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# Diurnal variations and source apportionment of ozone at the summit of Mount Huang, a rural site in Eastern 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 ($O_{3\text{-INFLOW}}$) and the other half was formed by ozone precursors ($O_{3\text{-PBL}}$) emitted in eastern, central, and southern China. In the $O_{3\text{-PBL}}$, 3.0% of the ozone was from Mt. Huang reflecting the small local contribution ($O_{3\text{-LOC}}$) and the non-local contributions ($O_{3\text{-NLOC}}$) 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 $O_{3\text{-NLOC}}$ was highly related to the diurnal movements in boundary layer, the similar diurnal patterns between $O_{3\text{-NLOC}}$ and total ozone both indicated the direct influence of $O_{3\text{-NLOC}}$ and the importance of boundary layer diurnal variations in the formation of such distinct diurnal ozone variations at Mt. Huang.



## 1. Introduction

Tropospheric ozone ($O_3$) 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

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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: $SO_2$, $NO_X$, $NH_3$, CO, $CO_2$, NMVOC (non-methane volatile organic compounds), BC (black carbon), OC (organic carbon), $PM_{10}$ (particulate matter with diameter less than or equal to 10 μm), and $PM_{2.5}$ (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 firstly 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