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Factors dominating 3-dimensional ozone distribution during high tropospheric ozone period☆

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ABSTRACT

Data from an in situ monitoring network and five ozone sondes are analysed during August of 2012, and a high tropospheric ozone episode is observed around the 8th of AUG. The Community Multi-scale Air Quality (CMAQ) model and its process analysis tool were used to study factors and mechanisms for high ozone mixing ratio at different levels of ozone vertical profiles. A sensitive scenario without chemical initial and boundary conditions (ICBCs) from MOZART4-GEOS5 was applied to study the impact of stratosphere-troposphere exchange (STE) on vertical ozone. The simulation results indicated that the first high ozone peak near the tropopause was dominated by STE. Results from process analysis showed that: in the urban area, the second peak at approximately 2 km above ground height was mainly caused by local photochemical production. The third peak (near surface) was mainly caused by the upwind transportation from the suburban/rural areas; in the suburban/rural areas, local photochemical production of ozone dominated the high ozone mixing ratio from the surface to approximately 3 km height. Furthermore, the capability of indicators to distinguish O_3-precursor sensitivity along the vertical O_3 profiles was investigated. Two sensitive scenarios, which had cut 30% anthropogenic NO_X or VOC emissions, showed that O_3-precursor indicators, specifically the ratios of O_3/NOy, H_2O_2/HNO_3 or H_2O_2/NO_Z, could partly distinguish the O_3-precursor sensitivity between VOCs-sensitive and NOx-sensitive along the vertical profiles. In urban area, the O_3-precursor relationship transferred from VOCs-sensitive within the boundary layer to NOx-sensitive at approximately 1–3 km above ground height, further confirming the dominant roles of transportation and photochemical production in high O_3 peaks at the near-ground layer and 2 km above ground height, respectively.

1. Introduction

China is widely undergoing continuous ozone (O_3) increases in recent years. Research on key regions, such as the Northern China Plain (NCP), Yangtze River Delta (YRD) and the Pearl River Delta (PRD) including Hong Kong, has observed increasing trends of surface ozone (Li et al., 2014a; Ma et al., 2016; Tang et al., 2008; Wang et al., 2009; Xu et al., 2008; Xue et al., 2014). Continuous data, based on a monitoring network set up by the Ministry of Environmental Protection (MEP) since 2013, show that mean surface ozone concentrations are increasing, while other major pollutants (SO_2, NO_X and suspended particulates) are more or less decreasing (www.mep.gov.cn) (Wang et al., 2016). As for the PRD region including Hong Kong, surface ozone concentrations increased at a rate of 0.88 μg/m^3 per year from 2006 to 2014 (Guangdong-Hong Kong-Macao Pearl River Delta Regional Air Quality Monitoring Network: A Report of Monitoring Results in 2014). However, annual concentrations of SO_2, NO_2 and respirable suspended particulates (PM_{10}) decrease during the same period from 47 μg/m^3, 46 μg/m^3 and 74 μg/m^3 to 16 μg/m^3, 37 μg/m^3 and 56 μg/m^3, respectively. The increasing pattern is not only found at the surface but is also observed vertically (Sun et al., 2016). Ozone is

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relatively becoming a more severe problem in many regions and may even be a tough problem for China (Wang et al., 2013).

Many factors can largely affect the vertical ozone distribution. Evidence has been revealed by observation experiments (Hocking et al., 2007) and numerical studies (Li and Rappenglück, 2014) that stratosphere-troposphere exchange (STE) of ozone plays an important role in mixing the ozone of the upper troposphere and lower stratosphere (UTLS) (Holton, 1995). Typhoons can largely affect the strength of the stratosphere-troposphere exchange, especially in eastern China and the western North Pacific Ocean. Within the typhoon's large-scale circulation, downward propagation of stratospheric ozone to the surface induces an elevated surface ozone mixing ratio (Jiang et al., 2015). As for the upper troposphere and lower stratosphere from approximately 200 hPa to 50 hPa, which lie in the top most levels of regional air quality models like the CMAQ and WRF-CHEM, a typhoon also redistributes the vertical ozone through its convective system (Fu et al., 2013). Therefore, O_3 at the surface and above ground can affect each other, suggesting the great necessity for the investigation of vertical O_3 distributions. In addition to stratosphere-troposphere exchange, other processes including local photochemical formation and atmospheric transportation (horizontal transport and vertical convection) could lead to high O_3 mixing ratios along the vertical profiles (Fiore, 2002; Jacob, 1999; Tang et al., 2008; Godowitch et al., 2015; Park et al., 2014), making it a complicated issue in tropospheric O_3 studies.

The relative contributions of the above influenced factors of vertical O_3 distributions in different environments are varied (Wang et al., 2010). By applying some O_3-precursor sensitivity indicators, Wang et al. (2011) found that it is usually VOCs-sensitive for megacity area and NO_X-sensitive for rural areas. However, research shows that there are limitations and accuracy problems in using indicators to investigate O_3-precursor relationships. For example, previous research mainly focused on the surface layer and the transition values of different indicators, i.e., the ratios of O_3/NOz, HCHO/NOy, H_2O_2/HNO_3 (Sillman, 1995), O_3/NOy, O_3/HNO_3 and H_2O_2/NOz (Sillman et al., 1997). And these indicators are more varied in different areas (Castell et al., 2009; Jiménez and Baldasano, 2004; Tonnesen and Dennis, 2000). In the PRD region, previous research showed that the ratio of H_2O_2/HNO_3 has good performances (Lam et al., 2005; Wang et al., 2011). In this study, we apply some of the indicators to analyse whether they are capable along the vertical direction or not, instead of horizontal dimensions like most other research. The transition values of those indicators are localized for our key region. Accompanied by the process analysis tool of CMAQ (Fan et al., 2015a, 2015b; Liu et al., 2015), we can distinguish vertical layers between O_3-producing and O_3-consuming ones.

The top layer of regional chemical transport models is usually set to 50 hPa or 100 hPa, inducing uncertainties in simulating the stratosphere-troposphere exchange effect, especially for regional chemical transport models. Therefore, challenges often remain in simulating the stratosphere-troposphere exchange effect. Ozone near the upper troposphere and lower stratosphere cannot be well simulated by regional chemical transport models. The WRF/CMAQ modelling system, which is used in this research (Byun and Schere, 2006), also faces the same challenge of modelling upper air ozone with its default initial conditions and boundary conditions (ICBCs) (Tang et al., 2008).

To improve the model performance of simulating the stratosphere-troposphere exchange of ozone, the results of global chemical models can be applied to our regional air quality model. GEOS-CHEM and MOZART4-GEOS5 have been widely used in recent years. A toolbox called "geos2cmaq" (http://wiki.seas.harvard.edu/geos-chem/index.php/GEOS-Chem_to_CMAQv5.0) and its updated version pncglobal2cmaq (Henderson et al., 2014) were developed by the GEOS-CHEM community to fit the GEOS-CHEM model outputs for initial and boundary conditions of CMAQ. There is also a linkage tool called "mozart2cmaq" for MOZART included in the CAMx package (www.camx.com). Previous studies found that ozone profiles could be simulated more reasonably by importing either the GEOS-CHEM or MOZART lateral boundary conditions (Li and Rappenglück, 2014; Tang et al., 2008). In this study, the simulation results of the WRF/CMAQ model imported with the above ICBCs further confirm the importance of the stratospheric O_3 boundary condition in modelling vertical O_3 profiles. Furthermore, the "ozone mixing ratios tongue" in the upper and middle troposphere near 9 km above ground level (AGL), which is probably underestimated in global chemical transport model (Zhang et al., 2012), was well captured in this study.

2. Methodology

2.1. In-situ monitoring data and ozone sondes data

Surface meteorological observations, including hourly temperature and wind speed, as well as relative humidity, are obtained by 74 Guangdong Meteorological Observatory (GMO) stations. Environmental monitoring in-situ data are obtained by the Pearl River Delta Regional Air Quality Monitoring Network (PRDRAQMN) which consists of stations in the three regions of Guangdong, Hong Kong and Macao. SO_2, NO_2, O_3 and PM_{10} concentration data are available from all stations in this monitoring network during the study period - August 2012, Fine Suspended Particulates ($PM_{2.5}$), NO_X and CO are additionally available from monitoring stations in Hong Kong. Five ozone sondes were launched at Kings Park by the Hong Kong Observatory during August 2012, on the 1st, 8th, 14th, 22nd and 29th. The locations of these stations are presented in Fig. S1. In this study, 9 PRDRAQM stations are mainly used: 6 stations in the Guangdong Province are in black, and 3 in Hong Kong are marked in red.

2.2. Models

In this study, we use the Weather Research and Forecasting model and the Community Multiscale Air Quality model (WRF/CMAQ) to simulate such a high ozone period. The domain of the WRF/CMAQ modelling system covers an area from 94.4°E to 133.3°E and 11.9°N to 44.4°N. The spatial resolution is 27 km, and there are 40 vertical levels with a model top height at 50 hPa. Increasing vertical resolution can somehow help the numerical model achieve a better performance in simulating boundary layer structures and meteorological factors. Approximately 16 levels are set within the boundary layer in this study in order to offer a better driven field for CMAQ chemical modelling.

In CMAQ version 5.1, some modified chemistry options are updated. The aero6i (ae6i) for aerosol chemistry has been updated from the aero6 (ae6) of former versions. A more detailed option (AQCHEM-KMTI) for aqueous-phase chemistry is updated as well (Pye et al., 2015). In our study, the chemistry mechanism option is set to SAPRC07tic in order to get more detailed gas-phase reaction formulas, which are important for ozone modelling. Other settings for our WRF/CMAQ model are listed in Table S1.

In our study, the process analysis (PA) method is used for providing different factors' contributions to ozone generation and consumption. Vertical advections, horizontal advections, vertical diffusions, horizontal diffusions, cloud effects, chemical reactions and dry depositions are the 7 PAs that account for ozone changes. PA values show how much the concentrations are contributed to by those 7 PAs during the concerned period.

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