Diurnal variation of surface ozone in mountainous areas: Case study of Mt. Huang, East China

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HIGHLIGHTS
• A distinct diurnal cycle of O3 at the summit of Mt. Huang in East China.
• The diurnal O3 pattern at the summit was driven by the regional O3 transport.
• The diurnal O3 change at high-altitude sites was associated with residual layer.

GRAPHICAL ABSTRACT

Abstract

To explore the variations in atmospheric environment over mountainous areas, measurements were made from an intensive field observation at the summit of Mt. Huang (30.13°N, 118.15°E, 1841 m above sea level), a rural site located in East China, from June to August 2011. The measurements revealed a diurnal change of surface O3 with low concentrations during the daytime and high concentrations during the nighttime. The causes of diurnal O3 variations over the mountain peak in East China were investigated by using a fairly comprehensive WRF-Chem and HYSPLIT4 modeling approach with observational analysis. By varying model inputs and comparing the results to a baseline modeling and actual air quality observations, it is found that nearby ozone urban/anthropogenic emission sources were contributing to a nighttime increase in mountaintop ozone levels due to a regional transport lag and residual layer effects. Positive correlation of measured O3 and CO concentrations suggested that O3 was associated with anthropogenic emissions. Sensitivity modeling experiments indicated that local anthropogenic emissions had little impact on the diurnal pattern of O3. The diurnal pattern of O3 was mainly influenced by regional O3 transport from the surrounding urban areas located 100–150 km away from the summit, with a lag time of 10 h for transport.

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http://dx.doi.org/10.1016/j.scitotenv.2015.08.096
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1. Introduction

Tropospheric O\textsubscript{3} has an important effect on air quality, tropospheric chemistry, climate change, as well as human health and vegetation growth (Gao et al., 2005; Lippmann, 2000; Sitch et al., 2007; Solomon et al., 2000; Yang et al., 2012). O\textsubscript{3} and other atmospheric constituents over remote mountains could represent the atmospheric background of environmental change (Aneja et al., 1994; Tan et al., 2015; Gheusi et al., 2011; Puxbaum et al., 1991; Ribas and Penuelas, 2006; Skelly et al., 1997; Van Ooy and Carroll, 1995). The O\textsubscript{3} variation over mountainous areas is more complex, reflecting the interactions of physical and chemical processes, especially the terrain effect on dynamic transport on different scales and the exchange of atmospheric constituents between the boundary layer and the free troposphere.

It is well-known that diurnal changes of surface O\textsubscript{3} between low daytime concentrations and high nighttime concentrations were observed at many mountaintop sites over the world (Gallardo et al., 2000; Oltmans, 1981; Oltmans and Komhyr, 1986; Ryan, 1997), which is the opposite of that observed for surface O\textsubscript{3} over plains and flat terrain. The distinct pattern of diurnal O\textsubscript{3} changes measured at high-altitude observatories of mountaintops was thought to be a consequence of terrain thermally induced circulations, for example, mountain-valley breezes (Cristofanelli et al., 2013; Oltmans and Komhyr, 1986; Oltmans and Levy, 1994; Zaveri et al., 1995) in association with the vertical distribution of O\textsubscript{3} in the lower troposphere (Bonasoni et al., 2000; Forrer et al., 2000; Gheusi et al., 2011; Zellweger et al., 2000, 2003). In remote mountainous areas, the O\textsubscript{3} vertical distribution shows a positive correlation with altitude within the troposphere because of less impact of anthropogenic sources (Chevalier et al., 2007). In these areas, up-slope winds during the day drive the transport of O\textsubscript{3}-poor air masses from the foothills to the mountaintop, and downdraft winds during the night bring O\textsubscript{3}-rich air aloft towards the mountaintop, driving the diurnal O\textsubscript{3} changes (Yang et al., 2012). The terrain height of mountains was found to be a key factor in driving the exchange of O\textsubscript{3} between boundary layer and free tropospheric, with a critical altitude of 1.0–1.2 km a.s.l (Chevalier et al., 2007; Monteiro et al., 2012).

The distinct pattern of diurnal O\textsubscript{3} changes over mountainous areas was also found related to air mass transport from pollutant emission sources. For example, polluted air masses from L’Aquila were transported to Mt. Portella (Italy) through breeze circulation at night (Cristofanelli et al., 2013). The diurnal O\textsubscript{3} pattern at Mt. Fuji (Japan) was built by regional transport and vertical mixing of thermal convection (Tsutsumi and Matsueda, 2000). Regional pollutant transport is believed to form the diurnal O\textsubscript{3} variations at Mt. Abu (India) as well (Naja et al., 2003). At Mt. Tai (northern China), the air pollutant transport within the boundary layer to the summit resulted in increases in afternoon O\textsubscript{3} concentrations (Li et al., 2008), however, the cause for the nighttime peak of O\textsubscript{3} at Mt. Tai is only speculated to be the effect of local mesoscale dynamic transport (Gao et al., 2005). The regional transport of O\textsubscript{3} from the surrounding emission sources to the receptor regions at mountaintops and its influences on the diurnal O\textsubscript{3} changes at mountaintops are complicated by the pathway and period of regional transport on different scales, physical and chemical processes as well as the exchange between the boundary layer and the free troposphere over the mountaintops, which is required to further understand.

The Mt. Huang is located in East China (Fig. 1), a major pollutant emission source region connecting with economic boom and dense population over past decades in China. The atmospheric environment over Mt. Huang is found to be affected by air pollutant emissions over the surrounding areas. An O\textsubscript{3} contribution of 20–50% from the Yangtze Delta and East China led to a high O\textsubscript{3} event at the summit of Mt. Huang (Wang et al., 2006b). Regional transport was a key factor in driving the seasonal changes of O\textsubscript{3} concentrations at Mt. Huang (Li et al., 2007). However, little is known about the mechanism of regional transport forming the diurnal variation in surface O\textsubscript{3} over the Mt. Huang. As such, this study aimed understanding causes on diurnal O\textsubscript{3} variation over mountainous areas in connection with regional environment change.

2. Experiment

2.1. Measurement site and O\textsubscript{3} concentrations

An intensive field observation including hourly meteorology and concentrations of O\textsubscript{3} and CO were simultaneously measured at the summit of Mt. Huang in summer 2011. The measurement site was located at the summit of Mt. Huang, at an elevation of 1841 m a.s.l, in the southern rural area of East China. The summit is approximately 280 km southwest of the Yangtze River Delta and overlooks the city of Huangshan, 45 km to the south. Around Mt. Huang, a number of cities are located within 100–150 km, such as Anqing and Chizhou to the northwest, Jingdezhen and Nanchang to the southwest, Quzhou and Jinhua to the southeast (Fig. 1). As a popular tourism destination in China, Mt. Huang receives a large number of tourists during summer (June, July, and August). Local pollutant emissions, such as carbon monoxide, PM\textsubscript{2.5} and volatile organic compounds from combustion sources are produced from small restaurants and temples.

Climatologically, the area around Mt. Huang is a typical monsoon region with significant changes in winds, temperature, humidity, and...
precipitation between summer and winter monsoons. In the summer months of June, July, and August, southwest summer monsoon winds prevail with frequent rainfall. During the measurements, rainy and foggy days were more than 70% of the entire period and the mean relative humidity was 86%.

The diurnal variation of measured \( \text{O}_3 \) at the summit of Mt. Huang was classified into two patterns of rainy days and non-rainy days, which are thought to be a strength index of mountain-valley breezes (Fig. 2). Overall, the both patterns in diurnal \( \text{O}_3 \) change presented low \( \text{O}_3 \) concentrations during the daytime and high \( \text{O}_3 \) concentrations during the night-time. The similar \( \text{O}_3 \) pattern in rainy days with the week mountain-valley circulation indicated that the mountain-valley breezes exerted less impact on the diurnal \( \text{O}_3 \) change over the summit of Mt. Huang. The \( \text{O}_3 \) concentration during the night was greater than 40 ppbv, which could cause visible leaf injury and plant damage (Sitch et al., 2007).

2.2. Model description and settings

The WRF-Chem (Weather Research and Forecasting model with Chemistry) version 3.6.1 was employed in this study (Grell et al., 2005). The grid spacing was set at 9, 3 and 1 km for three nested domains (Fig. 3) with 35 vertical layers extending from the surface to 100 hPa. Most of the cities surrounding Mt. Huang (Fig. 1) were included in domain 2. The National Center for Environmental Prediction Final Global Forecast System operational analysis data was used for the initial and boundary conditions of all meteorological variables in the WRF-Chem simulation. The physical parameterizations used in this study are provided in Table 1.

To reduce biases in the \( \text{O}_3 \) simulation during night-time, the CBMZ (carbon bond mechanism) and MOSAIC (Model for Simulating Aerosol Interactions and Chemistry) were selected in the simulation (Zaveri et al., 2008). Anthropogenic emissions of \( \text{NO}_x \) (nitrogen oxides), \( \text{CO} \) (carbon monoxide), \( \text{SO}_2 \) (sulfur dioxide), \( \text{VOCs} \) (volatile organic compounds), \( \text{PM}_{2.5}, \text{PM}_{10} \) (black carbon) and \( \text{OC} \) (organic carbon) were based on the Intercontinental Chemical Transport Experiment-Phase B (INTEX-B, 2006) field campaign emission inventory. Biogenic emissions were from the Model of Emission of Gases and Aerosol from Nature (MEGAN) (Guenther et al., 2006). Default model settings for initial and boundary chemistry conditions were used. The simulations were conducted for the period ranging from 00:00 Local State Time (LST) July 12, 2011 to 08:00 LST July 21, 2011 with the restart every 3 days, and the first 24 h used as spin-up time. Additionally, two sensitivity experiments (Table 2) were carried out to investigate the influences of local \( \text{O}_3 \) on the summit of Mt. Huang.

3. Results

3.1. Validation of simulated meteorology and \( \text{O}_3 \) concentrations

The WRF-Chem modeling results were evaluated through comparisons between measured and simulated wind speeds, wind directions, and \( \text{O}_3 \) concentrations from July 12–21, 2011. Fig. 4 presents the hourly series of observed and modeled surface wind speeds, wind directions, and \( \text{O}_3 \) concentrations, respectively. As seen in Fig. 4, the simulated meteorological variables exhibited a good agreement with measurements. For wind direction, the model depicted its temporal variation well, except for some rapid small changes. The correlation coefficient between the simulated and measured wind velocity is 0.33, passing the significant level of 0.001. Wind velocity was slightly overestimated by the model. This may be the unresolved boundary layer (PBL) scheme (Shimada and Ohsawa, 2011; Shimada et al., 2011), or the out-of-date USGS (United States Geological Survey) data used in the model (Gao et al., 2015). It should be noted that the summit in the model was only 1467 m a.s.l. because the model resolution of the innermost domain was 1 km, which could increase discrepancies between simulations and observations. Generally, the modeled \( \text{O}_3 \) diurnal variation

![Fig. 2. Diurnal variations in surface \( \text{O}_3 \) concentrations averaged over rainy and non-rainy days (curves), with standard errors (straight lines).](Fig. 2)

![Fig. 3. Map of the three model domains with the grid spacing of 9, 3 and 1 km.](Fig. 3)

<table>
<thead>
<tr>
<th>Table 1</th>
<th>WRF physical parameterizations used in the modeling study.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical management</td>
<td>Parameterization</td>
</tr>
<tr>
<td>Microphysics scheme</td>
<td>Lin et al.</td>
</tr>
<tr>
<td>Longwave radiation scheme</td>
<td>RRTM</td>
</tr>
<tr>
<td>Shortwave radiation scheme</td>
<td>Dudhia</td>
</tr>
<tr>
<td>Land surface scheme</td>
<td>Noah</td>
</tr>
<tr>
<td>Surface scheme</td>
<td>Monin–Obukhov</td>
</tr>
<tr>
<td>Planetary boundary layer scheme</td>
<td>YSU</td>
</tr>
<tr>
<td>Cumulus scheme</td>
<td>KF</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Settings of sensitivity experiments.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiments</td>
<td>MOD-1</td>
</tr>
<tr>
<td>Settings</td>
<td>Closing the anthropogenic emissions within domain 3</td>
</tr>
</tbody>
</table>
reasonably captured the measured pattern (Fig. 5) with most simulated points within a factor of two compared with the observations. The modeled O$_3$ concentrations were overestimated, especially at night. Overestimations of O$_3$ concentrations in the residual layer during nighttime were reported by WRF-Chem simulations because of low turbulence diffusion efficiencies in the YSU scheme (Hu et al., 2012), which was used in this study. Because the altitude of the summit is comparable to the height of the residual layer, constituents in the residual layer are likely to be present at the summit.

3.2. Impact of regional emissions

The correlation between tropospheric O$_3$ and CO has been extensively used in tropospheric chemistry studies to explore photochemical characteristics. As CO is a good indicator for industrial and biomass burning pollution (Logan et al., 1981), a positive correlation between CO and O$_3$ indicates that a region has experienced photochemical O$_3$ production from anthropogenic emissions including CO, while a negative correlation indicates that O$_3$ originated from the upper troposphere or the stratosphere (Fishman and Seiler, 1983).

The correlation coefficient between O$_3$ and CO at the summit of Mt. Huang was 0.56 (Fig. 6), which is similar to that reported for Mt. Tai during summer (Gao et al., 2005). This suggests that the Mt. Huang station was affected by anthropogenic emissions rather than transport from the upper troposphere or the stratosphere, because this upper layer is always rich in O$_3$ but poor in CO. For example, at Mt. Waliguan (WLC, 36.28°N, 100.90°E, 3816 m above sea level), a negative correlation between CO and O$_3$ was present because of the transport from upper tropospheric or lower stratospheric air (Wang et al., 2006a).

As previously discussed, realistic O$_3$ variations were predicted by the simulation, which is referred to as the control simulation (MOD-control). To further investigate the effects of anthropogenic emissions, two sensitivity simulations were preformed (Table 2 and Fig. 7).

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Fig. 4. Hourly observed (black squares) and modeled (red squares) wind direction (top panel), wind speed (middle panel), and O$_3$ mixing ratios (bottom panel).

Fig. 5. A scatterplot of observed and modeled O$_3$ concentrations. $R = 0.56$ is the correlation coefficient between simulated and measured O$_3$ with a linear regression line in black line. Three gray lines are two lines for a factor of two from observations and a line of best fit.

Fig. 6. A scatterplot of O$_3$ versus CO concentrations. The correlation coefficient $R = 0.56$ indicates that the Mt. Huang station was mostly affected by anthropogenic emissions.
Insignificant O₃ concentration differences between MOD-control and MOD-1, with high O₃ concentrations during daytime and low O₃ concentrations during nighttime, indicated that local emissions in domain 3 covering the city of Huangshan and some smaller towns, had little influence on O₃ variations at the summit of Mt. Huang. When anthropogenic emissions were ignored in the sensitivity experiment MOD-2, O₃ concentrations decreased markedly and the diurnal variation disappeared, indicating that anthropogenic emissions from domain 2 to 3 were closely related to the diurnal O₃ variation at the summit. Based on the mean wind speed of 3.5 ms⁻¹ over the study period at the summit and the distance of 100–150 km from the urban areas in domain 2 to 3 to the summit, it could be estimated that polluted air emitted from those urban areas would take approximately 10 h to be transported to the summit. This transport time is within the 2-day lifetime of O₃ in the low troposphere (Wang et al., 2011).

3.3. Regional transport to the summit

As discussed in Section 3.2, the diurnal O₃ variation at the summit of Mt. Huang was mainly influenced by anthropogenic emissions from domain 2 to 3. This highlights the importance of investigating how anthropogenic emissions affect O₃ concentrations.

Because O₃ concentrations at the summit of Mt. Huang were at their minimum and maximum at 12:00 and 22:00, respectively (Fig. 2), meteorological and chemical conditions at 12:00 and 22:00 were treated as daytime and night-time conditions, respectively. Sections A and B aligned with the wind direction in front of the summit, used for vertical distribution calculation of O₃ and wind speed in Fig. 8.

Fig. 7. Observed, MOD-control, MOD-1 and MOD-2 simulated hourly series of O₃ mixing ratios. The MOD-control simulation was the control experiment, and the simulations of MOD-1 and MOD-2 are described in Table 2.

Fig. 8. Simulated O₃ concentrations on the surface on July 16. (a) 12:00; (b) 22:00. The summit of Mt. Huang is marked with a black cross. The time 12:00 and 22:00 were treated as daytime and night-time conditions, respectively. Sections A and B aligned with the wind direction in front of the summit, used for vertical distribution calculation of O₃ and wind speed in Fig. 9.

Fig. 8a. At night, O₃ concentrations decreased in the urban regions because of deposition and chemical reactions (Fig. 8b). This diurnal pattern is the opposite of that at Mt. Huang. As previously estimated, polluted air masses emitted from the urban areas would take

Fig. 9. Vertical distribution of O₃ concentrations and wind velocities in front of the summit on July 16. The lines shown are: (O₃-A) 12:00, O₃ concentrations in the marked section A of Fig. 8a; (V-B) 22:00, wind velocities in the marked section B of Fig. 8b; (O₃-B) 22:00, O₃ concentrations in the marked section B of Fig. 8b; (V-A) 12:00, wind velocities in the marked section A of Fig. 8a.
approximately 10 h to reach the summit of Mt. Huang. This transport time is the same as the lag time between 12:00 and 22:00 (Fig. 8).

The vertical concentration profile of O₃ and the horizontal wind velocity in front of the summit presented different patterns between the day and the night (Fig. 9). We suggest that O₃ concentrations near the ground are enhanced because of solar radiation and emissions of O₃ precursors after sunrise, but the upper air mass in front of the summit (1840 m a.s.l.) has a low concentration of O₃ because of fewer precursors (Line O₃-A in Fig. 9). The horizontal wind velocity at 1840 m a.s.l. in front of the summit was 8.3 m/s and decreased rapidly below 1.5 km because of the development of a convective PBL, which could reduce advection (Line V-A in Fig. 9). These factors suggest that the low O₃ concentrations during daytime resulted from horizontal transport in front of the summit. It was also confirmed that local anthropogenic emissions had little effect on O₃ concentrations at the summit. The distribution of nocturnal O₃ in front of the summit revealed a low-high-low pattern as altitude increases, with peak concentrations between 1.0 and 1.5 km in the nocturnal residual layer (Line O₃-B in Fig. 9). We suggest that this pattern emerged because of deposition and chemical removal (Simmonds et al., 1997). Simultaneously, the layer above the SBL maintained the structure of the mixed layer because of slow cooling, forming the nocturnal residual layer. O₃ in this residual layer is far away from surface destruction, resulting in a longer lifetime of O₃ than that in the SBL. The distinct vertical distribution of O₃ at 22:00 in front of the summit was caused by the formation of a residual layer. Because O₃ concentrations in the residual layer were comparable with those at the summit (Figs. 4 and 9) and wind in the residual layer was relatively strong (Line V-B in Fig. 9), the enhancement of nocturnal O₃ concentrations at the summit was mainly driven by regional transport in the residual layer.

To determine transport processes and the source regions of O₃, a backward trajectory analysis of the HYSPLIT4 model was performed by using WRF-Chem-simulated results from domain 2. As discussed in Section 3.2, the diurnal pattern of O₃ with the enhancement of nocturnal O₃ concentrations at the summit resulted from the O₃ transport time of approximately 10 h to the summit. 10 h backward trajectories were calculated from the summit of Mt. Huang from July 12 to 20 twice per day respectively starting at 12:00 and 22:00 LST for the minimum (12:00) and maximum (22:00) O₃ concentrations (Fig. 2). The transport pattern at night (22:00) revealed that most trajectories from the summit of Mt. Huang originated from urban areas, especially southern cities such as Jinhua, Quzhou, and Shangrao (Fig. 10b) within 900–940 hPa.
indicating similar source regions between the day and night. The differences starting at 12:00 (Figs. 10a and 11a) was similar to those at 22:00, indicating similar source regions between the day and night. The difference was the summit experienced low O3 levels at day, which mostly originated from urban areas before sunrise.

Regional transport was a major driving force on O3 concentration variations during the daytime and nighttime; and the transport of O3 in the nocturnal residual layer enhanced O3 concentrations at the summit of Mt. Huang during the nighttime. This process was responsible for the observed diurnal pattern of O3 concentrations.

4. Conclusions

A typical diurnal of O3 variation at high-altitude sites was measured from an intensive field observation at the summit of Mt. Huang, East China. The diurnal pattern featured high concentrations during the night and low concentrations during the day. The factors contributing to the diurnal O3 pattern at the summit of Mt. Huang were investigated by using measurements and modeling with the WRF-Chem and HYSPLIT4 models.

By varying model inputs and comparing the results to a baseline model and actual air quality observations, our study concluded that nearby ozone urban/anthropogenic sources are contributing to a nighttime increase in mountaintop ozone concentrations due to a regional transport lag and residual layer effects. A positive correlation between measured CO and O3 concentrations indicated that the summit was affected by photochemical O3 production from anthropogenic emissions.

Two sensitivity experiments with zero anthropogenic emissions from all domains and only domain 3 showed that local emissions played little role. The enhancement of O3 during the night was mainly driven by regional transport in the nocturnal residual layer. During the daytime, because of the 10-h lag time, the summit received air masses with low O3 concentrations that originated from urban areas before sunrise. The new findings and the information could be useful for future studies on regional environmental changes over mountainous areas.

This study at the summit of Mt. Huang in summer highlights the dominance of regional transport and residual layer of O3 in driving the diurnal pattern of O3 over the mountaneous areas. The distribution and variation of surrounding emission sources affecting the role of regional transport in O3 change over mountainous areas as well as the height of mountain altering the vertical exchange of the boundary layer and the free troposphere for the mountaintop O3 will be addressed in comprehensive studies on atmospheric environment over mountainous areas.

Acknowledgments

This study was sponsored by the National Natural Science Foundation of China (Grant No. 41030962), National Scientific and Technology Project (2014BAC22B04), the Key Basic Research Program (2014CB441203), Science and Technology Support Program of Jiangsu Province (BE2012771) and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

References


