Integrated studies of a regional ozone pollution synthetically affected by subtropical high and typhoon system in the Yangtze River Delta region, China

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Abstract: Severe high ozone (O_3) episodes usually have close relations to synoptic systems. A regional continuous O_3 pollution episode was detected over the Yangtze River Delta (YRD) region in China during August 7-12 2013, in which the O_3 concentrations in more than half of the cities exceeded the national air quality standard. The maximum hourly concentration of O_3 reached 167.1 ppb. By means of the observational analysis and the numerical simulation, the characteristics and the essential impact factors of the typical regional O_3 pollution are integratedly investigated. The observational analysis shows that the atmospheric subsidence dominated by Western Pacific subtropical high plays a crucial role in the formation of high-level O_3. The favorable weather conditions, such as extremely high temperature, low relative humidity and weak wind speed, caused by the abnormally strong subtropical high are responsible for the trapping and the chemical production of O_3 in the boundary layer. In addition, when the YRD cities are at the front of Typhoon Utor, the periphery circulation of typhoon system can enhance the downward airflows and cause worse air quality. But when the typhoon system weakens the subtropical high, the prevailing southeasterly surface wind leads to the mitigation of the O_3 pollution. The Integrated Process Rate (IPR) analysis incorporated in the Community Multi-scale Air Quality (CMAQ) Model is applied to further illustrate the combined influence of subtropical high and typhoon system in this O_3 episode. The results show that the vertical diffusion (VDIF) and the gas-phase chemistry (CHEM) are two major contributors to O_3 formation. During the episode, the

30   contributions of VDIF and CHEM to O_3 maintain the high values over the YRD region. On August

31   10-12, the cities close to the sea are apparently affected by the typhoon system, with the

32   contribution of VDIF increasing to 28.45 ppb/h in Shanghai and 19.76 ppb/h in Hangzhou. In

33   contrast, the cities far away from the sea can hardly be affected by the periphery circulation of

34   typhoon system. When the typhoon system significantly weakens the subtropical high, the

35   contribution values of all individual processes decrease to a low level in all YRD cities. These

36   results provide an insight for the O_3 pollution synthetically impacted by the Western Pacific

37   subtropical high and the tropical cyclone system.

38   **Keyword**: Ozone; subtropical high; typhoon; the Yangtze River Delta region; heat wave

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40   **1. Introduction**

41   Ground-level ozone (O_3) is a secondary air pollutant generated by a series of complicated

42   photochemical reactions involving nitrogen oxides (NO_x) and hydrocarbons (HC) (Crutzen, 1973;

43   Sillman, 1999; Jenkin et al., 2000; Wang et al., 2006b; Xie et al., 2014; 2016b). Severe O_3

44   pollution events usually occur in the presence of sunlight and under favorable meteorological

45   conditions, with the abundance of O_3 precursors (NO_x and HC) (Wang et al., 2006b). These O_3

46   pollutions in troposphere can deteriorate the air quality, and thereby cause adverse effects on

47   human health and vegetation (Feng et al., 2003; Fann and Risley, 2013; Landry et al., 2013).

48   Consequently, the formation mechanism and the integrated prevention of O_3 pollution are of great

49   concern in many megacities all over the world (Xie et al., 2016b).

50   Over the past decades, along with the rapid industrial and economic development, many areas

51   in China have been suffering from high levels of O_3 pollution. Especially in the most economically

52   vibrant and densely populated areas, such as the Yangtze River Delta (YRD) region, the Pearl

53   River Delta (PRD) region, and the Beijing-Tianjin-Hebei (BTH) area, the severe O_3 pollution

54   episode has frequently occurred (Lam et al., 2005; Wang et al., 2006b; An et al., 2007; Chan and

55   Yao, 2008; Duan et al., 2008; Jiang et al., 2008; Zhang et al., 2008; Guo et al., 2009; Shao et al.,

56   2009; Ma et al., 2012) , and the background air pollutant concentrations have steadily increased

57   (Chan and Yao, 2008; Zhang et al., 2008; Tang et al., 2009; Wang et al., 2009a; Ma et al., 2012;

58   Liu et al., 2013). Many studies on the O_3 pollution, including satellite data analyses, field

59   experiments, and model simulations, have been carried out over China in order to investigate the

temporal and spatial characteristics of surface photochemical pollutions (Lu and Wang, 2006; Wang et al., 2006a; Tu et al., 2007; Zhang et al., 2007; 2008; Geng et al., 2008; Tang et al., 2008; 2009; Chen et al., 2009; Han et al., 2011; Ding et al., 2013; Xie et al., 2016b), nonlinear photochemistry of O_3 and its precursors (Lam et al., 2005; Ran et al., 2009; Liu et al., 2010; Li et al., 2011; Xie et al., 2014), interactions between O_3 and aerosols (Lou et al., 2014; Shi et al., 2015), the effects of urbanization on O_3 formation (Wang et al., 2007; 2009b; Liao et al., 2015; Li et al., 2016; Xie et al., 2016a; Zhu et al., 2016), and other essential impact factors (Jiang et al., 2012; Li et al., 2012; Wei et al., 2012; Liu et al., 2013; Gao et al., 2016).

The Yangtze River Delta (YRD) region is a highly developed area of urbanization and industrialization. With the accelerated economic development and remarkable increase in energy consumption, the photochemical smog with high level of O_3 concentration is becoming more and more prominent and frequent, tending to present the characteristics of regional pollution (Chan and Yao, 2008; Ma et al., 2012; Li et al., 2012). Being located on the southeastern coast of China, YRD features a typical subtropical monsoon climate and is strongly affected by the Western Pacific subtropical high in summer. So, high O_3 concentrations are usually observed in late spring and summer by in-situ monitoring (Ding et al., 2013; Xie et al., 2016b). Severe high O_3 episodes usually have close relations to synoptic systems (Huang et al., 2005; 2006; Wang et al, 2006b; Jiang et al., 2008; Cheng et al., 2014; Hung and Lo, 2015). Horizontal and vertical transport processes from upwind O_3-rich air masses as well as poor atmospheric diffusion conditions can lead to the accumulation of surface O_3 concentrations and aggravating the photochemical pollution (Wang et al., 2006b). In previous studies on high O_3 pollution in the YRD region, some researchers have discussed this issue. For example, Jiang et al. (2012) investigated the spring O_3 formation over East China, and suggested that O_3 concentrations over the YRD region were transported and diffused from surrounding areas. Li et al. (2012) presented quantitative analysis on atmospheric processes affecting O_3 concentrations in the typical YRD cities during a summertime regional high O_3 episode, and found that the maximum concentration of photochemical pollutants was usually related with the process of transportation. Gao et al. (2016) evaluated the O_3 concentration during a frequent shifting wind period, and revealed that vertical mixing played an important positive role in the formation of surface O_3. However, these investigations only focused on the O_3 formation mechanism for one megacity (such as Shanghai, Nanjing and Hangzhou, etc.)

90 or just a single station. Up to now, studies on the process analysis of high ozone episodes over the

91 YRD are quite limited (Li et al., 2012). So, more studies should pay attention to the typical

92 weather systems and the exact formation mechanism of the regional O_3 pollution in this region.

93 During August 7-12 2013, there was a typical regional O_3 pollution episode in the YRD

94 region, which might be synthetically influenced by the Western Pacific subtropical high and

95 Typhoon Utor. To better understand the important factors impacting O_3 formation from the

96 regional scale, we investigated the exact roles of these two typical weather systems in this

97 pollution episode by using observational analysis and numerical simulations. The observational

98 analysis was performed to identify the temporal and spatial characteristics of the episode. The

99 WRF/CMAQ modeling system, which consists of the Weather Research and Forecasting model

100 (WRF) and the Community Multi-scale Air Quality Model (CMAQ), was used to reveal the exact

101 formation mechanism. With the aid of the Integrated Process Rate (IPR) analysis coupled in

102 CMAQ, the qualitative and the quantitative analysis on the contributions of individual atmospheric

103 processes were conducted as well. In this paper, the brief description of observational data and

104 model configurations are shown in Section 2. The detailed observational analysis of air quality and

105 meteorological conditions are given in Section 3. The evaluation of model performance and the

106 formation mechanism of O_3 explored by IPR technique are presented in Section 4. In the end, a

107 summary of main findings is given in Section 5.

108

109 **2. Methodology**

110 **2.1 Observed meteorological and chemical data**

111 The air quality observational data are used to identify the regional characteristics of the O_3

112 episode in August 2013. Fifteen cities are selected as the representative research objects to better

113 reflect the status of O_3 pollution over the YRD region. The locations of these cities are shown in

114 Fig. 1b, which contains Shanghai, 8 cities in Jiangsu province (Changzhou, Nanjing, Nantong,

115 Suzhou, Taizhou, Wuxi, Yangzhou, and Zhenjiang), and 6 cities in Zhejiang province (Hangzhou,

116 Huzhou, Jiaxing, Ningbo, Shaoxing, and Zhoushan). The in-situ monitoring data for the hourly

117 concentrations of O_3, CO, NO_2, SO_2, $PM_{2.5}$ and PM_{10} can be acquired from National

118 Environmental Monitoring Center (NEMC) (http://106.37.208.233:20035). The assurance/quality

119 control (QA/QC) procedures for monitoring strictly follow the national standards (State

120   Environmental Protection Administration of China, 2006). The hourly pollutant concentration for

121   a city is calculated as the average of the pollutant concentrations from several national monitoring

122   sites in that city, which can better characterize the pollution level of the city. In order to identify

123   invalid or lacking data, a checking procedure for these data is performed following the work of

124   Chiqueto and Silva (2010). Finally, only less than 0.2% of the primary data are ignored in the

125   calculation. Moreover, the observed data of total VOCs (TVOC) during August 4-10 at an urban

126   site in Shanghai (SAES, 31.17°N, 121.43°E) is also used. They are provided by Shanghai

127   Academy of Environmental Sciences. The sampling height is about 15 m, and individual VOC

128   species are continuously measured every 30 min by two on-line high performance gas

129   chromatograph with flame ionization detector (GC-FID) systems (Chromato-sud airmoVOC

130   C2-C6 #5250308 and airmoVOC C6-C12 #2260308, France). The details for measurement and

131   QA/QC can refer to Wang et al. (2013).

132   The weather charts and the observed surface meteorological records are used to analyze the

133   synoptic systems during the episode. The weather charts for East Asia are accessible from Korea

134   Meteorological Administration (http://www.kma.go.kr/chn/weather/images/analysischart.jsp). The

135   hourly meteorological data at the observation sites of SH (31.40°N, 121.46°E) located in Shanghai,

136   HZ (30.23°N, 120.16°E) in Hangzhou, and NJ (32.00°N, 118.80°E) in Nanjing can be obtained

137   from the University of Wyoming (http://weather.uwyo.edu/wyoming/), where 2-m air temperature,

138   2-m relative humidity, 10-m wind speed and 10-m wind direction are available.

139   Meteorological and air quality observation data are also used to validate the reliability of

140   simulations in this study. Comparisons of the modeling results with the observation data are

141   performed in Shanghai, Nanjing, and Hangzhou. Shanghai is the most populous city in China, and

142   also a global financial and transportation center. Locating to the northwest of Shanghai, Nanjing is

143   the capital of Jiangsu Province and the second largest commercial center in East China. Hangzhou

144   is the capital of Zhejiang Province and located to the southwest of Shanghai. These cities are the

145   provincial capitals and the typical metropolis in the YRD region. They are highly urbanized and

146   industrialized, and all suffer from severe O_3 pollution.

147

148   **2.2 Model description and configurations**

149   In this study, WRF/CMAQ, which consists of WRF model version 3.4.1 and CMAQ Model

150   version 4.7.1, is applied to simulate the high O_3 episode over the YRD region in August 2013.

151   Developed at the National Center for Atmospheric Research (NCAR), WRF is a new generation of

152   meso-scale weather forecast model and assimilation system. Numerous applications have proven

153   that it shows a good performance in all kinds of weather forecasts and has broad application

154   prospects in China (Jiang et al., 2008; 2012; Wang et al., 2009b; Liu et al., 2013; Xie et al., 2014;

155   2016a; Liao et al., 2014; 2015; Li et al., 2016; Zhu et al., 2016). WRF provides off-line

156   meteorological fields as the input for the chemical transport model CMAQ. CMAQ is a third

157   generation of regional air quality model developed by the Environmental Protection Agency of

158   USA (USEPA). A set of up-to-date compatible modules and control equations for the atmosphere

159   is incorporated in the model, which can fully consider atmospheric complicated physical processes,

160   chemical processes and the relative contribution of different species (Byun and Schere, 2006;

161   Foley et al., 2010). CMAQ has been widely applied in China and proven to be a reliable tool in

162   simulating air quality from city scale to meso scale (Li et al., 2012; Wei et al., 2012; Liu et al.,

163   2013; Zhu et al., 2016).

164   The simulation run is conducted from 08:00 (local standard time, LST) on August 2 to 08:00

165   (LST) on August 16 2013, in which the first 48 h is taken as the spin-up time. Three one-way

166   nested domains are used in WRF with a Lambert Conformal map projection. The domain setting is

167   shown in Fig. 1. The outermost domain (domain 1, d01) covers the most areas of East Asia and

168   South Asia, with the horizontal grids of 88×75 and the grid spacing of 81 km. The nested domain

169   d02 covers the southeastern part of China, with the horizontal grids of 85×70 and the grid spacing

170   of 27 km. The finest domain (domain 3, d03) covers the core areas of the YRD region, with the

171   grid system of 70×64 and the resolution of 9 km. For all domains, there are 23 vertical sigma

172   layers from the surface to the top pressure of 100 hPa, with about 10 layers in the planetary

173   boundary layer. The detailed configuration options for the dynamic parameterization in WRF are

174   summarized in Table 1. Additionally, the SLAB scheme that does not consider urban canopy

175   parameters is adopted to model the urban effect. In order to reflect the rapid urban expansion in

176   the YRD region, the default United States Geological Survey (USGS) land-use archives are

177   updated by adding the present urban land-use conditions from 500-m Moderate Resolution

178   Imaging Spectroradiometer (MODIS) data, based on the work of Liao et al. (2014; 2015). The

179   initial meteorological fields and boundary conditions are from 1° resolution global reanalysis data

180   provided by National Center for Environmental Prediction (NCEP). The boundary conditions are

181   forced every 6 h.

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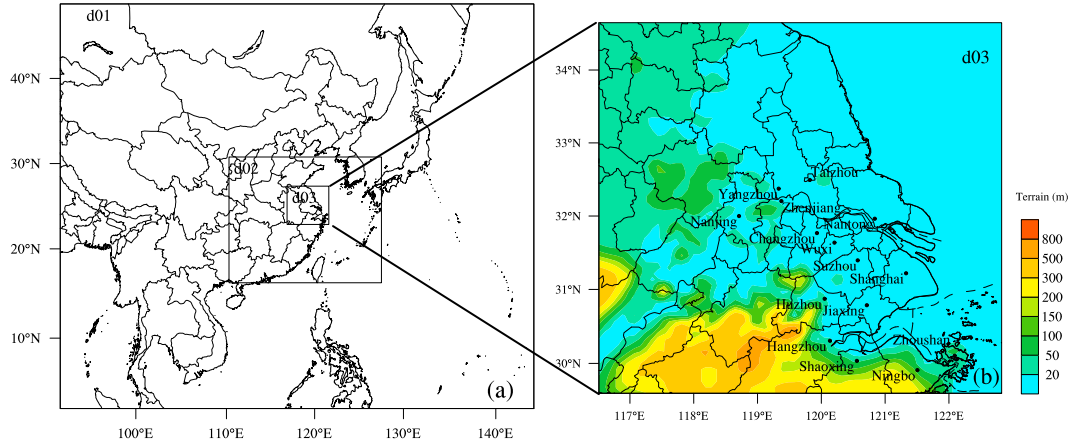
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184   **Fig. 1. Domain settings, include (a) the three nested modeling domains and (b) the nested domain 3 (d03)**
185   **with the terrain elevations and the locations of 15 main cities in the YRD region.**

186

187   **Table 1. The grid settings and the physical options for WRF in this study.**

Items	Options
Dimensions (x, y)	(88, 75), (85, 70), (70, 64)
Grid spacing (km)	81, 27, 9
Microphysics	WRF Single-Moment 5-class scheme (Hong et al., 2004)
Longwave Radiation	RRTM scheme (Mlawer et al., 1997)
Shortwave Radiation	Goddard scheme (Kim and Wang, 2011)
Surface layer	Moni-Obukhov scheme (Monin and Obukhov, 1954)
Land-surface layer	Noah Land Surface Model (Chen and Dudhia, 2001)
Planetary Boundary layer	YSU scheme (Hong et al., 2006)
Cumulus Parameterization	Grell-Devenyi ensemble scheme (Grell and Devenyi, 2002)

188

189   With respect to the air quality model, CMAQ uses the same vertical levels and the similar

190   three nested domains as those adopted in the meteorological simulation, whereas the CMAQ

191   domains are one grid smaller than the WRF domains. The Meteorology Chemistry Interface

192   Processor (MCIP) is used to convert WRF outputs to the input meteorological files needed by

193   CMAQ. The Carbon Bond 05 chemical mechanism (CB05) (Yarwood et al., 2005) is chosen for

194   gas-phase chemistry, and the 4rd generation CMAQ aerosol module (Byun and Schere, 2006) is

195   adopted for aerosol chemistry. The initial and outmost boundary conditions are obtained from the

196 Model for Ozone and Related Chemical Tracers version 4 (MOZART-4) (Emmons et al., 2010),

197 while those for the two nested inner domains are extracted from the immediate concentration files

198 of their parent domains. The anthropogenic emissions are mainly from the 2012 Multi-resolution

199 Emission Inventory for China (MEIC) with $0.25° \times 0.25°$ resolution, which is re-projected for the

200 grids of China in both domains. For the grids outside of China, the inventory developed for the

201 Intercontinental Chemical Transport Experiment-Phase B (INTEX-B) by Zhang et al. (2009) is

202 used. The natural O_3 precursor emissions are calculated by the natural emission model developed

203 by Xie et al. (2007; 2009; 2014), including NO from soil, VOCs from vegetations, and CH_4 from

204 rice paddies and terrestrial plants. The biomass burning emissions are acquired from the work of

205 Xie et al. (2014; 2016a).

206 **2.3 Integrated Process Rate (IPR) analysis method**

207   The CMAQ modeling system contains process analysis module (PROCAN), which consists

208 of the Integrated Process Rate (IPR) analysis and the Integrated Reaction Rate (IRR) analysis

209 (Byun and Schere, 2006). IPR has the capability of calculating the hourly contributions of

210 individual physical processes and the net effect of chemical reaction compared to the overall

211 concentrations, and thereby can determine the quantitative contribution of each process in a

212 specific grid cell. The atmospheric processes considered in IPR include the horizontal advection

213 (HADV), the vertical advection (ZADV), the horizontal diffusion (HDIF), the vertical diffusion

214 (VDIF), the emissions (EMIS), the dry deposition (DDEP), the cloud processes with the aqueous

215 chemistry (CLDS), the aerosol processes (AERO) and the gas-phase chemistry (CHEM). IPR has

216 been widely applied to investigate the regional photochemical pollutions, and proven to be an

217 effective tool to show the relative importance of every process and provide a fundamental

218 interpretation (Goncalves et al., 2009; Li et al., 2012; Liu et al., 2013; Zhu et al., 2016). In this

219 paper, the period from August 4 to 15 is selected for the IPR analysis. With the aid of IPR, we

220 assess the roles of the individual physical and chemical processes involved in O_3 formation over

221 the YRD region, and further present those in the typical cities (Shanghai, Nanjing and Hangzhou).

222 **2.4 Evaluation method**

223   Comparisons of the modeling results in the finest domain (d03) with the hourly observation

224 data are performed for meteorological factors and air pollutants in Shanghai, Hangzhou, and

225 Nanjing. The correlation coefficient (R), the normalized mean bias (NMB) and the

226 root-mean-square error (RMSE) are used to evaluate the model performance. These statistic values

227 are calculated as follows:

$$R = \frac{\sum_{i=1}^{N}(S_i - \bar{S})(O_i - \bar{O})}{\sqrt{\sum_{i=1}^{N}(S_i - \bar{S})^2}\sqrt{\sum_{i=1}^{N}(O_i - \bar{O})}} \tag{1}$$

$$NMB = \frac{\sum_{i=1}^{N}(S_i - O_i)}{\sum_{i=1}^{N}O_i} \times 100\% \tag{2}$$

$$RMSE = [\frac{1}{N}\sum_{i=1}^{N}(S_i - O_i)^2]^{\frac{1}{2}} \tag{3}$$

231 where S_i and O_i represent the simulated and the observed value, respectively. N means the total

232 number of valid data. Generally, the model performance is acceptable if the values of NMB and

233 RMSE are close to 0 and that of R is close to 1.

234

235 **3. Characteristics of the continuous ozone episode**

236 **3.1 Basic characteristic of the regional ozone episode in August 2013**

237 Fig. 2 shows the temporal variation of the hourly O_3 concentrations observed in 15 typical

238 cities over the YRD region from 00:00 (Universal Time Coordinated, UTC) August 4 to 23:00

239 (UTC) August 15 in 2013. Obviously, from August 7 to 12, high O_3 concentrations over 93.5 ppb

240 (approximately equal to the hourly national air quality standard of 200 μg/m^3) have been

241 frequently recorded in 13 cities, which means O_3 concentrations in most cities over the YRD

242 region exceed the national air quality standard. So, this high O_3 pollution episode is a typical

243 regional O_3 pollution episode that can affect the people and the ecosystem in a large area. In

244 general, for each city, there is a remarkable continuous growth in O_3 concentrations before the O_3

245 episode, followed by the lasting heavy O_3 pollution period. Though the O_3 concentrations in

246 Shaoxing and Nanjing meet the national O_3 standard, their time series still show the similar

247 tendency to those of the other cities in the same region. The excessive level of O_3 occurring in

248 Huzhou, Jiaxing, Nantong, Yangzhou and Shanghai lasts for more than six consecutive days,

249 reflecting the regional continuous characteristics of this O_3 pollution episode.

250 According to the temporal variation characteristics of O_3 illustrated in Fig. 2, the

251 abovementioned 15 typical YRD cities can be classified into three categories: (1) the cities in the

252 Southeast Coastal Region (SCR), including Shanghai, Suzhou, Jiaxing, Ningbo, Shaoxing, and

253 Zhoushan; (2) the cities in the Central Inland Region (CIR), including Hangzhou, Huzhou, Wuxi,

254 Changzhou, and Nantong; and (3) the cities in the Northwestern Inland Region (NIR), including

255 Nanjing, Yangzhou, Zhenjiang, and Taizhou. The classification is primarily on basis of the

256 observational facts that the maximum O_3 concentrations occur on August 10-11, 12, and 13, and

257 begin to synchronously decrease on August 12, 13 and 14 in SCR, CIR and NIR, respectively. As

258 shown in Fig. 2, in the Southeast Coastal Region (SCR), Zhoushan firstly exceeds the national O_3

259 standard on August 4, followed by Jiaxing, Shanghai, Suzhou and Ningbo. The peak hourly O_3

260 concentration of SCR occurs in Jiaxing on August 10, with the value up to 162.4 ppb. In the

261 Central Inland Region (CIR), Huzhou is the first city exceeding the national O_3 standard, followed

262 by the order of Nantong, Changzhou, Wuxi, and Hangzhou. The high-level O_3 pollution in

263 Huzhou lasts during August 5-13. In Nantong and Changzhou, the maximum hourly O_3

264 concentration reaches 167.1 ppb on August 10 and 166.1 ppb on August 12, respectively. As for

265 the Northwest Inland Region (NIR), Yangzhou, Zhenjiang, and Taizhou successively exceed the

266 national O_3 standard. It is also noteworthy that the date when O_3 concentration exceeds the

267 national air quality standard in coastal region is ahead of that in inland regions, so is the date of O_3

268 decrease. The different start time of O_3 decreasing in different regions might be related to the

269 strong southeast wind in accordance with the movement of Typhoon Utor, which is discussed in

270 Sect. 3.2 in detail.

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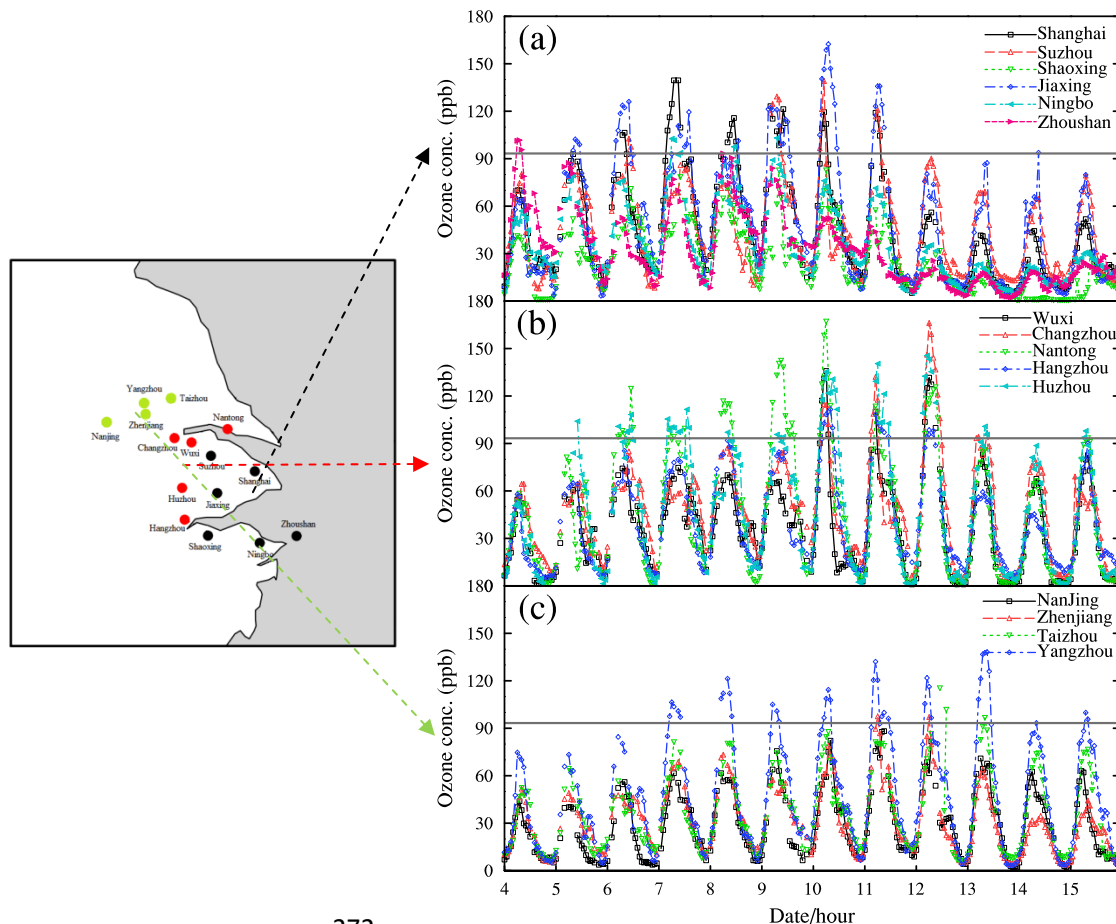
Fig. 2. The time series of the observed O$_3$ concentrations in 15 typical cities from August 4 to 15 2013 over the YRD region, which can be divided into three areas: (a) the Southeast Coast Region (SCR), including Shanghai, Suzhou, Shaoxing, Jiaxing, Ningbo, and Zhoushan; (b) the Central Inland Region (CIR), including Wuxi, Changzhou, Nantong, Hangzhou, and Huzhou; (c) the Northwest Inland Region (NIR), including Nanjing, Zhenjiang, Taizhou and Yangzhou. The gray solid lines in (a), (b), and (c) represent the national standard for the hourly O$_3$ concentration, which is 200 μg/m^3.

Table 2 presents the maximum and the average concentrations of O$_3$ and NO$_2$ in 15 YRD cities during August 7-12 2013. It illustrates that the mean concentrations of NO$_2$ in different YRD cities range from 7.7 to 24.5 ppb during the O$_3$ episode, indicating the heterogeneity of the spatial distribution of O$_3$ precursor emissions. For O$_3$, the highest hourly concentration (167.1 ppb) occurs in Nantong, followed by 166.1 ppb in Changzhou and 162.4 ppb in Jiaxing. These values are all nearly 2 times of the national air quality standard. It seems that O$_3$ concentrations are higher in the cities around Shanghai, where the concentrations of O$_3$ precursors are more adequate as well. High concentrations of O$_3$ and its precursors imply that there may be stronger photochemical reactions.

290 **Table 2. The maximum and average concentrations of O_3 and NO_2 observed in 15 cities during August 7-12**

291 **2013 (ppb).**

Sites		O_3		NO_2	
		Max	Mean	Max	Mean
Southeast Coast Region (CSR)	Shanghai	139.5	55.1	35.1	15.6
	Suzhou	139.1	50.9	50.6	19.7
	Jiaxing	162.4	61.1	52.1	17.1
	Ningbo	113.4	41.9	31.2	12.4
	Shaoxing	82.6	31.9	27.8	12.7
	Zhoushan	93.6	35.5	27.3	7.8
Central Inland Region (CIR)	Hangzhou	111.5	48.6	30.2	16.7
	Huzhou	145.6	57.2	43.8	20.8
	Wuxi	135.8	43.2	39.9	18.8
	Changzhou	166.1	55.7	58.4	24.5
	Nantong	167.1	56.0	48.2	20.9
Northwest Inland Region (NIR)	Nanjing	88.2	34.1	41.4	21.9
	Yangzhou	132.1	54.1	36.0	17.1
	Zhenjiang	97.5	37.7	38.5	20.1
	Taizhou	115.3	40.5	18.5	7.7

292

293 Fig. 3 demonstrates the hourly variations of the observed NO_2 concentrations in Shanghai,

294 Nanjing and Hangzhou from August 4 to 15 2013, and the time series of TVOC observed at SAES

295 in Shanghai from August 4 to 10 2013. Obviously, there are two peaks in the diurnal cycles of

296 NO_2 and VOC at all sites, which should be related with the rush hours in cities. The photolysis of

297 NO_2 dominates O_3-VOC-NO_x chemistry after 8:00, and thereby makes the concentrations of

298 precursors (NO_2 and VOC) begin to decrease. Thus, the related reactions form O_3 and increase its

299 concentration until about 14:00. These diurnal variations of O_3 and its precursors follow the

300 typical patterns in the polluted areas and reflect the close relationships between O_3, VOC and NO_x

301 (Wang et al., 2013; Xie et al., 2016b). Moreover, the daily variations of NO_2 and VOC show good

302 agreement with those of O_3. For VOC, the concentration in Shanghai largely increases since

303 August 6, which corresponds well with the over-standard O_3 concentrations since then (Fig. 2).

304 For NO_2, the higher values occur from August 6 to 11 in all cities, but the concentrations start to

305 decrease on August 12, 13 and 14 in Shanghai, Hangzhou and Nanjing, respectively. It seems that

306 the changes of O_3 precursors (NO_2 and VOC) are also affected by the movement of Typhoon Utor.

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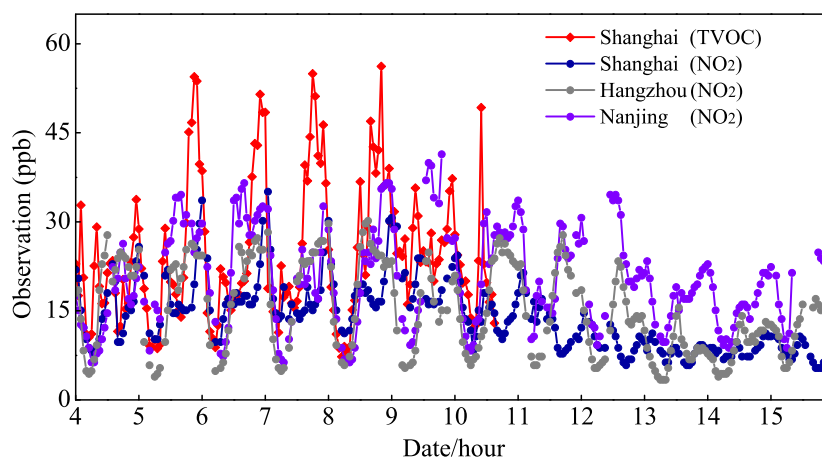
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309 **Fig. 3. Temporal variations of the observed NO$_2$ concentrations at Shanghai, Nanjing and Hangzhou**
310 **stations from August 4 to 15 2013 and the observed TVOC concentration at SAES (31.17°N, 121.43°E) in**
311 **Shanghai from August 4 to 10 2013.**

312

3.2 Meteorological condition and its effect

314   Favorable weather conditions have large impacts on the formation of severe O$_3$ pollution

315 (Huang et al., 2005; 2006; Wang et al, 2006b; Jiang et al., 2008; Cheng et al., 2014; Hung and Lo,

316 2015). High-level O$_3$ episodes often take place in hot seasons, when the meteorological conditions

317 with high temperature and strong solar radiation are beneficial to the photochemical reactions of

318 O$_3$ (Lam et al., 2005). Fig. 4 shows the variations of the surface meteorological parameters that are

319 related to this photochemical pollution episode during August 4-15, including 2-m air temperature,

320 2-m relative humidity, 10-m wind speed and 10-m wind direction at the meteorological sites in

321 Shanghai (SH) of SCR, Hangzhou (HZ) of CIR, and Nanjing (NJ) of NIR.

322   As shown in Fig. 4a, the hot weather at SH, HZ and NJ exists for nearly a week from August

323 7 to 12, with the hourly maximum temperature reaching the value over 40 ^{o}C. Meanwhile, the

324 variations of 2-m relative humidity show the negative correlation with those of 2-m air

325 temperature. The minimum 2-m relative humidity at SH and HZ occur on August 9 and August 10

326 respectively, with the value below 75%. These minimum values are also lower than the values

327 before and after the O$_3$ episode, suggesting that high-level O$_3$ episodes usually occur under the

328 weather conditions with high temperature and low humidity. The value of 2-m relative humidity at

329 NJ is relatively higher than those at SH and HZ and remains more stable. This extremely hot and

330   dry weather condition at SH, HZ, and NJ are successively relieved on August 12, 13 and 15, which

331   coincide well with the reduction of surface O_3 concentrations in Shanghai, Hangzhou, and Nanjing

332   (Fig. 2). With respect to the observed surface wind (Fig. 4b), the 10-m wind speed at SH and HZ is

333   comparatively lower during the period of the O_3 episode, while it is suddenly intensified after

334   August 12. Meanwhile, the wind direction is fluctuating from August 7 to 12, while it maintains

335   southeasterly wind after August 12 as well. The growth of wind speed is more distinct at SH, with

336   the maximum value of approximately 10 m/s. The wind speed at NJ has an obviously diurnal

337   variation from August 4 to 8, and the minimum value occurs on August 10.

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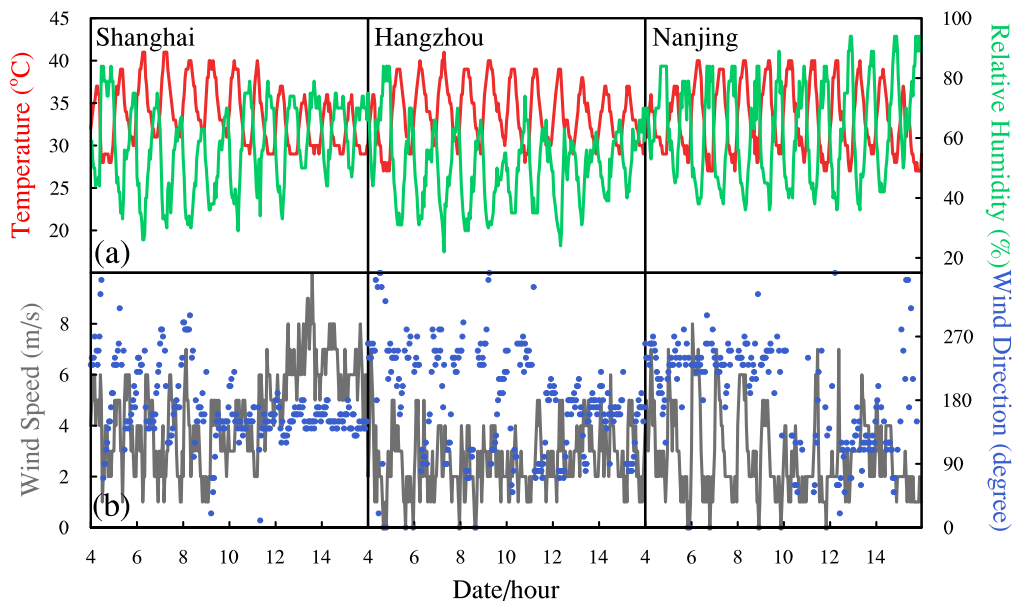
339

340 **Fig. 4. Temporal variations of the main meteorological parameters at Shanghai, Hangzhou and Nanjing**

341 **meteorological stations during August 4-15 2013, including (a) 2-m air temperature (the red solid line) and**

342 **2-m relative humidity (the green solid line); (b) 10-m wind speed (the gray solid line) and 10-m wind**

343 **direction (the blue scatter points).**

344

345   Fig. 5 displays the weather charts for the 500 hPa layer over the East Asia at 00:00 (UTC) on

346   August 6, 8, 10, and 12 2013, which can illustrate the main synoptic patterns causing the O_3

347   pollution. Obviously, during the period of the selected O_3 episode, the whole YRD region is under

348   the control of the strong Western Pacific subtropical high, which is stronger and extends much

349   farther west than normal. The anomaly of the subtropical high might be the direct and leading

350   cause of the abnormally high temperature shown in Fig. 4a (Peng et al., 2014). The intensity of the

351 subtropical high is usually characterized by the area index, defined as the total number of grid

352 points that have geopotential heights of 588 decameters or greater in the region of 110-180°E and

353 northward of 10°N. As shown in Fig. 5, the 588-decameter area covers most of southeast China,

354 and the high pressure center (592-decameter area) is located in the southeastern coastal areas as

355 well as the surrounding sea areas, which means the subtropical high is very intensive. This high

356 pressure strengthens and remains over the YRD region for several days (from August 6 to 12),

357 implying that the air subsides to the ground. The downward air acts as a dome capping the

358 atmosphere, and helps to trap heat as well as air pollutants at the surface. Without the lift of air,

359 there is little convection and therefore little cumulus clouds or rains. The end result is a continual

360 accumulating of solar radiation and heat on the ground, which may greatly enhance the

361 photochemical reactions between the abundant build-up air pollutants.

362   The other weather system worthy of note is Typhoon Utor (shown in Fig. 5c and d). Typhoon

363 Utor is one of the strongest typhoons in the 2013 Pacific typhoon season. It is formed early on

364 August 8, develops into a tropical storm on August 9, undergoes an explosive

365 intensification within a half of day, and achieves typhoon status on early August 10. After landing

366 in Luzon of the Philippines on late August 11, it reemerges in the South China Sea on August 12.

367 Typhoon Utor hits the land of Guangdong Province in China on August 14, and thereby is finally

368 weakened into a tropical storm. In the end, it is ultimately dissipated on August 18. It was reported

369 that ozone episodes during the hot season are usually associated with the passage of tropical

370 cyclones close to the territory (Huang et al., 2005; Wang et al., 2006b; Jiang et al., 2008; Cheng et

371 al., 2014; Hung and Lo, 2015). When a site is at the front of moving typhoon system, it can be

372 controlled by the downward airflow induced by the typhoons' peripheral circulation. So, the

373 typhoon system can cause the local weather around the site with high temperature, low humidity,

374 strong solar radiation and small wind for a short time, before it is close enough to bring winds and

375 rains. All these changes of meteorological conditions can help to form the severe continuous O_3

376 pollution (Jiang et al., 2008). In this O_3 episode, the YRD region may be influenced by the

377 peripheral circulation of Typhoon Utor as well. Especially on August 10-11, the downward airflow

378 in the troposphere is significantly strengthened (shown in Fig. 7), which may enhance the build-up

379 of heat and air pollutants, and thereby result in worse air quality shown in Fig. 2.

380   Moreover, with the approaching of Typhoon Utor from August 12 to 14, the near-surface

381   breeze over the YRD region gradually turns to be the prevailing southeasterly or southerly wind

382   (Fig. 5d), with the highest wind speed up to 6-10 m/s in Shanghai (Fig. 4). The strengthened wind

383   can bring the clean marine air from ocean to inland, and thereby effectively mitigate the O_3

384   pollution. Meantime, Typhoon Utor also gradually affects the position and strength of the Western

385   Pacific subtropical high. As the typhoon continuously approaching and finally landing on

386   Guangdong, the high pressure system is forced to retreat easterly and move northwards. When the

387   high pressure center completely moves to the oceans, the YRD region is totally under the control

388   of the typhoon system. In the end, the hot weather is relieved and the O_3 pollution is mitigated.

389   The coastal cities in CSR are closer to the typhoon system, so they are firstly influenced during

390   this period. Thus, the wind at SH in CSR firstly changes, followed by HZ in CIR and NJ in NIR.

391   In the same way, 2-m air temperature and O_3 concentrations also successively decrease from

392   southeast (SH in CSR) to northwest (NJ in NIR) owing to the scavenging effect.

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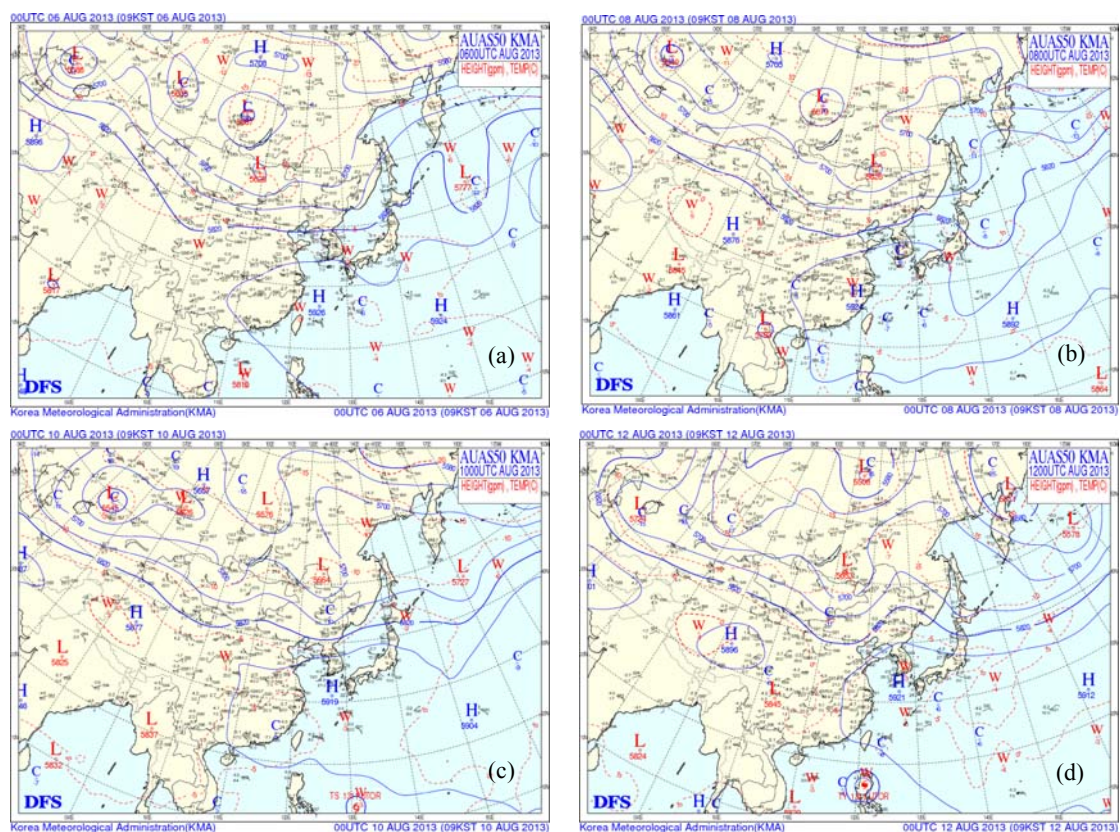
394   **Fig. 5. Weather charts at the 500 hPa layer over the East Asia at 00:00 (UTC) on (a) August 6, (b) August 8,**

395   **(c) August 10, and (d) August 12 2013 (from Korea Meteorological Administration).**

396

397   **4 Modeling results and discussions**

4.1 Evaluation of model performance

To evaluate the simulation performance, the hourly modeling results during the period of August 4-15 2013 are compared with the observation records. Table 3 presents the performance statistics, including the values of the correlation coefficient (R), the normalized mean bias (NMB), and the root-mean-square error (RMSE), which are all calculated for 2-m air temperature (T_2), 2-m relative humidity (RH_2), 10-m wind speed ($Wspd_{10}$), 10-m wind direction ($Wdir_{10}$), surface ozone concentrations (O_3), and surface nitrogen dioxide concentrations (NO_2) in Shanghai (SH), Nanjing (NJ), and Hangzhou (HZ).

As indicated in Table 3, the simulated results of surface air temperature and relative humidity from WRF show good agreement with the observations. The highest correlation coefficient of 2-m air temperature (T_2) is found to be 0.91 at SH, followed by 0.84 at NJ and 0.80 at HZ (statistically significant at 95% confident level). The corresponding correlation coefficients for 2-m relative humidity (RH_2) are 0.85, 0.83 and 0.78, respectively. The values of RMSE for T_2 at SH, NJ and HZ are 4.15, 2.91and 3.09 ^{o}C, and those for RH_2 are 19.3%, 9.41% and 13.96%, respectively. Our simulation underestimates T_2 and overestimates RH_2 to some certain extent, with the values of NMB for T_2 at SH, NJ and HZ being -5.68%, -5.98% and -6.53%, and those for RH_2 being 12.64%, 4.52% and 16.36%. These biases might be attributed to the uncertainty caused by the SLAB scheme, which can underestimate temperature in summer (Liao et al., 2014). However, according to the relevant studies (Li et al., 2012; Liao et al., 2015; Xie et al., 2016a), this level of over- or under-estimation is still acceptable. The wind components are closely related to the transport processes. As shown in Table 3, our modeling results of wind speed and direction basically reflect the characteristics of wind fields. For 10-m wind speed (W_{spd10}), R is 0.77 at SH, 0.74 at NJ, and 0.75 at HZ, respectively. Though the values of NMB (1.53%, 5.92%, and 9.21%) and RMSE (2.18, 2.41 and 2.39) display that the simulated wind speeds are a little overestimated, the biases are still reasonable and acceptable. For 10-m wind direction (W_{dir10}), the simulated values also fit the observation records well, with the R values of 0.63 at SH, 0.57 at NJ and 0.58 at HZ. Comparing the mean values from SIM and OBS, we can find that WRF model generally simulates the prevailing wind direction during this period. In summary, the abovementioned performance statistics numbers illustrate that the WRF simulation can reflect the major characteristics of meteorological conditions of this O_3 episode, and the meteorological outputs can

428 be used in the pollutant concentration simulation.

429

430 **Table 3. Comparisons between the simulations and the observations at Shanghai, Nanjing and Hangzhou**
431 **stations during August 4-15 2013.**

Sites [a]	Vars [b]	Mean		R [e]	NMB [f]	RMSE [g]
		OBS [c]	SIM [d]			
SH	T_2 (°C)	33.27	31.38	0.91	-5.68%	4.15
	RH_2 (%)	57.91	65.23	0.85	12.64%	19.3
	$Wspd_{10}$ (m s^{-1})	4.59	4.66	0.77	1.53%	2.18
	$Wdir_{10}$ (°)	176.34	182.57	0.63	3.53%	41.44
	O_3 (ppb)	87.77	82.5	0.81	-6.00%	38.79
	NO_2 (ppb)	29.01	38.25	0.54	31.85%	28.95
NJ	T_2 (°C)	32.95	30.98	0.84	-5.98%	2.91
	RH_2 (%)	63.28	66.14	0.83	4.52%	9.41
	$Wspd_{10}$ (m s^{-1})	3.21	3.4	0.74	5.92%	2.41
	$Wdir_{10}$ (°)	197.68	194.58	0.57	-1.57%	71.19
	O_3 (ppb)	69.7	78.15	0.81	12.12%	36.8
	NO_2 (ppb)	41.44	40.09	0.61	-3.26%	22.4
HZ	T_2 (°C)	33.25	31.08	0.8	-6.53%	3.09
	RH_2 (%)	52.76	61.39	0.78	16.36%	13.96
	$Wspd_{10}$ (m s^{-1})	3.04	3.32	0.75	9.21%	2.39
	$Wdir_{10}$ (°)	186.45	186.2	0.58	-0.13%	69.44
	O_3 (ppb)	76.57	84.51	0.83	10.37%	33.95
	NO_2 (ppb)	31.06	27.21	0.66	-12.40%	16.86

432 [a] Sites indicates the city where the observation sites locate, including Shanghai (SH), Nanjing (NJ), and Hangzhou
433 (HZ); [b] Vars indicates the variables under validation, including 2-m air temperature (T_2), 2-m relative humidity
434 (RH_2), 10-m wind speed ($Wspd_{10}$), 10-m wind direction ($Wdir_{10}$), ozone (O_3), and nitrogen dioxide (NO_2). The
435 words between the parentheses behind variables indicate the unit; [c] OBS indicates the observation data; [d] SIM
436 indicates the simulation results from WRF/CMAQ; [e] R indicates the correlation coefficients, with statistically
437 significant at 95% confident level; [f] NMB indicates the normalized mean bias; [g] RMSE indicates the
438 root-mean-square error.

439

440 Fig. 6 shows the comparisons between the modeling results from CMAQ and the observed

441 hourly concentrations of O_3 in Shanghai, Nanjing, and Hangzhou during August 4-15 2013.

442 Obviously, the observations and the simulated results present reasonable agreement at each site,

443 with the correlation coefficients of 0.81 to 0.83, NMB of -6% to 12.12%, RMSE of 33.95 to 38.79

444 ppb. Moreover, the simulation also reproduces the diurnal variation of O_3, which shows that the

445 concentration reaches its maximum at around noon time and gradually decreases to its minimum

446   after midnight. With respect to the O_3 precursor, comparisons of NO_2 concentrations between

447   simulation results and observations show that the correlation coefficient at each city is about 0.6

448   (given in Table 3), which further prove that the process of O_3 formation is captured reasonable

449   well over the YRD region and throughout the episode. However, CMAQ overestimates NO_2 and

450   underestimates O_3 in Shanghai, while underestimates NO_2 and overestimates O_3 in Nanjing and

451   Hangzhou. These biases of O_3 and NO_2 should mainly be attributed to the uncertainties in

452   emissions of O_3 precursors (NO_x and VOC_s) (Li et al., 2012; Liao et al., 2015; Xie et al., 2016).

453   Because of the VOC-sensitive O_3 chemistry in the daytime and NO_x titration at night in the YRD

454   region (Xie et al., 2014), higher estimation of NO_x emission in Shanghai may lead to higher NO_2

455   and lower O_3 predictions, while lower NO_x estimations in Nanjing and Hangzhou may result in

456   lower NO_2 and higher O_3 modeling results. The undervalued NO_2 and overvalued O_3 in Nanjing

457   and Hangzhou can also be related with the overestimations in WS_{10} and the negative biases in T_2.

458   Moreover, the uncertainties in nonlinear chemical reactions coupled in CMAQ may also have

459   important effects on model predictions. For example, the modeling results cannot catch the low O_3

460   values observed at night in Nanjing and Hangzhou (Fig. 6), implying there may be some

461   imperfections in the nocturnal chemistry of CMAQ. Nevertheless, the performance of CMAQ

462   model is comparable to the other applications (Goncalves et al., 2009; Li et al., 2012; Zhu et al.,

463   2016). Compared to these previous related studies, the simulation in this study attains an

464   acceptable and satisfactory result. Thus, the consistency of simulation and observation

465   demonstrates that the modeling results are capable of capturing and reproducing the characteristics

466   and changes of photochemical pollutants, and can be used to provide valuable insights into the

467   governing processes of this O_3 episode.

468

150

Ozone conc. (ppb)

120

90

60

0

Shanghai   Hangzhou   Nanjing

4 6 8 10 12 14   4 6 8 10 12 14   4 6 8 10 12 14

Date/hour

469

470
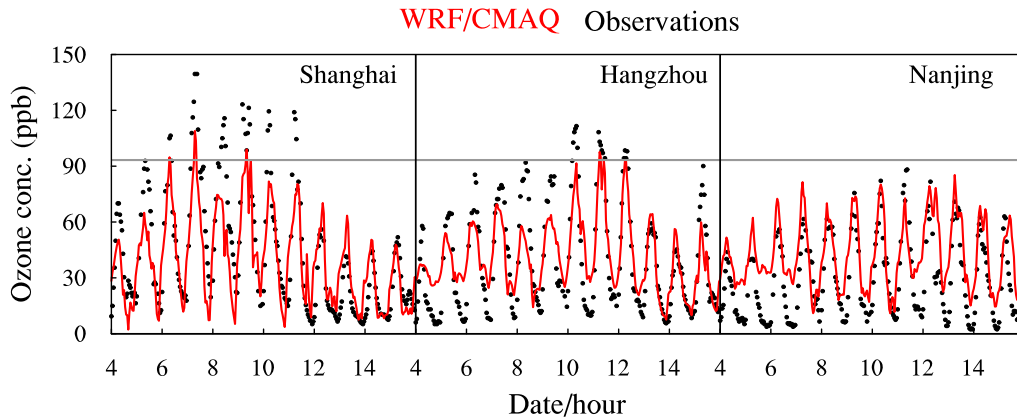
Fig. 6. Hourly variations of the observed and the simulated O$_3$ concentrations in Shanghai, Nanjing, and Hangzhou during August 4 to 15 2013. The red solid lines show the modeling results, the black dot lines give the observations, and the solid gray lines represent the national standard for the hourly O$_3$ concentration, which is 200 μg/m^3.

475

4.2 Characteristics of the vertical airflows

Fig. 7 presents the daytime vertical wind velocity as well as the vertical distribution of O$_3$ concentrations from 116.5°E to 122.9°E along the latitude of 31.40°N (where Shanghai is located) during August 7-12 2013. The simulation results clearly illustrate that there are strong downward airflows over the YRD region during the period of the regional high-level O$_3$ pollution, which can be attributed to the fact that these areas are under the control of the subtropical high and the sinking airflow is predominant (as discussed in Sect. 3.2).

From August 7 to 9 2013, except for the mentioned regional sinking airflows, there are still some local thermal circulations continually occurring at the lower atmospheric layers (< 2 km) along the vertical cross-section of Hangzhou (HZ) - Nanjing (NJ). These circulations are related with urban heat islands. Usually high pressures are accompanied by more stagnant and fair dry weather, so the upward and the downward flows caused by urban-breeze circulations can easily appear in the urban areas. For the vertical distribution of O$_3$, its high concentrations (> 50 ppb) generally appear from the surface to 1.5 km height above the cities. As discussed in Sect. 3.2, air pollutants tend to be trapped on the ground due to the regional sinking airflows. Moreover, the local circulations over the cities make the urban areas to be the convergence zones, and thereby more air pollutants can be accumulated in and around these cities. Under the weather conditions induced by the subtropical high, such as high air temperature, stronger solar radiation and less

494   water vapor, the chemical reactions between the build-up air pollutants can be enhanced to form

495   the high-level O_3 pollution. Additionally, Fig. 7a-c also show that there are maximum O_3

496   concentrations (> 90 ppb) occurring near the surface in and around SH. This phenomenon should

497   be explained by the fact that the coastal city (SH) is firstly affected by Typhoon Utor

498   From August 10 to 12, with the approaching of Typhoon Utor, the vertical air movements

499   over the YRD region are not restricted at the lower atmosphere any more. As shown in Fig. 7d-f,

500   there are stronger downward airflows from the surface to the top of troposphere. As discussed in

501   Sect. 3.2, the YRD cities are at the front of the moving typhoon system, so the peripheral

502   circulation of Typhoon Utor may enhance the sinking of atmosphere, which can lead to higher air

503   temperature, lower humidity, and stronger solar radiation. Affected by the enhanced downward air

504   movement as well as the relevant changes of meteorological conditions, O_3 concentrations over

505   the YRD region maintain a high pollution level, with the O_3 concentrations over 60 ppb below the

506   height of 1.5 km (Fig. 7d-f). Furthermore, the high value center of O_3 concentrations (> 90 ppb)

507   moves westwards during August 10-12, implying that the peripheral circulation of Typhoon Utor

508   can drive the air from the coastal areas to the inland areas.

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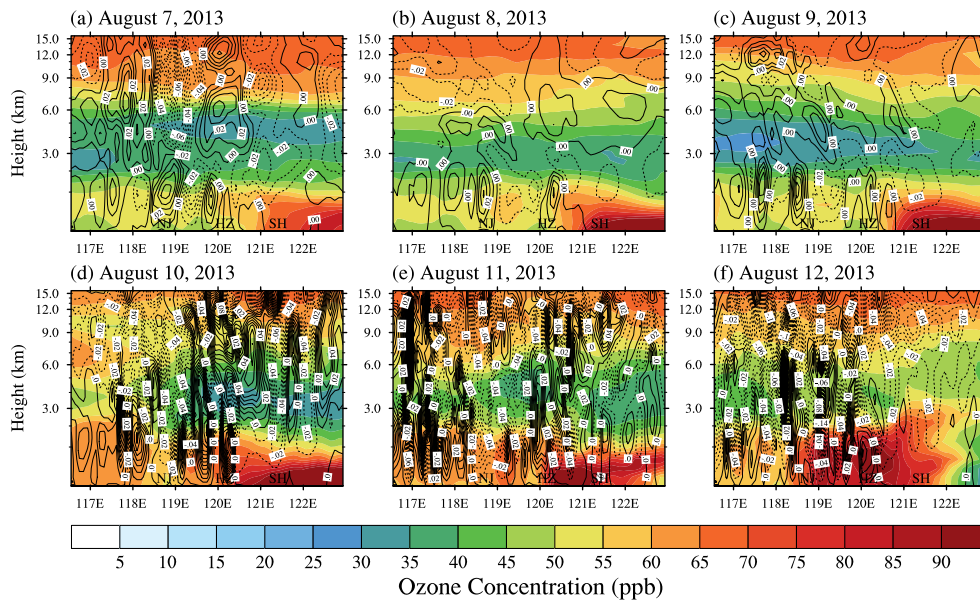
510

511   **Fig. 7. Simulated daytime vertical wind velocity and vertical distribution of O_3 concentrations from 116.5°E**

512   **to 122.9°E along the latitude of 31.40°N (where Shanghai is located) during August 7 to 12 2013. The marks**

513   **of SH, HZ and NJ point out the longitudes of Shanghai, Hangzhou, and Nanjing, respectively. The dotted**

514   **lines show the negative wind speeds and represent downward airflow, while the solid lines show the positive**

515   **wind speeds and zero vertical velocity. The interval is 0.01 m/s.**

516

The vertical changes of wind velocity and O_3 concentrations above Shanghai, Hangzhou and Nanjing are further illustrated in Fig. 8. Similarly, the atmospheric subsidence can also be found in the troposphere (usually occur at more than 1 km above the surface) during the period of the high-level O_3 pollution. With respect to Shanghai, affected by the extremely high temperature, more active photochemical reactions lead to higher O_3 concentrations in the whole atmospheric boundary layer. The downward airflows induced by the subtropical high trap and enhance the accumulation of surface O_3 as time passes. Thus, high O_3 concentrations are formed below 2 km above the urban areas of Shanghai, and the high concentration centers occur near the surface below 500 m. It is interesting that O_3 concentration on August 8 is comparatively lower, which can be seen in Fig. 2 as well. This phenomenon can be explained by the fact that the transient upward airflow occurs at above 300 m over Shanghai and inhibits the accumulation of the O_3 pollution at the surface (shown in Fig. 8a). Additionally, Fig. 8a also presents the possible effects of Typhoon Utor on the formation of O_3. On August 10, when the typhoon system approaches to the eastern coastal areas of China, the sinking air above Shanghai is apparently strengthened, and thereby enhances the intensity of O_3 pollution as well as the scope of the pollution. But after August 12, when Typhoon Utor changes the wind and even impacts the subtropical high, high temperature is alleviated and the build-up O_3 is transported to other places. Thus, the pollution is mitigated. As to Hangzhou (Fig. 8b), from August 7 to 9, owing to weaker photochemical reactions, lower O_3 concentrations than that in Shanghai are found in the boundary layer. However, the O_3 concentration can exceed the national standard from August 10 to 12 (Fig. 2), which should be influenced by the typhoon system. The influence process is similar to the above discussion for Shanghai, that is, the upper downward airflows (over 1 km above the surface) are enhanced significantly since August 10. But for Nanjing, the O_3 concentration does not exceed the national O_3 standard during August 7-12 (Fig. 2 and 8), which should be attributed to the fact that Nanjing is far away from the coastal areas and thereby hardly affected by the downward flow in the typhoon periphery. Though the O_3 concentration in Nanjing increases on August 12, it should mainly be caused by the local photochemical reactions because the vertical movement below 2 km above Nanjing is dominated by upward airflows.

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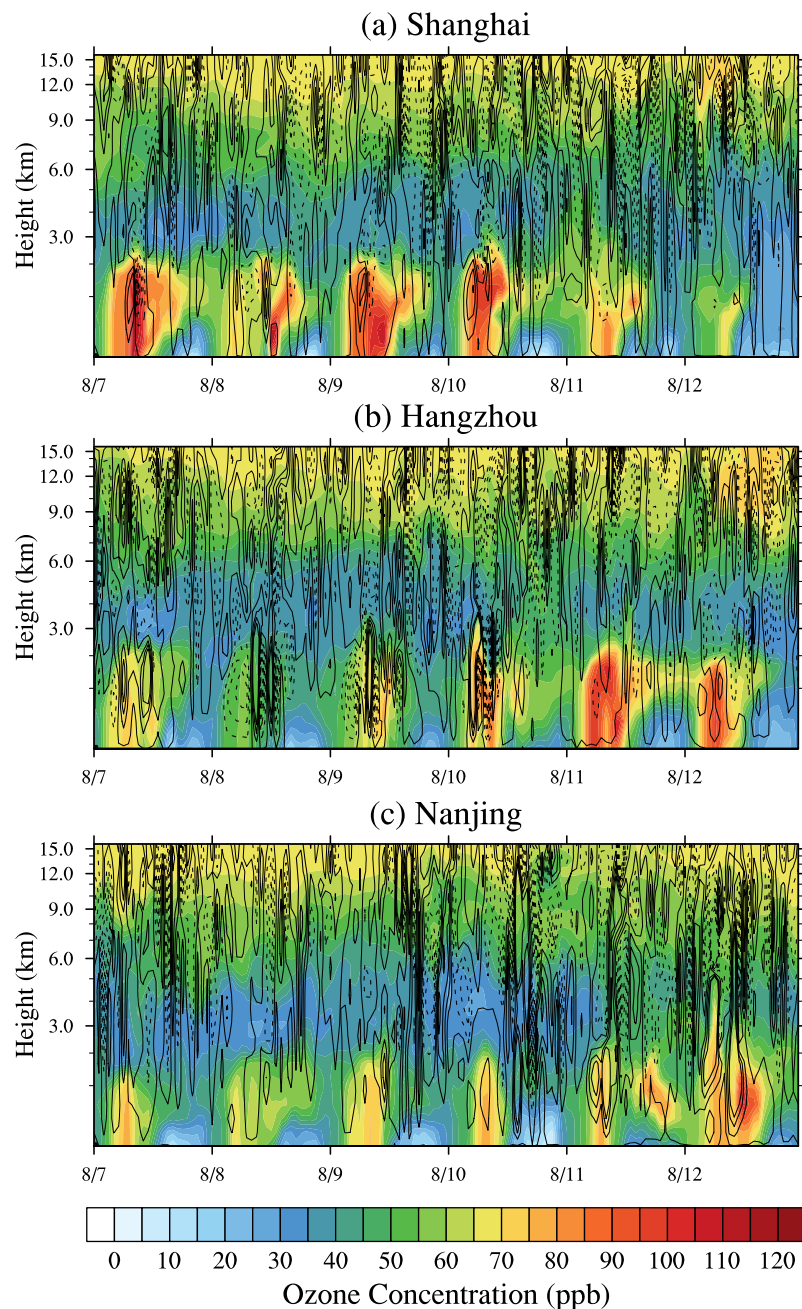
Fig. 8. Temporal variations of the vertical wind velocity and the vertical distribution of O₃ concentrations above (a) Shanghai, (b) Hangzhou and (c) Nanjing during August 7 to 12 2013. The dotted lines show the negative wind speeds and represent the downward airflows, while the solid lines show the positive wind speeds and zero vertical velocity. The interval is 0.005 m/s.

It is also should be mentioned that the near-surface vertical velocities around these cities are much lower than those at higher altitudes (Fig. 8). Especially in the planetary boundary layer (< 1 km), lots of zero-velocity lines appear near the ground. This phenomenon may be related with the upward airflow caused by Urban Heat Islands. Thus, the maximum centers of O₃ occur near the surface below 500 m, and the vertical diffusion process plays a more important role in the

558   accumulation of surface O_3. The essential role of the vertical diffusion process in the O_3 episode is

559   similar to that reported by Zhu et al. (2015).

560

561   **4.3 Process analysis for ozone formation**

562   **4.3.1 Typical cities in the YRD region**

563   Fig. 9 shows the daytime mean contributions of different atmospheric processes to the

564   formation of O_3 in Shanghai (SH), Nanjing (NJ), and Hangzhou (HZ) at the first modeling layer

565   from August 4 to 15 2013. As shown in the figure, for all cities during this period, the major

566   contributors to high O_3 concentrations include the vertical diffusion (VDIF), the dry deposition

567   (DDEP), the gas-phase chemistry (CHEM), and the total advection (TADV). TADV is the sum of

568   the horizontal advection (HADV) and the vertical advection (ZADV). In this study, HADV and

569   ZADV are considered together as TADV because they are inevitably linked as the inseparable

570   parts of air circulation. As discussed in Sect. 3.2, the strong sinking air causes slow wind on the

571   ground and little clouds in the sky, so the contributions of horizontal diffusion (HDIF) and cloud

572   processes (CLDS) are quite small during this episode.

573   In the first layer of the urban areas of Shanghai (Fig. 9a), the averaged contributions from the

574   vertical diffusion (VDIF), the gas-phase chemistry (CHEM), the advection process (TADV), and

575   the dry deposition (DDEP) during the daytime of August 4-15 are 9.95, 10.10, -11.74 and -7.28

576   ppb/h, respectively. Obviously, VDIF and CHEM exhibit significant positive contributions to O_3

577   during most days, while TADV and DDEP mainly show the consumption contributions. The

578   sinking air caused by the weather system discussed in Sect. 3.2 can trap heat and air pollutants on

579   the ground, and make VDIF be the most import source of surface O_3. Meanwhile, the hotter and

580   dryer weather with more sunshine, above 40 ^{o}C and comparatively low relative humidity (shown

581   in Fig. 4), which is related with the sinking air, can enhance the photochemical reactions. So,

582   CHEM can form more O_3 on the ground. Compared with the time series of CHEM and DDEP in

583   which there are no obvious fluctuations, the values of VDIF and TADV significantly change with

584   the time, with the daytime mean contributions varying from 3.99 to 28.45 ppb/h for VDIF and

585   from -2.56 to -28.13 ppb/h for TADV. These time variations should be related with the changes of

586   vertical air movement. For example, the value of VDIF on August 8 is only 3.99 ppb/h, which can

587   be attributed to the local transient upward airflow over Shanghai (shown in Fig. 8a). On August 10,

588 however, VDIF can contribute 28.45 ppb O_3 per hour, which may be related with the enhanced

589 downward air movement caused by the peripheral circulation of Typhoon Utor. Moreover, during

590 the high-level O_3 episode from August 7-12, the mean values for VDIF, CHEM, TADV and DDEP

591 are 13.41, 11.21, -8.37 and -14.74 ppb/h. But after August 12, the mean contributions of VDIF,

592 CHEM, TADV and DDEP decrease to 5.35, 9.53, -5.52 and -10.85 ppb/h. These reductions should

593 be related with the process that the subtropical high moves eastward and northward forced by

594 Typhoon Utor (Fig. 5d). By quantifying the relative importance of each process to O_3 formation,

595 the IPR analysis provides a fundamental explanation for the synthetical influence of the high

596 pressure and the typhoon system, which has been discussed in Sect. 3.2 and 4.1, and further

597 illustrates the exact mechanism.

598   Fig. 9b presents the result of IPR analysis for Hangzhou. During August 4-15, VDIF and

599 CHEM are the major source of surface O_3 with the average contribution of 5.36 ppb/h for VDIF

600 and 10.97 ppb/h for CHEM, while TADV and DDEP are two important sinks for O_3 with the

601 average contribution of -9.63 ppb/h for TADV and -5.14 ppb/h for DDEP. Synthetically impacted

602 by Western Pacific subtropical high and Typhoon Utor, the mean contributions during the O_3

603 episode (from August 7 to August 12) for VDIF, CHEM, TADV and DDEP increase to 7.21, 12.61,

604 -11.51 and -5.92 ppb/h, respectively. The highest VDIF contribution occurs on August 10-11, and

605 the over-standard of O_3 concentration appears on August 10-12 as well, which may be attributed to

606 the effect of typhoon's peripheral circulation, implying Typhoon Utor also plays an essential role

607 in the formation of O_3 pollution in Hangzhou. After Typhoon Utor approaches close enough to

608 Hangzhou, the wind direction is mainly dominated by the southeast wind (Fig. 4b), and the mean

609 values of VDIF, CHEM, TADV and DDEP finally decrease to 4.84, 10.08, -8.92 and -4.78 ppb/h,

610 respectively. In a word, Hangzhou is located close to Shanghai, so the temporal variations of VDIF,

611 CHEM, TADV and DDEP in Hangzhou are similar to those in Shanghai.

612   However, the similar variation pattern of VDIF, CHEM, TADV and DDEP occurring in

613 Shanghai and Hangzhou does not appear in Nanjing. As shown in Fig. 9c, the mean contributions

614 of VDIF, CHEM, TADV and DDEP to surface O_3 in Nanjing are 11.31, 9.55 -1.34 and -17.57

615 ppb/h during the whole period, while the values during 7-12 August are 10.32, 10.70, -0.99 and

616 -18.42 ppb/h. There are no apparent fluctuations or sudden increases of these contributors during

617 the period from August 4 to 15, so are the O_3 concentration (Fig. 2), temperature and relative

618   humidity (Fig. 4a), implying Nanjing is generally under the control of the Western Pacific

619   subtropical high and can hardly be affected by the typhoon system. As a typical city in the

620   northwest inland area of the YRD region (NIR), Nanjing is located far away from the sea, which

621   means it may not be easily affected by the peripheral circulation of the typhoon system.

622   Additionally, at the altitude of 500 m and 1500 m above Shanghai, Nanjing, and Hangzhou

623   (not shown), CHEM is also the major contributor to O_3 formation, with the values a litter lower

624   than those at the surface, suggesting that there are strong photochemical reactions in the whole

625   boundary layer of these YRD cities. In contrast, VDIF has an opposite effect in the middle of the

626   boundary layer, with the negative contributions for O_3 of -3.26 ppb/h in Shanghai, -2.37 ppb/h in

627   Hangzhou, and -3.21 ppb/h in Nanjing, respectively (not shown). The loss of O_3 at higher

628   atmospheric level caused by VDIF further proves the essential role of the downward vertical

629   movement in this O_3 episode.

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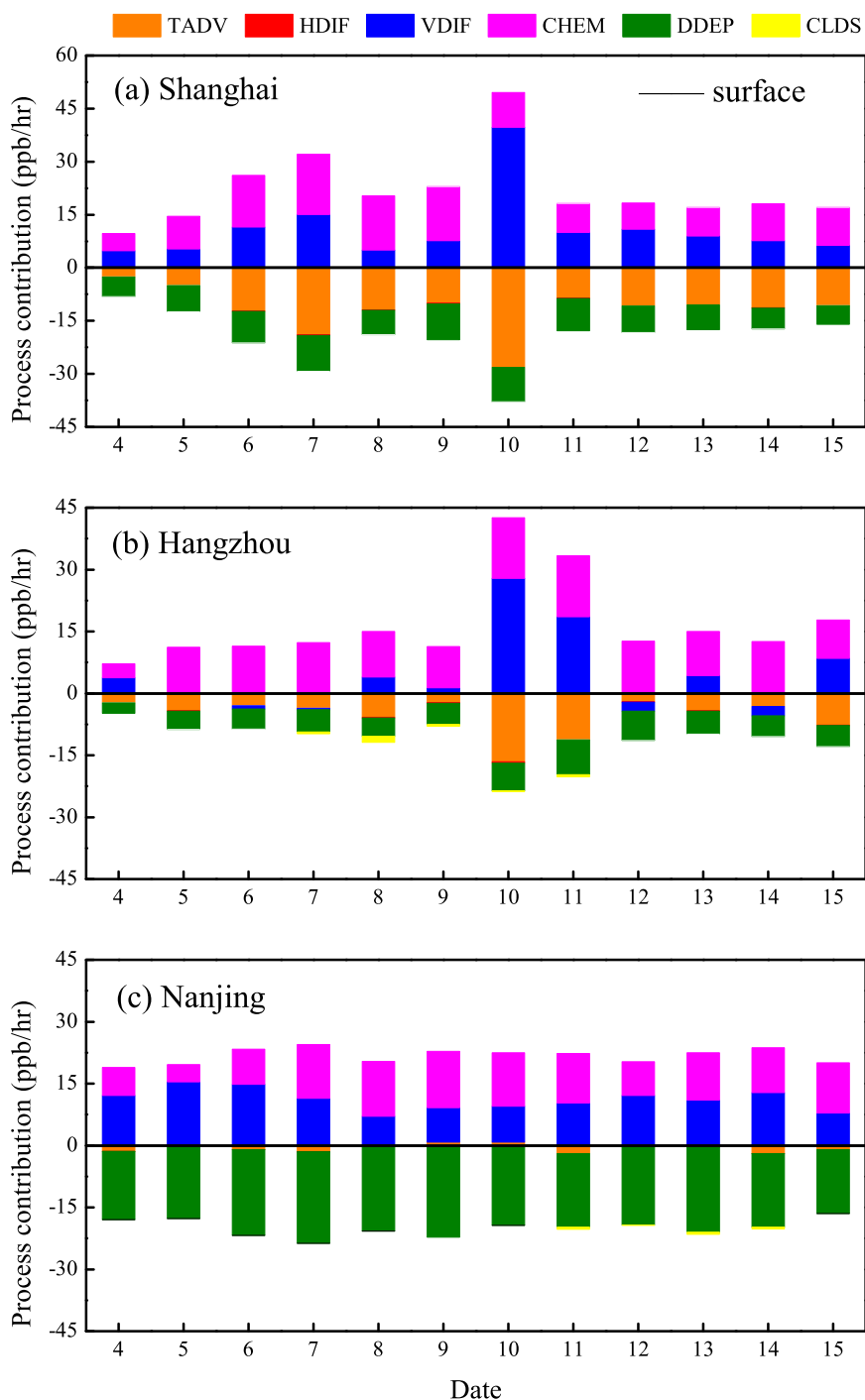
Fig. 9. Variations of the daytime mean values for the contributions of individual processes to O₃ formation in
(a) Shanghai, (b) Hangzhou, and (c) Nanjing from August 4 to 15 2013 at the surface layer. The contributors
include the total advection (TADV), the horizontal diffusion (HDIF), the vertical diffusion (VDIF), the
gas-phase chemistry (CHEM), the dry deposition (DDEP), and the cloud processes with the aqueous
chemistry (CLDS).

4.3.2 Spatial distribution of the contributors for the O₃ episode over the YRD region

    Fig. 10 demonstrates the spatial distribution of the daytime mean contributions of main

640   processes (VDIF, CHEM, DDEP and TADV) to the ozone formation at the lowest modeling layer

641   in domain 3 during this high-level O_3 episode. The modeling results from 7 to 12 August are

642   averaged to provide the mean values.

643   Similar to the results shown in Fig. 9, Fig. 10 illustrates that the vertical diffusion (VDIF) and

644   the gas-phase chemistry (CHEM) exhibit significant positive contributions to O_3 over the YRD

645   region and the surrounding areas during the high-level O_3 episode. The contributions of VDIF in

646   domain 3 (Fig. 10a) range from 5 to 25 ppb/h, with the high values (> 20 ppb/h) occurring in the

647   southeast coastal areas. For CHEM (Fig. 10b), the contributions vary within the range of 0-15

648   ppb/h, with the high values over 10 ppb/h appearing in and around the big cities. As discussed

649   above, these regional positive contributions of VDIF and CHEM over domain 3 should be related

650   to the facts that the whole region is under the control of the Western Pacific subtropical high. With

651   respect to the higher contributions of CHEM in the urban areas, they should be attributed to the

652   spatial distribution of the emissions of O_3 precursors, which is also higher in the cities.

653   Furthermore, higher air temperature in the cities related with the urban heat island may enhance

654   the chemical reactions and form more O_3 in these areas as well.

655   For DDEP, it is the main critical factor of the consumption of O_3, with the negative

656   contributions varying from 0 to -25 ppb/h over the modeling domain 3 (Fig. 10c). Small values

657   usually occur on the water, which may be related with less air pollution over rivers, lakes and

658   oceans. High values can be found on land, especially in the southeast coastal areas. For the

659   contributions of TADV, the values in domain 3 range from -10 to 10 ppb/h, with the positive

660   contributions generally occurring on land while the negative ones appearing on the water (Fig.

661   10d). The maximum positive contributions of TADV are usually found along the boundary

662   between the land and the water, which should be explained by the facts that the land-sea breeze

663   circulations can play an important role in the redistribution of the formed O_3. On account of the

664   high-pressure system and so-caused sinking airflows in the YRD region, the background wind is

665   relatively weak in comparison to the local atmospheric circulation, thus the sea breeze can easily

666   bring more generated O_3 to the seashore.

667
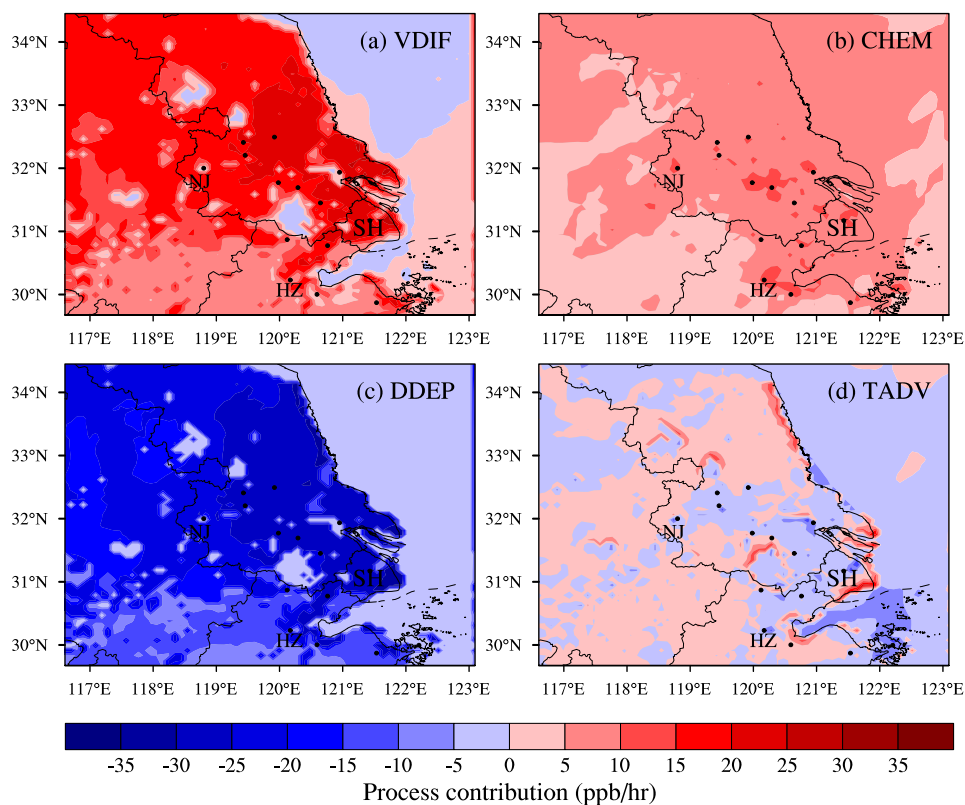
Fig. 10. The daytime mean contributions of main processes to O_3 formation over the YRD region, including (a) vertical diffusion (VDIF), (b) gas chemistry (CHEM), (c) dry deposition (DDEP), and (d) total advection (TADV). The values are averaged from August 7 to 12 2013.

From the discussion in Section 3 and 4.2, it can be deduced that typhoon Utor plays an important role in the formation of ozone over the YRD region during August 10-12. To clearly clarify the effect of the typhoon system in this O_3 pollution episode, we firstly average the modeling results of VDIF, CHEM, DDEP and TADV during August 10-12 to show their contributions to O_3 formation when the typhoon system plays an important role. Secondly, the modeling results of these processes from August 7 to 9 are also averaged to provide their contributions when only the subtropical high dominates the episode. Finally, the differences of the contributions of VDIF, CHEM, DDEP and TADV between the period of August 7-9 and August 10-12 are calculated to reveal the role of the typhoon system in this severe high O_3 episode (Fig. 11). As shown in Fig. 11a, when YRD is affected by the peripheral circulation of Typhoon Utor, the contributions of VDIF over the YRD region increase by 0-15 ppb/h, with the higher increment values (> 30 ppb/h) occurring in the southeast coastal region (SCR) and center inland region (CIR),

686 implying that SCR and CIR can be largely affected by the peripheral subsidence airflows of the

687 typhoon system. As to the contributions of CHEM, the increases caused by the typhoon system are

688 0-5 ppb/h over the YRD region, and the higher increment also appears in the coastal areas (Fig.

689 11b). For DDEP, influenced by typhoon Utor, its negative contributions decrease by up to -20

690 ppb/h, with the largest reduction along the coastline (Fig. 11c). For TADV, with the approaching of

691 typhoon Utor, the contributions of TADV particularly decrease by 0-20 ppb/h, especially in the

692 southeast coastal region (Fig. 11d).

693   In all, during this high-level O_3 pollution episode, more active photochemical reactions and

694 the vertical diffusion play a significant role in the accumulation of surface O_3 over the YRD region.

695 The major driving factor should be the Western Pacific subtropical high. Moreover, the changes in

696 the contributions of VDIF, CHEM, DDEP, and TADV between August 7-9 and August 10-12

697 exhibit a similar spatial pattern with the high values mostly concentrating in the southeast coastal

698 areas (Fig. 12), implying the Typhoon Utor also plays a collaborative effect.

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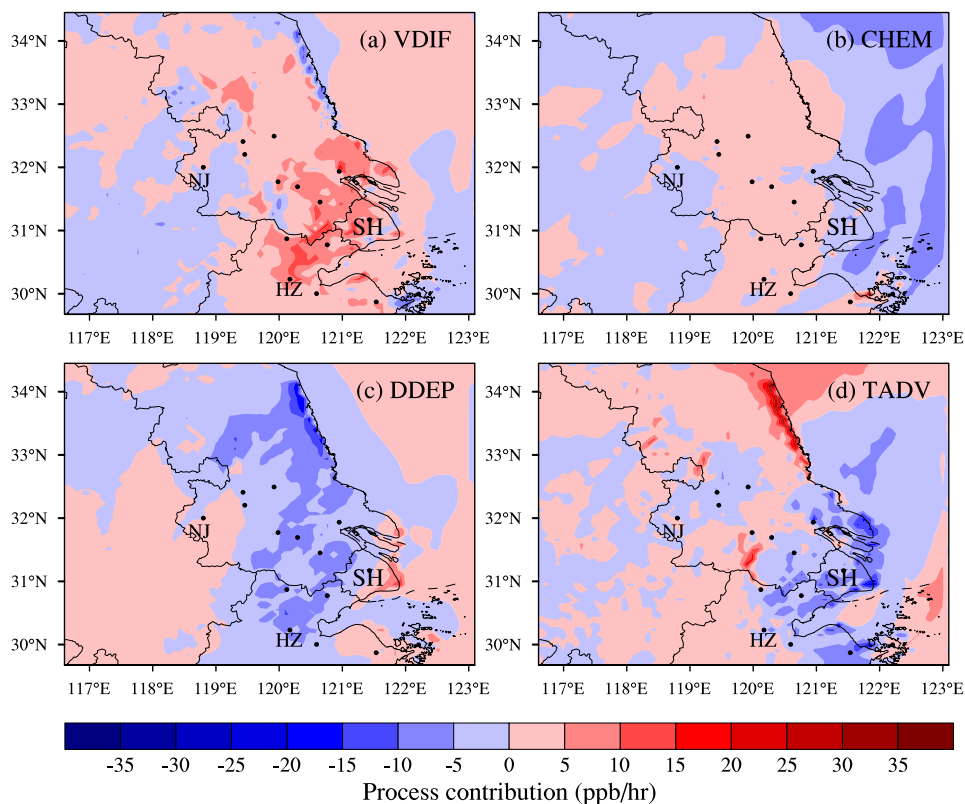
701 **Fig. 11. The difference of daytime mean contributions of main processes to O_3 formation over the YRD**

702 **region between the period of August 10-12 and August 7-9, including (a) vertical diffusion (VDIF), (b) gas**

703 **chemistry (CHEM), (c) dry deposition (DDEP), and (d) total advection (TADV) .**

704

5. Conclusions

In this study, the characteristics and the essential impact factors of a typical regional continuous O_3 pollution over the YRD region are investigated by means of observational analysis and numerical simulation. The episode lasted for nearly a week from August 7 to 12 2013, with the O_3 concentration exceeding the national air quality standard in more than half of the cities over the YRD region. The analysis of weather systems and the modeling results from WRF/CMAQ all illustrate that the continuous strong Western Pacific subtropical high is the leading factor of the abnormally high temperature weather and the heavy O_3 pollution, by inducing more sinking air to trap heat as well as air pollutants at the surface. Meanwhile, the development of this episode is closely related to the movement of Typhoon Utor as well. The temporal variations of the vertical wind velocity and O_3 concentrations show that when the YRD region is at the front of moving typhoon system, the downward airflow is enhanced in the boundary layer with fine weather, and thereby the air pollutants are trapped and accumulated near the surface. Moreover, in the last stage of the O_3 episode, the activity of Typhoon Utor weakens the strength of the subtropical high and forces it to retreat easterly and move northward, and the prevailing southeasterly surface wind related with the approaching of Typhoon Utor contributes to the mitigation of the O_3 pollution.

The Integrated Process Rate (IPR) analysis implemented in CMAQ is specially carried out to quantify the relative contributions of individual processes and give a fundamental explanation. During the high-level O_3 episode from August 7-12, the vertical diffusion (VDIF) and the gas-phase chemistry (CHEM) exhibit significant positive contributions to surface O_3 over the YRD region, with the high values over 20 ppb/h for VDIF and over 10 ppb/h for CHEM. The dry deposition (DDEP) is the major sink of surface O_3, while the total advection (TADV) can give the positive contribution on land and the negative contribution on the water. Moreover, on August 10-12, the YRD region is apparently affected by the periphery circulation of Typhoon Utor, with the contributions of VDIF over the YRD region increasing by 0-15 ppb/h, the contributions of CHEM increasing by 0-5 ppb/h, and the contributions of DDEP and TADV decreasing. Especially in the coastal cities, such as Shanghai and Hangzhou, the effects of the typhoon system are more obvious. In contrast, the cities in the northwest inland area of the YRD region, which are far away from the sea, can hardly be affected by the typhoon system. In the end, when the typhoon system

734 significantly weakens the high pressure system, the contributions of VDIF, CHEM, TADV, and

735 DDEP decrease to a low level in all cities.

736   The WRF/CMAQ modeling system shows a relatively good performance in simulation of the

737 O_3 episode, with the simulated meteorological conditions and air pollutant concentrations

738 basically in agreement with the observations in most YRD cities. Our results in this study can

739 provide an insight for the formation mechanism of regional O_3 pollution in East Asia, and help to

740 forecast the O_3 pollution synthetically impacted by the Western Pacific subtropical high and the

741 tropical cyclone system.

742

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947