% if Boulder is excluded). These results confirm a significant contribution of stratospheric O₃ to the tropospheric budget and the model’s ability to give a reasonable representation of the overall stratospheric contribution.

5.3. Boundary Layer Terms

The boundary layer height (PBLH) and the integrated boundary layer O₃ amount for the sondes and the model budgets are compared in Figure 9. The PBLH for Houston, Huntsville and Boulder is well represented by the model, but at all other sites the model shows an underestimate. The average PBLH over all sites from the LID budget is 1.1 ± 0.1 km compared to 0.7 ± 0.4 km for the model. The overall lower bias in PBLH in the model probably contributes to the high bias in surface O₃ discussed in section 4, however, the end result is less integrated boundary layer O₃ compared to the LID analysis. The mean bias over all sites is 2.6 ± 1.5 DU, with the model about a factor of 2 lower compared to the LID budget. The largest disagreements are over sites in the northeast. Despite the absolute bias, the model represents the spatial correlation between the sites with a correlation of 0.76. Both model and LID analysis identify Sable Island and Trinidad Head as the sites with the lowest PBL O₃ column amount.
We also used the model tracers to estimate individual contributions to the $O_3$ amount in the boundary layer (Table 2). U.S. sources are the major contributor at all sites. They explain up to 96% of the PBL column for sites on the east coast. Smallest United States contributions are found for Sable Island (62%), Pellston (61%), Boulder (63%), and Trinidad Head (66%). At the latter three sites we find the largest Eurasian contributions (7–8%). For all other sites the Eurasian contribution does not exceed 2%. The largest impact from the Alaska wildfires is estimated for Pellston (10%) and Trinidad Head (9%). Note from Figure 3e that there is actually significant transport of $O_3^{\text{FIRE}}$ along the West Coast. Sources not covered by the model tracers account for as little as a few percent at some of the locally polluted east coast sites up to 34% at Sable Island. Boulder, owing to its high elevation, has highest contributions from $O_3^{\text{STRAT}}$ (3%) and $O_3^{\text{LIGHT}}$ (4%). For Houston, even though lightning explains about 15% of the tropospheric column, only 3% accounts for the boundary layer $O_3$, because, as was shown earlier, the majority of $O_3^{\text{LIGHT}}$ is produced and remains at higher altitudes.

5.4. Other Terms

In this Section we identify a number of encouraging cases where LID and model budget complement each other and give motivation for future work. For this purpose we refer back to Figure 6 where the terms for both the modeled and the LID budget are included. One such case study is Houston. With 15% (8.5 DU), Houston has the largest $O_3^{\text{LIGHT}}$ contribution of the sites considered. At the same time, it also has the largest RCL (regional convection plus lighting) terms in the LID budget (7.5 DU or 14%) and the lowest relative contribution from ADV (50%). Besides Houston, we see large RCL for Sable (7.3 DU or 16%) and Yarmouth (7.3 DU or 13%). We cannot relate this to a single MOZART tracer, but both sites are on the higher end of contributions from $O_3^{\text{LIGHT}}$ and $O_3^{\text{EURASIA}}$, on the order of 10% and 30%, respectively.

Trinidad Head, owing to its location on the West Coast, is most exposed to inflow from the Pacific and has the lowest $O_3^{\text{U.S.}}$ contribution from all sites (2.6 DU or 6%) and highest contributions from $O_3^{\text{EURASIA}}$ (12.3 DU or 28%). This is in line with the LID budget, which has a rather small RCL term (3.8 DU or 8%) and at the same time a large contribution from ADV (27.3 DU or 61%). Generally, the largest relative contributions from ADV are determined for Trinidad Head, Boulder, and Pellston. These are all sites that have large inflow from sources outside the contiguous United States ($O_3^{\text{EURASIA}}$ and/or $O_3^{\text{FIRE}}$) in the model budget.

Last we compare the impact of the boreal fires between the two budgets. Morris et al. [2006] find large $O_3$ increases as far south as Houston during 19–20 July owing to the fires. In the MOZART budget some of the largest contributions from $O_3^{\text{FIRE}}$ are seen for the same time period. While the column amount of $O_3^{\text{FIRE}}$ is below 0.2 DU on most days it is 0.84 DU and 0.89 DU for 19 and 20 July, respectively. Fire emissions contribute to the ADV term in the LID budget, which reaches a value of close to 40 DU for 20 July for Houston, one of the highest values for the time period considered.

6. Conclusions

Ozone plays a major role in atmospheric chemistry, climate and air quality. Understanding current $O_3$ concentrations and how they may change in the future requires an

Table 2. Boundary Layer Ozone Column for LID Analysis and Model as Well as Model Tracer Contributions

<table>
<thead>
<tr>
<th>Site</th>
<th>$O_3^{\text{BL,LID}}$</th>
<th>$O_3^{\text{BL,MOZ}}$</th>
<th>$O_3^{\text{STRAT}}$</th>
<th>$O_3^{\text{LIGHT}}$</th>
<th>$O_3^{\text{EURASIA}}$</th>
<th>$O_3^{\text{U.S.}}$</th>
<th>$O_3^{\text{FIRE}}$</th>
<th>$O_3^{\text{REST}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trinidad, Calif.</td>
<td>3.77</td>
<td>1.13</td>
<td>&lt;1</td>
<td>2</td>
<td>8</td>
<td>66</td>
<td>9</td>
<td>14</td>
</tr>
<tr>
<td>Boulder, Colo.</td>
<td>6.68</td>
<td>3.89</td>
<td>3</td>
<td>4</td>
<td>8</td>
<td>63</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>Houston, Tex.</td>
<td>6.86</td>
<td>7.31</td>
<td>&lt;1</td>
<td>3</td>
<td>1</td>
<td>88</td>
<td>&lt;1</td>
<td>8</td>
</tr>
<tr>
<td>Huntsville, Ala.</td>
<td>8.08</td>
<td>7.17</td>
<td>1</td>
<td>3</td>
<td>2</td>
<td>82</td>
<td>1</td>
<td>11</td>
</tr>
<tr>
<td>Pellston, Mich.</td>
<td>4.23</td>
<td>2.31</td>
<td>1</td>
<td>1</td>
<td>7</td>
<td>61</td>
<td>10</td>
<td>18</td>
</tr>
<tr>
<td>Beltsville, Md.</td>
<td>7.30</td>
<td>3.14</td>
<td>&lt;1</td>
<td>1</td>
<td>1</td>
<td>91</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>Wallops Island, Va.</td>
<td>5.48</td>
<td>3.89</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>90</td>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td>Narragansett, R.I.</td>
<td>6.14</td>
<td>2.10</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>96</td>
<td>&lt;1</td>
<td>3</td>
</tr>
<tr>
<td>Yarmouth, N.S.</td>
<td>5.09</td>
<td>1.88</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>79</td>
<td>3</td>
<td>14</td>
</tr>
<tr>
<td>Sable Island, N.S.</td>
<td>3.67</td>
<td>0.47</td>
<td>&lt;1</td>
<td>2</td>
<td>2</td>
<td>62</td>
<td>&lt;1</td>
<td>34</td>
</tr>
<tr>
<td>Ron Brown</td>
<td>6.09</td>
<td>1.52</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>88</td>
<td>2</td>
<td>8</td>
</tr>
</tbody>
</table>

*Model tracer contributions are in percent. Boundary layer ozone column for LID analysis ($O_3^{\text{BL,LID}}$) and for model ($O_3^{\text{BL,MOZ}}$) are in Dobson Units (DU).
understanding of the relative importance of the various sources. In this study we used a comprehensive network of ozonesonde measurements together with two independent budget analysis methods to estimate the factors contributing to tropospheric \(O_3\) over the summertime contiguous United States as well as their range of uncertainty. The observations are provided by the IONS-04 network that was assembled over North America during the INTEX-A field campaign in summer 2004. Evaluation of the MOZART-4 model with these data shows that the model gives a good representation of the general characteristics of the spatial and vertical ozone field. However, this study also discloses a number of uncertainties associated with modeling the tropospheric \(O_3\) budget such as simulating the \(NO_x\) production from lightning or representing boundary layer dynamics.

The tropospheric \(O_3\) budget is determined via two different methodologies. One is based on five synthetic ozone tracers in the MOZART model: stratosphere, lightning, North American boreal wildfires, and anthropogenic and biomass burning sources in the contiguous United States and in Eurasia. The other methodology, an \(O_3\) laminar identification analysis, is a more empirical approach for extracting information about contributions of stratospheric \(O_3\), advection and convection from ozonesonde observations.

Averaged over the IONS-04 locations, the tropospheric contributions for the model tracers are 25 ± 9% for U.S. sources, 13 ± 5% for Eurasian sources, 3 ± 2% for North American boreal fires and 10 ± 2% from lightning. The stratospheric contribution in the model budget is 26 ± 6%. Model evaluation and comparison to other studies indicate that the lightning term in the model budget may be biased low, while the stratospheric term is likely biased high. The overestimate in the stratospheric term is expected to be not larger than a few percent, because the corresponding LID estimate of 20 ± 7% gives a lower limit to the modeled stratospheric term.

Evaluation of modeled \(NO_x\) fields to aircraft measurements in the upper troposphere show a low model bias. Other studies [Cooper et al., 2006; Hudman et al., 2007] suggest this discrepancy may be due to an underestimate in the lightning source. However, analysis of the \(NO_x\) contributions from tagged sources indicates that increasing the magnitude of the lightning source is unlikely to fully explain the model-measurement discrepancy in the upper troposphere.

Variations in the tracer contributions across the different sites can be large, but the budget estimated by the model for the entire United States is similar to the budget averaged over the IONS-04 sites. From this we conclude that the sample of locations and launch days conveys a proper representation of the \(O_3\) budget for the contiguous United States. In the boundary layer the dominant contribution comes from sources within the contiguous United States, but other terms might play a significant role as well. The results indicate the importance of understanding the impact of nonlocal sources, even when studying the lowermost troposphere. Eurasian sources can contribute on average up to 8% to the boundary layer ozone, and lightning up to 4%. The impact from the North American boreal fires was found to be as high as 10%.

In Figure 10 we summarize the findings and show the variation in the \(O_3\) budget across the contiguous United States by plotting a west-east cross section of the various budget terms. Further we include the modeled and LID budgets for the West Coast IONS site Trinidad Head and contrast that to an average over a set of east coast sites. The two most prominent features in the modeled budget are the increasing United States and decreasing Eurasian contributions when going from the west to the east coast. The tropospheric column amount of \(O_3^{U.S.}\) increases from an average of 4DU on the West Coast to 14 DU on the West Coast and \(O_3^{ASIA}\) decreases from 11 DU to 5 DU, respectively. This agrees with the LID analysis showing higher RCL contributions in the east. Longitudinal variations in the lightning and stratospheric contributions are less pronounced, because these tracers have a stronger north–south than west–east gradient. Model and laminae both show

![Figure 10](image-url)
increased boundary O$_3$ in the east, but the model terms are smaller owing to a lower PBLH. We also see that fires impacted ozone concentrations across the United States, with the effects most dominant in the eastern half of the country. [65] Acknowledgments. The authors acknowledge Mijeong Park and Simone Tilmes for valuable input to the manuscript and two anonymous reviewers who significantly contributed to improving the quality of this study. The authors acknowledge the ICARTT teams for providing an extensive and unique set of measurements. The work was supported by NASA grants EOS/03-0601-0145 and NNG04GA45. NCAR is operated by the University Corporation of Atmospheric Research under sponsorship of the National Science Foundation.

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