We thank the two reviewers for their comments. Reviewer comments are shown in red. Our responses are shown in blue, with new text in bold. Line numbers referenced here refer to the tracked-changes version of the document.

Anonymous Referee #1

1) I believe the research flights usually conduct spiral maneuverings and was wondering that the spiral profiles can be utilized the ozone the vertical distribution analysis presented in Section 6.

This is sometimes true, but was not the case for SEAC^{4}RS. We added the following text on page 8 line 15, and page 12, lines 5-6 to address this comment.

"Aircraft observations do not effectively probe that region of the atmosphere but ozonesondes do."

"and additional profile observations of the evolution of meteorological tracers, ozone and other long-lived chemical species in the boundary layer are essential to testing model parameterizations."

2) Maybe I missed something but the vertical ozone distribution with suppressed the top-down mixing presented in Figure 6 has substantial bias with observed ozone in the lower mixed layer in terms of values although the shape is reasonably simulated for the cloudy day simulation. Discussion on this would be beneficial.

We added the following text on page 9, lines 27-28,

"These specific days have free tropospheric **and surface** biases but our interest here is in the simulation of the PBL vertical gradient **which is unaffected by these biases**."

And the following text on Page 10, lines 18-22,

"The model underestimate of ozone above the mixed layer shown in Figure 6 cannot explain the missing model gradient because any additional entrained ozone will rapidly into a smooth vertical profile due to the fast mixing in the current scheme. Figure 5 shows several profiles where model ozone is overestimated above the mixed layer but the gradient below is unaffected."

Anonymous Referee #2

I think that the issue that this paper raises, the modeling of vertical gradients of ozone, is interesting and potentially important. However, there are too many shortcomings to the modeling to give a definitive analysis of the issue. An obvious shortcoming is that the lowest model level is 60 m while the measurements are at 10 m. Most other air quality models use much finer grid resolution near the surface.

It is true that regional models have finer grid resolution near the surface, but this is not true of global models. CAM-Chem (Lamarque et al, 2012) has the same vertical levels as GEOS-Chem when using assimilated meteorology. We correct for the coarseness of our lowest model level in Section 3. We add the following text to page 3, line 30.

"**,typical for global CTMs (i.e. Lamarque et al, 2012)"**

Furthermore, I strongly object to using different PBL schemes for meteorology and chemistry.

We perform a sensitivity test using both schemes within the GEOS-5 GCM and find very little difference in the ozone vertical structure in the boundary layer, as expected. See lines 1-2 on page 9, and line 1 on page 10 : "We conducted a sensitivity on-line simulation in the GEOS-5 GCM using the GEOS-Chem chemical module (Long et al., 2015) and including the GEOS-5 PBL mixing scheme of Lock et al. (2000), but found the same excessive downward mixing of ozone as in the off-line GEOS-Chem."

Not only has the PBL height been reduced for the chemistry but the Kz is also reduced and non-local term eliminated for the proposed correction. This is unjustified. If the same scheme does not give realistic results for both meteorology and chemistry, it should not be used for combined meteorology and air quality modeling.

The mixing depths from GEOS are purely diagnostic, since mixing is done online in GEOS-5. The non-local term is actually calculated online We add the following clarifying text to page 3, line 32 and page 4 line 3,

"The parameterization uses **diagnostic** mixing depths …"
"**These diagnostic** mixing depths…"

and remove the reference on page 4, line 18 ("daytime mixing depths (Zhu et al, 2016) to avoid confusion.

The other corrections and adjustments, such as reducing NOx emissions, that are made in order to get better results also call into question the validity of the study and its findings.

The other corrections and adjustments, such as reducing NOx emissions, are strongly supported by Travis et al, 2016. See page 4, lines 23-28.

P2 ln17-19: The statement: "we showed that the NOx National Emission Inventory (NEI) from the US Environmental Agency (EPA, 2015) was too high by 30-50 %." Is much too strong. All they should say is that this model with its many demonstrated errors better predicts ozone and NOx with a 30-40% emission cut. I do not believe that it's been proven that the NEI is over predicting NOx emissions by this amount.

We softened this language throughout, including changing the text on page 1, line 19 "After correcting for a 30-50 % NOx emission overestimate in the US EPA National Emission Inventory…" to

"Some of the model bias appears due to an overestimate of NOx emissions, and after correcting for this overestimate…"

and removed the discussion starting with "One the basis of observations…" on page 2.

P3 ln6-7: I don't understand how the mixing depth (h) can be defined by Kh values when according to Holtslag and Boville (1993) the Kh is a function of h which is defined by bulk Richardson number. Also, if the mixing depth is 40% too high, then this problem should be diagnosed and fixed. It is not reasonable to "correct" this in Geos-Chem. The result would be inconstancies between chemical concentration profiles and meteorological profiles which would lead to many errors in the chemical simulation including incorrect advection, errors in temperature and humidity especially above the GEOS-Chem h but below the GEOS h. I think that such "corrections" in AQ modeling should not be acceptable practice.

The mixing depth from the GEOS-5 simulation is purely diagnostic, they do not represent how mixing in the GEOS-5 system is actually calculated online. We add the following text on page 3, line 32,

"The parameterization uses **diagnostic** mixing depths…"

P3 ln20-22: More explanation and justification should be provided for the corrections and adjustments to PBL, emissions, and chemistry. The reader should not have to look up these other papers to know what was done.

We suggest that this type of referencing is standard practice.

The mixing height correction needs much better explanation. Even after reading Zhu et al. (2016) it is not clear how or if the Kh values were adjusted after the 40% mixing height correction. The fact that GEOS overpredicts mixing height so much indicates significant errors in surface fluxes or air temperature or winds which could adversely affect the AQ simulation.

See response above, the mixing depth from GEOS provided to GEOS-Chem is diagnostic only.

The emission adjustments are also not sufficiently explained or justified. Over predictions of NOx concentrations do not necessarily indicate emission over prediction, especially when the meteorology simulation has such large errors. The isoprene corrections are not explained at all. I think that these adjustments are very questionable. The fact that you get better results is not sufficient justification. It is likely that you are adding errors to compensate for other errors.

We remove references to the NOx overestimate and other previous work on page 2, lines 30-34, and page 3, lines 1-2, since it is not relevant to this study.

P3 ln33: More needs to be said than just "simply explained by numerical diffusion". An AQ model that cannot get the high end of ozone distribution is not very useful.

We removed the text "explained by numerical diffusion" and clarified our meaning on page 4, lines 24-25 by adding the following,

"…attributed to spatial averaging in the model…"

P4 ln 7-10: Were model values for u*, L, Vd, Ra used in the 10 m calculations or the "typical" values given in the text? In any case, this technique has its limitations and uncertainties that should be noted since ozone is not an inert tracer. The ozone profile between 60m and 10m is affected not only by deposition flux but also chemical reactions with NOx and VOCs that usually have the opposite gradients from ozone. It would be preferable to run both the meteorology and chemical models at finer vertical resolution near the ground so that the model explicitly simulates 10m concentrations.

We changed to text on page 5, line 20 from We combine… to
"For example,…"
to clarify that this is an example calculation for illustration purposes. We also add the following clarification on page 5, lines 23-24 to address the comment about chemical reactions.

"This assumes conservation of the vertical ozone flux in the 10-60 m column, a safe assumption since the transport time is only a few minutes."

P4 ln4-18: The large underprediction of cloud cover is another significant deficiency in this model. This, combined with the large overpredictions of mixing height, suggest that meteorology model is not sufficiently realistic for modeling boundary layer air quality.

Page 7, line 11 – we explain that missing cloud is a typical model problem not unique to GEOS.

Climate models in general tend to underestimate low cloud cover (Zhang, 2005; Mueller et al., 2006; Chepfer et al., 2008; Naud et al., 2010; Kay et al., 2012; Nam et al., 2012).

P7 ln1-2: This statement is way too strong considering the other errors in the model system!

We changed the sentence on page 9, lines 19-20 "This confirms that the model overestimate of surface ozone …" To:

"This confirms that **a source of** model **bias in simulating** surface …"

P7 ln9: Is the grey shading defined by model or observations?

The caption of Figure 6 states: "The grey shading in the bottom left panel indicates the cloud vertical extent as diagnosed from the ozonesonde relative humidity measurement."

P7 ln 12-15: There is asymmetry in the Hotslag&Boville93 scheme for potential temperature. However, how this is applied to chemical concentrations is not explained.

P7 ln22-24: Removing the non-local term actually removes the asymmetry which contradicts the findings of Wyngaard and Brost and others.

We add the following to clarify that we are arguing against counter-gradient transport for subsiding air masses on page 10, line 10.

"Additional non-local **(counter-gradient)…"**

Section 6: Another possible reason for the poor modeling of the ozone gradient could be that the model underpredicts the ozone concentrations above the mixing layer. On both days the ozone profile increases throughout the PBL and above the PBL. Having high concentration above the PBL to entrain would tend to increase concentrations in the upper part of the PBL. The greater gradient from the "corrected" GEOS-Chem is simply due to decreased mixing from an arbitrarily reduced Kz profile.

We added the following clarifying text on Page 10, lines 15-19,

"The model underestimate of ozone above the mixed layer shown in Figure 6 cannot explain the missing model gradient because any additional entrained ozone will rapidly into a smooth vertical profile due to the fast mixing in the current scheme. Figure 5 shows several profiles where model ozone is overestimated above the mixed layer but the gradient below is unaffected."

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Resolving ozone vertical gradients in air quality models

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Abstract. Models severely overestimate surface ozone in the Southeast US during summertime ~~and this overestimation has implications for the design of air quality regulations.~~. We use the GEOS-Chem model to interpret ozone observations over that region from aircraft (SEAC^{4}RS), ozonesondes (SEACIONS), and surface sites (CASTNET) in August-September 2013. ~~After correcting for a 30-50 % NO_x emission overestimate in the US EPA National Emission Inventory,~~Some of the model bias appears due to an overestimate of NO_x emissions, and after correcting for this overestimate we find that the model is unbiased relative to aircraft observations below 1 km. However, surface observations of maximum daily 8-h average (MDA8) ozone are still biased high in the model (averaging 48 ± 9 ppb) compared to observations (40 ± 9 ppb). The low tail in the observations (MDA8 ozone < 25 ppb) is associated with rain and is not captured by the model. The model bias decreases by 3 ppb when accounting for the subgrid vertical gradient between the lowest model level (centered 60 m above ground) and the measurement altitude (10 m). ~~The model underestimates low cloud cover, but this underestimate is insufficient to explain the remaining surface ozone bias because the response of model ozone to cloud cover is weaker than observed.~~ Midday ozonesondes at Huntsville, Alabama show mean ozone decreases ~~in ozone~~ from 1 km to the surface of 4 ppb under clear-sky and 7 ppb under low cloud, whereas the model decreases by only 1 ppb under both conditions. By contrast, potential temperature below 1 km is well-mixed in both the observations and the model. The observations thus imply a strong asymmetry between top-down and bottom-up mixing that is missing from GEOS-Chem and appears to be insufficiently represented in current air quality models. A sensitivity simulation ~~reducing~~using slower top-down eddy diffusion ~~and removing top-down non-local vertical transport of ozone~~ can reproduce the observed ozone gradients in the mixed layer.

1 Introduction

Ground-level ozone is harmful to human health and vegetation. Ozone is produced in the troposphere when volatile organic compounds (VOCs) and carbon monoxide (CO) are photochemically oxidized in the presence of nitrogen oxide radicals ($NO_x \equiv NO+NO_2$). Natural sources of VOCs, CO, and NO_x from the biosphere, wildfires, and lightning contribute an ozone background. Anthropogenic sources, mainly from fuel combustion, increase ozone levels. The chemistry involved is complex and non-linear. Air pollution control strategies rely on chemical transport models (CTMs) to identify the most effective emission reductions, but confidence in these models can be limited by their inability to reproduce ozone observations. The Southeast US in summer is a particularly problematic region, as models tend to greatly overestimate surface ozone levels (Lin et al., 2008; Fiore et al., 2009; Reidmiller et al., 2009; Chai et al., 2013; Brown-Steiner et al., 2015; Canty et al., 2015; Travis et al., 2016; Lin et al., 2017). An intercomparison of 21 models by Fiore et al. (2009) showed an average overestimate of 25 ppb in the Southeast in August. Here we use a combination of aircraft, ozonesonde, and surface observations in summer 2013 to better understand this overestimate and draw general insights for ozone air quality modeling.

The Southeast US in summer is characterized by relatively high NO_x emissions, very high emissions of biogenic isoprene, strong insolation, and frequent regional stagnation, all conditions favorable for producing elevated ozone. A range of explanations have been proposed for the model overestimates of ozone in that region including excessive ozone background over the Gulf of Mexico (Fiore et al., 2003), uncertainty in isoprene emissions and chemistry (Fiore et al., 2005; Horowitz et al., 2007; Squire et al., 2015), insufficient ozone dry deposition (Lin et al., 2008), missing halogen chemistry (McDonald-Buller et al., 2011), and excessive NO_x emissions in current inventories (Travis et al., 2016).

Detailed probing of the chemical environment of the Southeast US took place in summer 2013 with surface and aircraft observations from the Southeast Atmosphere Studies (SAS) in June-July (Carlton ~~et al.,~~and Co-authors, 2016), the NASA SEAC^{4}RS aircraft campaign in August-September (Toon et al., 2016), and the SEACIONS ozonesonde network (https://tropo.gsfc.nasa.gov/seacions/), adding to the long-term ozone air quality monitoring network. In previous work by Travis et al. (2016), we applied the GEOS-Chem CTM at $0.25^o \times 0.3125^o$ spatial resolution to the simulation of SEAC^{4}RS observations. ~~The standard model overestimated ozone by 12 ppb below 1.5 km altitude. On the basis of observations of NO_x and its oxidation products, together with national nitrate wet deposition data, we showed that the NO_x National Emission Inventory (NEI) from the US Environmental Agency (EPA, 2015) was too high by 30-50 %. This finding was subsequently supported by SAS observations (Miller et al., 2017). Previous studies had documented such a NO_x NEI bias in urban areas (Fujita et al., 2012; Yu et al., 2012; Brioude et al., 2013;~~

~~Anderson et al., 2014), but our results suggest that the bias is national in extent. After correcting this NO_x emission overestimate in GEOS-Chem, we found that we could match the SEAC^{4}RS aircraft observations below 1.5 km altitude, but the model mean bias against surface network observations was still 6 ± 14 ppb.~~We found that we could match the SEAC^{4}RS ozone observations below 1.5 km altitude with no significant bias, but the model mean bias against surface network observations was still 6 ± 14 ppb. Midday ozonesonde observations showed an increase of ozone with altitude in the lowest 1 km of the atmosphere that the model failed to capture. Here we examine the origin of this ozone vertical gradient and the implications for modeling surface ozone.

2 GEOS-Chem simulation

The GEOS-Chem simulation used here is as described by Travis et al. (2016). It is based on GEOS-Chem version 9.02 with detailed oxidant-aerosol chemistry (www.geos-chem.org) and is driven by assimilated meteorological data from the Goddard Earth Observing System – Forward Processing (GEOS-FP) product of the NASA Global Modeling and Assimilation Office (GMAO) using the GEOS-5.11.0 general circulation model (GCM). The GEOS-FP data have a native horizontal resolution of 0.25° latitude by 0.3125° longitude, with 72 levels in the vertical and a temporal resolution of 3 h (1 h for surface variables and mixing depths). This native $0.25^o \times 0.3125^o$ horizontal resolution is used in GEOS-Chem over North America and adjacent oceans (130° - 60° W, 9.75° - 60° N), with boundary conditions from a global simulation with 4° × 5° horizontal resolution.

The model representations of planetary boundary layer (PBL) mixing and ozone deposition are particularly relevant for this work. The PBL is defined as the column of air in contact with the surface on a daily basis. Observations show that the PBL over the Southeast US in summer extends to 1-3 km altitude and is capped by a semi-permanent subsidence inversion (Toon et al., 2016). Within the PBL, the unstable mixed layer driven by surface heating rises rapidly in the morning to reach a maximum altitude (mixing depth) of 1.7 ± 0.4 km by afternoon, as observed in SEAC^{4}RS by aerosol lidar (Zhu et al., 2016), before collapsing in the evening. The afternoon mixed layer is often capped by shallow fair-weather cumuli (cloud convective layer) constituting the upper part of the PBL.

The PBL is resolved in the GEOS-FP ~~data~~meteorological fields (and hence in GEOS-Chem) by 18 vertical levels below 3 km, and 8 below 1 km of approximately equal thickness. The lowest level is centered at 60 m above ground, typical for global CTMs (i.e. Lamarque et al, 2012). Turbulence in the mixed layer follows ~~a~~the clear-sky non-local parameterization from Holtslag and Boville (1993), as implemented in GEOS-Chem by Lin and McElroy (2010). The parameterization uses diagnostic mixing depths from the

GEOS-FP data, ~~which are diagnosed~~defined as the GCM ~~model~~ level above which the eddy diffusivity for heat (~~K_h~~) falls below a threshold value of 2 m^2 s^{-1} (McGrath-Spangler and Molod, 2014). ~~GEOS-FP~~These diagnostic mixing depths were found to be 40 % too high compared to the SEAC^{4}RS aerosol lidar data and ~~this was corrected in~~ were reduced accordingly for application of the Holstag and Boville (1993) parameterization in GEOS-Chem ~~simulations~~ (Zhu et al., 2016). ~~Additional turbulence due to cloud cooling at the PBL top is included in the GEOS-5.11.0 GCM following Lock et al. (2000) but not in the Holtslag and Boville (1993) scheme.~~

Ozone deposition in GEOS-Chem follows the resistance-in-series scheme of Wesely (1989) as implemented by Wang et al. (1998) and further modified for SEAC^{4}RS conditions by Travis et al. (2016). The mean ~~daytime (09:00-16:00 local)~~midday ozone deposition velocity over the Southeast US in the model is 0.~~7~~8 ± 0.3 cm s^{-1} during August-September 2013. Comparison with ozone deposition measurements by Finkelstein et al. (2000) at Duke Forest, North Carolina shows good agreement with a mean ozone deposition velocity of 0.8 cm s^{-1} during daytime. Aircraft eddy covariance flux measurements over the Ozarks forest during SEAC^{4}RS indicate a daytime ozone deposition velocity of 0.8 ± 0.1 cm s^{-1}, in agreement with the local GEOS-Chem value of 0.9 cm s^{-1} (Wolfe et al., 2015).

Detailed evaluations of GEOS-Chem with SAS and SEAC^{4}RS observations have been reported in previous studies. Initial evaluations led to corrections of ~~daytime mixing depths (Zhu et al., 2016),~~ NEI NO_x emissions (Travis et al., 2016~~),~~) and isoprene chemistry (Fisher et al., 2016; Travis et al., 2016). After these corrections, the model was found to be successful in reproducing surface and aircraft observations of aerosol composition (Kim et al., 2015b; Marais et al., 2016) and organic nitrates (Fisher et al., 2016), and aircraft observations of formaldehyde (Zhu et al., 2016), glyoxal (Miller et al., 2017), and ozone and its precursors (Travis et al., 2016; Yu et al., 2016). Travis et al. (2016) presented successful model comparisons to observations of (1) NO_x, (2) the relationship of ozone to NO_x oxidation products (a measure of the ozone production efficiency), and (3) isoprene nitrates and peroxides tracking the high-NO (ozone-producing) and low-NO pathways for isoprene oxidation. This evaluation lends some confidence in the model simulation of ozone chemistry.

3 Ozone frequency distributions in the mixed layer and surface air

Figure 1 (left panel) shows the frequency distribution of afternoon (12-18 local time) ozone concentrations in August-September 2013 measured by the SEAC^{4}RS DC-8 aircraft in the mixed layer at 0.4-1.0 km altitude. The mean ozone in the mixed layer as measured by the aircraft is 50 ± 10 ppb. The model sampled along the aircraft tracks is in good agreement (52 ± 10 ppb, r=0.54). The model does not capture the

observed extremes and this can be simply ~~explained by numerical diffusion~~attributed to spatial averaging in the model (Yu et al., 2016~~).~~) and targeted sampling by the aircraft. In particular, observations above 75 ppb are associated with focused sampling of urban (Houston) and agricultural fire plumes that may not be properly represented or located in the model (Travis et al., 2016).

Also shown in Figure 1 (right panel) is the frequency distribution of maximum daily 8-hour average (MDA8) ozone at the CASTNET regional air quality surface network for the same period (https://www.epa.gov/castnet). ~~CASTNET monitors air quality in rural areas and is therefore representative of regional air quality.~~ The mean MDA8 ozone measured at CASTNET sites is 40 ± 9 ppb, while the corresponding model mean sampled at the lowest grid level is 48 ± 9 ppb, for a high mean bias of 8 ± 9 ppb. ~~The model shows only a 4 ppb difference between the mixed layer sampled by the aircraft and the surface, but the observations imply a 10 ppb difference.~~

Part of the ~~surface~~ bias in the model ~~can be simply attributed~~comparison to ~~representation error. The~~ the CASTNET data can be corrected by taking into account the vertical gradient between the lowest model grid~~-point in GEOS-Chem is centered at~~ level (60 m ~~above~~) and the ~~local surface. The~~10-m altitude at which the CASTNET measurements are typically ~~at 10 m altitude. Implicit model ozone concentrations at 10 m can be inferred from the values at 60 m and the local ozone deposition velocity by applying the model~~ made. This gradient is effectively implied by the local model aerodynamic resistance (R_a) ~~between 60 and 10 m. The formula for this correction~~used to compute ozone dry deposition, and it is ~~presented in~~ readily extracted from the model output (Zhang et al~~.~~ (., 2012). ~~We combine~~For example, a typical friction velocity u^* = 0.4 ~~cm~~m s^{-1}~~,~~ and daytime Monin-Obhukov length $|L|$ = ~~40~~100 m~~, and~~ yields R_a = 0.07 s cm^{-1} between 60 and 10 m; combining this with an ozone deposition velocity of 0.8 cm s^{-1} ~~and find~~implies an ~~average~~ ozone decrease of approximately 3 ppb between ~~60 m and 10 m.~~ the two altitudes. This assumes conservation of the vertical ozone flux in the 10-60 m column, a safe assumption since the transport time is only a few minutes.

The right panel of Figure 1 ~~includes~~shows the ~~implied~~ model pdf of ozone concentrations at 10 m altitude, as inferred from the local model values of R_a~~, the~~. The model mean is 45 ± 8 ppb. The mean bias relative to observations decreases to 5 ± 9 ppb. We apply this correction in all following model comparisons.

The relatively low surface ozone measured at CASTNET sites in August-September 2013 reflects lower-than-average but not anomalous conditions. Figure 2 (top panel) shows the long-term trend of August-September MDA8 ozone in the Southeast US from 1987 to 2015. There is a 0.4 ppb a^{-1} decrease due to emission controls (Cooper et al., 2012). The 2013 data are 2 ppb below the linear fit to that long-term trend, and this may be due to cooler and wetter conditions than average (bottom panel).

The frequency distribution of MDA8 ozone at the CASTNET sites in Figure 1 shows a population of very low ozone concentrations below 25 ppb that the model does not capture at all. Previous work has suggested that this population could be due to tropical air transported from the Gulf of Mexico (Fiore et al., 2002; McDonald-Buller et al., 2011). ~~However, we find that the observed occurrence of low values is distributed across the Southeast and is not related to distance from the Gulf.~~ Four SEAC^{4}RS flights sampled air over the Gulf of Mexico and showed a median ozone concentration of 26 ppb below 1.5 km with the model in close agreement (Travis et al., 2016). Rain may be an additional factor driving low ozone occurrences in the Southeast, as discussed below.

4 Relationship to cloud cover and precipitation

We examined whether the 5 ± 9 ppb mean model bias in simulating MDA8 ozone at surface sites could be attributed to cloudy and rainy conditions. ~~Such a bias would not affect the comparison to aircraft observations, which generally targeted clear-sky conditions.~~ For this purpose we segregated the frequency distributions of ozone at CASTNET sites between (1) clear-sky~~,~~ days, (2) dry low-cloud ~~with no rain, and~~ days, (3) rainy days, and (4) other days. Low cloud in the observations was diagnosed by 20-minute averaged data at nearby airports from the automated surface observing system network (ASOS) sensors collected by the Iowa Environmental Mesonet (IEM) with 371 locations in the Southeast US (http://mesonet.agron.iastate.edu/request/download.phtml). Cloud data below 680 hPa are reported in oktas. Low-cloud ~~conditions~~days are defined here ~~as~~by an average daytime cloud fraction greater than 3 oktas (3/8 cloud fraction), excluding rainy conditions, and clear-sky ~~conditions~~days are defined as less than 0.5 oktas (0.5/8 cloud fraction). Rainy ~~conditions~~days are defined by daily average rainfall exceeding 6 mm in the PRISM data regridded to $0.25^o \times 0.3125^o$. Rainy ~~conditions~~days in the model are diagnosed in the same way as in the observations, while cloudy ~~conditions~~days are diagnosed from cloud fractions at different vertical levels below 680 hPa using the maximum random overlap scheme (MRAN) of Liu et al. (2006). In the remainder of this paper, "cloudy" conditions refer to ~~low-cloud conditions.~~dry low-cloud conditions. The "other days" category includes days with partial low cloud cover, high-altitude cloud cover, or light rain; they are not discussed further.

Figure 3 shows the segregated pdfs of surface ozone in the observations and the model. The days for a given sky condition are not necessarily the same in the observations and the model. We see that ozone decreases from clear to low-cloud to rainy conditions in both the observations and the model. The model meteorology is ~~heavily~~ biased toward clear-sky. The average daytime low-cloud cover across the entire

Southeast is ~~32 ± 9~~29 ± 8 % from the ASOS sensors but only ~~7 ± 3~~8 ± 2 % in the GEOS-FP data. The GEOS-5 GCM ~~underlying~~from which the GEOS-FP data are derived uses a critical RH to trigger cloud formation (Molod et al., 2012; Molod et al., 2015) and the cloud bias could result from the setting of this trigger (Naud et al., 2010). The low-cloud bias in GEOS-FP is also apparent in comparison to satellite observations from the Clouds and the Earth's Radiant Energy System (CERES) instruments (Minnis et al., 1995; Minnis et al., 2011).

Figure 4 compares CERES low-cloud fractions in August-September 2013 in the Southeast with GEOS-FP values. The mean observed low-cloud fraction is 21 ± 4 % as compared to 9 ± 2 % in GEOS-FP. The mean in-cloud optical depth is 45 ± 3 in both CERES and GEOS-FP. Thus the optical depth of low clouds in GEOS-FP is consistent with observations but the cloud frequency is too ~~small~~low. Table 1 shows that the underestimate in GEOS-FP cloud fraction is mainly due to a lack of fair-weather cumulus. Climate models ~~generally~~in general tend to underestimate low cloud cover (Zhang, 2005; Mueller et al., 2006; Chepfer et al., 2008; Naud et al., 2010; Kay et al., 2012; Nam et al., 2012). The GEOS-Chem underestimate of sulfate aerosol production in SEAC^{4}RS, previously attributed by Kim et al. (2015) to a missing SO_2 oxidation pathway involving Criegee biradicals, could instead be due to insufficient cloud processing.

We see from Figure 3 that the mean bias between model and observed surface ozone vanishes when only clear-sky conditions are considered, but persists under low-cloud and rainy conditions. Thus the bias cannot be simply attributed to insufficient cloud in the model. If we apply the observed frequencies of clear-sky, cloudy, and rainy days from Figure 3 to the model mean ozone concentrations for each category, we decrease the mean model MDA8 ozone bias at CASTNET sites by only 1 ppb. This is because of the weaker response in the model to cloud cover and rain (4 ppb relative to clear-sky) than observed (7 ppb and 11 ppb respectively). Kim et al. (2015a) previously observed a 1 ppb decrease in ozone per 10 % increase in cloud cover over the contiguous United States, and found that their model response to cloud (from the NOAA National Air Quality Forecast) was approximately half that, a similar bias to our model. We conducted a model sensitivity study with the low cloud fraction adjusted to the mean observed value of ~~32~~29 % from the ASOS observations~~. This simulation perturbs~~, perturbing model photolysis but ~~does~~ not ~~modify~~modifying other meteorological variables. We find an ozone decrease of only 1 ppb and thus photolysis appears to be only a minor effect. ~~Previous urban-scale model studies have found larger cloud effects on surface ozone from changes in photolysis (Pour-Biazar et al., 2007;Tang et al., 2015), but larger-scale studies find a weaker effect consistent with our findings (Voulgarakis et al., 2009). SEAC^{4}RS observations of actinic fluxes in SEAC^{4}RS show cloud effects consistent with radiative transfer models (Ryu et al., 2017).~~

The largest difference between model and observations occurs on rainy days. Rainy days account for over half of all days with observed MDA8 ozone below 25 ppb. ~~Thus, the~~The inability of the model to reproduce the low tail in the observed ozone distribution appears to be due in large part to positive bias on rainy days. ~~This~~This cannot be due to wet scavenging, considering the low solubility of ozone in water, but could reflect vertical stratification from surface evaporative cooling that is not properly captured in the model. ~~The effect of precipitation on ozone through wet scavenging is negligible.~~ Rainfall or dew may also enhance the non-stomatal component of ozone dry deposition (Finkelstein et al., 2000;~~-~~Altimir et al., 2006;~~-~~Potier et al., 2017) but the mechanism for this enhancement is uncertain~~ and is not included in the model~~.

5 Ozone vertical profiles at Huntsville

The analysis above suggests that ~~insufficient model response to cloud conditions and rain~~excessive vertical mixing in the model below 1 km could be the cause of the remaining surface ozone bias. ~~We examined whether this could be related to excessive vertical mixing in the model by using~~Aircraft observations do not effectively probe that region of the atmosphere but ozonesondes do. We therefore turned to the SEACIONS ozonesonde data from Huntsville, Alabama (31 launches at 10-13 local time during August-September 2013; https://tropo.gsfc.nasa.gov/seacions/). The ozonesondes measure ozone at approximately 5-m resolution from the surface through the stratosphere but the 5-m resolution data are ~~averaged and reported at coarser resolution to achieve reasonable noise statistics. We interpolate~~noisy. Here we average the data ~~to~~on the model vertical ~~resolution (approximately 130 m)~~grid and down to 10 m above ground. Huntsville is a small-sized city at 200-m ASL with forested land cover and little topography, and the ozonesonde data can be viewed as regionally representative (Newchurch et al., 2003).

The top panel of Figure 5 compares the time series of ozonesonde observations at Huntsville up to 12 km altitude to the corresponding GEOS-Chem values. The model successfully captures the large-scale features in the free troposphere above 3 km with no significant bias (1 ± ~~14~~12 ppb). A comparison of the modeled and observed mean profile at Huntsville is shown in Travis et al. (2016).

The bottom panel of Figure 5 shows the ozonesonde vertical profiles with more resolution below 3 km. As for the CASTNET data, we infer model ozone at 10 m for each ozonesonde launch from the simulated concentration at the lowest model level (60 m) and local values of the aerodynamic resistance and ozone deposition flux. For the ensemble of ozonesonde launches, we find a mean 10-60 m aerodynamic resistance of 0.04 s cm^{-1} and an ozone deposition velocity of 0.8 cm s^{-1}, resulting in a mean model difference of 1~~.6 ± 0.5~~ ± 1 ppb ozone between 60 and 10 m. This is less than the mean 3 ppb effect found for MDA8 ozone at

CASTNET sites (Section 3), because the MDA8 8-h averaging window includes periods with greater stability than midday. The implied model gradient at Huntsville is consistent with the mean observed difference of ~~0.7 ± 0.9~~2 ± 1 ppb in the ozonesonde data between 60 and 10 m.

We find that surface (10 m) ozone at Huntsville shows similar behavior to the CASTNET network. Mean observed surface ozone from the ozonesondes (43 ± ~~12~~13 ppb) compares well with the observed CASTNET MDA8 ozone shown in Figure 1. Ozone is lowest on rainy days (n=6, 36 ± 12 ppb), diagnosed from the PRISM data, similar to our finding at CASTNET sites in Figure 3. The lowest ozone (18 ppb) on September 21 occurred on the day with the most rainfall in the time series (50 mm), in air originating from the Gulf of Mexico. We do not find a significant difference in surface ozone at Huntsville between cloudy conditions (n=14, 43 ± 13 ppb) and clear conditions (n = 5, 44 ± 13 ppb), but this may be due to the small sample size. The modeled surface ozone for the ozonesonde launches is 48 ± 9 ppb and the mean model bias is 5 ± 9 ppb (r=0.67), same as at the CASTNET sites.

The mean ozone decrease from 1 km down to the surface is steeper in the observations (6 ± 5 ppb) than in GEOS-Chem (1 ± 3 ppb) and agrees well with the implied gradient shown in Figure 1 between the SEAC^{4}RS aircraft and CASTNET surface observations. The mean observed decrease is 4 ± 5 ppb on clear days (n=5) and 7 ± 6 ppb on cloudy days (n=14) but this difference is not statistically significant (p = 0.2). The model decrease is less than 1 ppb on either clear (n=15) or cloudy (n=3) days. This confirms that ~~the~~a source of model ~~overestimate of~~bias in simulating surface ozone is due to underestimate of the gradient in the lowest km, particularly under cloudy conditions but also under clear-sky conditions.

6 Top-down PBL mixing of ozone

Figure 6 shows ozone and potential temperature profiles on two typical days where model and observations agree on the clear and low-cloud classification. These specific days have free tropospheric and surface biases but our interest here is in the simulation of the PBL vertical gradient which is unaffected by these biases. On the clear-sky day (Sep 4), the model is well-mixed throughout the lowest km but the observations show a vertical gradient, particularly in the lowest 300 m. The potential temperature profile is well-mixed in both the observations and model. On the cloudy day (Aug 16) there is a steady gradient below 1 km in the observations that the model does not reproduce. The grey shading on Figure 6 shows the convective cloud layer in the upper part of the PBL and again the model does not capture the gradient in that layer. We conducted a sensitivity on-line simulation in the GEOS-5 GCM using the GEOS-Chem chemical module (Long et al., 2015) and including the GEOS-5 PBL mixing scheme of Lock et al. (2000),

but found the same excessive downward mixing of ozone as in the off-line GEOS-Chem. The inconsistency between potential temperature, which is well-mixed in both the observations and the model, and ozone, for which the observations show a vertical gradient absent from the model, suggests a bottom-up vs. top-down asymmetry in vertical mixing that is missing from both the Holtslag and Boville (1993) and Lock et al. (2000) PBL schemes.

Wyngaard and Brost (1984) used large-eddy simulations to investigate top-down vs. bottom-up differences in eddy diffusion parameterizations of PBL mixing. They show that eddy diffusion coefficients (K_z) for top-down transport should be about 60 % lower than for bottom-up transport, due to the role of surface-driven buoyant plumes in contributing to bottom-up transport. Additional non-local (counter-gradient) vertical transport in PBL schemes, developed originally for heat flux, is mostly intended to resolve buoyant plumes (Deardorff, 1966; Holtslag and Moeng, 1991) and should be formulated differently for top-down transport (Xie and Fung, 2014). We conducted a sensitivity simulation ~~for the two sample days of Figure 6~~ where the Holtslag and Boville (1993) mixing scheme was modified for ozone to decrease K_z by 60 % and remove the non-local term. As shown in Figure 6, this fully corrects the ozone gradient~~.~~ on the two sample days of Figure 6. The model underestimate of ozone above the mixed layer shown in Figure 6 cannot explain the missing model gradient because any additional entrained ozone will rapidly into a smooth vertical profile due to the fast mixing in the current scheme. Figure 5 shows several profiles where model ozone is overestimated above the mixed layer but the gradient below is unaffected.

The need for asymmetric top-down vs. bottom-up PBL mixing for air quality applications has long been recognized (Pleim and Chang, 1992), and is presently implemented in the EPA Community Multiscale Air Quality (CMAQ) and in the Comprehensive Air ~~Quality~~quality Model with Extensions (CAMx) using the Asymmetrical Convection Model version 2 (ACM2) (Pleim, 2007a, b). The ACM2 has the same eddy diffusion component as Holtslag and Boville (1993) but a different form of ~~non local~~nonlocal parameterization. It treats upward convective transport with a ~~non local~~nonlocal buoyant component, but downward transport as a slower, layer-by-layer process. However, comparisons to ozonesonde and aircraft observations suggest that ACM2 still has excessive mixing for ozone down to the surface (Tang et al., 2011; Goldberg, 2015).

7 Conclusions

Models overestimate summertime surface ozone in the Southeast US. ~~We showed previously using the GEOS-Chem model that~~Some of this ~~overestimate is due in part~~bias may be attributed to an overestimate of NO_x

emissions in the US EPA National Emission Inventory (Travis et al., 2016). However, midday ozonesondes also show a large vertical gradient of decreasing ozone below 1 km altitude that is at odds with the strong mixing expected from models. Here we investigated the cause of this discrepancy through the combined analysis of August-September 2013 ozone observations from aircraft (SEAC^{4}RS), surface (CASTNET), and ozonesondes (SEACIONS).

Statistical comparison of the GEOS-Chem model to aircraft observations of ozone below 1 km shows no significant bias (50 ± 10 ppb observed, 52 ± 10 ppb model), but the maximum daily 8-h average (MDA8) surface ozone at CASTNET sites is overestimated by 8 ± 9 ppb (40 ± 9 ppb observed, 48 ± 9 ppb model). ~~The~~ Part of that discrepancy is simply due to a subgrid ozone gradient between 60 m altitude (lowest model grid level ~~is centered at 60 m above ground while~~) and 10 m (where the ~~observations~~measurements are ~~at 10 m; thus~~typically made). Increasing vertical grid resolution is not necessary as a subgrid correction ~~must~~can be readily applied using the model aerodynamic resistance to dry deposition~~.~~ under the assumption of uniform vertical flux. This correction, which is generally ignored in models, averages 3 ppb in our case~~; it is relatively large because the MDA8 8-hour window can include convectively stable conditions.~~ The resulting model ozone at 10 m altitude is 45 ± 8 ppb, still significantly higher than observed. August-September 2013 was cooler and wetter than average but the effect on ozone was small, averaging 2 ppb at CASTNET sites. The low tail of observed MDA8 ozone (<25 ppb) was largely associated with rainy conditions.

The GEOS-FP meteorological data driving GEOS-Chem are biased toward clear-sky, and this bias would be expected to contribute to the overestimate of ozone. However, we find that the model MDA8 ozone is only 4 ppb lower under low-cloud and rainy conditions than in clear sky, whereas in the observations that difference is 7 ppb under low-cloud conditions and 11 ppb under rainy conditions. Midday ozonesonde data from Huntsville, Alabama show a 6 ppb decrease from 1 km to the surface (4 ppb under clear-sky, 7 ppb under low cloud), whereas the model shows only a 1 ppb decrease. Thus the model has excessive top-down mixing of ozone; this is seen using both the Holtslag and Boville (1993) PBL scheme in the off-line GEOS-Chem and the Lock et al. (2000) scheme in the GEOS-5 GCM. By contrast, potential temperature shows similar strong vertical mixing in the observations and the model. Bottom-up mixing (as for heat) is known to be faster than top-down mixing (as for ozone) because of buoyant plumes but the two above schemes do not include this asymmetry. The ACM2 scheme (Pleim, ~~2007a, b~~2007b, a) includes this asymmetry, but previous evaluations suggest that this scheme still has excessive downward mixing of ozone. We find in a sensitivity simulation that decreasing top-down eddy diffusion following Wyngaard and Brost (1984) and suppressing top-down non-local vertical transport allows GEOS-Chem to successfully simulate the observed ozone gradient in the mixed layer. More work is needed to describe the top-down mixing of

ozone for air quality applications. and additional profile observations of the evolution of meteorological tracers, ozone and other long-lived chemical species in the boundary layer are essential to testing model parameterizations.

8 Data availability

Cloud data from the Automated Surface Observing System (ASOS) can be downloaded here: http://mesonet.agron.iastate.edu/request/download.phtml. PRISM temperature and precipitation data can be downloaded here: http://www.prism.oregonstate.edu/historical/. The SEACIONS ozonesonde data can be accessed here: https://tropo.gsfc.nasa.gov/seacions. The CERES cloud fraction and cloud optical depth observations are available at http://doi.org/10.5067/Aqua/CERES/ISCCP-D2LIKE-MERG00_L3.003. The SEAC^{4}RS aircraft data can be found here: https://www-air.larc.nasa.gov/missions/seac4rs/DC8-Extract.html. CASTNET data are available ~~at~~here: https://www.epa.gov/castnet.

9 Competing Interests

The authors declare that they have no conflict of interest.

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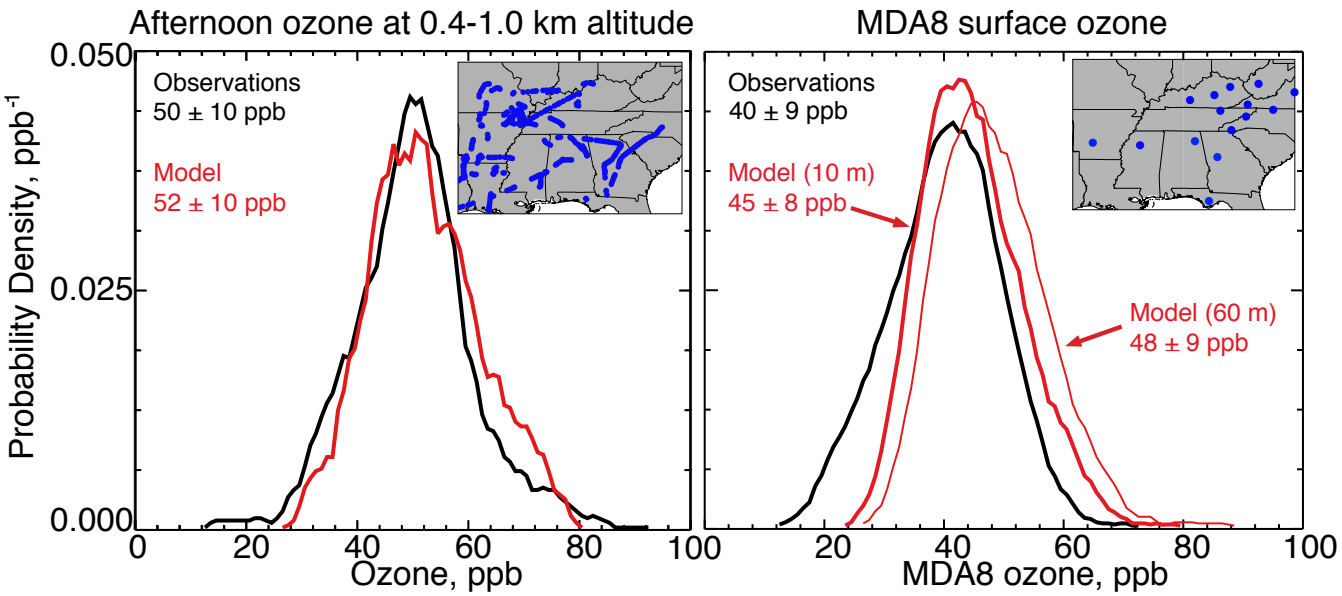
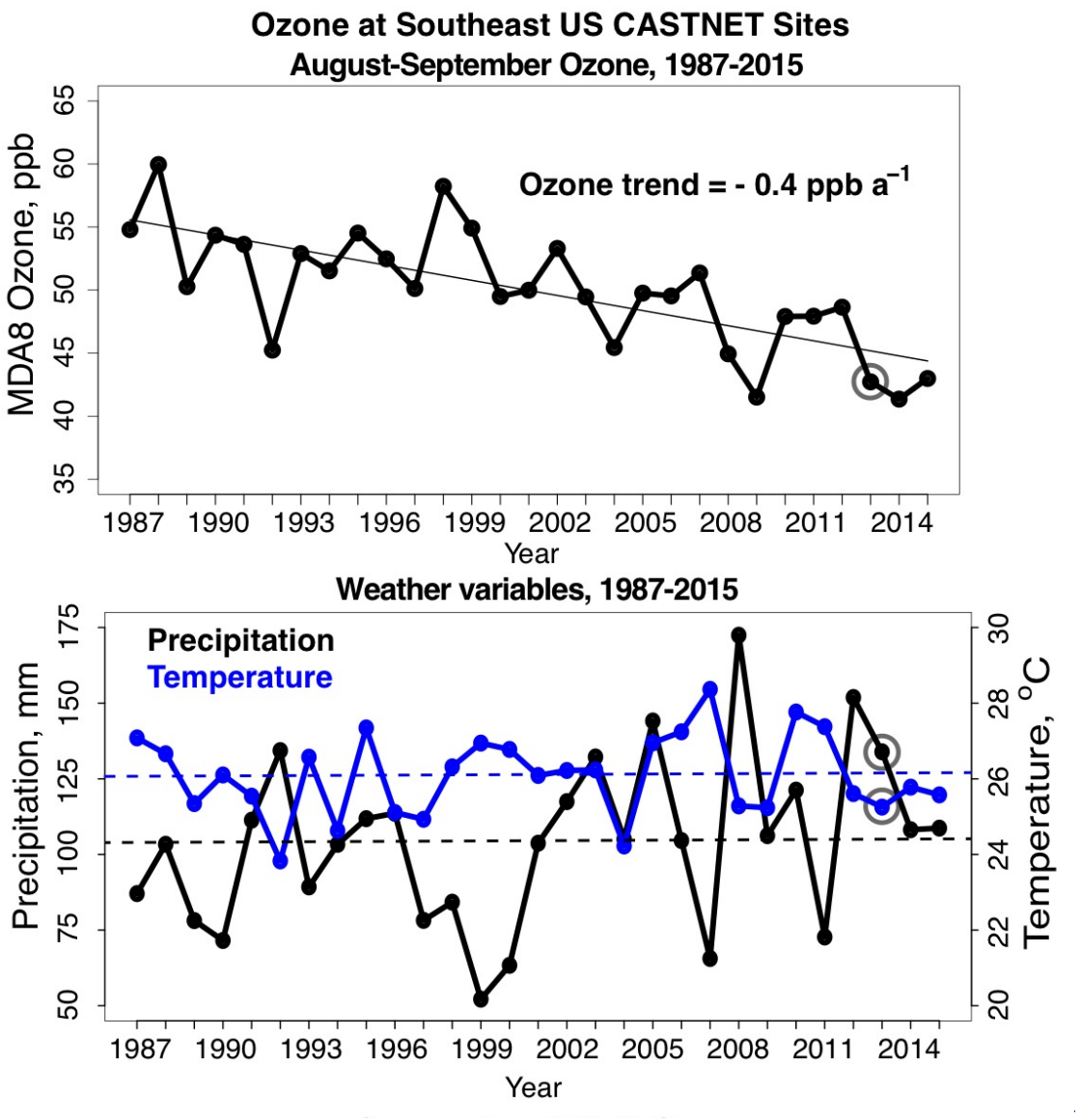


Figure 1 – Probability density functions (pdfs) of ozone concentrations in the Southeast US (94.5-80 W, 29.5-38 N, maps inset with sampling locations indicated) in August-September 2013. Mean and standard deviation are given in the legend for each pdf. The left panel shows afternoon (12-18 local time) mixed layer values measured by the SEAC^{4}RS DC8 aircraft at 0.4-1.0 km altitude (n = 370). The right panel shows maximum 8-hour daily average (MDA8) near-surface values (about 10 m above the local surface) measured at the CASTNET network of 15 rural sites. Also shown are the corresponding GEOS-Chem model pdfs sampled at the locations and times of the observations. The thin red line in the right panel is the model pdf for the lowest model level (centered at 60 m above ground). The thick red line is the implied model value at 10 m above ground (see text).


Ozone at Southeast US CASTNET Sites
August-September Ozone, 1987-2015
MDA8 Ozone, ppb
Ozone trend = - 0.4 ppb a^{-1}
Year
Weather variables, 1987-2015
Precipitation
Temperature
Precipitation, mm
Temperature, °C
Year

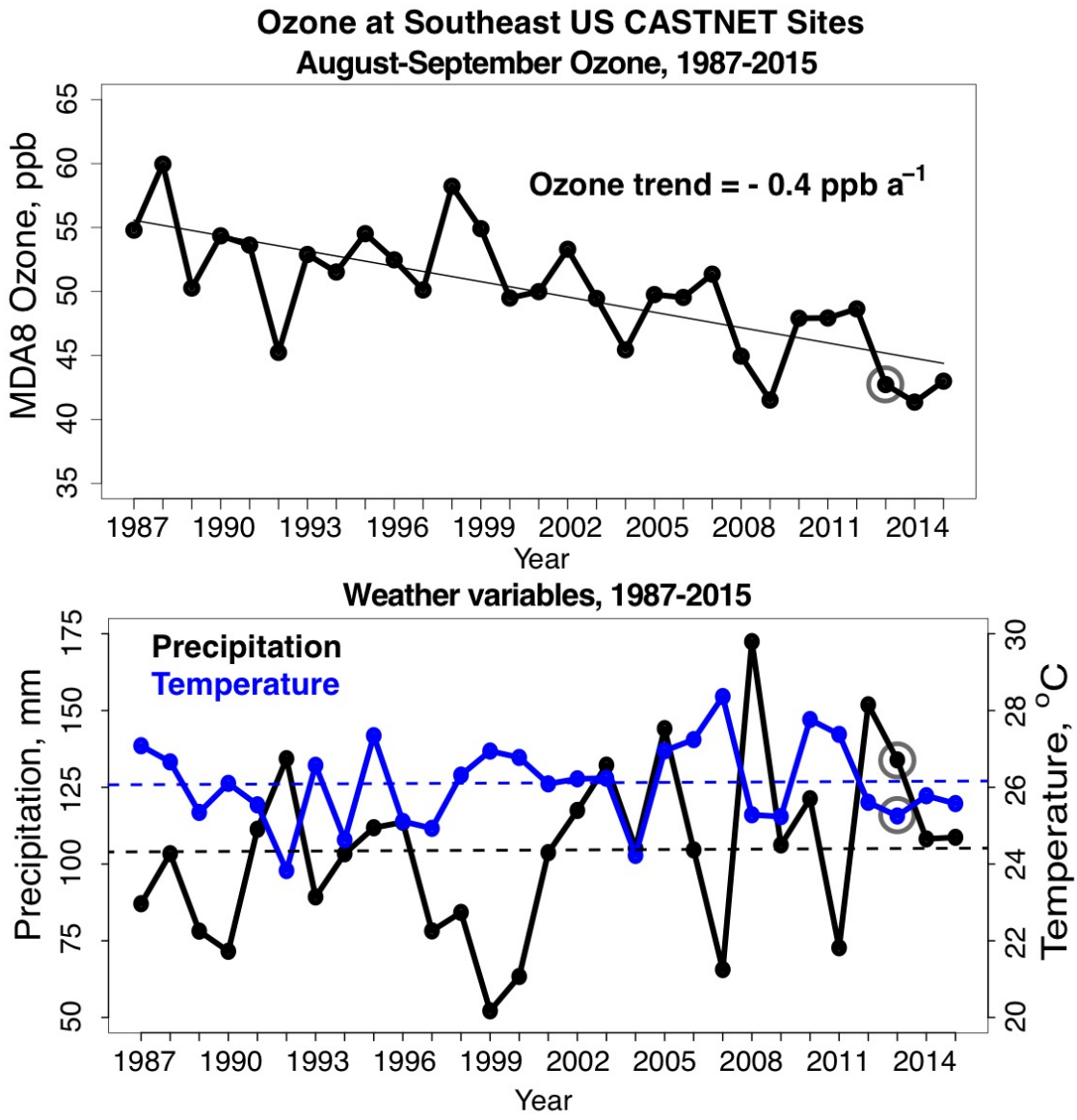


Figure 2 – Ozone and weather variables averaged over the 15 Southeast US CASTNET sites of Figure 1~~,~~ and over August-September 1987-2015. The top panel shows the ~~1987-2015~~ trend ~~in August-September MDA8 ozone, with~~ and linear regression ~~indicated.~~in MDA8 ozone. The bottom panel shows ~~1987-2015 August-September average~~mean daily temperature (~~blue) and~~ average of ~~August and September total~~daily minimum and maximum temperatures) and precipitation ~~(black)~~ from the PRISM Climate Group datasets (http://www.prism.oregonstate.edu). Dashed lines indicate the 1987-2015 mean values. ~~Grey circles~~Circles highlight 2013.

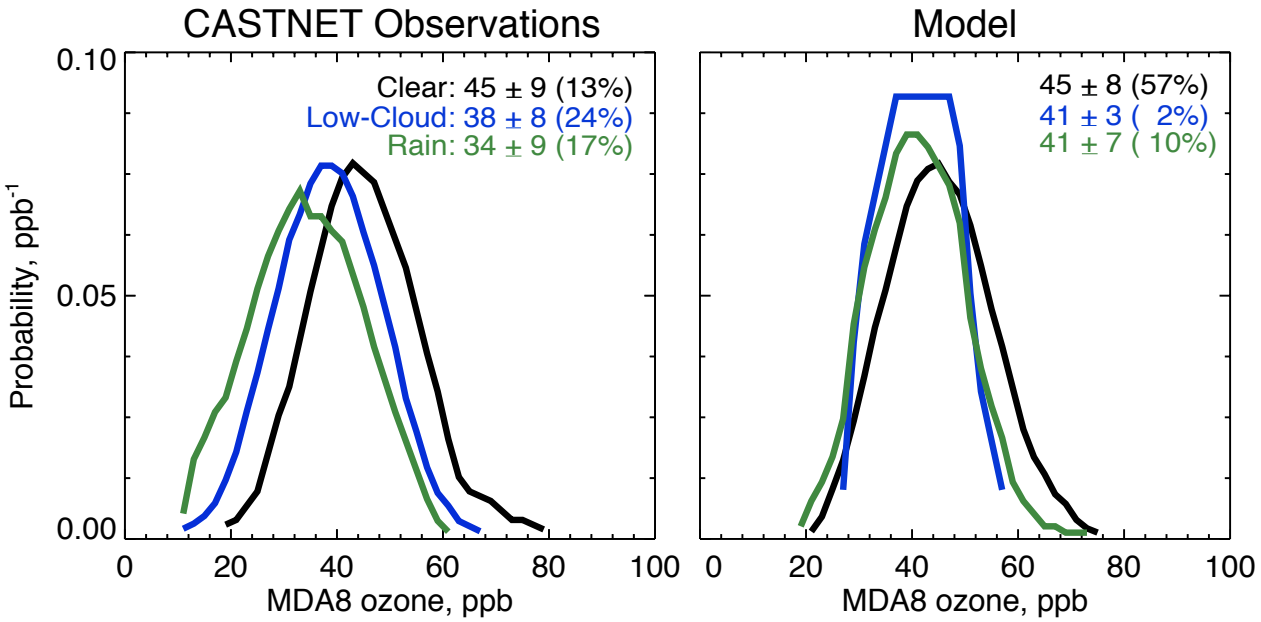


Figure 3 – ~~Maximum daily 8-h average (MDA8) ozone probability~~Probability density functions (pdfs) of MDA8 ozone at CASTNET sites in the Southeast US in August-September 2013. The pdfs are segregated between clear-sky, low cloud, and rainy conditions as described in Section 4. The model pdfs include the correction for 10 m ozone described in Section 3. For each sky condition, the mean ozone and its standard deviation are given inset with the frequency of that sky condition in parentheses. The frequencies do not add up to 100 % because partial low-cloud cover (0.5-3 oktas) is not included.

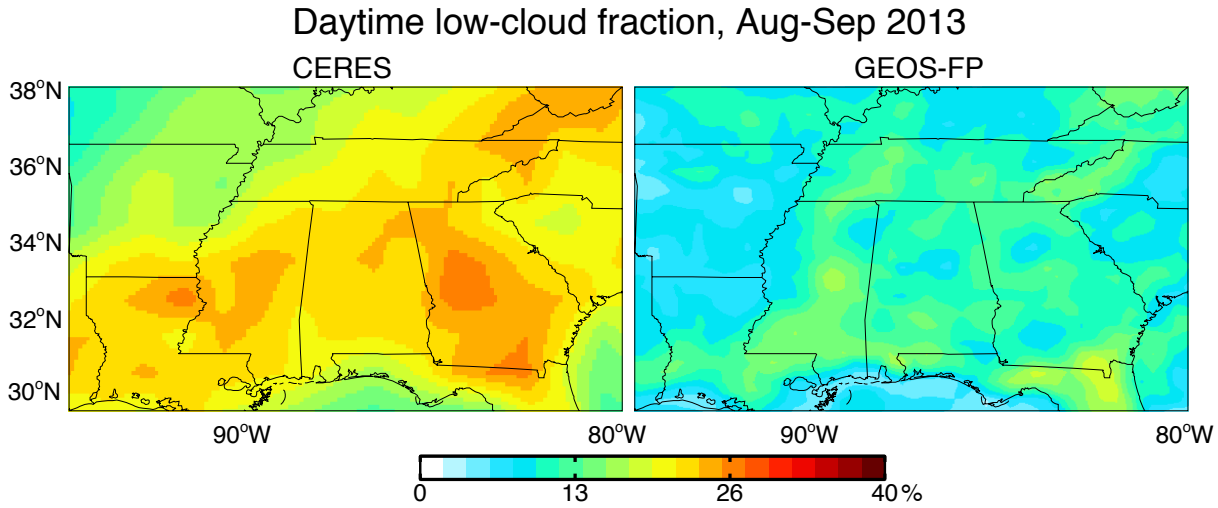
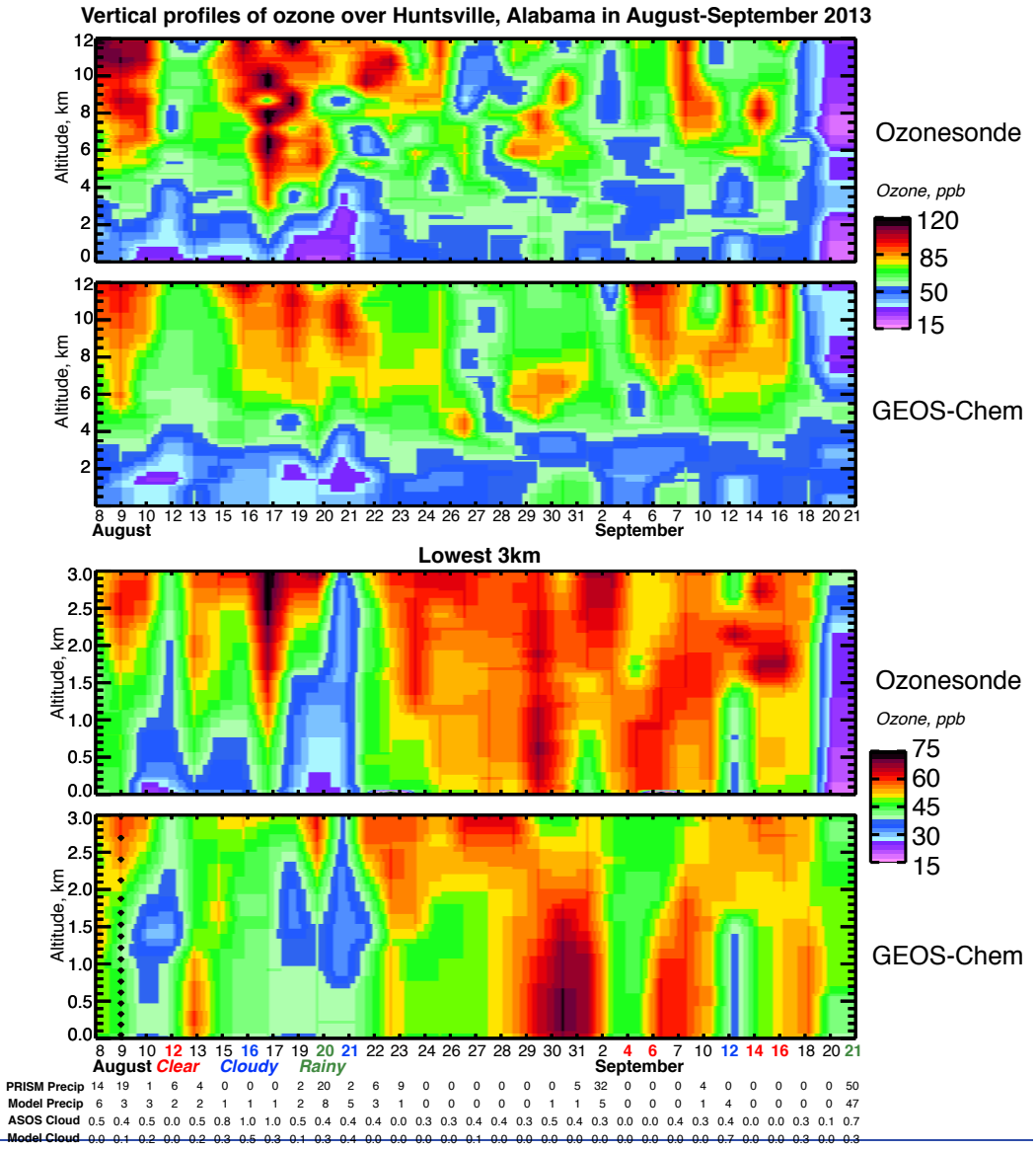


Figure 4 – Average daytime low-cloud fraction (below 680 hPa, 9-17 local time) in August-September 2013. The left panel shows satellite data from the CERES ISCCP-D2like product (CERES Science Team, Hampton, VA, USA: NASA Atmospheric Science Data Center, accessed May, 2016, at http://doi.org/10.5067/Aqua/CERES/ISCCP-D2LIKE-MERG00_L3.003A). This merged product combines 3-hourly, daytime cloud properties from Terra and Aqua on the Moderate Resolution Imaging Spectroradiometer (MODIS) and geostationary meteorological satellites mapped on a 1°×1° grid (Minnis et al., 2011). The right panel shows data from GEOS-FP, where cloud fraction and in-cloud optical depth are provided for each model level, using the maximum random overlap scheme (MRAN) to derive total cloudiness below 680 hPa (Liu et al., 2006).

Table 1 - CERES and GEOS-FP low-cloud frequencies in the Southeast US.[1]

	CERES Low-Cloud		GEOS-FP Low-Cloud	
	Fraction	**Optical Depth**	**Fraction**	**Optical Depth**
Cumulus	11%	1.6	<1%	1.3
Stratocumulus	9%	8	6%	13
Stratus	1%	36	3%	31

[1]Data from August-September 2013 for the domain of Figure 4. The classification of low-cloud type is done by CERES according to optical depth below 680 hPa: cumulus (0.02-3.55), stratocumulus (3.55-22.63), and stratus (22.63-378.65).



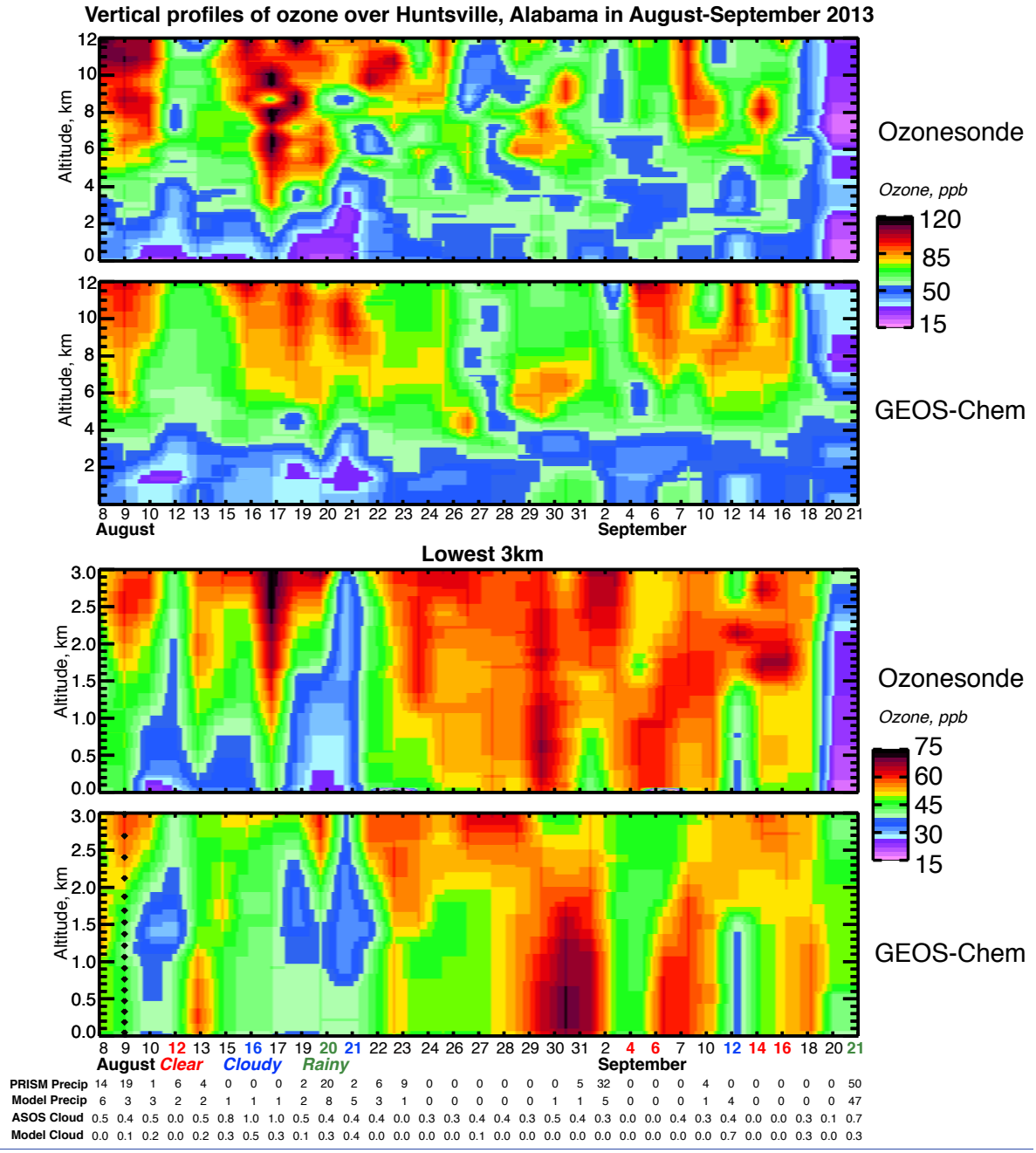


Figure 5 – Midday vertical profiles of ozone over Huntsville, Alabama (35.3 N, 86.6 W) for the full troposphere (up to 12 km, top) and for the PBL (up to 3 km, bottom). Ozonesonde observations (n = 31 during 08 August – 21 September 2013, launched at 10-13 local time) are compared to GEOS-Chem model profiles sampled at the same location and times. Values are interpolated in time between launches and are not intended to resolve the diurnal cycle of ozone. The ASOS low-cloud fraction at the time of the ozonesonde launch and daily PRISM precipitation (mm d^{-1}) are also shown along with the corresponding model values. Clear, low-cloud, and rainy days following the criteria of Section 4 are labeled in color in the abscissa. The black diamonds on the bottom plot show midpoints of the model grid levels.

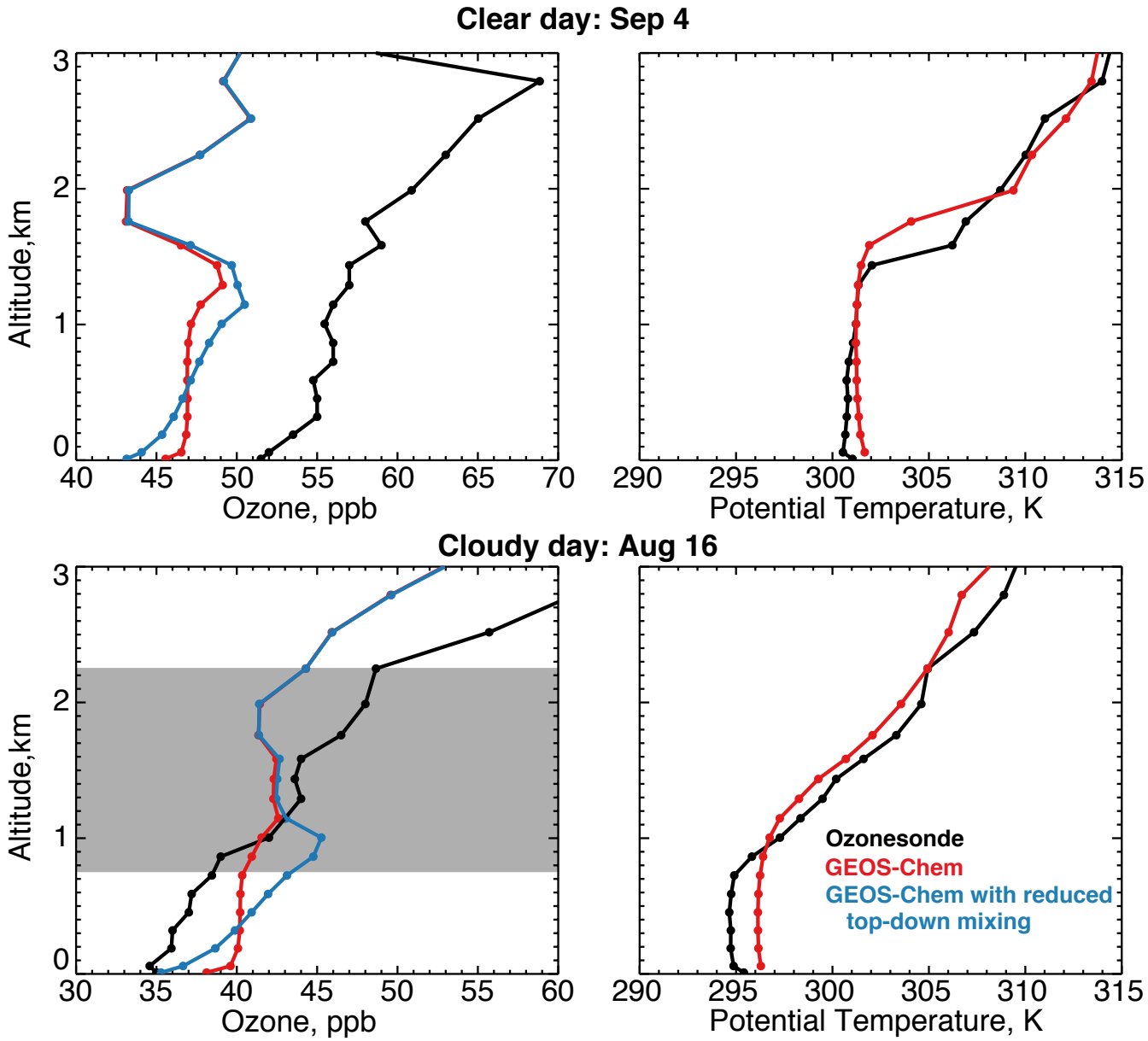


Figure 6 - Vertical profiles of ozone concentrations and potential temperature at the SEACIONS Huntsville site on representative clear-sky and low-cloud days from the record of Figure 5. The left panels include the sensitivity simulation with reduced top-down mixing in the mixed layer as described in Section 5. The grey shading in the bottom left panel indicates the cloud vertical extent as diagnosed from the ozonesonde relative humidity measurement.