Impact of the Vertical Mixing Induced by Low-level Jets on Boundary Layer Ozone Concentration

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1st submitted on June 5, 2012

Revision on 9/11/2012 11:10 AM

Abstract

After sunset, a stable boundary layer (SBL) develops close to the ground, while the upper region of the daytime mixed layer becomes the residual layer (RL). Mixing between the SBL and RL is often quite limited and the RL is thought to be a reservoir for daytime mixed-layer pollutants under such conditions. However, ozone (O_3) profiles observed in Maryland, U.S. suggest that the RL is not always a reservoir of O_3 in that region. Nocturnal low-level jets (LLJs) and/or other mechanisms are speculated to enhance vertical mixing between the SBL and RL, which influences the vertical O_3 redistribution.

Nocturnal surface O_3 maxima, a RL with reduced O_3 levels, and a concurrent strong LLJ were observed in Maryland on the night of August 9-10, 2010. Surface O_3 measurements in the region and three-dimensional air quality simulations suggest that horizontal advection cannot explain the nocturnal O_3 maxima and concurrent decrease of O_3 levels within the RL. A sensitivity study with a single column (1D) chemistry model was performed to investigate the role of LLJs in generating turbulent mixing within the nighttime boundary layer and to identify related impacts on O_3 concentrations at night and on the following day. The strong shear associated with the LLJ enhanced turbulent mixing and weakened the decoupling of the RL and SBL substantially. Ozone was actively mixed down from the RL to the surface, causing secondary nocturnal surface O_3 maxima. Near the surface, O_3 was efficiently removed by chemical reactions and dry deposition, which resulted in lower O_3 peak values on the next day.

1. Introduction

Following the traditional picture of the diurnal evolution of the atmospheric boundary layer, radiational cooling after sunset results in the development of a stable boundary layer (SBL) near the surface that is typically quite shallow. Above the SBL is a residual layer (RL) with characteristics similar to those of the previous day's mixed layer (Stull, 1988). In the absence of strong disturbances, mixing and dispersion of pollutants between the RL and SBL become limited, and within the RL the concentration of pollutants remains at similar levels as in the mixed layer before its decay, which is why the RL is often viewed as a reservoir of pollutants (Stull, 1988). The pollutants trapped within the RL from the previous day can be entrained downward into the re-developing mixed layer on the following day. In places such as the northeastern United States, such downward mixing of ozone (O_3) and its precursors is shown to contribute substantially to ground-level O_3 buildup in the morning in addition to chemical production (Zhang et al., 1998; Zhang and Rao 1999). The downward transport of the RL O_3 in the morning also contributes to the maximum O_3 levels observed near the surface during daytime (Neu et al., 1994; Aneja et al., 2000; Yorks et al., 2009; Morris et al., 2010; Tong et al., 2011). Accurate information regarding the RL O_3 is thus critical for correctly simulating the daytime O_3 near the surface (Herwehe et al., 2011). Due to its relative inaccessibility, the actual detection of the properties of the RL at high temporal and spatial scales has been limited in the past. Recent field experiments (e.g., Balsley et al., 2008) showed that the classical view of a quiescent RL may have been oversimplified. Sporadic turbulence exists at night, weakening the decoupling between the RL and SBL, and the vertical mixing in the nighttime boundary layer may be significant, even compared to that in the daytime convective boundary layer (Poulos et al., 2002; Tjernstrom et al., 2009). Enhanced nighttime turbulence may be triggered by mesocale motions

such as low-level jets (LLJ), Kelvin-Helmholtz instabilities, gravity waves, wake vortices, and density currents (Sun et al., 2002, 2003; Salmond and McKendry, 2005; Fritts et al., 2009). Such intense turbulence can affect the vertical structure of the nighttime boundary layer and vertical distribution of pollutants. The view of the quiescent RL as a reservoir of pollutants may be challenged under such conditions. Recent observations (Hu et al., 2012) have suggested that the RL is leaky at times, i.e., active vertical exchange of air exists between the RL and the SBL. As a result, the O_3 levels in the RL may be highly variable and surface O_3 may not decrease as fast as anticipated based on the assumption of having a completely decoupled RL and SBL. In some cases, there are even secondary nighttime O_3 maxima reported, which were typically associated with periods of enhanced mixing (Corsmeier et al., 1997; Reitebuch et al., 2000; Salmond and McKendry, 2002; Talbot et al., 2005; Hu et al., 2012). Therefore, it is important to further investigate the dynamics and mixing of nocturnal boundary layers to better understand the temporal variability, absolute levels, and deposition rates of surface layer O_3 concentrations.

In Beltsville, Maryland (MD), nighttime vertical O_3 profiles have been measured during the summertime since 2004 (Yorks et al., 2009; Hu et al., 2012). Beltsville is located between Washington, D.C. and Baltimore, MD, in the middle of the Mid-Atlantic urban corridor of the United States. Heavy emissions of O_3 precursors and favorable meteorological conditions frequently lead to extreme O_3 events in this area (Ryan et al., 1998). Within the RL, O_3 levels at the Beltsville site at times resemble those found in the free troposphere with concentrations that are significantly lower than those in the previous day's atmospheric mixed layer. Ozone in the RL inherited from the daytime mixed layer appears to be readily mixed down to the surface, contributing to elevated O_3 at night (Hu et al., 2012). Previous studies have shown that LLJs occur frequently in the Mid-Atlantic region of the United States during the period between 1900-

89 0600 hours local time (LT), with peak winds ranging from 8 to 23 m s^{-1} (Ryan, 2004; Zhang et
90 al., 2006). Such strong LLJs may cause the RL to become leaky (Banta et al., 2007). Thus, the
91 LLJs are hypothesized to contribute to the formation of leaky RL and nighttime surface O_3
92 maxima in the Mid-Atlantic region.

93 In the current study, the impacts of a LLJ observed in the Beltsville area on surface O_3 and
94 vertical O_3 profiles are investigated in detail using different numerical modeling approaches.
95 Initially, a three-dimensional model is employed to examine the spatial extent of the LLJ and to
96 diagnose its role in modulating boundary layer O_3. A single column model is then applied to
97 isolate the impacts of the LLJ on boundary layer mixing, nocturnal O_3 dispersion, and O_3 built-
98 up on the subsequent day. This study, for the first time, provides direct modeling evidence that
99 LLJs induce substantial turbulence and reduce the RL O_3 significantly; as a result, the O_3 level in
100 the daytime boundary layer on the following day is lowered.

101

102 **2. Methods**

103 During summer 2010, a research field campaign (Hu et al., 2012) was conducted at Howard
104 University's Atmospheric Research Site in Beltsville, MD (39.06^{o}N, 76.88^{o}W). The
105 meteorological variables and mixing ratios of chemical species (O_3, NO, NO_2, CO, SO_2) were
106 measured at 5 m above ground level (AGL). The mixing ratios of chemical species were
107 recorded every second. During several intensive observation periods, balloon-borne
108 meteorological and O_3 sondes were used to obtain vertical profiles of temperature, humidity,
109 wind speed and direction, and O_3. On the night of August 9-10, 2010, a secondary O_3 maximum
110 and a concurrent LLJ were observed at this research site. This event will be the focus of the
111 current study. In addition to the night of August 9-10, O_3 sondes were also launched in the

112 afternoon of August 9, which provided the unique opportunity during the field campaign to
113 investigate the O_3 variation from the daytime convective boundary layer to the nighttime
114 boundary layer. LLJs commonly occur in the Mid-Atlantic region (Zhang et al., 2006). This case
115 study demonstrates potential impacts of the frequently occurring phenomenon of nocturnal LLJs
116 on boundary layer O_3.

117 Three-dimensional (3D) air quality simulations, using the Weather Research and Forecasting
118 model with Chemistry (WRF/Chem, Grell et al., 2005), for the 2010 summer campaign were
119 applied in Hu et al. (2012) to investigate regional transport of O_3 and illustrate certain caveats in
120 3D air quality simulations. As part of the current study, output from these WRF/Chem
121 simulations along with hourly O_3 data recorded at the AIRNOW sites in the region were first
122 used to examine the spatial extent and the potential causes of elevated nocturnal surface O_3
123 concentrations during the night of August 9-10, 2010. Details about the model set-up and
124 domains of the WRF/Chem simulations can be found in Hu et al. (2012).

125 To further investigate the impacts of the strong LLJ observed on the night of August 9-10,
126 2010 near the Beltsville site on the vertical distribution of O_3, a single column photochemical
127 model CACHE (Forkel et al., 2006) is employed in this study. In the vertical direction, 40 model
128 layers extend from the surface to the 2.64-km height, with a vertical grid spacing of 1 m for the
129 lowest layer and 500 m for the uppermost layer; such a setup appears to adequately capture the
130 boundary layer structure during both nighttime and daytime. The multi-layered photochemical
131 model solves the following system of equations:

132 $$\frac{\partial \chi_{i,j}}{\partial t} = E_{i,j} + D_{i,j} + C_{i,j} + \frac{\partial}{\partial z}\left(K \frac{\partial \chi_{i,j}}{\partial z_j}\right) \quad (1)$$

133 where subscripts *i* and *j* denote the i^{th} chemical species and the j^{th} model layer, respectively, with

134 χ being the concentration of a chemical species. Terms *E*, *D* and *C* are the rates of change due
135 to emissions, dry deposition, and chemical reactions, respectively. The estimation method of
136 emissions of volatile organic compounds, *E*, was updated to use the formula of Guenther (2006).
137 The dry deposition, *D*, is treated using the methods of Wesely (1989) and Gao et al. (1993). The
138 chemical reaction rate, *C*, is computed using the Regional Atmospheric Chemistry Mechanism
139 (RACM) gas-phase mechanism (Stockwell et al., 1997). The atmospheric turbulent transport
140 term, i.e., the last term of (1), is parameterized using a first-order closure scheme. The eddy
141 diffusivity *K* is described using a mixing-length approach, in which *K* is expressed as a function
142 of mixing length l, the vertical wind shear S, and the stability function $f(Ri)$:

143 $$K = l^2 S f(Ri) \qquad (2)$$

144 This first-order parameterization is widely applied in operational NWP and climate models
145 (Beare et al., 2006; Cuxart et al., 2006). The stability function *f* is parameterized using the
146 Richardson number *Ri*; a larger/smaller *Ri* leads to a smaller/larger value of the stability function.
147 The Richardson number *Ri*, a dynamic stability parameter, represents the ratio of thermally to
148 mechanically produced turbulence in a defined air layer.

149 Two simulations are conducted with the single column model. In the control simulation,
150 a calm condition (no LLJ) is considered while in a sensitivity simulation a LLJ is included. The
151 simulations are initialized at 1400 LT on August 9, 2010, and run for 34 hours. The initial
152 concentrations of O_3 and nitrogen oxides (NO_x) come from field observations while the initial
153 concentrations of other species come from the WRF/Chem simulation conducted in Hu et al.
154 (2012). The shortwave radiation is constrained by the observed values. The simulated mixing
155 ratio of NO_x in the boundary layer is nudged to the observed values at 5m AGL every half-hour.
156 Advection is not considered in the single column model. The boundary layer advection pathway

in Maryland changed during the daytime of August 10, 2010 (Hu et al., 2012). Thus bias of the simulated mixed layer O_3 on August 10 by the single column model is expected. However, the goal of the single column model simulations is to isolate the impact of the vertical mixing induced by a LLJ on boundary layer O_3 by examining the difference between the control and the sensitivity simulations.

3. Observations and three-dimensional WRF/Chem simulations

The measured O_3, NO_x and the corresponding meteorological variables on August 9-10, 2010 at the Beltsville research site, 5 m AGL, are shown in Fig. 1. Due to the diurnal cycle of photochemical production, O_3 maxima typically occur in the afternoon in the continental atmospheric boundary layer. During summer nights, NO_x mixing ratios are ~7 ppbv and NO titration and dry deposition usually result in continuously decreasing O_3 concentrations near the surface in Beltsville (Hu et al., 2012). During our study period, however, a secondary O_3 maximum was recorded on the night of August 9-10, 2010; O_3 mixing ratios between 0000 and 0300 LT were elevated by ~15 ppbv. By 0700 and 0800 LT, the O_3 mixing ratio decreased to ~10 ppbv due to NO titration and dry deposition. The secondary O_3 maximum was accompanied by a decrease of the NO_x mixing ratio and increase of temperature. Southwesterly winds (~2 m s^{-1}) were maintained during the period of 0000-0500 LT, suggesting that a similar footprint and air mass persisted during this period. These factors suggest that the secondary O_3 maximum at the surface on the night of August 9-10, 2010 was due to downward mixing of RL O_3, as was also reported in Talbot et al. (2005) and Hu et al. (2012). Since the upper layers typically had higher O_3 mixing ratios, lower NO_x mixing ratios, and higher potential temperatures, one can conclude that vertical mixing between the SBL and RL persisted during the night, which led to

180 an increase in surface O_3 and temperature, and a decrease in surface NO_x.

181 Similar secondary nocturnal O_3 maxima were also recorded at the majority of AIRNOW
182 sites (60% of 45 sites) along the Virginia-to-Connecticut corridor on the same night. Other
183 AIRNOW sites along this corridor also experienced elevated O_3 on this night, but an isolated
184 secondary O_3 maximum was not apparent. The concentration variations for ten exemplary sites
185 are shown in Fig. 2. Figure 3 illustrates the locations of those sites. These AIRNOW sites are
186 located across a wide region with different characteristics such as urban and rural land use types.
187 Their upstream O_3 mixing ratios varied significantly according to the WRF/Chem simulation
188 (Fig. 4), which can be explained by the different elevation of the monitoring sites (Fig. 3) and
189 spatially variable precursor emission rates within the domain. Ozone was removed more
190 efficiently by NO titration around anthropogenic emission sources such as big cities and traffic
191 roads. Factors contributing to higher nighttime O_3 concentrations at elevated locations (e.g., in
192 the Appalachian Mountains) included (1) a more explicit influence of O_3-richer air from the free
193 troposphere, (2) lower anthropogenic emission rates, and (3) limited transport of NO into these
194 regions. Despite the heterogeneous upstream O_3 mixing ratios, almost concurrent nocturnal
195 secondary O_3 maxima were observed at the AIRNOW sites along the Virginia-to-Connecticut
196 corridor. Given the large variability in O_3 concentrations near each site, advection cannot
197 explain these nearly simultaneous secondary maxima. The distance between the south-west (S.
198 MARYND) and north-east (Mt Ninham) sites along the corridor is ~600 km. Even with a wind
199 speed as high as 20 m s^{-1}, it would take more than eight hours for an air mass to travel across this
200 distance. The secondary O_3 maximum at Mt Ninham would be expected to occur several hours
201 later than at the S. MARYND site if they were due to advection of an O_3-richer air mass, which
202 was clearly not observed. Given the difficulties in reproducing the structure of the nocturnal

boundary layer and nighttime chemistry, the simulated vertical profile of chemical species can be biased (Zhang et al., 2009; Herwehe et al., 2011; Hu et al., 2012). Thus, the results from the WRF/Chem simulations should not be over interpreted. It can be noted, however, that the general O_3 patterns remain similar throughout the entire period from 0000 LT to 0400 LT (Figure not shown), which is another indication that advection did not play a crucial role in the formation of the nighttime secondary O_3 maxima. The small variations in the onset times of the secondary O_3 maxima among the ten sites (Fig. 2) do not show any systematic trends related to the position of the site along the SW-NE corridor. They can likely be explained by the local characteristics of each site (e.g., urban vs. rural and different elevation), which resulted in different nocturnal O_3-depletion rates, vertical O_3 distributions, and turbulent mixing at each site.

Boundary layer structures on August 9-10, 2010 are clearly illustrated by the measured vertical profiles of O_3 (Fig. 5a). During daytime, elevated O_3 mixing ratios due to photochemical production are confined in the mixed layer, which is the lower ~1.7 km AGL. The O_3 mixing ratio in the daytime mixed layer on August 9, 2010 was as high as 100 ppbv (Fig. 5a). During nighttime, strong vertical gradients of O_3 mixing ratios develop in the stable boundary layer (~ 600 m AGL) due to efficient O_3 removal by NO titration and dry deposition near the surface. If the stable boundary layer developing near the surface is decoupled form the RL, we would expect to observe low O_3 concentrations close to the surface, but concentrations inside the RL would remain close to the values observed within the previous day mixed layer (~100 ppbv in the studied case). However, O_3 concentrations decreased throughout the RL (0.8-1.7 km AGL) on the night of August 9-10, 2010 to as low as 50-60 ppbv, which more closely resemble the values in the free troposphere. The decrease of the RL O_3 concentrations by nearly a factor of 2 compared to the previous day mixed-layer values, confirms that active dispersion of RL O_3

persisted on this night. At the same time, a strong LLJ over the Beltsville research site was recorded during the study period. The wind speed exceeded 15 m s^{-1} at 500 m AGL at 0252 LT on August 10 (Fig. 5b). Along the western, mountainous side of the Virginia-to-Connecticut corridor, strong radiative cooling near the ground results in lower nighttime temperatures than on the eastern side. Such a horizontal temperature gradient, caused by the terrain effects (Fig. 3), can induce a southwesterly thermal wind in the nocturnal boundary layer (Ryan, 2004), and contribute to the formation of the nighttime LLJ. The meridional variation of the Coriolis parameter could also accelerate the northward-blowing LLJ (Wexler, 1961; Zhong et al., 1996). The results from WRF/Chem simulations reported in Hu et al. (2012) also showed that a persistent low-level jet formed east of the Appalachian Mountains over the Virginia-to-Connecticut corridor (Fig. 6). Compared with the observed wind profiles, the maximum LLJ wind speed was however significantly underestimated by WRF (Fig. 7). Beltsville and all the sites experiencing secondary O_3 maximum shown in Fig. 2 are located in the corridor affected by the LLJ. As it was already discussed, neither the observations nor the model results indicate that advection of O_3 triggered the secondary, nighttime O_3 maxima. Instead, it is hypothesized that the LLJ induced strong turbulence, which weakened the decoupling between the SBL and RL and triggered enhanced mixing of O_3 from the RL to the ground, causing the observed increase in surface O_3. To prove this hypothesis, a one-dimensional modeling study was conducted that allowed us to isolate the role of the LLJ.

4. Impact of LLJ-induced vertical mixing in one-dimensional simulations

The 3D WRF/Chem simulation predicted that a LLJ formed and persisted throughout the early morning hours. However, it significantly underestimated the strength of the LLJ (Fig. 7),

249 which meant that the WRF/Chem model would not accurately reproduce the vertical mixing in
250 the NBL. However, even if the simulation had correctly reproduced the LLJ strength, it would
251 still be difficult to identify the contribution of the LLJ in moderating the vertical O_3 distribution
252 because the interplay of several processes (e.g., vertical mixing and horizontal advection) cannot
253 be easily separated in 3D simulations. Therefore, simulations are conducted in this study using a
254 single-column model to examine the impact of LLJ-induced vertical mixing on August 10, 2010.
255 The environmental wind profile is manually set up in the model using the observed wind profile
256 as guidance. Two simulations are conducted; the control simulation has a calm condition while a
257 sensitivity experiment has a LLJ profile between 0000 LT and 0600 LT of day 2; the latter is
258 otherwise the same as the control simulation. The maximum wind speed (WSP) of the LLJ at
259 440 m AGL is set as 20 m s^{-1}. The single column model does not consider directional wind
260 shear. Instead, the maximum WSP of the LLJ is set at a higher value than the observation to
261 account for the effect of directional shear-induced turbulence.

262 The simulations with the single column model captured the meteorological conditions (e.g.,
263 temperature and relative humidity) reasonably well (Fig. 8). In the sensitivity simulation, the
264 impacts of LLJ-induced vertical mixing on meteorological conditions near the surface are
265 successfully captured. An abrupt increase of temperature and decrease of relative humidity near
266 the surface are reproduced at the onset of the LLJ, i.e., 0000 LT on August 10, 2010.

267 The simulated time series of O_3 mixing ratios near the surface are shown in Fig. 9a. At the
268 onset of the LLJ (0000 LT), O_3 mixing ratios near the surface increased by ~18 ppbv in the
269 sensitivity simulation. At the same time, surface temperature increased (Fig. 8). These results
270 are consistent with the observed secondary O_3 maximum shown in Fig. 1. The surface O_3 was
271 nearly depleted on the calm night in the control simulation due to dry deposition and NO titration,

while it was elevated in the sensitivity simulation with the LLJ (Fig. 9a). Such difference of the surface O_3 caused by LLJs was also reported in previous studies (Banta et al., 2007). These results therefore confirm the hypothesis that the LLJ played an important role in downward mixing of O_3 during the night of August 9-10, 2010.

The simulated vertical profiles of O_3 are shown in Fig. 10. The LLJ played an important role in removing O_3 in the RL at night. According to the formula (2), elevated wind shear in the presence of the LLJ will cause an increase of the eddy diffusivity. As a result of the shear-enhanced turbulence, the temperature inversion weakened, *Ri* further decreased, which, according to (2), as a whole contributed to a substantial increase in eddy diffusivity in the presence of a LLJ. The enhanced vertical mixing played a critical role in modulating the vertical redistribution of O_3 in the boundary layer. On a calm night, O_3 in the RL was mostly conserved while the RL O_3 was reduced by ~25 ppbv at 0800 LT in the presence of the LLJ (Fig. 10 and Fig. 9b). LLJs have also been reported to induce mechanical turbulence that can vertically mix O_3 in the nocturnal boundary layer in other regions such as Texas (Tucker et al., 2010). The significant reduction of O_3 in the RL in both observations (Fig. 5a) and simulation (Fig. 10b) indicates that the RL may not be a reservoir of pollutants in the presence of strong LLJs. The simulated reduction of the RL O_3 from the daytime mixed layer by the sensitivity simulation (~25 ppbv, Fig. 10b) was smaller than the observed reduction (~40 ppbv, Fig. 5a). Such discrepancy may be due to the exclusion of advection processes in the single column model and/or model errors. Model errors in the treatments of vertical mixing in meteorological and air quality models are shown to lead to substantial bias of simulated profiles of meteorological and chemical variables (Hu et al., 2010, 2012; Nielsen-Gammon et al., 2010).

Due to the enhanced turbulence induced by the LLJ, more O_3 was transported to the surface, where it was subjected to NO titration and enhanced dry deposition. The dry deposition velocity was correlated to the friction velocity u_*, with larger u_* values leading to larger dry deposition velocities. Enhanced turbulent mixing in the presence of a LLJ resulted in an increase in u_*, and thus higher dry deposition rates. As a result, the LLJ affected the O_3 budget at night, which in turn affected the O_3 concentration in the daytime mixed layer on the following day. Figure 10 shows that the mixed-layer O_3 at 1400 LT on the second day was reduced by ~8 ppbv due to the influence of the LLJ compared to the control simulation without the LLJ. The simulated maximum surface O_3 on August 10, 2010 was reduced by ~8 ppbv with the LLJ while the maximum 8-hour running average O_3 was reduced by ~6 ppbv (Fig. 9a). Compared with the observed O_3 profile at 13:54 LT on August 10 (~80 ppbv in the mixed layer), the predicted O_3 in the mixed layer on the second day by the sensitivity simulation is higher by ~10 ppbv. The discrepancy is likely due to the change of transport pathways during the daytime of August 10, 2010 (Hu et al., 2012), which is not considered in the single column model.

The time-height diagrams of simulated O_3 are shown in Fig. 11. Without the LLJ, the RL O_3 is mostly conserved (Fig. 11a). When the daytime mixed layer grows, the O_3-rich RL air is entrained into the mixed layer below, thereby contributing to the rapid increase in O_3 in the mixed layer in the morning. Such a scenario is described in Zhang and Rao (1999) and confirmed by other studies (Aneja et al., 2000; Yorks et al., 2009; Morris et al., 2010; Tong et al., 2011). However, in the presence of the LLJ, the RL O_3 is removed at night (Fig. 11b). In the following morning, entrainment contributes much less to the O_3 in the mixed layer (Fig. 11b), thus the increase of surface O_3 is much slower comparing to the control simulation (Fig. 9a).

5. Conclusions and discussion

Profiles of O_3 and meteorological variables in both nighttime and daytime have been measured in summertime since 2006 in Beltsville, Maryland (Hu et al., 2012). The data sets provided a unique opportunity to investigate the pollutants in the residual layer (RL) and their contribution to the daytime boundary layer pollution. It is shown that the RL was at times not a reservoir of O_3 at night. A case study was conducted for August 9-10, 2010, when a strong LLJ and elevated surface O_3 were observed at night. During this night, the RL O_3 was 50-60 ppbv, which was much lower than the O_3 level in the mixed layer on the previous day (~100 ppbv). Thus, O_3 appeared to be mixed from the RL to the ground preventing the RL from acting like a reservoir. Simulation results from a single-column model containing O_3 chemistry confirm that the LLJ causes a nocturnal secondary O_3 maximum and a significant reduction of the RL O_3. The LLJ-induced strong turbulence, which transports O_3-rich RL air to the surface where O_3 is efficiently removed by chemical reactions and enhanced dry deposition. These processes impact the O_3 budget: the enhanced nocturnal vertical mixing reduces the increase in surface O_3 the following morning and, compared to the results of a control simulation with calm conditions, the maximum O_3 is ~ 8 ppbv lower for the simulation containing a LLJ.

Salmond and McKendry (2002) found that secondary surface O_3 maximum due to enhanced nocturnal mixing rarely exceeded 50 ppbv. They concluded that the nocturnal secondary O_3 maximum is unlikely to be significant enough to affect human health. Our study shows that such nocturnal mixing may play an important role in modulating the O_3 levels in the daytime boundary layer on the following day; it may thus have a more important implication for public health than it had been previously realized.

339 Ryan (2004) investigated the climatology of LLJs in Maryland, USA and found that the
340 weather patterns favorable for the development of LLJs are normally also suitable for the
341 occurrence of Mid-Atlantic high O_3 episodes. Thus, the influence of LLJs on the O_3 episodes
342 can be hardly discerned from other factors that are conducive to O_3 accumulation. Due to the
343 difficulty in accurately reproducing LLJs and the interplay of several processes (e.g., vertical
344 mixing and horizontal advection) in three dimensional air quality simulations, a previous study
345 on this case (Hu et al. 2012) did not isolate the impact of LLJs on the vertical distribution of O_3.
346 Using a single column chemistry model that allows for easier setup of sensitivity experiments in
347 this study, the impact of LLJs on the boundary layer O_3 pertaining to stronger vertical mixing is
348 isolated. The effects of horizontal long-range transport due to LLJs are not considered in this
349 study. One implication of this study for long-range transport is: the pollutants in the RL may
350 leak out during the horizontal transport due to enhanced vertical mixing, reducing the impact of
351 urban plumes in downwind areas.

352 LLJs have been reported in many regions (Whiteman et al., 1997; Song et al., 2005; Zhang et
353 al., 2006); the LLJs in other regions (e.g., the Great Plains of the United States) may be much
354 stronger and more extensive than those in the Mid-Atlantic region (Zhang et al., 2006). Thus,
355 the impact of LLJs on the boundary layer O_3 may have important implications for air quality in
356 many regions. Apart from LLJs, mesocale motions such as Kelvin-Helmholtz instabilities,
357 gravity waves, wake vortices, and density currents can also cause enhanced nighttime turbulence
358 (Sun et al., 2002, 2003; Salmond and McKendry, 2005; Fritts et al., 2009), which may also make
359 the RL leaky. In addition to O_3, nocturnal mixing events may have appreciable effects on the
360 dispersion and budget of other species such as carbon dioxide and volatile organic compounds
361 (Acevedo et al., 2006; Ganzeveld et al., 2008). In one-dimensional simulations for the boundary

362 layer over a tropical forest using a single column chemistry-climate model, Ganzeveld et al.
363 (2008) showed that unresolved nocturnal vertical mixing processes likely lead to a nocturnal
364 accumulation of formaldehyde in the RL, which is later on entrained into the daytime convective
365 boundary layer where it affects daytime photochemistry. Further investigations regarding such
366 mixing processes and their impacts are warranted. Future field campaigns that aim at improving
367 our understanding of atmospheric chemistry in the atmospheric boundary layer should include
368 measurements of the chemical composition/transformation in combination with detailed
369 measurements of turbulence inside the RL.

370 Although the current study focuses on demonstrating the importance of vertical mixing
371 processes for vertical dispersion of boundary layer O_3, the contribution of other processes,
372 including advection (Banta et al., 2005; Zhang et al. 2007; Tucker et al., 2010), dry deposition
373 (Lin and McElroy, 2010) and chemical reactions in different chemical regimes at different height
374 above the ground (Brown et al., 2007), cannot be always ignored. To more accurately quantify
375 their contributions, meteorological and air chemistry measurements throughout the atmospheric
376 boundary layer are needed to further improve boundary-layer parameterizations, particularly for
377 nighttime conditions, and to facilitate the development and evaluation of more sophisticated
378 three-dimensional chemistry simulations.

379

380 *Acknowledgement. This work was supported by funding from the Office of the Vice President*
381 *for Research at the University of Oklahoma. The second author was also supported through the*
382 *NSF Career award ILREUM (NSF ATM 0547882). DCD received support from NASA (grant*
383 *number NNX08BA42A) to participate in the field studies. JDF received support from the*
384 *National Science Foundation to participate in this research (award ATM 0914597).*

Observations at Howard University Beltsville Campus were supported through grants from Maryland Department of the Environment, NASA (grant number NNX08BA42A) and NOAA (grant number NA17AE1625).

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Figure

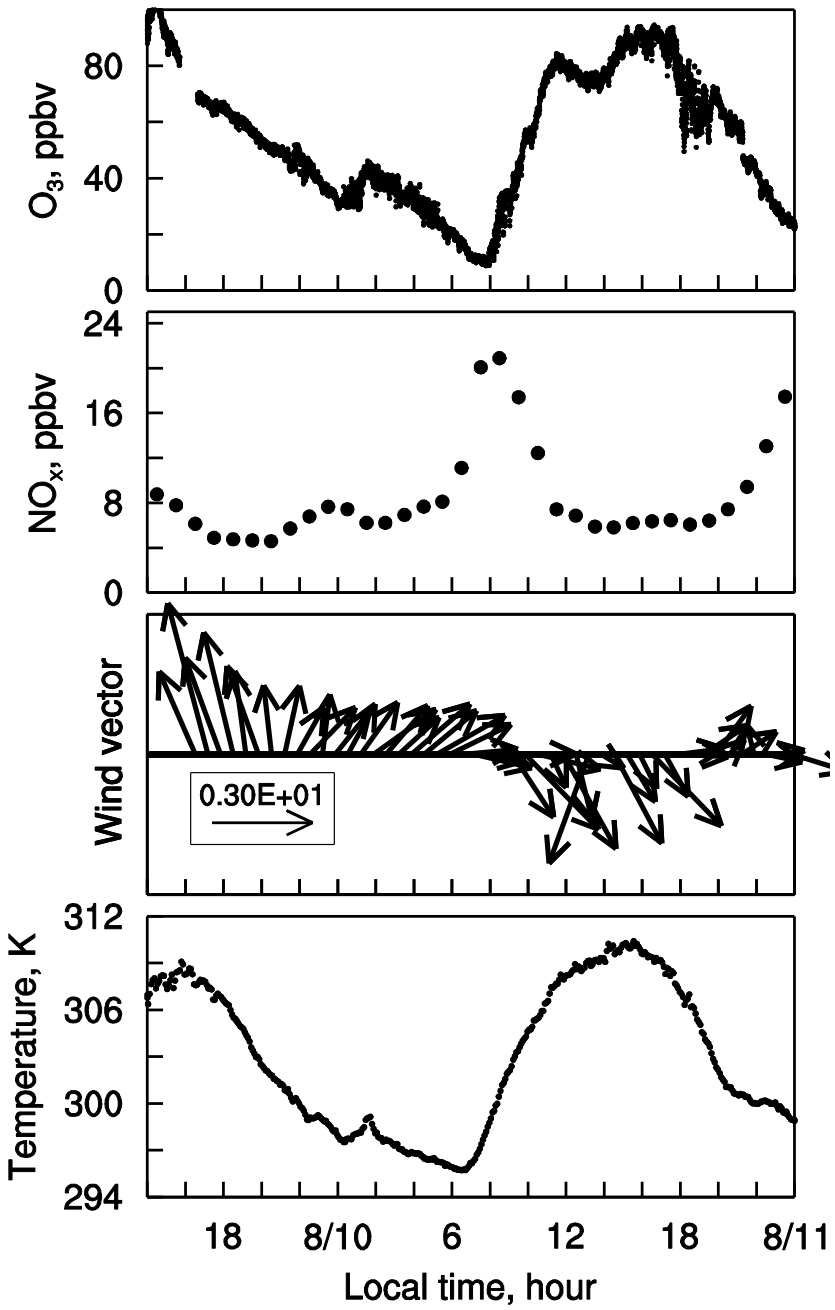

Figure 1. Observed (top to bottom) O_3, NO_x, wind vector, and temperature at Beltsville, Maryland on August 9-10, 2010.

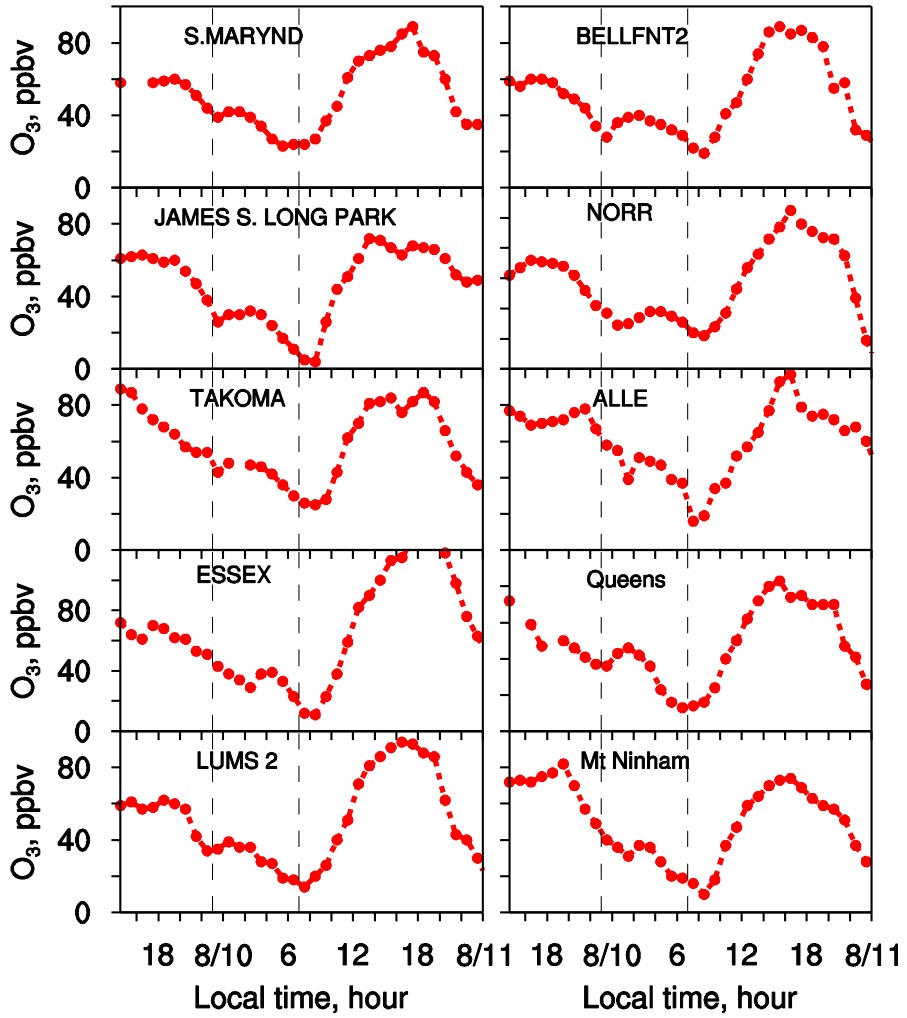

Figure 2. Time series of observed O_3 mixing ratios on Aug. 9-10, 2010 at 10 AIRNOW sites. The locations of these sites are marked in Fig. 3. The nighttime secondary O_3 maxima are confined in the time window between 2300 local time (LT), Aug. 9 and 0700 LT, Aug. 10, which are marked by the dashed lines.

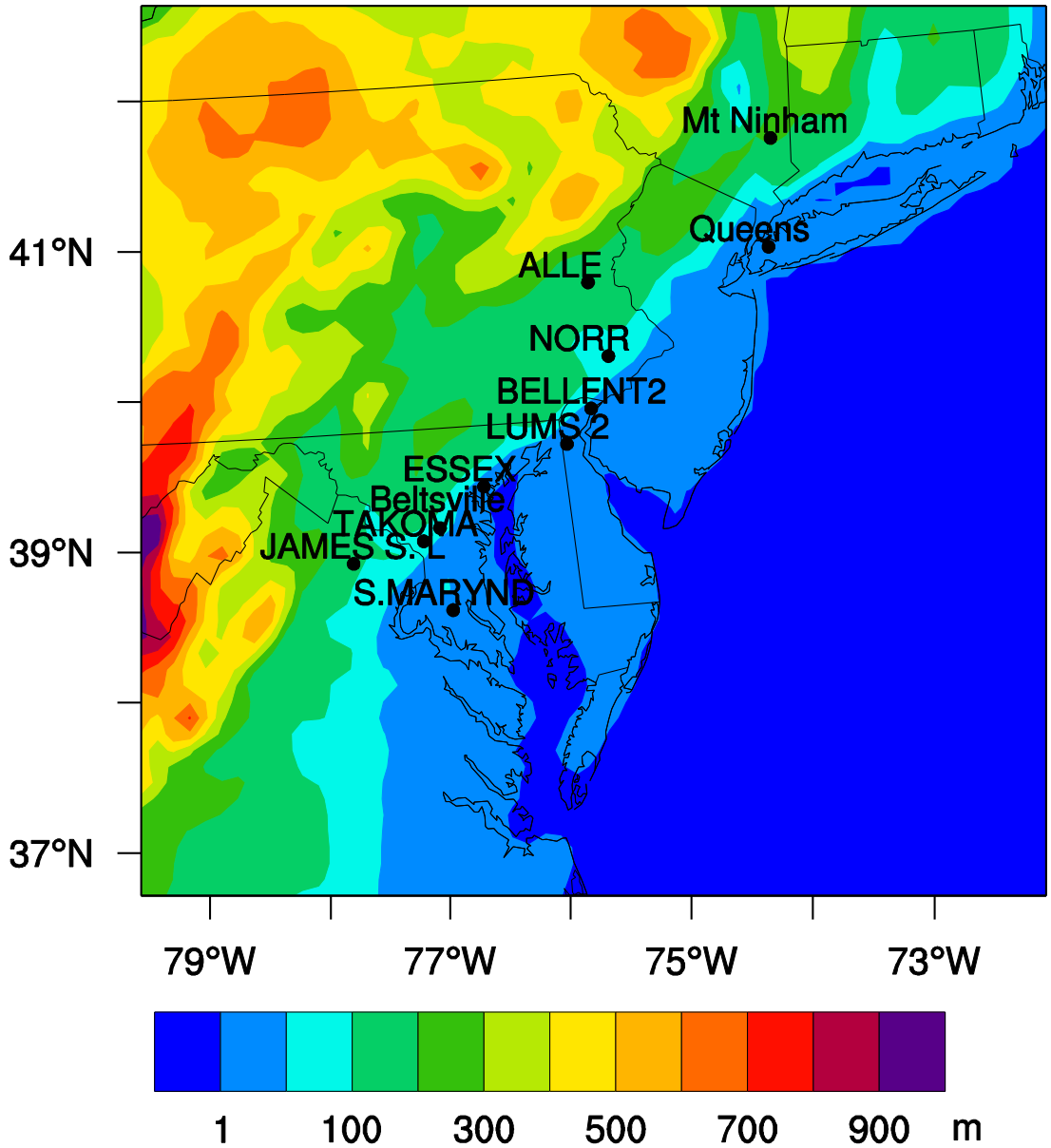

Figure 3. Terrain height of the study area. Locations of the AIRNOW sites are marked.

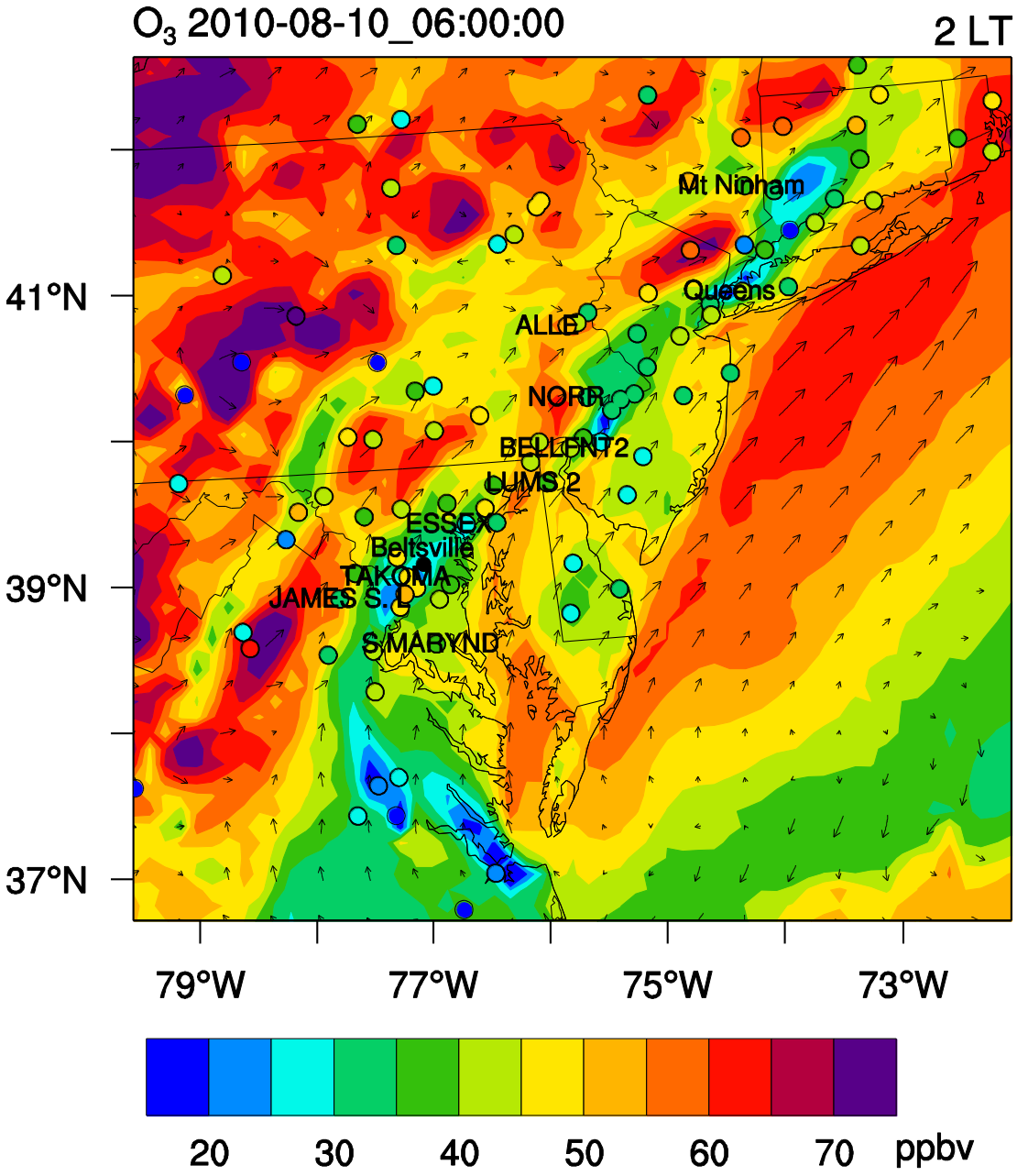

Figure 4. Spatial distribution of O_3 at 0200 local time (LT) on August 10, 2010 simulated by the WRF/Chem model. The observed O_3 values at the AIRNOW sites are indicated by shaded circles.

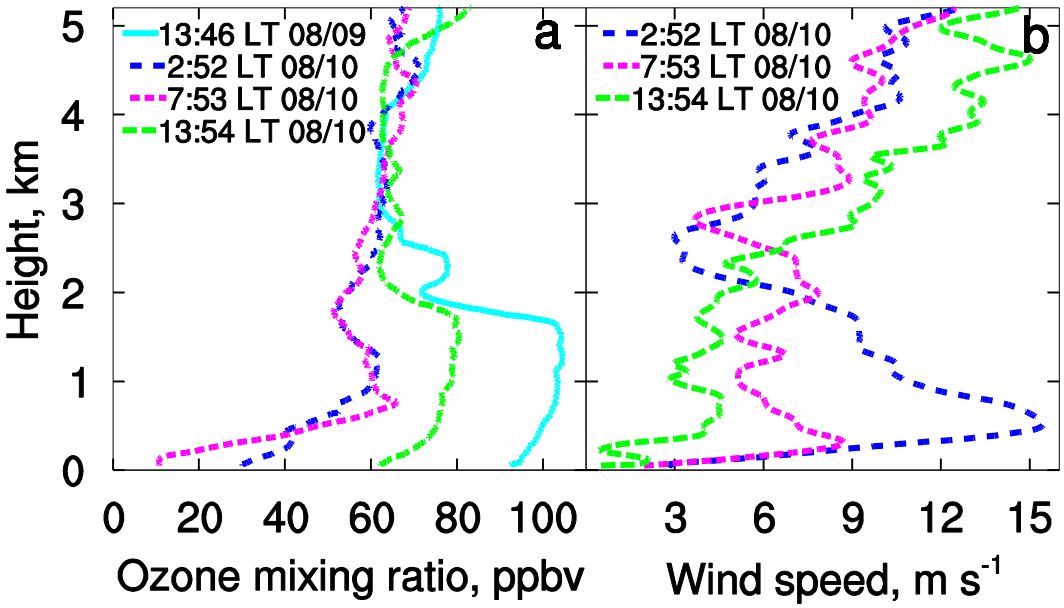

Figure 5. Observed vertical profiles of (a) O_3 and (b) wind speed at Beltsville, Maryland on August 9-10, 2010.

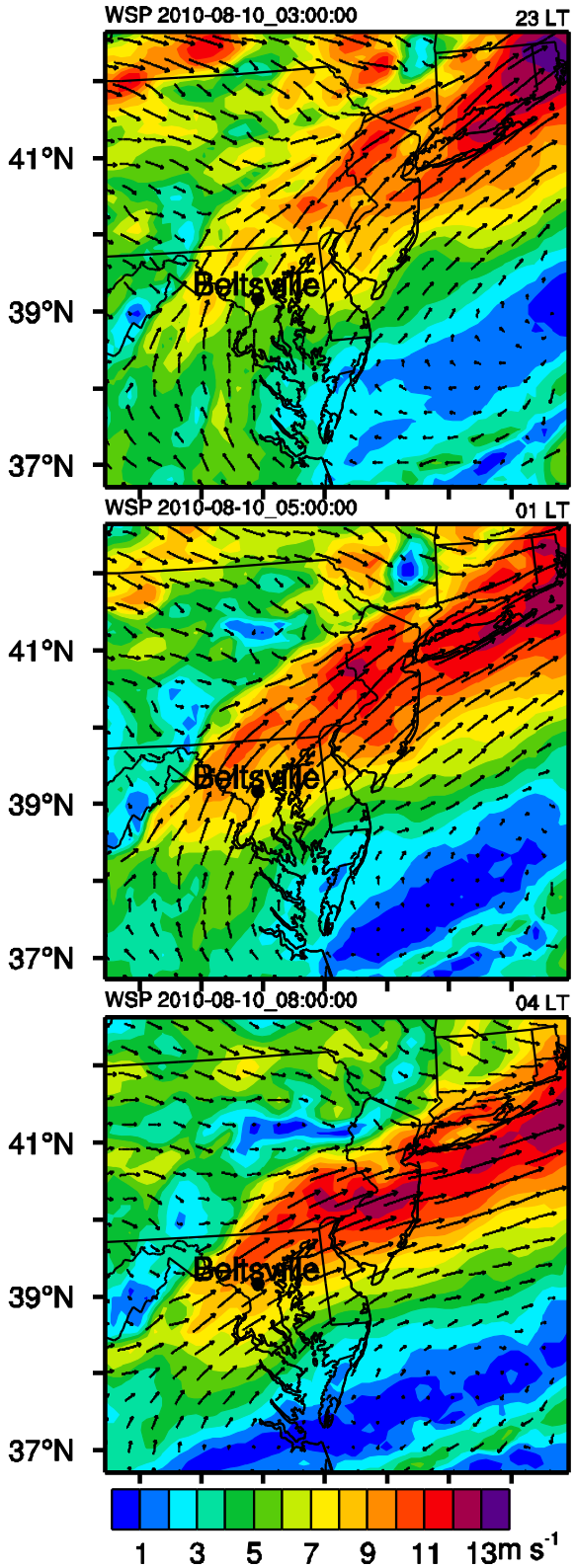

Figure 6. (top to bottom) Wind field at ~370 m AGL at 2300 LT on August 9, 0100 LT, and 0400 LT on August 10, 2010 simulated by WRF/Chem.

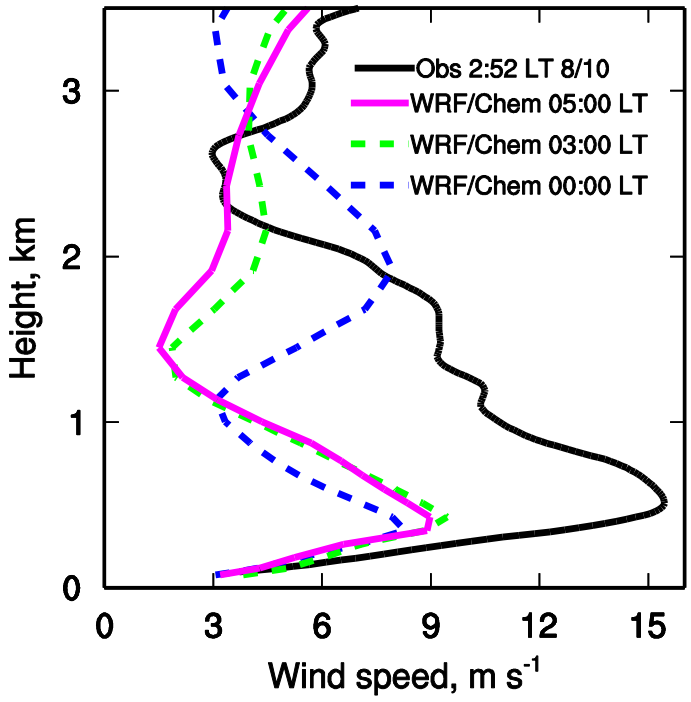

Figure 7. Simulated and observed vertical profiles of wind speed at Beltsville, Maryland on the night of August 9-10, 2010.

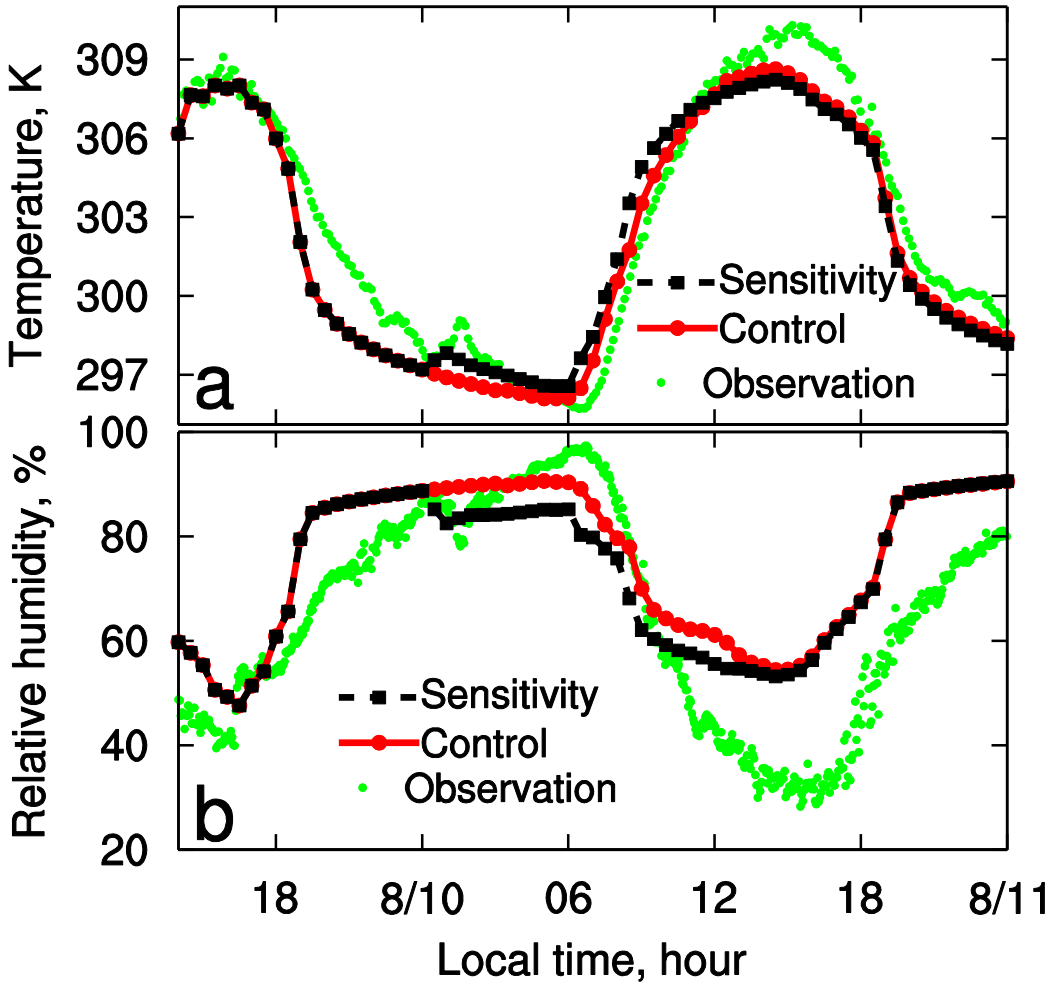

Figure 8. Observed and simulated time series of (a) temperature and (b) relative humidity near the surface.

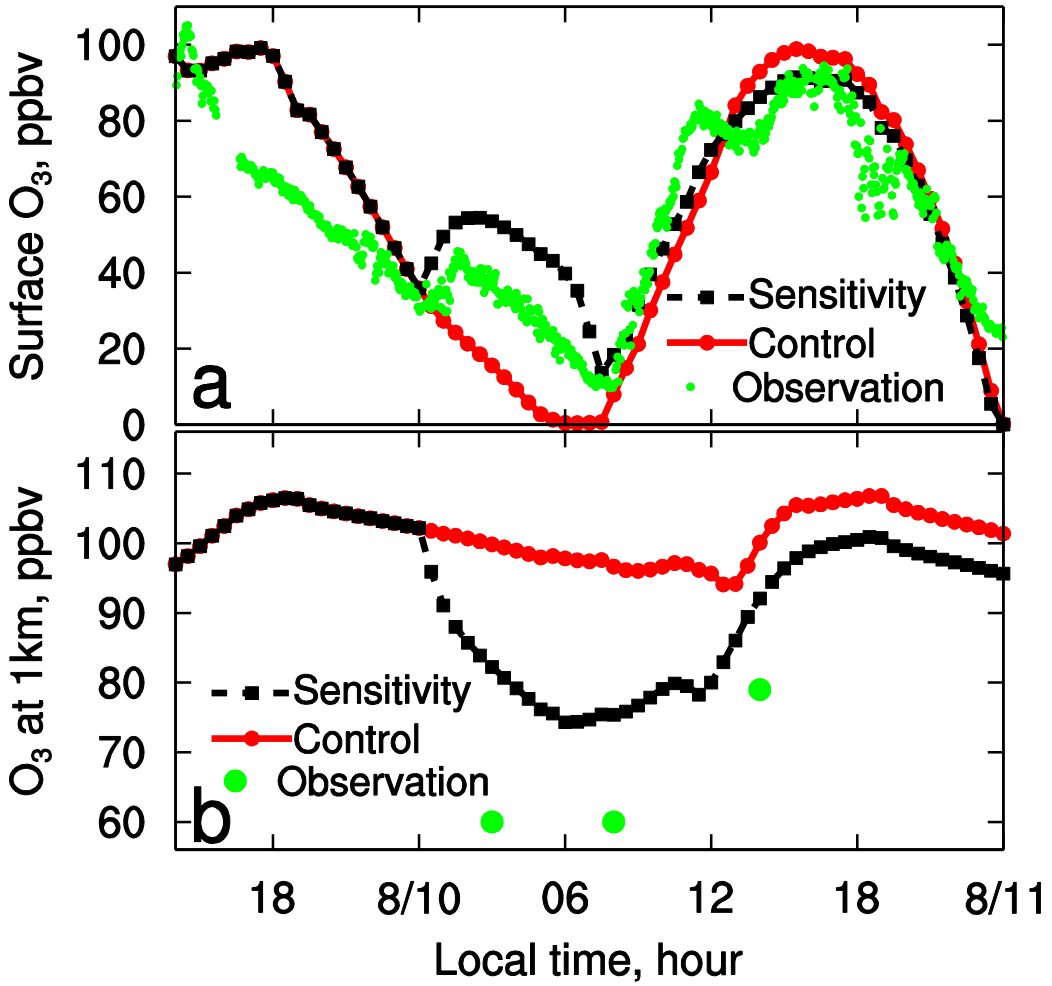

Figure 9. Time series of O_3 (a) near the surface and (b) at 1 km AGL (in the RL at night). Dots show observed O_3 near the surface (panel a) and observed O_3 at 1km AGL by Ozonesondes (panel b).

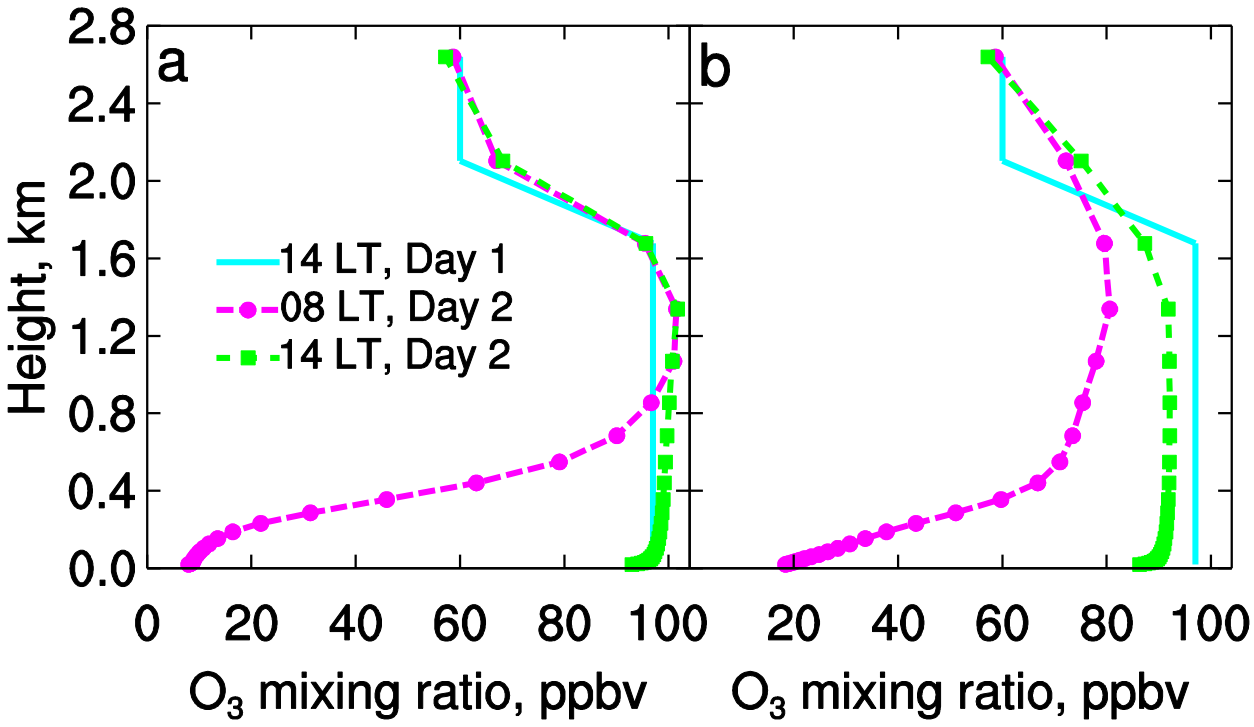

Figure 10. Profiles of simulated O_3 mixing ratio from (a) the control simulation and (b) sensitivity simulation.

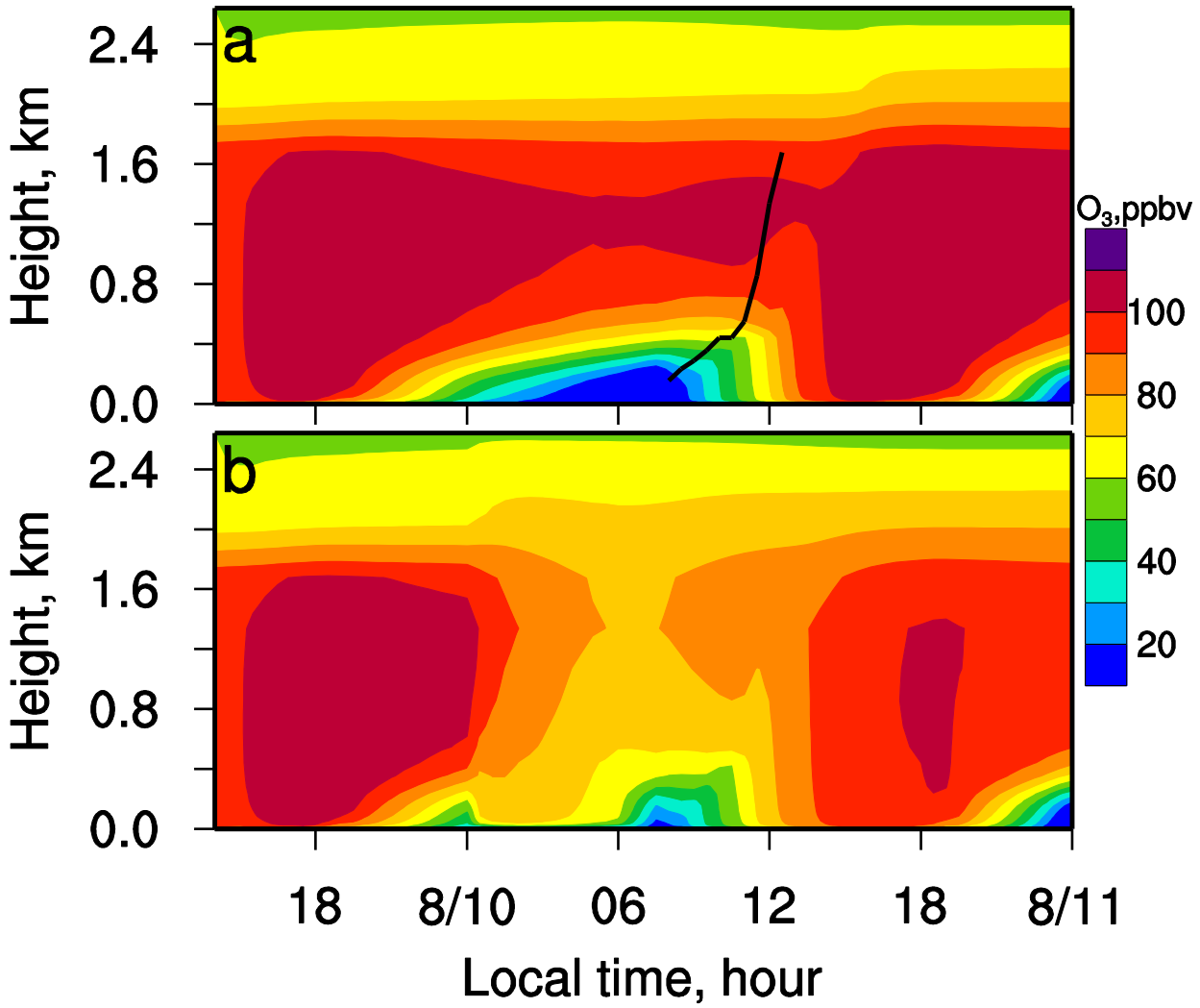

Figure 11. Time-height diagram of simulated O_3 mixing ratio from (a) the control simulation and (b) sensitivity simulation. The black line in the top panel indicates the top of the mixed boundary layer between 0730 and 1300 local time, which is diagnosed using the 1.5-theta-increase method (Hu et al., 2010). The 1.5-theta-increase method defines boundary layer top as the level at which the potential temperature first exceeds the minimum potential temperature within the boundary layer by 1.5 K.

Impact of the Vertical Mixing Induced by Low-level Jets on Boundary Layer Ozone Concentration

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1st submitted on June 5, 2012

Revision on 9/12/2012 3:59 PM

Abstract

After sunset, a stable boundary layer (SBL) develops close to the ground, while the upper region of the daytime mixed layer becomes the residual layer (RL). Mixing between the SBL and RL is often quite limited and the RL is thought to be a reservoir for daytime mixed-layer pollutants under such conditions. However, ozone (O_3) profiles observed in Maryland, U.S. suggest that the RL is not always a reservoir of O_3 in that region. Nocturnal low-level jets (LLJs) and/or other mechanisms are speculated to enhance vertical mixing between the SBL and RL, which influences the vertical O_3 redistribution.

Nocturnal surface O_3 maxima, a RL with reduced O_3 levels, and a concurrent strong LLJ were observed in Maryland on the night of August 9-10, 2010. Surface O_3 measurements in the region and three-dimensional air quality simulations suggest that horizontal advection cannot explain the nocturnal O_3 maxima and concurrent decrease of O_3 levels within the RL. A sensitivity study with a single column (1D) chemistry model was performed to investigate the role of LLJs in generating turbulent mixing within the nighttime boundary layer and to identify related impacts on O_3 concentrations at night and on the following day. The strong shear associated with the LLJ enhanced turbulent mixing and weakened the decoupling of the RL and SBL substantially. Ozone was actively mixed down from the RL to the surface, causing secondary nocturnal surface O_3 maxima. Near the surface, O_3 was efficiently removed by chemical reactions and dry deposition, which resulted in lower O_3 peak values on the next day.

1. Introduction

Following the traditional picture of the diurnal evolution of the atmospheric boundary layer, radiational cooling after sunset results in the development of a stable boundary layer (SBL) near the surface that is typically quite shallow. Above the SBL is a residual layer (RL) with characteristics similar to those of the previous day's mixed layer (Stull, 1988). In the absence of strong disturbances, mixing and dispersion of pollutants between the RL and SBL become limited, and within the RL the concentration of pollutants remains at similar levels as in the mixed layer before its decay, which is why the RL is often viewed as a reservoir of pollutants (Stull, 1988). The pollutants trapped within the RL from the previous day can be entrained downward into the re-developing mixed layer on the following day. In places such as the northeastern United States, such downward mixing of ozone (O_3) and its precursors is shown to contribute substantially to ground-level O_3 buildup in the morning in addition to chemical production (Zhang et al., 1998; Zhang and Rao 1999). The downward transport of the RL O_3 in the morning also contributes to the maximum O_3 levels observed near the surface during daytime (Neu et al., 1994; Aneja et al., 2000; Yorks et al., 2009; Morris et al., 2010; Tong et al., 2011). Accurate information regarding the RL O_3 is thus critical for correctly simulating the daytime O_3 near the surface (Herwehe et al., 2011). Due to its relative inaccessibility, the actual detection of the properties of the RL at high temporal and spatial scales has been limited in the past. Recent field experiments (e.g., Balsley et al., 2008) showed that the classical view of a quiescent RL may have been oversimplified. Sporadic turbulence exists at night, weakening the decoupling between the RL and SBL, and the vertical mixing in the nighttime boundary layer may be significant, even compared to that in the daytime convective boundary layer (Poulos et al., 2002; Tjernstrom et al., 2009). Enhanced nighttime turbulence may be triggered by mesocale motions

such as low-level jets (LLJ), Kelvin-Helmholtz instabilities, gravity waves, wake vortices, and density currents (Sun et al., 2002, 2003; Salmond and McKendry, 2005; Fritts et al., 2009). Such intense turbulence can affect the vertical structure of the nighttime boundary layer and vertical distribution of pollutants. The view of the quiescent RL as a reservoir of pollutants may be challenged under such conditions. Recent observations (Hu et al., 2012) have suggested that the RL is leaky at times, i.e., active vertical exchange of air exists between the RL and the SBL. As a result, the O_3 levels in the RL may be highly variable and surface O_3 may not decrease as fast as anticipated based on the assumption of having a completely decoupled RL and SBL. In some cases, there are even secondary nighttime O_3 maxima reported, which were typically associated with periods of enhanced mixing (Corsmeier et al., 1997; Reitebuch et al., 2000; Salmond and McKendry, 2002; Talbot et al., 2005; Hu et al., 2012). Therefore, it is important to further investigate the dynamics and mixing of nocturnal boundary layers to better understand the temporal variability, absolute levels, and deposition rates of surface layer O_3 concentrations.

In Beltsville, Maryland (MD), nighttime vertical O_3 profiles have been measured during the summertime since 2004 (Yorks et al., 2009; Hu et al., 2012). Beltsville is located between Washington, D.C. and Baltimore, MD, in the middle of the Mid-Atlantic urban corridor of the United States. Heavy emissions of O_3 precursors and favorable meteorological conditions frequently lead to extreme O_3 events in this area (Ryan et al., 1998). Within the RL, O_3 levels at the Beltsville site at times resemble those found in the free troposphere with concentrations that are significantly lower than those in the previous day's atmospheric mixed layer. Ozone in the RL inherited from the daytime mixed layer appears to be readily mixed down to the surface, contributing to elevated O_3 at night (Hu et al., 2012). Previous studies have shown that LLJs occur frequently in the Mid-Atlantic region of the United States during the period between 1900-

89 0600 hours local time (LT), with peak winds ranging from 8 to 23 m s^{-1} (Ryan, 2004; Zhang et
90 al., 2006). Such strong LLJs may cause the RL to become leaky (Banta et al., 2007). Thus, the
91 LLJs are hypothesized to contribute to the formation of leaky RL and nighttime surface O_3
92 maxima in the Mid-Atlantic region.

93 In the current study, the impacts of a LLJ observed in the Beltsville area on surface O_3 and
94 vertical O_3 profiles are investigated in detail using different numerical modeling approaches.
95 Initially, a three-dimensional model is employed to examine the spatial extent of the LLJ and to
96 diagnose its role in modulating boundary layer O_3. A single column model is then applied to
97 isolate the impacts of the LLJ on boundary layer mixing, nocturnal O_3 dispersion, and O_3 built-
98 up on the subsequent day. This study, for the first time, provides direct modeling evidence that
99 LLJs induce substantial turbulence and reduce the RL O_3 significantly; as a result, the O_3 level in
100 the daytime boundary layer on the following day is lowered.

101

102 **2. Methods**

103 During summer 2010, a research field campaign (Hu et al., 2012) was conducted at Howard
104 University's Atmospheric Research Site in Beltsville, MD (39.06^{o}N, 76.88^{o}W). The
105 meteorological variables and mixing ratios of chemical species (O_3, NO, NO_2, CO, SO_2) were
106 measured at 5 m above ground level (AGL). The mixing ratios of chemical species were
107 recorded every second. During several intensive observation periods, balloon-borne
108 meteorological and O_3 sondes were used to obtain vertical profiles of temperature, humidity,
109 wind speed and direction, and O_3. On the night of August 9-10, 2010, a secondary O_3 maximum
110 and a concurrent LLJ were observed at this research site. This event will be the focus of the
111 current study. In addition to the night of August 9-10, O_3 sondes were also launched in the

112 afternoon of August 9, which provided the unique opportunity during the field campaign to
113 investigate the O_3 variation from the daytime convective boundary layer to the nighttime
114 boundary layer. LLJs commonly occur in the Mid-Atlantic region (Zhang et al., 2006). This case
115 study demonstrates potential impacts of the frequently occurring phenomenon of nocturnal LLJs
116 on boundary layer O_3.

117 Three-dimensional (3D) air quality simulations, using the Weather Research and Forecasting
118 model with Chemistry (WRF/Chem, Grell et al., 2005), for the 2010 summer campaign were
119 applied in Hu et al. (2012) to investigate regional transport of O_3 and illustrate certain caveats in
120 3D air quality simulations. As part of the current study, output from these WRF/Chem
121 simulations along with hourly O_3 data recorded at the AIRNOW sites in the region were first
122 used to examine the spatial extent and the potential causes of elevated nocturnal surface O_3
123 concentrations during the night of August 9-10, 2010. Details about the model set-up and
124 domains of the WRF/Chem simulations can be found in Hu et al. (2012).

125 To further investigate the impacts of the strong LLJ observed on the night of August 9-10,
126 2010 near the Beltsville site on the vertical distribution of O_3, a single column photochemical
127 model CACHE (Forkel et al., 2006) is employed in this study. In the vertical direction, 40 model
128 layers extend from the surface to the 2.64-km height, with a vertical grid spacing of 1 m for the
129 lowest layer and 500 m for the uppermost layer; such a setup appears to adequately capture the
130 boundary layer structure during both nighttime and daytime. The multi-layered photochemical
131 model solves the following system of equations:

132 — — — (1)

133 where subscripts *i* and *j* denote the i^{th} chemical species and the j^{th} model layer, respectively, with

χ being the concentration of a chemical species. Terms *E*, *D* and *C* are the rates of change due to emissions, dry deposition, and chemical reactions, respectively. The estimation method of emissions of volatile organic compounds, *E*, was updated to use the formula of Guenther (2006). The dry deposition, *D*, is treated using the methods of Wesely (1989) and Gao et al. (1993). The chemical reaction rate, *C*, is computed using the Regional Atmospheric Chemistry Mechanism (RACM) gas-phase mechanism (Stockwell et al., 1997). The atmospheric turbulent transport term, i.e., the last term of (1), is parameterized using a first-order closure scheme. The eddy diffusivity *K* is described using a mixing-length approach, in which *K* is expressed as a function of mixing length , the vertical wind shear , and the stability function :

(2)

This first-order parameterization is widely applied in operational NWP and climate models (Beare et al., 2006; Cuxart et al., 2006). The stability function *f* is parameterized using the Richardson number *Ri*; a larger/smaller *Ri* leads to a smaller/larger value of the stability function. The Richardson number *Ri*, a dynamic stability parameter, represents the ratio of thermally to mechanically produced turbulence in a defined air layer.

Two simulations are conducted with the single column model. In the control simulation, a calm condition (no LLJ) is considered while in a sensitivity simulation a LLJ is included. The simulations are initialized at 1400 LT on August 9, 2010, and run for 34 hours. The initial concentrations of O_3 and nitrogen oxides (NO_x) come from field observations while the initial concentrations of other species come from the WRF/Chem simulation conducted in Hu et al. (2012). The shortwave radiation is constrained by the observed values. The simulated mixing ratio of NO_x in the boundary layer is nudged to the observed values at 5m AGL every half-hour. Advection is not considered in the single column model. The boundary layer advection pathway

in Maryland changed during the daytime of August 10, 2010 (Hu et al., 2012). Thus bias of the simulated mixed layer O_3 on August 10 by the single column model is expected. However, the goal of the single column model simulations is to isolate the impact of the vertical mixing induced by a LLJ on boundary layer O_3 by examining the difference between the control and the sensitivity simulations.

3. Observations and three-dimensional WRF/Chem simulations

The measured O_3, NO_x and the corresponding meteorological variables on August 9-10, 2010 at the Beltsville research site, 5 m AGL, are shown in Fig. 1. Due to the diurnal cycle of photochemical production, O_3 maxima typically occur in the afternoon in the continental atmospheric boundary layer. During summer nights, NO_x mixing ratios are ~7 ppbv and NO titration and dry deposition usually result in continuously decreasing O_3 concentrations near the surface in Beltsville (Hu et al., 2012). During our study period, however, a secondary O_3 maximum was recorded on the night of August 9-10, 2010; O_3 mixing ratios between 0000 and 0300 LT were elevated by ~15 ppbv. By 0700 and 0800 LT, the O_3 mixing ratio decreased to ~10 ppbv due to NO titration and dry deposition. The secondary O_3 maximum was accompanied by a decrease of the NO_x mixing ratio and increase of temperature. Southwesterly winds (~2 m s^{-1}) were maintained during the period of 0000-0500 LT, suggesting that a similar footprint and air mass persisted during this period. These factors suggest that the secondary O_3 maximum at the surface on the night of August 9-10, 2010 was due to downward mixing of RL O_3, as was also reported in Talbot et al. (2005) and Hu et al. (2012). Since the upper layers typically had higher O_3 mixing ratios, lower NO_x mixing ratios, and higher potential temperatures, one can conclude that vertical mixing between the SBL and RL persisted during the night, which led to

180 an increase in surface O_3 and temperature, and a decrease in surface NO_x.

181 Similar secondary nocturnal O_3 maxima were also recorded at the majority of AIRNOW
182 sites (60% of 45 sites) along the Virginia-to-Connecticut corridor on the same night. Other
183 AIRNOW sites along this corridor also experienced elevated O_3 on this night, but an isolated
184 secondary O_3 maximum was not apparent. The concentration variations for ten exemplary sites
185 are shown in Fig. 2. Figure 3 illustrates the locations of those sites. These AIRNOW sites are
186 located across a wide region with different characteristics such as urban and rural land use types.
187 Their upstream O_3 mixing ratios varied significantly according to the WRF/Chem simulation
188 (Fig. 4), which can be explained by the different elevation of the monitoring sites (Fig. 3) and
189 spatially variable precursor emission rates within the domain. Ozone was removed more
190 efficiently by NO titration around anthropogenic emission sources such as big cities and traffic
191 roads. Factors contributing to higher nighttime O_3 concentrations at elevated locations (e.g., in
192 the Appalachian Mountains) included (1) a more explicit influence of O_3-richer air from the free
193 troposphere, (2) lower anthropogenic emission rates, and (3) limited transport of NO into these
194 regions. Despite the heterogeneous upstream O_3 mixing ratios, almost concurrent nocturnal
195 secondary O_3 maxima were observed at the AIRNOW sites along the Virginia-to-Connecticut
196 corridor. Given the large variability in O_3 concentrations near each site, advection cannot
197 explain these nearly simultaneous secondary maxima. The distance between the south-west (S.
198 MARYND) and north-east (Mt Ninham) sites along the corridor is ~600 km. Even with a wind
199 speed as high as 20 m s^{-1}, it would take more than eight hours for an air mass to travel across this
200 distance. The secondary O_3 maximum at Mt Ninham would be expected to occur several hours
201 later than at the S. MARYND site if they were due to advection of an O_3-richer air mass, which
202 was clearly not observed. Given the difficulties in reproducing the structure of the nocturnal

boundary layer and nighttime chemistry, the simulated vertical profile of chemical species can be biased (Zhang et al., 2009; Herwehe et al., 2011; Hu et al., 2012). Thus, the results from the WRF/Chem simulations should not be over interpreted. It can be noted, however, that the general O_3 patterns remain similar throughout the entire period from 0000 LT to 0400 LT (Figure not shown), which is another indication that advection did not play a crucial role in the formation of the nighttime secondary O_3 maxima. The small variations in the onset times of the secondary O_3 maxima among the ten sites (Fig. 2) do not show any systematic trends related to the position of the site along the SW-NE corridor. They can likely be explained by the local characteristics of each site (e.g., urban vs. rural and different elevation), which resulted in different nocturnal O_3-depletion rates, vertical O_3 distributions, and turbulent mixing at each site.

Boundary layer structures on August 9-10, 2010 are clearly illustrated by the measured vertical profiles of O_3 (Fig. 5a). During daytime, elevated O_3 mixing ratios due to photochemical production are confined in the mixed layer, which is the lower ~1.7 km AGL. The O_3 mixing ratio in the daytime mixed layer on August 9, 2010 was as high as 100 ppbv (Fig. 5a). During nighttime, strong vertical gradients of O_3 mixing ratios develop in the stable boundary layer (~ 600 m AGL) due to efficient O_3 removal by NO titration and dry deposition near the surface. If the stable boundary layer developing near the surface is decoupled form the RL, we would expect to observe low O_3 concentrations close to the surface, but concentrations inside the RL would remain close to the values observed within the previous day mixed layer (~100 ppbv in the studied case). However, O_3 concentrations decreased throughout the RL (0.8-1.7 km AGL) on the night of August 9-10, 2010 to as low as 50-60 ppbv, which more closely resemble the values in the free troposphere. The decrease of the RL O_3 concentrations by nearly a factor of 2 compared to the previous day mixed-layer values, confirms that active dispersion of RL O_3

persisted on this night. At the same time, a strong LLJ over the Beltsville research site was recorded during the study period. The wind speed exceeded 15 m s^{-1} at 500 m AGL at 0252 LT on August 10 (Fig. 5b). Along the western, mountainous side of the Virginia-to-Connecticut corridor, strong radiative cooling near the ground results in lower nighttime temperatures than on the eastern side. Such a horizontal temperature gradient, caused by the terrain effects (Fig. 3), can induce a southwesterly thermal wind in the nocturnal boundary layer (Ryan, 2004), and contribute to the formation of the nighttime LLJ. The meridional variation of the Coriolis parameter could also accelerate the northward-blowing LLJ (Wexler, 1961; Zhong et al., 1996). The results from WRF/Chem simulations reported in Hu et al. (2012) also showed that a persistent low-level jet formed east of the Appalachian Mountains over the Virginia-to-Connecticut corridor (Fig. 6). Compared with the observed wind profiles, the maximum LLJ wind speed was however significantly underestimated by WRF (Fig. 7). Beltsville and all the sites experiencing secondary O_3 maximum shown in Fig. 2 are located in the corridor affected by the LLJ. As it was already discussed, neither the observations nor the model results indicate that advection of O_3 triggered the secondary, nighttime O_3 maxima. Instead, it is hypothesized that the LLJ induced strong turbulence, which weakened the decoupling between the SBL and RL and triggered enhanced mixing of O_3 from the RL to the ground, causing the observed increase in surface O_3. To prove this hypothesis, a one-dimensional modeling study was conducted that allowed us to isolate the role of the LLJ.

4. Impact of LLJ-induced vertical mixing in one-dimensional simulations

The 3D WRF/Chem simulation predicted that a LLJ formed and persisted throughout the early morning hours. However, it significantly underestimated the strength of the LLJ (Fig. 7),

249 which meant that the WRF/Chem model would not accurately reproduce the vertical mixing in
250 the NBL. However, even if the simulation had correctly reproduced the LLJ strength, it would
251 still be difficult to identify the contribution of the LLJ in moderating the vertical O_3 distribution
252 because the interplay of several processes (e.g., vertical mixing and horizontal advection) cannot
253 be easily separated in 3D simulations. Therefore, simulations are conducted in this study using a
254 single-column model to examine the impact of LLJ-induced vertical mixing on August 10, 2010.
255 The environmental wind profile is manually set up in the model using the observed wind profile
256 as guidance. Two simulations are conducted; the control simulation has a calm condition while a
257 sensitivity experiment has a LLJ profile between 0000 LT and 0600 LT of day 2; the latter is
258 otherwise the same as the control simulation. The maximum wind speed (WSP) of the LLJ at
259 440 m AGL is set as 20 m s^{-1}. The single column model does not consider directional wind
260 shear. Instead, the maximum WSP of the LLJ is set at a higher value than the observation to
261 account for the effect of directional shear-induced turbulence.

262 The simulations with the single column model captured the meteorological conditions (e.g.,
263 temperature and relative humidity) reasonably well (Fig. 8). In the sensitivity simulation, the
264 impacts of LLJ-induced vertical mixing on meteorological conditions near the surface are
265 successfully captured. An abrupt increase of temperature and decrease of relative humidity near
266 the surface are reproduced at the onset of the LLJ, i.e., 0000 LT on August 10, 2010.

267 The simulated time series of O_3 mixing ratios near the surface are shown in Fig. 9a. At the
268 onset of the LLJ (0000 LT), O_3 mixing ratios near the surface increased by ~18 ppbv in the
269 sensitivity simulation. At the same time, surface temperature increased (Fig. 8). These results
270 are consistent with the observed secondary O_3 maximum shown in Fig. 1. The surface O_3 was
271 nearly depleted on the calm night in the control simulation due to dry deposition and NO titration,

while it was elevated in the sensitivity simulation with the LLJ (Fig. 9a). Such difference of the surface O_3 caused by LLJs was also reported in previous studies (Banta et al., 2007). These results therefore confirm the hypothesis that the LLJ played an important role in downward mixing of O_3 during the night of August 9-10, 2010.

The simulated vertical profiles of O_3 are shown in Fig. 10. The LLJ played an important role in removing O_3 in the RL at night. According to the formula (2), elevated wind shear in the presence of the LLJ will cause an increase of the eddy diffusivity. As a result of the shear-enhanced turbulence, the temperature inversion weakened, *Ri* further decreased, which, according to (2), as a whole contributed to a substantial increase in eddy diffusivity in the presence of a LLJ. The enhanced vertical mixing played a critical role in modulating the vertical redistribution of O_3 in the boundary layer. On a calm night, O_3 in the RL was mostly conserved while the RL O_3 was reduced by ~25 ppbv at 0800 LT in the presence of the LLJ (Fig. 10 and Fig. 9b). LLJs have also been reported to induce mechanical turbulence that can vertically mix O_3 in the nocturnal boundary layer in other regions such as Texas (Tucker et al., 2010). The significant reduction of O_3 in the RL in both observations (Fig. 5a) and simulation (Fig. 10b) indicates that the RL may not be a reservoir of pollutants in the presence of strong LLJs. The simulated reduction of the RL O_3 from the daytime mixed layer by the sensitivity simulation (~25 ppbv, Fig. 10b) was smaller than the observed reduction (~40 ppbv, Fig. 5a). Such discrepancy may be due to the exclusion of advection processes in the single column model and/or model errors. Model errors in the treatments of vertical mixing in meteorological and air quality models are shown to lead to substantial bias of simulated profiles of meteorological and chemical variables (Hu et al., 2010, 2012; Nielsen-Gammon et al., 2010).

Due to the enhanced turbulence induced by the LLJ, more O_3 was transported to the surface, where it was subjected to NO titration and enhanced dry deposition. The dry deposition velocity was correlated to the friction velocity u_*, with larger u_* values leading to larger dry deposition velocities. Enhanced turbulent mixing in the presence of a LLJ resulted in an increase in u_*, and thus higher dry deposition rates. As a result, the LLJ affected the O_3 budget at night, which in turn affected the O_3 concentration in the daytime mixed layer on the following day. Figure 10 shows that the mixed-layer O_3 at 1400 LT on the second day was reduced by ~8 ppbv due to the influence of the LLJ compared to the control simulation without the LLJ. The simulated maximum surface O_3 on August 10, 2010 was reduced by ~8 ppbv with the LLJ while the maximum 8-hour running average O_3 was reduced by ~6 ppbv (Fig. 9a). Compared with the observed O_3 profile at 13:54 LT on August 10 (~80 ppbv in the mixed layer), the predicted O_3 in the mixed layer on the second day by the sensitivity simulation is higher by ~10 ppbv. The discrepancy is likely due to the change of transport pathways during the daytime of August 10, 2010 (Hu et al., 2012), which is not considered in the single column model.

The time-height diagrams of simulated O_3 are shown in Fig. 11. Without the LLJ, the RL O_3 is mostly conserved (Fig. 11a). When the daytime mixed layer grows, the O_3-rich RL air is entrained into the mixed layer below, thereby contributing to the rapid increase in O_3 in the mixed layer in the morning. Such a scenario is described in Zhang and Rao (1999) and confirmed by other studies (Aneja et al., 2000; Yorks et al., 2009; Morris et al., 2010; Tong et al., 2011). However, in the presence of the LLJ, the RL O_3 is removed at night (Fig. 11b). In the following morning, entrainment contributes much less to the O_3 in the mixed layer (Fig. 11b), thus the increase of surface O_3 is much slower comparing to the control simulation (Fig. 9a).

5. Conclusions and discussion

Profiles of O_3 and meteorological variables in both nighttime and daytime have been measured in summertime since 2006 in Beltsville, Maryland (Hu et al., 2012). The data sets provided a unique opportunity to investigate the pollutants in the residual layer (RL) and their contribution to the daytime boundary layer pollution. It is shown that the RL was at times not a reservoir of O_3 at night. A case study was conducted for August 9-10, 2010, when a strong LLJ and elevated surface O_3 were observed at night. During this night, the RL O_3 was 50-60 ppbv, which was much lower than the O_3 level in the mixed layer on the previous day (~100 ppbv). Thus, O_3 appeared to be mixed from the RL to the ground preventing the RL from acting like a reservoir. Simulation results from a single-column model containing O_3 chemistry confirm that the LLJ causes a nocturnal secondary O_3 maximum and a significant reduction of the RL O_3. The LLJ-induced strong turbulence, which transports O_3-rich RL air to the surface where O_3 is efficiently removed by chemical reactions and enhanced dry deposition. These processes impact the O_3 budget: the enhanced nocturnal vertical mixing reduces the increase in surface O_3 the following morning and, compared to the results of a control simulation with calm conditions, the maximum O_3 is ~ 8 ppbv lower for the simulation containing a LLJ.

Salmond and McKendry (2002) found that secondary surface O_3 maximum due to enhanced nocturnal mixing rarely exceeded 50 ppbv. They concluded that the nocturnal secondary O_3 maximum is unlikely to be significant enough to affect human health. Our study shows that such nocturnal mixing may play an important role in modulating the O_3 levels in the daytime boundary layer on the following day; it may thus have a more important implication for public health than it had been previously realized.

339 Ryan (2004) investigated the climatology of LLJs in Maryland, USA and found that the
340 weather patterns favorable for the development of LLJs are normally also suitable for the
341 occurrence of Mid-Atlantic high O_3 episodes. Thus, the influence of LLJs on the O_3 episodes
342 can be hardly discerned from other factors that are conducive to O_3 accumulation. Due to the
343 difficulty in accurately reproducing LLJs and the interplay of several processes (e.g., vertical
344 mixing and horizontal advection) in three dimensional air quality simulations, a previous study
345 on this case (Hu et al. 2012) did not isolate the impact of LLJs on the vertical distribution of O_3.
346 Using a single column chemistry model that allows for easier setup of sensitivity experiments in
347 this study, the impact of LLJs on the boundary layer O_3 pertaining to stronger vertical mixing is
348 isolated. The effects of horizontal long-range transport due to LLJs are not considered in this
349 study. One implication of this study for long-range transport is: the pollutants in the RL may
350 leak out during the horizontal transport due to enhanced vertical mixing, reducing the impact of
351 urban plumes in downwind areas.

352 LLJs have been reported in many regions (Whiteman et al., 1997; Song et al., 2005; Zhang et
353 al., 2006); the LLJs in other regions (e.g., the Great Plains of the United States) may be much
354 stronger and more extensive than those in the Mid-Atlantic region (Zhang et al., 2006). Thus,
355 the impact of LLJs on the boundary layer O_3 may have important implications for air quality in
356 many regions. Apart from LLJs, mesocale motions such as Kelvin-Helmholtz instabilities,
357 gravity waves, wake vortices, and density currents can also cause enhanced nighttime turbulence
358 (Sun et al., 2002, 2003; Salmond and McKendry, 2005; Fritts et al., 2009), which may also make
359 the RL leaky. In addition to O_3, nocturnal mixing events may have appreciable effects on the
360 dispersion and budget of other species such as carbon dioxide and volatile organic compounds
361 (Acevedo et al., 2006; Ganzeveld et al., 2008). In one-dimensional simulations for the boundary

362 layer over a tropical forest using a single column chemistry-climate model, Ganzeveld et al.
363 (2008) showed that unresolved nocturnal vertical mixing processes likely lead to a nocturnal
364 accumulation of formaldehyde in the RL, which is later on entrained into the daytime convective
365 boundary layer where it affects daytime photochemistry. Further investigations regarding such
366 mixing processes and their impacts are warranted. Future field campaigns that aim at improving
367 our understanding of atmospheric chemistry in the atmospheric boundary layer should include
368 measurements of the chemical composition/transformation in combination with detailed
369 measurements of turbulence inside the RL.

370 Although the current study focuses on demonstrating the importance of vertical mixing
371 processes for vertical dispersion of boundary layer O_3, the contribution of other processes,
372 including advection (Banta et al., 2005; Zhang et al. 2007; Tucker et al., 2010), dry deposition
373 (Lin and McElroy, 2010) and chemical reactions in different chemical regimes at different height
374 above the ground (Brown et al., 2007), cannot be always ignored. To more accurately quantify
375 their contributions, meteorological and air chemistry measurements throughout the atmospheric
376 boundary layer are needed to further improve boundary-layer parameterizations, particularly for
377 nighttime conditions, and to facilitate the development and evaluation of more sophisticated
378 three-dimensional chemistry simulations.

379

380 *Acknowledgement. This work was supported by funding from the Office of the Vice President*
381 *for Research at the University of Oklahoma. The second author was also supported through the*
382 *NSF Career award ILREUM (NSF ATM 0547882). DCD received support from NASA (grant*
383 *number NNX08BA42A) to participate in the field studies. JDF received support from the*
384 *National Science Foundation to participate in this research (award ATM 0914597).*

Observations at Howard University Beltsville Campus were supported through grants from Maryland Department of the Environment, NASA (grant number NNX08BA42A) and NOAA (grant number NA17AE1625).

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