Diurnal variations and source apportionment of ozone at the summit of Mount Huang, a rural site in Eastern China

J. Gao a, b, B. Zhu a, b, *, H. Xiao c, H. Kang a, b, X. Hou a, b, Y. Yin a, b, L. Zhang a, b, Q. Miao d

*a Collaborative Innovation Center on Forecast and Evaluation of Meteorological Disasters, Nanjing University of Information Science and Technology, Nanjing, China
b Key Laboratory for Aerosol-Cloud-Precipitation of China Meteorological Administration, Nanjing University of Information Science and Technology, Nanjing, China
c Institute of Tropical and Marine Meteorology, China Meteorological Administration, Guangzhou, China
d Suzhou Environment Monitor Center, Suzhou, China

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ABSTRACT

Comprehensive measurements were conducted at the summit of Mount (Mt.) Huang, a rural site located in eastern China during the summer of 2011. They observed that ozone showed pronounced diurnal variations with high concentrations at night and low values during daytime. The Weather Research and Forecasting with Chemistry (WRF-Chem) model was applied to simulate the ozone concentrations at Mt. Huang in June 2011. With processes analysis and online ozone tagging method we coupled into the model system, the causes of this diurnal pattern and the contributions from different source regions were investigated. Our results showed that boundary layer diurnal cycle played an important role in driving the ozone diurnal variation. Further analysis showed that the negative contribution of vertical mixing was significant, resulting in the ozone decrease during the daytime. In contrast, ozone increased at night owing to the significant positive contribution of advection. This shifting of major factor between vertical mixing and advection formed this diurnal variation. Ozone source apportionment results indicated that approximately half was provided by inflow effect of ozone from outside the model domain (O3-INFLOW) and the other half was formed by ozone precursors (O3-PBL) emitted in eastern, central, and southern China. In the O3-PBL, 3.0% of the ozone was from Mt. Huang reflecting the small local contribution (O3-LOC) and the non-local contributions (O3-NLOC) accounted for 41.6%, in which ozone from the southerly regions contributed significantly, for example, 9.9% of the ozone originating from Jiangxi, representing the highest geographical contributor. Because the origin and variation of O3-NLOC was highly related to the diurnal movements in boundary layer, the similar diurnal patterns between O3-NLOC and total ozone both indicated the direct influence of O3-NLOC and the importance of boundary layer diurnal variations in the formation of such distinct diurnal ozone variations at Mt. Huang.

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1. Introduction

Tropospheric ozone (O3) is an important air pollutant formed through physical processes and photochemical reactions (Crutzen, 1973). As a typical secondary pollutant, its impact on air quality, climate change, human health, and vegetation is well established (NRC, 1991), and represents a subject of public concern. Ozone in remote mountainous regions can reflect atmospheric background changes (Ribas and Penuelas, 2006; Gheusi et al., 2011; Tan et al., 2015). A number of researchers have observed diurnal variations of ozone at mountaintops, with concentrations being lower during the daytime and higher during the nighttime (Oltmans and Komhyr, 1986; Ryan, 1997; Gallardo et al., 2000), and an opposite pattern being observed above plains and/or low attitude environments (Geng et al., 2011; Jiang et al., 2012; Zhu et al., 2015).

Some previous studies have concluded that the ozone diurnal patterns at mountaintops relate to diurnal changes of mountain-valley breezes (Zaveri et al., 1995; Yang et al., 2012; Cristofanelli...
et al., 2013). In this scenario, up-slope winds carry air masses with low ozone concentrations during the day (Weiss-Penzias et al., 2006), while down-slope winds bring air aloft with high ozone concentrations down to the mountaintops at night. Another factor which was thought to be closely related to the distinct diurnal feature was the transport effects; for example, Naja et al. (2003) suggested that the diurnal variations in ozone at Mt. Abu reflected regional transport from upwind pollutant regions, while Li et al. (2008) showed that both transport and weak photochemical reactions could be responsible for low daytime ozone and high nighttime ozone at Happo. In addition, the location (Chevalier et al., 2007) and altitude of a mountain (Monteiro et al., 2012), and ozone vertical distributions (Forrer et al., 2000; Zellweger et al., 2003; Gheusi et al., 2011) have also been considered as possible explanations for ozone diurnal patterns at mountaintops. Studies on ozone diurnal variation at mountaintops have also been carried out in China. For example, comprehensive meteorological analyses and atmospheric pollutant measurements (Chen et al., 2014; Li et al., 2014) conducted at the summit of Mount Huang (Mt. Huang). Mt. Huang is located in eastern China, where the environment is strongly affected by air pollution from the surrounding areas, especially the ones with highly polluting industries and power plants, through transport effects. Wang et al. (2006) analyze an ozone episode occurred over Mt. Huang during 23–25 May 2004. They suggested that 20–50% of the ozone at the summit of the Mt. Huang was contributed from the Yangtze Delta and eastern China. Zhang et al. (2015) found that ozone from surrounding urban areas had a lag time of 10 h for transport to the Mt. Huang summit, concluding that this explained the high nighttime concentrations.

Each of these studies showed one or two possible factors leading to distinct diurnal variations in ozone concentration at the mountaintops. However, the changes in ozone concentrations are the result of a combination of various physical and chemical processes. Focusing on only one factor could thus put limitations on the analysis of diurnal variations in ozone. The impacts of all the relevant processes in the formation of ozone diurnal pattern require further investigation.

In this work, the Weather Research and Forecasting with Chemistry (WRF-Chem) model was applied to simulate the ozone concentrations at the summit of Mt. Huang in June 2011 as a case study. Using process analysis, impacts of the physical and chemical processes in boundary layer during each time period in the formation of ozone diurnal variations were established. And ozone source regions and their quantified contributions were indentified accurately by ozone tagging results. This paper appears to be a further research on the ozone diurnal variation and source apportionment at the summit of Mt. Huang. The results also provide valuable finding for studying the features of ozone in remote mountainous area in Eastern China.

2. Methodology

2.1. Measurement site

Hourly meteorological data (wind, temperature, wind direction, and wind speed) and ozone concentrations were collected at the summit of Mt. Huang (about 30°13′ N, 118°15′ E, 1840 m above sea level) during the summer of 2011. Mt. Huang is located southwest to the Yangtze River Delta, which is one of the most developed areas in China. A number of cities are located within 100–150 km of Mt. Huang; for example, Anqing and Chizhou (Anhui Province) to the northwest; Jingdezhen and Nanchang (Jiangxi Province) to the southwest; and Quzhou and Jinhua (Zhejiang Province) to the southeast (Zhang et al., 2015). Mt. Huang is one of the most popular tourist resorts known for providing a great sightseeing experience, and attracts visitors from all over the world every year. The relatively low level of development and also fewer heavy industries in the immediate vicinity mean that the ozone concentrations in this region generally represent the regional background levels in eastern China.

Mt. Huang experiences a typical subtropical monsoon climate with well-defined seasonal winds, precipitation, temperature, and humidity. In summer, southwesterly winds prevail (i.e., the summer monsoon) and warm and wet air is transported to Mt. Huang, leading to frequent rainy days. During June 2011, southwesterly winds accounted for 58% of the recorded winds, while the mean temperature and relative humidity were 16 °C and 90%, respectively. A total of 76% of the days in June were rainy or foggy. These synoptic features were close to the summer weather in the entire Mt. Huang region (17 °C mean temperature; 91% relative humidity; 70% rainy or foggy days). Further, with measured ozone concentration in June of a satisfactory data quality (nearly a whole month of continuous observations with few default data were obtained), we attempted to simulate ozone concentrations in June as a case study to investigate the causes of ozone diurnal variations at the summit of Mt. Huang. We defined the daytime and nighttime by relying on the time of sunrise and sunset: the daytime duration was about 14 h (from 05:00 to 19:00 LT) in June, and the nighttime duration was about 10 h.

2.2. Model description and data

In this study, we used version 3.4 of the WRF-Chem model. Detailed descriptions of the meteorological and chemical components of this model are available in Skamarock et al. (2008) and Grell et al. (2005). Two domains (Fig. 1a) were set up with horizontal resolutions of 9 km and 3 km with grids of 160 × 160 and 120 × 120 for domains D1 and D2, respectively. D1 covered most of eastern China and the corresponding simulations provided meteorological and chemical boundary conditions for the inner domain (D2). D2 covered Mt. Huang and the surrounding areas, which belong to the Anhui, Jiangsu, Jiangxi, and Zhejiang provinces. The vertical structure of the atmosphere was set using 38 sigma levels from the surface to 50 hPa, including 12 levels within the lowest 2 km. The simulation ran from 2 to 30 June 2011, with the initial and boundary meteorological conditions taken from National Centers for Environment Prediction (NCEP) final (FNL) Operational Global Analysis data files with 1° × 1° horizontal spatial resolution and 6-h temporal resolution. In order to reduce integral errors, FNL data were also used for data assimilation using the Grid Nudging method (Stauffer and Seaman, 1990). Initial and boundary chemical conditions were provided by the output of the Model of Ozone and Related Chemical Tracers (MOZART-4; Emmons et al., 2010) with a temporal resolution of 6 h. The gas-phase chemical mechanism Carbon Bond Mechanism version Z (CBMZ; Zaveri and Peters, 1999) was used as the gas mechanism. Other parameterizations are detailed in Table 1.

The initial anthropogenic emissions used relied on the MIX Asian emission inventory (Li et al., 2015), which has a 0.25° × 0.25° horizontal resolution. The target year of this inventory was 2010, close to our simulation year. MIX includes both gaseous and aerosol species, including: SO2, NOx, NH3, CO, CO2, NMVOC (non-methane volatile organic compounds), BC (black carbon), OC (organic carbon), PM10 (particulate matter with diameter less than or equal to 10 μm), and PM2.5 (particulate matter with diameter less than or equal to 2.5 μm). Considering the resolutions of our study, before interpolating emission data into the resolution of each domain, the MIX database was firsty interpolated in agreement with the distributions of nighttime light data for 2011 with a horizontal resolution of 1 km × 1 km, which were provided by the Defense
Meteorological Satellite Program (DMSP; Oda and Maksyutov, 2011). In addition, biogenic emissions, which are also very important to the formation of ozone, were generated using the Model of Emissions of Gas and Aerosols from Nature (MEGAN; Guenther et al., 2006) by obeying the resolution of each domain.

2.3. Ozone tagging method

2.3.1. Description of ozone tagging method

The ozone tagging method was coupled into the WRF-Chem model and then applied to quantify the ozone contributions from different source regions at the summit of Mt. Huang. Our ozone tagging method was similar to the Ozone Source Apportionment Technology (OSAT; Yarwood et al., 1996) in the Comprehensive Air quality Model with extensions (CAMx; ENVIRON, 2011) and some modifications were made to suit the requirements of the WRF-Chem model.

As a typical secondary air pollutant, the formation of tropospheric ozone is highly dependent on photochemical reactions with attendance of ozone precursors (NOX and VOCs); therefore, quantifying the contributions of ozone requires the consideration of both NOX limited and VOCs limited conditions in the regional-scale air quality model system. The ozone tagging method used in this study considered both these ozone control conditions. This approach uses a mass balance technique to identify the different geographical source contributions to overall ozone in a particular location or region within one simulation. In this method, ozone and its precursors were tracked as independent variables from various source regions. They undertook the effects of all the relevant calculations as the normal simulation do, but did not perturb the normal calculations. For each time step decays, ozone with identified by i in any grid cell is equal to:

\[
O_3^{\text{new}}_i = O_3^{\text{old}}_i + \frac{dO_3}{dt}_i
\]  

In equation (1), \( O_3^{\text{new}}_i \) and \( O_3^{\text{old}}_i \) represent the ozone concentrations after and before the integral, respectively, and \( \frac{dO_3}{dt}_i \) is the change rate of \( O_3^i \) at this time step which can be treated as follows:

\[
\frac{dO_3}{dt}_i = P03_i - DO3_i \times \frac{O_3^i}{\sum O_3^i}
\]  

where \( P03_i \) is the chemical production formed by ozone precursors from region i and the total ozone destruction (DO3) is allocated based on the rate of ozone concentration identified in i with respect to the total ozone concentration. We used the ratio of HCHO and NOy concentrations (HCHO/NOy) described by Sillman (1995) as an indicator to judge if the grid cell is under the NOX or VOCs limited condition in each grid cell. For different ozone controlled conditions, \( P03_i \) is allocated in the following ways:

(1) NOX limited:

\[
P03_i = P03 \times \frac{NOX_i}{\sum NOX_i}
\]  

(2) VOCs limited:

\[
P03_i = P03 \times \frac{VOCs_i}{\sum VOCs_i} = P03 \times \frac{\sum VOC_{ij} \times kOH_j \times MIR_j}{\sum VOC_{ij} \times kOH_j \times MIR_j}
\]  

PO3 represents the total ozone chemical production calculated as described by Davis et al. (2003). NOX, and VOCs are the concentrations of NOX and VOCs from region i, respectively.
Considering that the reactivity and ozone forming potential of each VOC species are different, two weighted factors \((kOH)\) and \((\text{MIR})\) for each VOC species \(j\) were introduced. \(kOH\) is the OH-reactivity of each VOC species generated by the calculation from the WRF-Chem model framework. The other weighted factor \(\text{MIR}\) is described in Carter (1994), and it is used to approximate the ozone forming potential of each VOC species.

2.3.2. Source region setting

In our simulations, the Mt. Huang region covered the mountainous area around Mt. Huang \((-1.4 \times 10^6 \text{ km}^2)\), with the observation site being nearly in the center (Fig. 1). Considering the transport effect on ozone, the ozone contributions from surrounding regions could be significant to the ozone at Mt. Huang, especially from regions with highly developed industries and economies. The surrounding source regions included Anhui Province (AH), Jiangsu Province and Shanghai Municipality (JS&SH), Zhejiang Province (ZJ), Jiangxi Province (JX), and Fujian Province (FJ). More distal regions included in the simulation included N-CHN (i.e., Henan Province, and some parts of the Shandong, Shanxi, Hebei, and Shaanxi provinces, where heavy industries have been significantly developed and heavy environment problems occur frequently), C-CHN (i.e., most of Hebei and Hunan provinces), and S-CHN (i.e., most of Guangdong Province, one of the most developed areas in China, and a small part of Guangxi Province). The TW&SEA area of the simulation represented Taiwan, the Bohai Sea, the Huanghai Sea, the East China Sea, and the islands within these seas. The ozone contributions from all the source regions mentioned above represented the ozone formed by ozone pre-cursors released into the planet boundary layer (PBL) within the model domain, and we named this component as \(O3_{-PBL}\). While the ozone contributions from all the geographical source regions were included in \(O3_{-PBL}\), they were independent from each other. In addition, the chemical boundaries provided by MOZART-4 were defined as an independent contribution \(O3_{-INFLOW}\), which was considered to originate outside of D1. The initial conditions for D1 and D2 were also tracked as independent sources.

3. Results and discussion

3.1. Model evaluations

Fig. 2 presents the measured and simulated data for temperature, wind speed, wind directions, and ozone concentrations at the summit of Mt. Huang. With regard to meteorological variables, a good level of agreement between the measured data and modeled results, especially the wind shifting features, implied that the model successfully captured the synoptic features. For ozone concentrations (Fig. 2d), the simulated results and the observed data showed similar patterns, especially during three following periods: (I) June 9–13, (II) June 17–18, (III) June 23–24 which is when the variation trend of the modeled results agreed well with the observed results.

Some statistical metrics including the correlation coefficient \((r)\), Index of Agreement \((\text{IOA})\), mean bias \((\text{MB})\), root mean square error \((\text{RMSE})\) and normalized mean bias \((\text{NMB})\) were used to further examine the model performance for these simulations; the results are shown in Table 2. Some of the values have been given a recommended criterion (EPA, 1991; Emery et al., 2001), and we also present these benchmarks in brackets beside the corresponding statistical metric value. The IOA of the wind direction was according to the report of Kwok et al. (2010), and IOA values for the other variables were calculated following the approach of Liu et al. (1997). IOAs for temperature and wind speed \((0.85 \text{ and } 0.80\text{, respectively})\) reached the criterion and high IOAs for wind direction and ozone \((0.96 \text{ and } 0.84\text{, respectively})\) were comparable to other studies (Li et al., 2012; Gao et al., 2016). Additionally, with the correlation coefficients for the four variables ranged from 0.47 to 0.78, and the time series patterns of simulated and observed values agreed well. Small values of mean bias for temperature \((-0.40 \degree C)\) and wind speed \((-0.49 \text{ m s}^{-1})\) confirmed sufficient model performance for these two variables, however, the MB for wind direction exceeded the benchmark. There was an over-estimation of ozone, as indicated by the positive mean bias value \((8.05 \text{ ppbv})\). RMSE for wind speed exceeded the recommended criteria a little and the others were close to other simulations in this region (Wang et al., 2006; Li et al., 2007; Hu et al., 2016). The NMB for ozone was a slightly larger than the recommended criteria. Besides, the NMB for the three meteorological factors were small and comparable to other studies (Li et al., 2013). Basically, our simulations for the time series of ozone concentrations and meteorological variables at the summit of Mt. Huang were reasonable. In addition, similar comparisons on ozone concentrations and meteorological factors at other sites were also conducted and these results are presented in the supplementary material (Fig. S1). The acceptable model performance not only at the summit of Mt. Huang but also at other sites in model domain suggests that our model system had the capability to reproduce ozone concentrations and capture the transport features in Eastern China during this period.

Uncertainties in the emission inventory and errors in parameterization often lead to deviations in simulations, making it challenging to reproduce reality exactly. For simulations on mountainous area, complex terrain and changeable synoptic conditions (e.g., valley winds) introduce additional uncertainties; therefore, deviations between simulations and observation are hard to avoid completely. To analyze ozone diurnal variations at the mountaintop more accurately, we selected the three periods for which observed and simulated data were best matched \((9–13 \text{ June, } 17–18 \text{ June, } 23–24 \text{ June}; \text{Fig. 2})\). For these three periods, the mean diurnal variations in simulations were similar to the measured data (Fig. 3), with low concentrations during the daytime and high concentrations at night. This pattern was consistent across the monthly mean diurnal pattern at the summit of Mt. Huang (Zhang et al., 2015), which suggests that the modeled results performed well and captured the distinct ozone.

3.2. Diurnal variations in ozone and relevant processes at the summit of Mt. Huang

Process analysis was applied to explain the development of diurnal variations in ozone under the influence of the atmospheric diurnal cycle, with the following process tendencies considered: 1) advection \((\text{adv})\) transport-related process; 2) the net value of chemical calculations in the model system \((\text{chem})\); and 3) vertical mixing \((\text{vmix})\) caused by atmospheric turbulence and vertical ozone concentration gradient. Convection processes \((\text{conv})\), which are mainly caused by dynamic and thermodynamic effects, were not found to be significant in the study area, and were therefore not considered. For full details, please check Zhang et al. (2014), Gao et al. (2016) and the WRF-Chem users’ guide.

The results showed that advection and vertical mixing influenced ozone concentration significantly at the summit of Mt. Huang (Fig. 4). Advection process made a positive contribution, while the contribution of vertical mixing was negative. A tiny positive contribution from photochemical process appeared during the middle of the day, reflecting low concentrations of ozone precursors (Zhang et al., 2015) over this region. During the morning hours, the contribution of vertical mixing was significant and offset the positive contribution of advection; as a result of which, the ozone concentration decreased. The tiny contribution from
photochemical reactions during midday indicated a lack of enough supplements for ozone formation, which was different from high photochemical contribution at the plains (Gao et al., 2016), and this made the net contribution to be maintained at a negative value until 15:00; therefore, the ozone concentrations fell during the daytime, reaching a minimum value in the afternoon. During the nighttime, contribution from advection offset the negative contribution (vertical mixing) and resulted in an increase in the ozone concentration. Owing to the shift in the major contributor, the ozone concentration showed distinct diurnal variations exhibiting low concentrations during the daytime and high concentrations at night at the summit of Mt. Huang.

3.3. Diurnal-altitude distribution for photochemical reactions and vertical mixing processes

The mean diurnal-altitude distribution (from the summit of Mt. Huang to a height of 5 km) of the chemical processes confirmed a tiny positive contribution both at the surface and beneath the PBL (Fig. 5a) during midday. This was different from the significant contribution that appeared on the plains in the neighboring region (Jiang et al., 2012). In troposphere, ozone chemical production is formed, usually with the presence of NO (Tie et al., 2009). During period of the observation, the observed NO concentrations were very low or even below the lower limitation of instrument most of the time. The low concentrations of NO also suggested that the local photochemistry was not significant at the summit of Mt. Huang. With the small positive contribution of ozone chemical production, ozone at the summit of Mt. Huang could not get enough ozone which provided favor conditions for the ozone concentration kept on decreasing till the afternoon (Fig. 4). The vertical mixing
tendencies showed significant negative values in the lowest altitude layers (Fig. 5b). Some positive values were also shown in the upper layers, especially at noon. The opposite contributions between the neighboring layers suggested that ozone exchange occurred between the lower and upper layers through vertical mixing. This led to a stronger negative contribution by vertical mixing during midday than during any other time of the day.

The latitude-altitude cross-sections for total ozone (O3-TOTAL), O3-INFLOW, and O3-PBL showed that during the midday (02–06 UTC), the measurement site was located within the upper PBL, which extended up to nearly 2 km. The ozone concentration at the summit of Mt. Huang was about 4–5 ppb higher than that between 2 and 3 km (Fig. 6a). Under these conditions, vertical mixing leading to ozone exchange between the layers resulted in poor ozone aloft being brought down to the surface and rich ozone at surface being brought up to the upper layer. That is why vertical mixing tendencies showed opposite behaviors between the neighboring layers during midday. A similar vertical structure appeared at night (Fig. 6d), but with ozone concentrations being higher in the lower layer, and the low-concentration upper layer extending to a height of 3–4 km, reflecting the influence of wind fields. Ozone concentrations changed little from the measurement site up to the top of the PBL; this meant that there was no significant gradient, and in addition, opposite contributions did not occur near the top of the PBL at night as atmospheric turbulence was weak. The negative contribution from vertical mixing was mainly caused by dry deposition. Ozone vertical structures contained a slightly low-concentration zone (5 ppb) in the free troposphere also had been observed in other regions (Pfister et al., 2013), suggesting that this type of ozone vertical structure is naturally occurring.

The total ozone (O3-TOTAL) concentrations from our simulation can be presented by the equation: $O_{3\text{-TOTAL}} = O_{3\text{-INFLOW}} + O_{3\text{-PBL}}$, where $O_{3\text{-INFLOW}}$ represents the ozone contribution from outside the model domain and $O_{3\text{-PBL}}$ represents the ozone component formed by ozone precursors emitted into the PBL within the model domain. The contribution from $O_{3\text{-INFLOW}}$ (Fig. 6b and e) decreased with decreasing altitude, which is consistent with the results of Pfister et al. (2013), while the $O_{3\text{-INFLOW}}$ was relatively low in the boundary layer. The $O_{3\text{-PBL}}$ (Fig. 6c and f) was primarily confined to the lowest 2 km and concentration decreased with altitude. More than 75% of the ozone in the free troposphere came from $O_{3\text{-INFLOW}}$ and the rates increased with increasing altitude. These results are also consistent with, Safeddine et al. (2014), who found that $O_{3\text{-INFLOW}}$ accounted for more than half of the ozone in the free troposphere over the Mediterranean during the summer. At higher altitudes, the $O_{3\text{-TOTAL}}$ concentration decreased downwards obeying the vertical structure of $O_{3\text{-INFLOW}}$; however, at lower altitudes, and especially in the lowest 2 km, supplemental ozone was provided by $O_{3\text{-PBL}}$, leading to higher total concentrations than those in the upper layer. With the different vertical distributions of $O_{3\text{-INFLOW}}$ and $O_{3\text{-PBL}}$, ozone concentrations were relatively low in the free troposphere at a height of 2–4 km. At noon, the low-concentration zone decreased in altitude to the top of the PBL owing to the wind fields and formed a vertical gradient of ozone from the top of the PBL down to the Mt. Huang; thereby, providing favorable conditions for ozone exchange through vertical mixing.

### 3.4. Ozone source apportionment at the summit of Mt. Huang

Owing to poor chemical production and positive contribution from advection, ozone at the summit of Mt. Huang is highly influenced by regional transport effects (Zhang et al., 2015). In this work, we used the ozone tagging results to quantify the ozone contributions from source regions at the summit of Mt. Huang. In order to avoid the impacts of initial conditions (Napelenok et al., 2008), the ozone contributions from each source region for the first 7 days were ignored. Nearly half, and sometimes more, of the ozone was provided by $O_{3\text{-INFLOW}}$ (Fig. 7), and the mean contribution (Table 3) reached 55.4% (24.6 ppb). The remaining (the other half) ozone was contributed by $O_{3\text{-PBL}}$ (44.6%). Zhu et al. (2016) suggested that half of the ozone at Mt. Huang is sourced from the eastern region in June. Considering a similar coverage between our model and their eastern region settings, the results of our study are consistent with the findings of Zhu et al. From 9 to 30 June, the ozone contribution from the local source region ($O_{3\text{-LOC}}$; i.e., Mt. Huang) was small, with a maximum contribution of 15 ppb (15 June) and a mean contribution of 3.0% (1.4 ppb). Non-local contributions ($O_{3\text{-NLOC}} = O_{3\text{-PBL}} - O_{3\text{-LOC}}$), which represented the contribution from the other geographical source regions, accounted for much more than the local contribution. Under the prevailing southerly winds, ozone was mainly sourced from regions to the south, for example, JX, FJ, and ZJ, with mean contributions of 9.9%, 7.5%, and 6.1%, respectively, accounting for more than the other geographical contributions. Ozone from JS&SH had a mean contribution of 4.7% across the entire period, however, it contributed more significantly when the wind direction was northerly. Further, the other source regions, such as S-CHN, C-CHN, and N-CHN contributed 3.3%, 2.3% and 3.8%, respectively.

When viewed as diurnal variations from all the source regions (Fig. 8), the mean contribution rates from $O_{3\text{-INFLOW}}$ and $O_{3\text{-PBL}}$ were 56.9% and 43.1%, respectively. The contribution rates of $O_{3\text{-INFLOW}}$ peaked during the day and decreased at night. In contrast, the contribution rates of $O_{3\text{-PBL}}$ increased at night, which meant the concentration of $O_{3\text{-PBL}}$ increased relatively significantly at night. As mentioned earlier, $O_{3\text{-PBL}}$ was mainly confined under the lowest 2 km. Its transport and diurnal variation was highly affected by...
atmospheric movement in the PBL. The mean value of O$_3$-LOC was 3.5%, with the maximum value (10.0%) occurring in the afternoon (16:00), reflecting the photochemical characteristics of tropospheric ozone. Contributions of O$_3$-NLOC accounted for 10 times more than the local contribution. Among the non-local source regions, those to the south, especially JX (14.2%) and FJ (8.6%), contributed the most, reflecting the prevailing southerly winds. The diurnal variations of O$_3$-LOC, O$_3$-NLOC, O$_3$-INFLOW and total ozone are provided in Fig. 5 as well. The comparison of the diurnal patterns revealed that O$_3$-NLOC showed the best agreement with the total ozone, and the correlation coefficient reached a value of 0.97. The good agreement between non-local and total diurnal variations in ozone indicated that diurnal variation in O$_3$-NLOC directly affected the occurrence of diurnal variations in ozone at the summit of Mt. Huang. Since concentrations O$_3$-NLOC was mainly confined under the height of lowest 2 km (Fig. 6c and f), the variation of O$_3$-NLOC was highly related to the atmospheric diurnal movements in boundary layer as well. Thus the similar diurnal variations also suggested the
importance of boundary layer diurnal variations in the formation of diurnal variations in ozone concentrations at the summit of Mt. Huang. The 50% contribution from O3-PBL and the tiny local contribution suggest that regional pollution should also be considered in the atmospheric studies of remote regions in eastern China.

4. Summary

In the summer of 2011, comprehensive meteorological and ozone data were collected at the summit of Mt. Huang, eastern China. The distinct diurnal variations in ozone featured high concentrations at night and low concentrations during the daytime. The WRF-Chem model was applied to study the causes of the distinct ozone diurnal variations and the ozone source apportionment problem. Acceptable agreement was achieved between observed and modeled results, indicating that the model was capable of accurately reproducing atmospheric ozone at the summit of Mt. Huang.

The processes analysis showed that the boundary layer diurnal cycle was very important in the formation of the distinct diurnal variations in ozone concentrations. At the summit of Mt. Huang, while the contribution from vertical mixing was negative, advection and photochemistry contributed positively, and photochemistry made only a minor contribution at noon. During the daytime, the contribution from vertical mixing was more significant than which from advection, resulting in a net negative contribution and a fall in ozone concentrations. With a favorable condition being provided by the ozone vertical structure, the low-concentration ozone aloft was entrained down to the mountaintop, which aggravated the negative contribution from vertical mixing during midday. The small contribution from the photochemical reactions did not supply enough ozone at noon, thus, the net contribution still showed negative values and the ozone concentration kept on decreasing till 15:00. In contrast, at night, the negative contribution of vertical mixing was weak and the positive contribution of advection impacted more significantly, leading to ozone accumulation. The shift in the major contribution with time led to the formation of this ozone diurnal variation at the summit of Mt. Huang.

Ozone source apportionment suggested that about half of the ozone at the summit of Mt. Huang was provided by O3-INFLOW from regions outside of the model domain. The remainder was sourced from the ozone precursors emitted in eastern China (O3-PBL), in which the contribution from Mt. Huang during the simulation period was about 3.0% reflecting the small local contribution (O3-LOC) and that was smaller than the non-local contributions (O3-NLOC: 41.6%). Among the non-local contributions, ozone from the southerly regions contributed significantly, while 9.9% of the ozone came from JX, which contributed the most among the all the geographical source regions. Diurnal changes in O3-NLOC was similar to that of total ozone which indicated that O3-NLOC had a direct effect on the formation of diurnal variations in ozone at the summit of Mt. Huang. Because the origin and variation of O3-NLOC was highly related to the diurnal movements in boundary layer, the similar diurnal variation also suggested the importance of boundary layer diurnal variations in the formation of diurnal variations in ozone concentrations at the summit of Mt. Huang.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2016.11.031

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