On the Origin of Surface Ozone Episode in Shanghai over Yangtze River Delta during a Prolonged Heat Wave

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ABSTRACT

A heat wave with temperatures over 35°C and sunny stagnant meteorological conditions occurred in Shanghai from 27 July to 5 August 2015, leading to a sustained episode of high ozone lasting 12 days. We have conducted a detailed source apportionment of surface ozone, by precursor source category and region, using a photochemical transport model. In this episode, a southwesterly wind prevailed over the Yangtze River Delta, and therefore precursors from the local Shanghai region and the region immediately to the south of Shanghai are the two major contributors (in total 90%) to ozone in Shanghai. The source apportionment reveals that local industrial sources and energy/biogenic sources in neighbouring regions are the principal causes for the high levels of ozone. By examining the contributions from individual physical and chemical processes, we show that ozone concentrations start to rise rapidly in the morning because chemical production dominates as the solar radiation increases, and while there is little removal by deposition when ozone remains low. In general, chemical production, horizontal advection and vertical diffusion contribute to increase ozone concentration during daytime, and deposition and vertical advection reduce ozone concentrations.

Keywords: Ozone; Source apportionment; Process analysis; Heat wave; Shanghai.

INTRODUCTION

High ozone (O₃) episodes are one of the most severe air pollution issues experienced in megacities (Wild et al. 2004; Shao et al., 2006; Streets et al., 2007; Yang et al., 2008; Zhang et al., 2008). Severe O₃ pollution events in troposphere can cause adverse effects on human health, crop productivity and ecosystems (Feng et al., 2003; Fann and Risley, 2013; Landry et al., 2013). In recent years, the O₃ concentrations exceeding moderately polluted level (the daily maximum 8-h moving average O₃ concentration > 100 ppbv defined by the National Ambient Air Quality Standard of China) have been frequently observed in China (Wang et al., 2001; Wang et al., 2006a; Ding et al., 2008; Xu et al., 2008; Ran et al., 2009; Shao et al., 2009; Tang et al., 2009; Wang et al., 2009; Ding et al., 2013).

O₃ concentrations are affected by chemical formation and loss related to local precursors emissions, and by transport of O₃ and its precursors from other regions. For chemical formation, O₃ is a secondary pollutant formed nonlinearly by chemical reactions involving nitrogen oxides (NOₓ) and volatile organic compounds (VOCs) in the presence of solar radiation (Crutzen et al., 1999; Kumar et al., 2008). High O₃ concentrations are also affected by favorable weather conditions, such as extremely high temperature, strong solar radiation, low relative humidity and weak wind speed (Shu et al., 2016). These weather conditions are usually accompanied by strong subtropical high, and play a crucial role in transport, accumulation and fast chemical production of O₃ in the boundary layer. Shanghai as well as surrounding city cluster (namely as Yangtze River Delta, YRD), locate on the eastern coast of China, and are generally affected by the western Pacific subtropical high in summertime. Therefore, high-level O₃ events are observed in summertime with relationship to synoptic systems (Huang et al., 2006; Jiang et al., 2012; Ding et al., 2013; Xie et al., 2016).

O₃ pollutions in the YRD have been previously analyzed (Wang et al., 2006b; Geng et al., 2008; Ran et al., 2009; Jiang et al., 2012), but some properties controlling O₃ behavior in this area remain uncertain, especially during a typical weather system in this region. Effective attainment of ground-level O₃ concentration depends upon a reliable
understanding of how O₃ responds to control of its precursors (Cohan et al., 2007). In this study, we apply the Comprehensive Air Quality Model with Extensions model (CAMx) to study the typical weather system and the exact formation mechanism of the O₃ pollution over YRD region. A better understanding of O₃ source-receptor relationship in the YRD can be accomplished through the identification of the geophysical sources as well as sectoral sources contribution. Such information is considerable for designing adequate control strategies regarding tropospheric O₃ concentration. Furthermore, process analysis tool provides an insight on qualitative and quantitative contributions of individual atmospheric processes.

**METHODOLOGY AND DATA**

*Model Description and Setup*

We apply an air quality model CAMx v6.20 (ENVIRON, 2015) to simulate an O₃ episode from 25 July to 6 August, 2015. CAMx simulates the emission, advection, dispersion, chemical transformation and physical removal of air pollutants on an Eulerian three-dimensional grid. Fig. 1 shows the model domain used in this study, which has a 265 × 265 grids at 9 km resolution on a Lambert conformal map projection. Vertically, we use 20 terrain-following layers from the surface to 20 km, with the lowest 10 layers below 2 km. The meteorological conditions were provided from the Weather Research and Forecasting model (WRF v3.2.1, http://www2.mmm.ucar.edu/wrf/users/docs/user_guide_V3.2/ARWUsersGuideV3.pdf), using NCEP/NCAR FNL reanalysis data (1° × 1°) for initial and boundary conditions. Four-dimensional data assimilation (Otte, 2009), based on 6-h 3-D analyses of temperature, water vapor mixing ratio and horizontal wind speeds, was used with a nudging coefficient of 3.0 × 10⁻⁴ for all the above components over this domain. Monthly-average concentrations from the MOZART model were used for chemical boundary conditions. The simulation was made from 14 July to 7 August 2015, using the first four days as a spin-up period.

The anthropogenic emissions in China were obtained from the Multi-resolution Emission Inventory for China (MEIC, http://www.meicmodel.org/) at 0.25° × 0.25° resolution, while emissions in other countries were derived from the bottom-up Regional Emission inventory in Asia (REAS 2.1) (Kurokawa et al., 2013). To improve the distribution of anthropogenic emissions at the 9 km resolution used here, we spatially reallocated the coarse resolution emissions over East Asia based on relevant proxies. For example, residential emissions were spatially allocated by population data; vehicle emissions were distributed according to road length data; and agricultural emissions were allocated based on cropland intensity data. All the static data including population, road length and land category data are obtained through http://www.dsac.cn, with spatial resolution of 1 km and data year of 2015. Biogenic emissions were obtained from a biogenic emission model (MEGANv2) provided by NCAR (http://accent.aero.jussieu.fr/database_table_inventories.php).

In this study, we use surface NO₂ and O₃ concentration measurements from a monitoring network maintained by the Ministry of Environmental Protection (http://106.37.208.233:20035). The locations of surface sites (273 sites within the model domain) are shown in Fig. 1. Hourly meteorological
variables (wind, temperature, relative humidity and solar radiation) were taken from automatic meteorological stations operated by the Shanghai Meteorological Service, and the data shown in Fig. 2 was collected at Pudong station (31.22°N, 121.55°E), which represents an urban area in Shanghai.

Source Apportionment

O₃ source apportionment technology (OSAT, Yarwood et al., 1996) uses multiple tracer species to track the fate of O₃ and its precursors by monitoring the effects of emissions, chemical reactions, transport, diffusion and deposition within CAMx. These tracers allow O₃ formation from multiple “source groupings” to be tracked simultaneously within a single simulation. A source grouping is defined in terms of geographical area and/or emission category, and the CAMx boundary conditions (BC) and initial conditions (IC) are tracked as separate source groupings. OSAT employs four types of tracers for each source grouping: \( N_i \) and \( V_i \) (tracking NOₓ and VOCs originating from source grouping \( i \), respectively), and \( O_{3N_i} \) and \( O_{3V_i} \) (tracking O₃ formation under NOₓ-limited and VOCs-limited conditions attributed to source grouping \( i \), respectively). The ratio of the production rates of hydrogen peroxide to nitric acid is used as an indicator of the O₃ formation sensitivity to NOₓ and VOCs. Sillman (1995) proposed that O₃ formation is NOₓ-limited when the ratio exceeds 0.35 and VOCs-limited when the ratio is less than 0.35. The \( O_{3N} \) and \( O_{3V} \) tracers for each source grouping accumulate a weighted fraction of the O₃ production (\( \Delta O_3 \)) that occurs in each grid cell at each time step (\( \Delta t \)):

\[
O_{3N_i}(t + \Delta t) = O_{3N_i}(t) + \Delta O_3 \times N_i(t) / \sum_{i=1}^{m} N_i(t)
\]

\[
O_{3V_i}(t + \Delta t) = O_{3V_i}(t) + \Delta O_3 \times V_i(t) \times \kappa_{OH_i} / \sum_{i=1}^{m} V_i(t) \times \kappa_{OH_i}
\]

where \( t \) represents time, \( m \) is the number of source groupings, and \( \kappa_{OH} \) is the average OH rate constant of VOCs for the \( i \) source grouping (ENVIRON, 2015).

Source Regions and Source Categories

Targeting a spatial-source analysis, we divide the model domain into eight source receptor areas based on province boundaries: Shanghai (SH), provinces north of Shanghai (NORTH2SH), provinces south of Shanghai (SOUTH2SH), northern China (NORTH_CHN), western China (WEST_CHN), southern China (SOUTH_CHN) and regions outside China (OUT_CHN) (see Fig. 1). NORTH2SH consists of Jiangsu, Anhui and Shandong provinces and SOUTH2SH consists of Zhejiang, Jiangxi and Fujian provinces.

Anthropogenic emissions from MEIC are categorized into industry, transport, residential, energy and agricultural sectors. Biogenic emissions are generated from the MEGAN model. These six categories, are defined as source groupings in the OSAT model. In addition, the initial and boundary conditions (IC and BC) are treated as individual source groupings.

Process Analysis

Process analysis (PA) allows for in-depth analysis of the contributions from individual physical and chemical processes operating within the model (Jeffries and Tonnesen, 1994). Using this approach, it is possible to investigate the complex interactions between different processes, and explain simulation results within the context of the model formulation. Integrated process rate analysis provides detailed rate information for each process in CAMx (i.e., advection, diffusion, deposition, emissions and chemistry) for selected grid cells and selected species (Wang et al., 1995).

Sensitivity Analysis

Sensitivity analysis is a widely used approach in which sources are quantified by perturbing emissions one at a time and simulating the difference in pollutant concentrations compared to unperturbed control scenarios. There are four sensitivity simulations as well as control run (BASE). Each sensitivity simulation is compared to the BASE run in order to assess the response of O₃ to emission perturbations during the episode.

RESULTS AND DISCUSSIONS

The Episode Review and Model Evaluation

The daily maximum temperature is more than 35°C for sustained 10 days from 27 July to 5 August 2015, in which 4 days of maximum temperature are over 37°C, which is a very powerful heat wave in Shanghai (Fig. 2). In the meantime, a continuous (12 days) O₃ pollution episode was detected in Shanghai over the Yangtze River Delta (YRD) region, in which the daily maximum 8-h moving average O₃ concentrations in 4 days exceeded moderately polluted level (> 100 ppbv), with the other 8 days exceeding lightly polluted level (> 75 ppbv). The hourly maximum observed O₃ concentration reached up to 130 ppbv, which significantly exceeded the moderately polluted level. During this period, the western Pacific subtropical high stayed over YRD region, and thereby led to this powerful heat wave in Shanghai. The relative humidity ranged from 40% to 80% and the total radiation, a key meteorological factor for O₃ formation, reached 1000 W m⁻², indicating that skies were clear. There is typically a positive correlation between O₃ and temperature because of a combination of meteorological and chemical factors. High temperatures lead to higher emissions of some O₃ precursors, greater electrical energy use, and more biogenic VOC emissions.

Fig. 2 also compares the simulated meteorological and O₃ concentration with observations, to assess the performance of the model. Before 27 July, there were lower temperatures, higher relative humidities, lower total radiation and lower O₃ concentrations. The comparisons demonstrate that the model can capture the temporal variation of meteorological variables over the study period very well compared to
Fig. 2. Comparison of hourly time-series for simulated (red) and observed (gray) wind, 2-m temperature, relative humidity, total radiation and ozone concentration at Shanghai station from 18 July to 7 August 2015.

observations. To evaluate how well the model captures the diurnal cycle of $O_3$, we calculate the episode-mean hourly $O_3$ concentrations, see Fig. 3. We find that the model catches the high $O_3$ during daytime but underestimates $O_3$ at nighttime. This may be due to overestimated NO emissions that leads to much chemical destruction at nighttime (Awang et al., 2015).

Fig. 4 shows the weather charts (http://web.kma.go.kr/chn/weather/images/analysischart.jsp) at 00UTC (08LST) each day. A subtropical high pressure is noted near Taiwan on 30 July, and the center moves north on 1 August. This synoptic pattern is disturbed when a typhoon approaches from the Pacific Ocean. The left panels display the simulated wind fields at the corresponding times (08:00LST), and daytime average $O_3$ concentrations (from 08:00 to 18:00 LST). The wind fields show that there was a high pressure over the ocean and the location is consistent with that in the weather charts on 30 July and 1 August. A southwesterly wind was induced by the high pressure prevailing along the east coast of China during the polluted heat wave period. The spatial distribution of $O_3$ shows that there were high concentrations in the north of China as well as on the east coast. On 6 August, the approaching typhoon brought easterly winds to Shanghai and the Yangtze River Delta region, along with cleaner marine air.

A suite of statistical metrics are considered to judge the performance of the model. We use the correlation coefficient (R), mean value of the observation (Obs) and simulation (Mod), root mean square error (RMSE) and mean bias (MB) of the hourly data over the full 20-day period. The spatial distributions of R and RMSE for each city are displayed in Fig. 5. The simulation generally agrees well with the observations and the correlation coefficients are greater than 0.7 for most of the cities. The RMSEs are below 15 ppbv in south China, but are 15–30 ppbv in north China. Table 1 summarizes the statistical metrics for $O_3$ and NO$_2$ for each region separately (region definitions are...
shown in Fig. 1). The correlation coefficients (R) for O3 are typically 0.6–0.8, indicating that the model can reproduce the O3 variations well in the study period. The R values for NO2 are lower than for O3, with values of 0.5–0.7. The mean bias shows that simulated O3 concentrations were underestimated over Shanghai (SH) and SOUTH2SH regions, but overestimated for the other regions. NORTH_CHN was the only region where NO2 was underestimated. In comparing different regions, it is worth noting that the model performed best over Shanghai and least well over NORTH_CHN. The NO2 emission over NORTH_CHN may be underestimated, and this is consistent with overestimation of O3 due to less urban titration. In general, based on this analysis, we infer that the CAMx model performs relatively well in simulating observed O3 concentrations.

Fig. 6 shows a scatterplot of hourly daytime O3 from the model and the observations at some points. The selected cities are Shanghai, Nanjing, Hangzhou, Hefei, Fuzhou, Nanchang, Jinan, Beijing, Changsha, Wuhan, Guangzhou and Xi’an, which are capitals of each province, respectively, over the east China (displayed in red points in Fig. 1). These data help to assess the model performance, showing that there is clearly a correlation between the model and observations, with the averaged correlation coefficient (R) of 0.69. The standard linear least square regression analysis reveals that the model somewhat overestimates the daytime O3 concentrations.

**Source Contribution Analysis**

Fig. 7 shows the daytime-average (08:00–18:00 LST) contributions to O3 for Shanghai area from different source regions and source categories. We find that Shanghai and SOUTH2SH are the two regions that contributed the most to O3 concentrations in Shanghai, together reaching as much as 90%. This is a consequence of the southwesterly flow during the study period (see Figs. 2 and 4), which brought pollutants and precursor emissions to Shanghai. In this period, the contributions from other regions were insignificant. The contributions of different emission categories show that the industrial sector contributes the most, followed by energy, biogenic and transport sectors. As expected, initial conditions (IC) were the major contributor at the beginning of the simulation, and it decreased significantly over the period. The contribution of boundary conditions (BC) was remarkably large on August 6, and this reflects the dominance of easterly flow in the Shanghai area on this day (see Fig. 4(c)).

Since Shanghai and SOUTH2SH are the dominant sources of O3 in Shanghai during this episode, it is interesting to examine the source apportionment by emission category from these two regions. For local emissions in Shanghai area (Fig. 8(a)), Industrial emissions were the largest source, with a contribution of 43%, and the contributions from energy, transport and biogenic sectors were 20%, 20% and 10%, respectively. In contrast (Fig. 8(b)), the largest source from SOUTH2SH region was not from industrial emissions but from energy and biogenic emissions which provided 28% and 28% of the O3 from this region to Shanghai. The contributions from industry and transport tailed off to 25% and 11%, respectively. In addition, 5–6% of O3 in Shanghai was attributed to initial and boundary conditions (IC + BC), and agriculture and residential emissions contributed very little.

The average diurnal O3 contributions for Shanghai area from different source regions during the episode period are shown in Fig. 9(a). It is clear that local and non-local emissions show distinct characteristics. The contribution of local emissions in Shanghai is heavily peaked, increasing during the morning, and with a maximum value around noon time. This is strongly related to chemical formation of O3 when solar radiation is high. The contributions from non-local sources (mostly from SOUTH2SH) are greatest in the morning and afternoon. During nighttime O3 is destroyed through titration by reaction with NO, and there is no O3 formation without solar radiation. Consequently, most of the O3 in Shanghai originates by transport from surrounding areas, and the contributions during nighttime are from non-local sources. The contribution of different source categories is shown in Fig. 9(b). The contribution of industrial emissions reveals similar features to the local emission in Shanghai, increasing during the morning, and reaching a maximum at noon. The contributions from energy, transport and biogenic emissions remain relatively similar over the course of daytime.

To evaluate the source contributions in this study, and to
Fig. 4. Simulated wind (left) and surface synoptic charts (right, http://web.kma.go.kr/chn/weather/images/analysischart.jsp) at 08:00 LST on 30 July, 1 August and 6 August 2015. Daytime averaged (08:00-18:00 LST) simulated ozone concentration (shaded) are also plotted on the left.
inform mitigation strategies for O\textsubscript{3} in Shanghai, several sensitivity simulations are conducted individually (described in Table 2). The sensitivity simulation results show that if all anthropogenic emissions in Shanghai were reduced by 50\% (SH0.5), the O\textsubscript{3} levels in Shanghai would have decreased by 12\% compared to the base run (BASE). When industrial or transport emissions were reduced by 50\% in both Shanghai and SOUTH2SH (IND0.5 and TRA0.5), the decrease in O\textsubscript{3} concentrations was 11\% or 6\%, respectively. If all industrial and transport emissions in both regions were reduced by 50\%, the O\textsubscript{3} concentrations would decrease by 18\%. This sensitivity analysis clearly demonstrates that the response of O\textsubscript{3} to emission reductions isn’t linear. And this leads to discrepancy between sensitivity analysis and source apportionment results. Because O\textsubscript{3} are most formed by chemical formations, the sensitivity simulations do not generate or lose equivalent concentrations of secondary O\textsubscript{3} when the simulations are run with fewer precursors. The Source apportionment method, which does not change any physical and chemical processes, can objectively allocate 100\% of the target O\textsubscript{3} to specified sources. Besides, the reduction of O\textsubscript{3} in IND\_TRA0.5 run is the biggest, even more significant than those in SH0.5 run. This illustrates that industrial and transport emissions are the main source of precursors in generating O\textsubscript{3} in Shanghai, and should be considered as the major target sectors for emission controls.
Process Analysis

The contributions of each modeled process to changes in O$_3$ in the model are calculated as average hourly values for each grid cell. Average rates in the surface layer for Shanghai area from July 27 0000 LST to August 5 2300 LST are shown in Fig. 10. The atmospheric processes that influence O$_3$ concentrations include chemistry, horizontal and vertical advection, horizontal and vertical diffusion and dry deposition. Positive values indicate that O$_3$ concentrations are increased by the process and negative values indicate a decrease. Note that there is no primary emission of O$_3$, so this process makes no direct contribution to O$_3$.

The diurnal cycle of O$_3$ concentration reveals that the build-up of O$_3$ in the morning is typically more rapid than the decline in the evening. During daytime, the model has a tendency to generate a broad daytime O$_3$ maximum, with the highest concentrations reached at noon. In the morning, chemical production dominates as the solar radiation increases, and there is little removal by deposition while O$_3$ remains low. Consequently, O$_3$ concentrations start to rise rapidly in the morning. The effect of chemical processes

![Fig. 6. Scatterplot of observed and simulated O$_3$ for daytime (08:00–18:00 LST) in the selected cites.](image)

![Fig. 7. Daytime-average (08:00 – 18:00 LST) O$_3$ contributions for Shanghai area from (a) different source regions, and (b) different source categories for grid cells corresponding to the observation sites in Shanghai. Note that the colors of the source regions are consistent with map in Fig. 1.](image)
remains positive from 0600LST to 1600LST, while at other times there is net chemical destruction of $O_3$ by titration. Horizontal advection of $O_3$ from neighboring regions also keeps daytime concentrations high. In contrast, vertical advection contributes to a decrease of $O_3$ as vertical mixing is enhanced during daytime, carrying $O_3$ away from the surface. The results also reveal that vertical diffusion has an important role in increasing $O_3$ concentrations during
afternoon and nighttime. We note above that the model underestimates the low \( \text{O}_3 \) levels at nighttime. This may be due to too much chemical destruction, excessive dry deposition, or to horizontal advection (see Fig. 9). While this may be a consequence of overestimated NO emissions or errors in dry deposition parameters, it may also reflect meteorological factors such as insufficient boundary layer mixing at nighttime. To summarize, chemical production, horizontal advection and vertical diffusion are the main contributors to increases in \( \text{O}_3 \) concentrations during daytime, while deposition and vertical advection reduce \( \text{O}_3 \) concentrations.

CONCLUSIONS

A sustained, 10-day episode of high \( \text{O}_3 \) occurred in the Yangtze River Delta from 27 July to 5 August 2015, with \( \text{O}_3 \) concentrations in the afternoon reaching more than 100 ppbv. During this \( \text{O}_3 \) episode, temperatures of more than 35°C and sunny stagnant meteorological conditions were observed, providing favorable conditions for \( \text{O}_3 \) formation. A numerical model was used to study this \( \text{O}_3 \) episode and comparisons between simulation and observations suggest that the model can reproduce the meteorological and chemical conditions during this \( \text{O}_3 \) episode well.

By applying source apportionment approaches, we have developed a detailed understanding of the precursor source region and source category contributions to surface \( \text{O}_3 \) in Shanghai. Spatially, precursors from local and nearby southerly provinces contributed 90% of \( \text{O}_3 \) concentrations in this episode. Normally synoptic high pressure systems in summertime over this region are associated with high temperatures and a southwesterly wind which brings \( \text{O}_3 \) and its precursors to Shanghai. Industrial emission was the largest local source, with a contribution of 41%, and the contributions from energy, transport and biogenic sectors were 19%, 19% and 12%, respectively. For precursors from southern provinces, energy and biogenic sectors were the largest sources, with contributions of 30% and 29%. Therefore, it is a priority to reduce industrial, energy and transport emissions through effective \( \text{O}_3 \) control strategies. However, biogenic emissions also play an important role in formation of \( \text{O}_3 \) at this time of year.

We have analyzed the contributions from individual physical and chemical processes during this episode. It is interesting to note that the build-up of \( \text{O}_3 \) in the morning was much more rapid than the decline in the evening. In the morning, chemical production made a large contribution in the presence of sunlight, while the removal of \( \text{O}_3 \) was much smaller. The results revealed that chemical production, horizontal advection and vertical diffusion contribute to the increase of \( \text{O}_3 \) concentrations during daytime. The underestimation of \( \text{O}_3 \) at nighttime may be due to too much destruction by chemistry, deposition or horizontal advection. This may be a consequence of overestimated NO emissions or errors in dry deposition parameters, it may also reflect meteorological factors such as insufficient boundary layer mixing at nighttime.

ACKNOWLEDGMENTS

This work is funded by the National Key Research and Development Program (2016YFC0208803), the National Natural Science Foundation of China (41505105, 41405119), the Environmental Public Welfare Research Project (201509014).

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Received for review, March 8, 2017
Revised, September 7, 2017
Accepted, September 27, 2017