1 **A measurement and model study on ozone characteristics in marine air at a remote**

2 **island station and its interaction with urban ozone air quality in Shanghai, China**

3 Yixuan Gu[a,b], Fengxia Yan[c], Jianming Xu[a,b,*], Yuanhao Qu[a,b], Wei Gao[a,b]

4 [a]Shanghai Typhoon Institute, Shanghai Meteorological Service, Shanghai 200030, China

5 [b]Shanghai Key Laboratory of Meteorology and Health, Shanghai Meteorological Service,

6 Shanghai 200030, China

7 [c]Meteorological Center of Traffic Management of East China, Shanghai 2000135, China

8 Corresponding to: Dr. Jianming Xu (metxujm@163.com)

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Abstract

To understand the characteristics and changes of baseline ozone (O_3) in oceanic air in East China, a six-year measurement of O_3 concentration was conducted from January 1 2012 to September 15 2017 at a remote offshore station located on the Sheshan Island (SSI) near the megacity of Shanghai. The observed monthly mean O_3 concentrations at SSI ranged from 33.4 to 61.4 ppbv during the study period, which were about 80% and 12% higher, respectively than those measured at downtown and rural sites in Shanghai. Compared to the remarkable O_3 increases observed at urban and rural sites in Shanghai, observed O_3 concentrations at SSI exhibited statistically insignificant increasing changes (1.12 ppbv yr^{-1}, $\alpha > 0.10$) during the observation period, suggesting less impacts of anthropogenic emissions on O_3 levels in oceanic air. In addition, an insignificant decreasing change (-0.72 ppbv yr^{-1}, $\alpha > 0.10$) was detected in O_3 concentrations at SSI in September and October when the influence of regional transport was minimum throughout the year, providing a good proxy to study the baseline oxidation capacity of the oceanic atmosphere. City plumes from Shanghai usually carried higher levels of NO_x, resulting in decreased O_3 concentrations at SSI during southwesterly and westerly winds. However, In MAM (March–May) and JJA (June–August), due to the enhanced production of oxygenated volatile organic compounds, O_3 could be continuously produced during daytime in aged city plumes, resulting in elevated O_3 concentrations transported to SSI. The impacts of the offshore O_3 on O_3 levels in Shanghai are quantified during an easterly wind dominant episode (September 1–30, 2014) using the WRF-Chem model. Sensitivity results suggest that O_3 in the oceanic air inflows can lead to 20–30% increases in urban

33 O_3 concentrations, which should be crucially considered in dealing with urban O_3 pollution

34 in large coastal cities like Shanghai.

35 1 Introduction

36 Ground-level ozone (O_3) is a harmful photochemical oxidant detrimental to air quality,

37 human health and land ecosystems (Yue and Unger 2014; Monks et al., 2015; Li et al.,

38 2019a). High ambient O_3 has been proved to increase the risks of respiratory and

39 cardiovascular mortality (Goodman et al., 2015) and enhance the greenhouse effect

40 (IPCC, 2013). In recent years, O_3 pollution has drawn increasing attention in China, since

41 O_3 pollution is getting worse in spite of the implementation of Chinese Clean Air Action

42 Plan. In contrast to the 28-40% decreases in $PM_{2.5}$ (fine particulate matter; diameter ≤ 2.5

43 μm) levels, the observed daily maximum 8-h average (MDA8) O_3 concentrations show

44 increasing rates of 1–3 ppb yr^{-1} in summer in megacities over eastern China during 2013–

45 2017 (Li et al., 2019b). To address the underlying causes of the increasing O_3 pollution

46 has become an urgent issue that triggers lots of discussions based on observational and

47 model studies worldwide (Yang et al., 2014; Lou et al., 2015; Fu et al., 2019).

48 Observational and model studies indicated that the elevated O_3 levels in urban and

49 rural areas in eastern China were strongly related to the changes in anthropogenic

50 emissions of O_3 precursors (Ma et al., 2016; Lu et al., 2018; Li et al., 2019b; Gu et al.,

51 2020). Since the O_3 formation was reported to be under volatile organic compound (VOC)

52 limited regime in most Chinese megacities (e.g. Beijing, Shanghai, and Guangzhou), the

53 sharp decreases in nitrogen oxides ($NO_x=NO+NO_2$) emissions combined with slight

54 increases in VOC levels were suggested to be main causes of the observed enhancement

55 of O_3 concentrations in East China (Gao et al., 2017; Xu et al., 2019). In remote areas,

56 changes of baseline O_3 also exhibit sensitive responses to human activities (Vingarzan,

57 2004; Meng et al., 2009; Wang et al., 2009; Lin et al., 2015). Based on 14-year

58 observations at a coastal site in Hong Kong, Wang et al. (2009) pointed out that enhanced

59 pollution flow from the upwind coastal regions contributed to most of the observed O_3

60 increases in the background atmosphere of South China during 1994–2007. And the

61 increase in background O_3, in turn, made a strong contribution of 81% to the increasing

62 rate of O_3 in urban Hong Kong. It is thus necessary to understand the background O_3

63 changes and their responses to different sources when developing long-term strategies to

64 mitigate local O_3 pollution. However, compared to the intensive field studies in polluted

65 cities and surrounding rural regions, continuous observations of O_3 at representative

66 background sites in China are relatively limited (Wang et al., 2017).

67   To better understand the characteristics of the background O_3 changes in mainland

68 China, the China Meteorological Administration (CMA) started to conduct continuous

69 measurements of surface O_3 at several regional background stations (e.g. Shangdianzi,

70 Linan, and Longfengshan) since 2005. Over 10-year records from those sites and

71 Waliguan, a baseline Global Atmospheric Watch (GAW) station in Tibetan Plateau region,

72 exhibited different increases in background continental O_3 concentrations especially

73 during daytime in China (Lin et al., 2008; Xu et al., 2008; Meng et al., 2009; Ma et al.,

74 2016; Xu et al., 2016). The detected positive trends of O_3 were in a range of 0.24–1.13

75 ppbv yr^{-1}, suggesting enhanced atmospheric oxidation capacity of continental air

76 responding to the rapid development of urbanization and industrialization in the past

77 decades. In addition to the changes at background O_3 in terrestrial stations mentioned

78 above, the characteristics of baseline O_3 at remote marine sites are also important. It is

79   because that large amounts of O_3 pollution events occurred in coastal urban

80   agglomerations in East China (Lu et al., 2018; Li et al., 2019a, b), affected by both city

81   plumes and oceanic air inflows (Tie et al., 2009; Shan et al., 2016). For example, model

82   work of Tie et al. (2009) suggested that sea air masses carried by oceanic inshore air

83   flows aggravated urban O_3 pollution in Shanghai under convergence conditions.

84   Understanding the O_3 characteristics in offshore oceanic regions is therefore an important

85   prerequisite for understanding the land-sea O_3 interactions and its impacts on O_3 pollution

86   in coastal cities. However, to our knowledge, studies on the characteristics and changes

87   of O_3 in marine air are quite limited in mainland China since it is very difficult to conduct

88   systematic and continuous observations under remote oceanic air conditions.

89   In this report, we present the first relatively long and continuous measurements of O_3

90   conducted on a remote offshore island (Sheshan Island, SSI) from January 2012 to

91   September 2017 in eastern China. The SSI is located at the confluence of the Yellow Sea

92   and the East China Sea, covering an area of about 0.4 km^2. Since there are no inhabitants

93   in the island, the observed O_3 is seldom affected by local anthropogenic emissions. The

94   collected O_3 data are used to understand the levels and variabilities of O_3 in the offshore

95   regions and their impacts on the O_3 concentrations in coastal city areas. First shown are

96   the general impacts of regional transport on the remote atmosphere over the SSI region.

97   Then the diurnal patterns of O_3 at SSI are investigated by comparing them with those

98   observed at a downtown site (XJH) in Shanghai. Multi-year changes of O_3 concentrations

99   at SSI are analyzed to examine the overall changes of baseline O_3 in marine air and

100   possible causes. Also analyzed are the impacts of urban plumes on O_3 levels in oceanic

101 air in offshore regions. At last, the influence of O_3 carried by oceanic air inflows on urban

102 O_3 air quality in Shanghai is assessed using the Weather Research and Forecasting

103 model coupled with Chemistry (WRF-Chem).

104 2 Material and methods

105 2.1 The SSI site and ozone observations

106 To investigate the characteristics and variabilities of O_3 in marine air and their interactions

107 with urban air quality in coastal areas, ground O_3 concentrations were continuously

108 measured at SSI site (31.4°N, 122.3°E, 73.5 m a.s.l.), which is approximately 75

109 kilometers away from the east edge of Shanghai city. Figure 1 shows the location of SSI

110 and the surrounding environment. As mentioned in Sect. 1, there is no resident and tourist

111 on the island. The observed O_3 at SSI site can represent the background O_3 conditions in

112 oceanic air which are seldom contaminated by anthropogenic emissions. Hourly O_3 data

113 was collected during January 1 2012 to September 15 2017, with a capture rate of 89.7%.

114 O_3 was measured using an analyzer from Ecotech, Australia (Model EC9810), which

115 combined microprocessor control with ultraviolet photometry. The instrument met the

116 technical specifications for United States Environmental Protection Agency, with a quality

117 control check every 3 days, filer replaced every 2 weeks and calibration every month.

118 2.2 Observational data at urban and rural sites in Shanghai

119 To better understand the characteristics of the offshore O_3 in oceanic air at SSI, O_3

120 observations obtained from a downtown site, Xujiahui (XJH) are used for comparisons.

121 The XJH site is located at downtown Shanghai, approximately 80 km west from the SSI.

122 Since measurements of NO_x, carbon monoxide (CO) and meteorological parameters (e.g.

123 wind direction and wind speed) were unavailable at SSI, observations obtained at an

124 adjacent site, Dongtan (DT), are substituted for the investigation. The DT site was set up

125 in a national nature reserve near the coast of Shanghai, where the observed pollutant

126 levels have been reported to well reflect the impacts of megacities in the Yangtze River

127 Delta (YRD) region on the remote atmosphere during the MIRAGE-Shanghai (Megacities

128 Impact on Regional and Global Environment at Shanghai) field campaign (Tie et al., 2013).

129 Similar to SSI, the DT site is also little affected by human activities. The obtained

130 observations of meteorology and pollutants are therefore applied for analyzing the

131 impacts of regional transport on observed O_3 concentrations at SSI. NO_x concentrations

132 were measured with a chemiluminescent trace level analyzer (TEI; Model 42iTL), with

133 detection limit of 0.025 ppb. CO concentrations were measured by the Model 48iTL

134 Enhanced CO analyzer, based on gas filter correlation technology. The wind speed and

135 wind direction were measured by using a DZZ4 Automatic Weather Station certificated by

136 the China Meteorological Administration. The geographical locations and surrounding

137 environment of XJH, DT, and SSI are displayed in Fig. 1.

138 2.3 The WRF-Chem model

139 We simulate O_3 using the regional chemical transport model WRF-Chem (version 3.8,

140 https://www2.acom.ucar.edu/wrf-chem), collaboratively developed through efforts of

141 several institutes, such as the National Center for Atmospheric Research (NCAR) and the

142 National Oceanic and Atmospheric Administration (the National Centers for Environmental

143 Prediction (NCEP). The model includes on-line calculation of meteorological parameters,

144 transport, mixing, emission, and chemical transformation of trace gases and aerosols

145 (Grell et al., 2005). The Regional Acid Deposition Model version 2 (RADM2, Stockwell et

146 al., 1990) gas-phase chemical mechanism is used for the O_3 formation chemistry.

147 Photolysis rates are calculated by using the fast radiation transfer module (FTUV)

148 followed those in Madronich and Flocke (1999) and Tie et al. (2003). ISORROPIA II

149 secondary inorganic (Fountoukis and Nenes, 2007) and the Secondary ORGanic Aerosol

150 Model (SORGAM) (Schell et al., 2001) schemes are used for aerosol chemistry. Dry

151 deposition follows the standard resistance-in-series model of Wesely (1989). The major

152 physical processes employed in the model follow the Lin microphysics scheme (Lin et al.,

153 1983), the Yonsei University (YSU) planetary boundary layer (PBL) scheme (Hong and

154 Lim, 2006), the Noah Land surface model (Chen and Dudhia, 2001), and the long-wave

155 radiation parameterization (Dudhia, 1989).

156 The model used in this study has a horizontal resolution of 6km×6km, including 150

157 un-staggered grids in west-east, 150 un-staggered grids in south-north, and 35 vertical

158 layers extending from the surface to 50 hPa. The domain encompasses Shanghai and its

159 surrounding region, centered at 31.3°N, 121.4°E. The NCEP FNL (Final) Operational

160 Global Analysis data are used for meteorological initial and boundary conditions, with

161 lateral meteorological boundary updated every 6 h. Basic chemical lateral boundary

162 conditions are constrained by a global chemical transport model (MOZART-4, Model for

163 OZone And Related chemical Tracers, version 4) (Tie et al., 2001; Emmons et al., 2010).

164 Anthropogenic emissions are derived from the Multi-resolution Emission Inventory for

165 China (MEIC inventory, http://www.meicmodel.org/; Li et al., 2014) for year 2010. Biogenic

166 emissions are calculated online using model of emissions of gases and aerosols from

167 nature (MEGAN2, Guenther et al., 2006).

168 2.4 Methods for assessing the trend of ozone

169 The daily mean O_3 concentrations are used to examine the overall changes in O_3

170 concentrations during the period 2012–2017, including all time of day with qualified

171 measurements. The trends are assessed using two nonparametric methods, which are

172 commonly used to detect trends of non-normally distributed data with seasonality (Xu et

173 al., 2016).The Mann-Kendall (MK) trend test (Mann, 1945; Kendall, 1975; Gilbert, 1987) is

174 used to examine the trend significance, and the Theil-Sen trend estimate method (Sen,

175 1968) is used to estimate the slope of trend, which could also be considered as the rate of

176 change, during the six-year period. Compared to the linear fitting analysis which requires

177 data to be independent and follow a Gaussian distribution, the non-parametric trend test

178 methods only need the data to be independent (Gocic and Trajkovic, 2013). To determine

179 if the calculated rate of change is statistically significant, the confidence level of at least 95%

180 is adopted in the MK trend test, with α value less than 0.05 being considered a statistically

181 significant trend. The trend significance is examined by comparing the value of a

182 standardized test statistic Z to that of a standard normal variate at a given significance

183 level (Z_α, α=0.05). If $|Z| > Z_{1-\alpha/2}$, then the dataset is non-stationary, exhibiting either an

184 increasing or a declining trend; If $|Z| \le Z_{1-\alpha/2}$, then the dataset is stationary with no

185 significant trend. Detailed calculation of Z can be referred to Xu et al. (2016).

186 3 Results and discussion

187 3.1 Regional transport characteristics at SSI

188 The observed O_3 concentrations at SSI were inevitably influenced by regional transport

189 depending on the prevailing winds in various seasons. Figure 2 displays the monthly wind

190 rose diagrams averaged over the period of 2012 to 2017 at DT. As mentioned in Sect. 2.2,

191 the DT site is a rural site located quite close to SSI. The observed wind speeds and wind

192 directions could then be applied to deduce the origins of the air mass arriving at SSI in

193 adjacent region. Generally, observed prevailing winds exhibited distinct seasonal

194 variabilities which were greatly affected by the East Asian monsoon. In warm seasons

195 (May-August), the site was predominately influenced by easterly and southeasterly winds,

196 accounting for 40–50% of the total winds. While in cold seasons (November-February),

197 the northwesterly and northerly winds became the predominant flows that affected SSI,

198 accounting for about 45% of total winds. During transitional months (e.g. March, April,

199 September and October), the dominant winds presented more diversities, with wind

200 directions dispersedly distributed in all the directions. The observed seasonal variations of

201 prevailing winds are typical at coastal cities at mid-latitude region (Shan et al., 2016; Xu et

202 al., 2019), suggesting that air masses arriving at SSI originated from various regions and

203 could result in different impacts on the offshore atmospheric composition in different

204 months.

205   Since CO has a relative long chemical lifetime of a few months, the observed CO

206 concentrations at DT could be regarded as a consequence of regional transport from

207 polluted regions (Tie et al., 2009). Figure 3 displays the observed monthly mean CO

208 mixing ratios under wind directions of north (N), northeast (NE), east (E), southeast (SE),

209 south (S), southwest (SW), west (W), and northwest (NW) at DT during the 2012–2017

210 period. Observed CO exhibited relative higher concentrations under SW and W winds in

211   all months, with mean mixing ratios of 0.44 and 0.56 ppmv, respectively during 2012–2017

212   (Table 1). The observed high CO mixing ratios suggested that the atmosphere

213   constituents at SSI could be more affected by regional transport of air pollutants under

214   SW and W wind conditions. As SSI is located to the northeast of the Shanghai city (Fig. 1),

215   air masses carried by the SW and W flows usually contain more urban pollutants from

216   upwind city areas, and those carried by E, SE, and NE flows mostly come from the ocean.

217   The oceanic air masses are less polluted compared to those from the cities, leading to

218   lower CO mixing ratio at SSI. For example, observed CO exhibited a mean concentration

219   of 0.23 ppmv under SE wind conditions, which was about 50% lower than that influenced

220   by W winds. To further examine the impacts of the SW and W winds on the atmosphere

221   constituents at SSI, Table 2 lists the calculated monthly mean occurrence frequency of the

222   SW and W winds in separate months during the studied period. The SW and S winds

223   were most infrequent in September (6.1 %) and October (5.2 %), suggesting that the

224   atmosphere at SSI during the two months could be less contaminated by pollutants

225   transported from the city and might be more close to the baseline oceanic air conditions.

226   3.2 The diurnal pattern of ozone at SSI

227   Figure 4 displays the monthly mean diurnal variations of O_3 at SSI and XJH in different

228   months during 2012–2017. The observed O_3 concentrations at the two sites exhibited

229   similar seasonal variations, with monthly mean values highest (61.4 ppbv for SSI and 35.9

230   ppbv for XJH) in May and lowest (33.4 ppbv for SSI and 12.5 ppbv for XJH) in December.

231   Since the O_3 formation in urban Shanghai is VOC-limited, observed O_3 could be

232   significantly depressed by large NO_x emissions at downtown site (XJH) (Gu et al., 2020).

233 In Fig. 4, observed O_3 levels at XJH were quite lower than those at SSI in all months, with

234 mean concentrations of 27.8 and 50.1 ppbv, respectively at XJH and SSI during the

235 observation period. The observed mean daily maximum 8-h average (MAD8) O_3

236 concentrations exhibited same differences between the two sites, which were 40.1 and

237 62.0 ppbv, respectively at XJH and SSI. The observed mean O_3 concentration at SSI was

238 also higher than that at DT (44.7 ppbv, Fig. S1) which is more close to the city, suggesting

239 that O_3 levels in marine air could be higher than those at continental urban and rural sites.

240 The observed diurnal patterns of O_3 at SSI and XJH in Fig. 4 were similar to those

241 reported for other sites in eastern China (Xu et al., 2008; Geng et al., 2015; Gao et al.,

242 2017), exhibiting minimums in early morning (06:00–08:00 LST) and maximums in the

243 afternoon (13:00–15:00 LST). However, compared to those at the urban site (XJH),

244 observed amplitudes of O_3 diurnal variations were much smaller at SSI. The diurnal

245 variations of surface O_3 can be mainly attributed to the O_3 production through

246 photochemical reactions in the daytime and O_3 depression via NO titration at nighttime

247 (Sillman, 2003). Due to few emissions of O_3 precursors (NO_x and VOCs), the O_3

248 production and depression could be weaker at remote site, resulting in flatter diurnal cycle

249 of O_3 compared to that at polluted urban site.

250 Since the amplitudes of O_3 diurnal variations usually exhibited much smaller values in

251 background areas compared to those in polluted urban regions, the ratio of daily

252 maximum O_3 concentration ($O_{3\text{-max}}$) to minimum O_3 concentration ($O_{3\text{-min}}$) was regarded as

253 an indicator to identify if the local O_3 pollution was significantly influenced by

254 anthropogenic emissions (Cvitas and Klasinc 1993; Vingarzan, 2004). The $O_{3\text{-max}}/O_{3\text{-min}}$

255   ratio displayed larger values in polluted regions (Cvitas et al., 1995) and lower values in

256   less contaminated rural regions. A ratio of about 1.4 suggested that the site could be

257   regarded as a typical background site (Scheel et al., 1997). For regional background sites

258   in China, the typical values of O_{3-max}/O_{3-min} were usually in the range of 2–3 (Xu et al.,

259   2008; Meng et al., 2009; Gu et al., 2020). In Lin'an, a continental background site in YRD

260   region, the ratio was reported to increase as a result of NO_x emission changes during past

261   decades, which could reach above 6 during summertime (Xu et al., 2008). In Fig. 4,

262   observed O_3 displayed different diurnal variabilities in various months at SSI. The

263   variations of the O_{3-max}/O_{3-min} ratio suggested different influence of regional transport on

264   O_3 levels in the marine atmosphere.

265   Figure 5 displays the calculated monthly mean O_{3-max}/O_{3-min} ratios at SSI and XJH,

266   respectively during 2012–2017. Generally, the observed ratios of O_{3-max}/O_{3-min} at SSI were

267   much lower than those at XJH in all the months, suggesting less impact of anthropogenic

268   emissions on O_3 levels. The calculated mean ratios were 3.03 and 5.20, respectively at

269   SSI and XJH, and most of the calculated values were larger than 4.50 at the urban site.

270   Besides, the ratios presented distinct seasonal differences at XJH and SSI sites. Higher

271   values were observed in summer, indicating stronger photochemical production of

272   daytime O_3 during June to August. At SSI, the O_{3-max}/O_{3-min} ratio exhibited relatively low

273   values in September and October, ranging from 1.61–2.35 during the studied period. The

274   values were consistent with the typical values of O_{3-max}/O_{3-min} observed at continental

275   background sites in China (Xu et al., 2008; Meng et al., 2009; Gu et al., 2020). Since the

276   observed temperature and solar radiation still exhibited higher values during the two

277   months in Shanghai (Gao et al., 2017), the observed low O_3 diurnal amplitudes should not

278   be attributed to the weakened photochemical formation of O_3 as those in winter. Due to

279   the persistent control of anticyclone, Shanghai and its neighboring areas are usually

280   dominated by stable weather conditions in September and October, resulting in more

281   gentle and diversified wind conditions. During the two months, the occurrences of more

282   polluted SW and W winds were lowest (6.1% and 5.2%) throughout the year. The

283   corresponding wind speed (2.49 and 2.50 m s^{-1}) also exhibited values 20% lower those in

284   other months (Table 2). The transport conditions led to fewer pollutants transported to the

285   SSI region, which could explain the observed weak diurnal variabilities of O_3 in September

286   and October. The transport conditions together with O_3 response further confirmed that

287   the transport of city pollutants had minimum impacts on the offshore O_3 levels in oceanic

288   air at SSI in September and October, providing a good proxy to study the baseline oceanic

289   O_3 and oxidation capacity of background atmosphere in eastern China.

290   3.3 Overall changes of ozone in oceanic air at SSI

291   Several studies have observed increasing trends of ground-level O_3 in metropolitan areas

292   over eastern China since 2013, suggesting that the O_3 increases were mostly attributed to

293   the NO_x emission reductions (Ma et al., 2016; Gao et al., 2017; Lu et al., 2018; Li et al.,

294   2019b). However, the O_3 changes at remote sites were relatively not well elucidated

295   during past years. Figure 6a presents the monthly variations of O_3 concentrations at SSI

296   and XJH during the 2012–2017 period. The statistical results of the MK test and Theil–

297   Sen trend estimate method indicated that observed monthly mean O_3 mixing ratios ($O_{3\text{-ave}}$)

298   exhibited increasing changes at both urban (XJH) and remote sites (SSI) in Shanghai,

299 with calculated increasing rate of 1.97 and 1.12 ppbv yr^{-1}, respectively in XJH and SSI.

300 Though an overall upward trend of O_3 was detected at SSI, the changes were not as

301 remarkable as those observed at XJH, which could not even pass the MK trend test at the

302 90% confidence level. The monthly mean MDA8 and daily extreme values of O_3 exhibited

303 similar differences between the two sites. The calculated increasing rates of MDA8 O_3,

304 O_{3-max} and O_{3-min} were 2.73, 2.77, and 1.35 ppbv yr^{-1} ($\alpha<0.05$), respectively at XJH, and

305 1.01, 1.35, and 1.27 ppbv yr^{-1} ($\alpha>0.10$), respectively at SSI. Compared to the rapid O_3

306 increases in urban Shanghai which was suggested to mostly result from the significant

307 NO_x emission reductions in the past decade (Gao et al., 2017; Xu et al., 2019), the

308 statistically insignificant changes of O_3 detected at SSI indicated that O_3 in the oceanic air

309 remained a relative constant level during the study period and was less influenced by the

310 decreases of NO_x emissions.

311 As discussed in Sect. 3.1, the prevailing winds carried different levels of pollutants to

312 the SSI, resulting in different impacts on the O_3 levels in different months. In September

313 and October, the frequencies of SW and W winds that carried high levels of pollutants

314 were lowest (Table 1–2), exerting least influence on the atmospheric composition at SSI.

315 Therefore, the variations of surface O_3 concentrations in September and October at SSI

316 were examined to further assess the changes of least contaminated O_3 in the oceanic air.

317 Figure 6b presents the overall changes of daily mean surface O_3 concentrations in

318 September and October at SSI and XJH, respectively during the six-year period. The

319 corresponding mean O_3 mixing ratios during the two months were 60.9 and 31.3 ppbv,

320 respectively at SSI and XJH. Compared to the significant elevated O_3 concentrations at

321 XJH (0.59 ppbv yr^{-1}, $\alpha<0.10$) in September and October, observed O_3 at SSI during same

322 months exhibited insignificant decreasing changes from 2017–2017. The changes (-0.72

323 ppbv yr^{-1}, $\alpha>0.10$) were somewhat different from the overall O_3 changes (+1.12 ppbv yr^{-1},

324 $\alpha>0.10$) at SSI, suggesting different causes of the observed O_3 changes in the oceanic air

325 during September and October.

326   To investigate possible drivers of the observed changes in the least contaminated O_3

327 in September and October at SSI, Table 3 displays the statistical results of the MK test

328 and Theil-Sen trend estimate for NO_x and CO mixing ratios, temperature, and wind speed

329 during the 2012–2017 period. Statistically significant upward trends were detected in wind

330 speed, with estimated increasing rates of 0.21 m s^{-1} yr^{-1} during the observation period

331 ($\alpha<0.05$). The significantly enhanced surface wind speeds were conducive to the diffusion

332 of O_3, which might be an important meteorological driver of the observed decreasing

333 changes in O_3 levels at SSI from 2012 to 2017. Observed NO_x and CO levels exhibited

334 increases of 0.48 ppbv yr^{-1} ($\alpha<0.05$) and 2.67 ppbv yr^{-1} ($\alpha>0.10$), respectively in

335 September and October during the six-year period, indicating enhanced transport of

336 pollutants to the oceanic area. Tie et al. (2013) suggested that the VOC-limited regime of

337 O_3 formation was not only confined in urban Shanghai, but also extended to a broader

338 regional area surrounding Shanghai. Thus, the elevated NO_x concentrations might not

339 only retard daytime O_3 production but also enhance nighttime O_3 depression at SSI.

340 Figure 6c further presents corresponding variations of daytime (10:00-16:00 LST) and

341 nighttime (23:00-04:00 LST) mean O_3 concentrations at SSI. Both daytime and nighttime

342 O_3 concentrations exhibited downward changes, reflecting the O_3 response to the

343   enhanced O_3 diffusion and depression in September and October. Therefore, the

344   enhanced diffusion and depression of O_3 induced by the elevated wind speed and NO_x

345   concentrations might be important causes of the observed O_3 changes in September and

346   October at SSI. It should be noted that the influence of radiation cannot be analyzed since

347   observations of solar radiation were not available during the study period. Therefore, more

348   measurements are still needed to further understand the O_3 changes and corresponding

349   drivers in the oceanic air.

350   3.4 Impacts of urban plumes on ozone in oceanic air at SSI

351   Due to the relatively long residence lifetime (about one month), O_3 produced at urban

352   regions could be transported several hundred kilometers away to downwind areas.

353   Meanwhile, the urban plumes become more aged with continuous production/depletion of

354   O_3 and its precursors, resulting in non-linear changes in O_3 in downwind areas (Geng et

355   al., 2011; Tie et al., 2009, 2013). Several studies suggested that there tended to be

356   considerable O_3 formations in aged urban plumes in the downwind region of Shanghai

357   (Geng et al., 2011; Tie et al., 2013). To investigate the impacts of urban plumes on the O_3

358   levels in oceanic air at SSI, the relationships between observed O_3 and NO_x under

359   different wind conditions at SSI and DT are investigated in this section.

360   Figure 7 presents the daytime and nighttime O_3/NO_x-wind relationships in MAM

361   (March–May), JJA (June–August), SON (September–November), and DJF (December–

362   February), respectively during 2012–2017. The SW and W winds were associated with

363   higher NO_x concentrations in both daytime and nighttime. The result was consistent with

364   the observed CO changes in Sect. 3.1. Since there is no local anthropogenic emission at

365   SSI, the higher levels of NO_x and CO were mainly resulted from the transport of more

366   polluted urban plumes by the SW and W winds. Generally, observed daytime O_3 and NO_x

367   concentrations presented opposite variations with the wind direction changes (Fig. 7a). In

368   SON and DJF, the correlation coefficients (Rs) between daytime O_3 and NO_x were -0.72

369   and -0.75, respectively, indicating that the O_3 formation was inhibited by increased NO_x

370   concentrations. The results are in accordance with Tie et al. (2013) and Xu et al. (2019),

371   who suggested that Shanghai and a broader regional area surrounding the city were all in

372   the VOC-limited O_3 formation regime during the study period. However, in MAM and JJA,

373   the daytime O_3-NO_x variations presented totally different patterns under SW and W wind

374   conditions. As wind directions turned from E-SE to SW-W, observed mean NO_x

375   concentrations increased from about 10 ppbv to 20 ppbv, while observed mean O_3

376   concentrations increased from 50–60 ppbv to 70–80 ppbv. The enhancements in daytime

377   O_3 levels suggested that there should be persistent production of O_3 in the polluted air

378   masses carried by the SW and W winds in MAM and JJA.

379   Based on observations and WRF-Chem simulations, Tie et al. (2013) suggested

380   considerable O_3 production in aged city plumes in the downwind area of Shanghai. Since

381   air masses affecting SSI site were directly originated from Shanghai under the SW and W

382   wind conditions (Fig. 1), the observed O_3 enhancements should be mainly attributed to the

383   O_3 production in the city plumes carried by SW and W winds. Studies during the

384   MIRAGE-Shanghai campaign suggested several factors that contributed to the O_3

385   enhancements in aged city plumes downwind Shanghai. First, as there is a large area of

386   forest located in the south of Shanghai, Geng et al. (2011) suggested that continuous

387   oxidation of isoprene emitted by the biogenic sources could result in enhanced production

388   of hydrogen radicals (HO_2) especially in warm seasons. Once the air massed were

389   transported north and mixed with high NO_x emissions, O_3 would be quickly produced.

390   However, the impacts of biogenic emissions on O_3 production were mainly limited in the

391   south part of Shanghai, which can hardly influence the atmosphere in the SSI region.

392   Then, Tie et al. (2013) further illustrated that the OH reactivity of alkane, alkene, aromatics,

393   and oxygenated VOCs (OVOCs) contributed to the O_3 formation in city plumes. Among

394   them, the influence of alkane, alkene and aromatics mostly occurred within or near the city,

395   while the OVOCs could be produced or emitted during the transport of the city plumes,

396   resulting in substantial O_3 enhancements in aged city plumes at 100–200 km downwind

397   Shanghai.

398   The SSI is located approximately 100 km northeast from the downtown area of

399   Shanghai. In MAM and JJA, the SW and W winds carried air masses with enhanced

400   OVOCs oxidation and O_3 production, resulting in elevated daytime O_3 levels on the island.

401   While in SON and DJF, the observed O_3 decreases at SSI during SW and W winds

402   suggested lower efficiency of O_3 productivity in the city plumes. That might be because

403   that fewer OVOCs were released or produced downwind the city due to the lower

404   temperature and weaker solar radiation (Cai et al., 2009). In addition, in SON and DJF, the

405   SW and W winds were usually related to low pressure system with large cloud cover and

406   rich water vapor in Shanghai, which could also lead to depressed photochemical reactions

407   and decreased O_3 levels. At night, observed O_3 and NO_x displayed totally opposite

408   changes with wind directions (Fig. 7b), indicating O_3 depression by nighttime NO_x titration

409   in all the seasons. High O_3 levels were observed under northeasterly, easterly and

410   southeasterly oceanic wind conditions, ranging from 50–60, 30-55, 55–60, and 40–50

411   ppbv respectively at night in MAM, JJA, SON, and DJF.

412   3.5 Impacts of offshore ozone on urban ozone air quality in Shanghai

413   As is presented in Sect. 3.2 and 3.3, observed O_3 concentrations at SSI were much higher

414   than those at urban site (XJH), suggesting higher levels of O_3 in oceanic air than those on

415   the continent. Therefore, sea breezes tend to bring more O_3 to the continent, aggravating

416   O_3 pollution in coastal cities. Shanghai is one of the largest cities located on the east coast

417   of China, experiencing severe O_3 pollution in recent years (Xu et al., 2019; Gu et al.,

418   2020). According to the cluster analysis results (Fig. S2), easterly winds from the ocean

419   greatly affected the Shanghai region, accounting for 64–78% of the total flows in

420   non-winter months during the period 2012–2017. To understand the impacts of higher O_3

421   in oceanic air on the urban air quality, numerical experiments are conducted using the

422   WRF-Chem model to examine the response of O_3 levels in Shanghai to various oceanic

423   air inflow conditions in this section.

424   Simulations are performed during September 1–30 2014 when the prevailing winds

425   were mostly northeasterly and easterly in the Shanghai region. The occurrence

426   frequencies of the northeasterly and easterly winds were 23% and 27% respectively,

427   during the simulation period, suggesting dominant influence of the oceanic air inflows on

428   the city of Shanghai. Consistent with above analysis, observed air O_3 concentrations were

429   much higher in oceanic regions than those in city areas, with monthly mean values of 30.9

430   and 57.7 ppbv, respectively at XJH and SSI in September 2014. The chemical boundary

431 conditions (BCs) of the regional model can represent the inflows conditions to explore

432 their impacts on surface concentrations of air pollutants over a certain continent region.

433 Using this method, Pfiter et al. (2011) proposed that chemical inflows taken from different

434 observational and model datasets could result in differences of ±15 ppbv in O_3 levels in

435 the US west coast region. Therefore, three sets of numerical experiments are conducted

436 as follows to access the impacts of oceanic O_3 air inflows on the urban O_3 air quality in

437 Shanghai. All the simulations are driven by the same emissions, initial conditions, physical

438 and chemical schemes.

439   (1) BC_40: O_3 concentrations at the eastern lateral boundary of the domain on the

440 ocean are assigned to 40 ppbv, which is provided by the MOZART-4 model, closed to the

441 observed urban O_3 levels (29.0–38.4 ppbv) in Shanghai in September. The chemical BCs

442 are updated every 6 hours.

443   (2) BC_50: Same as BC_40, but with O_3 concentrations setting to 50 ppbv at the

444 eastern lateral boundary of the domain.

445   (3) BC_60: Same as BC_40, but with O_3 concentrations at the eastern lateral

446 boundary of the domain setting to 60 ppbv according to the observed O_3 levels at SSI

447 (50.9–71.0 ppbv) in September.

448   Figure 8 displays the simulated and observed monthly mean distributions of surface

449 O_3 concentrations in BC_40, BC_50 and BC_60 scenarios, respectively. In addition to the

450 observations at XJH and SSI, O_3 measurements obtained from other three sites, Pudong

451 (PD, suburban), Sheshan (SS, rural), and Dongtan (DT, rural), during the same period

452 were introduced to evaluate the model's performance in simulating O_3 in Shanghai. The

453   O_3 concentrations at all the sites were measured using the same method as described in

454   Sect. 2.1. The calculated distributions of O_3 agree with observations, which exhibit lower

455   values in urban regions compared to those in rural and ocean areas, indicating strong O_3

456   depressions in the city of Shanghai due to the VOC-limited O_3 formation regime. The R

457   values between the simulated and observed O_3 concentrations are all larger than 0.50 at

458   continental sites (XJH, PD, SS, and DT), suggesting good prediction of O_3 variations by

459   the model.

460   Table 4 displays the statistical results of the comparisons between the simulated and

461   observed surface O_3 concentrations at different sites in Shanghai. Generally, the

462   WRF-Chem model underestimates O_3 concentrations at all the sites in most cases. Taken

463   the BC_40 scenario for example, the O_3 concentrations are underestimated by 9.4–27.6%

464   at continental sites and 36.1% at SSI, suggesting larger underestimation of O_3

465   concentrations in oceanic regions. Model results further suggest that elevated O_3 levels in

466   the eastern chemical BCs would lead to increases in O_3 concentrations at both urban and

467   remote sites when the prevailing winds are mostly easterly in Shanghai. With O_3

468   concentrations increasing from 40 to 60 ppbv in the easterly oceanic air inflows, the

469   simulated monthly mean O_3 concentrations increase by 7.0–9.7 ppbv at continental sites

470   and 10.4 ppbv at SSI. The underestimation of O_3 levels by the model is also greatly

471   improved in the BC_60 scenario, when the chemical BCs of O_3 are more close to the

472   observations. Compared to those in the BC_40 scenario, the normalized mean bias

473   (NMBs) of the predicted O_3 concentrations reduced at most sites in the BC_60 scenario,

474   for example from -36.1 % to -18.1 % at SSI and -27.6% to -4.6% at XJH, suggesting a

475 crucial role of the eastern oceanic air inflows in influencing O_3 air quality in Shanghai.

476 The calculated monthly mean differences in surface O_3 concentrations between

477 simulations in different scenarios are further presented in Fig. 9. Since the dominant winds

478 are easterly during the simulation period, distinct changes in surface O_3 concentrations

479 throughout Shanghai are generated, exhibiting generally gradient increases from the

480 ocean to the continent as O_3 increases in the oceanic air inflows. With every 10 ppbv

481 increases in O_3 levels in oceanic air, the simulated surface mean O_3 concentrations

482 increase by 3–6 ppbv in the land area and 4–7 ppbv in the offshore region. Due to the

483 strong O_3 depressions associated with high anthropogenic emissions, the simulated O_3

484 enhancements are relatively lower in the central urban region compared to those in

485 surrounding areas. Even so, simulated mean O_3 concentrations still exhibit 6–8 ppbv

486 increases in downtown Shanghai in the BC_60 scenario, accounting for approximately 30%

487 of the simulated O_3 concentrations in the BC_40 case. During the period 2012–2017,

488 most of the measured O_3 concentrations ranged between 50–60 ppbv at SSI in non-winter

489 seasons. Carried by the easterly inflows, these oceanic air masses with higher O_3 levels

490 (50–60 ppbv) could be transported to the coastal regions, resulting in approximately 20–

491 30% increases in urban O_3 concentrations in Shanghai according to the sensitivity results.

492 4 Conclusions

493 In this paper, we present the first relatively long and continuous measurements of oceanic

494 air O_3 conducted at an offshore monitoring station on the Sheshan Island during January 1

495 2012 to September 15 2017.The southwesterly and westerly winds are proved to carry

496 more pollutants to the SSI site, exerting greater influence of human activities on the

497 oceanic atmosphere over the offshore region of the East China Sea. Since the two kinds

498 of winds exhibited minimum occurrence frequencies and wind speeds in September and

499 October, atmosphere at SSI during the two months are considered to be less affected by

500 the transport of regional pollution.

501   Compared to those in urban (XJH) and rural (DT) sites, the observed O_3 levels were

502 higher at SSI, with a mean value of 50.1 ppbv during the observation period. Similar

503 seasonal and diurnal patterns of O_3 were observed at SSI and XJH; however, the

504 amplitudes of O_3 variations were much smaller at the offshore site (SSI). Since O_3

505 formation in Shanghai and its surrounding regions were VOC-limited, the observational

506 results suggested that the production and depression of O_3 could be weaker in the ocean

507 regions due to weak influence of the anthropogenic emissions. Observed mean

508 $O_{3\text{-max}}/O_{3\text{-min}}$ ratios also exhibited lower values at SSI (3.03) than those at XJH (5.20), with

509 minimum values ranging from 1.61–2.35 in September and October. The result further

510 illustrated that SSI was seldom affected by the anthropogenic emissions, especially in

511 September and October.

512   The multi-year changes of the oceanic O_3 at SSI are investigated using the

513 Mann-Kendall trend test and the Theil-Sen trend estimate method during 2012–2017.

514 Different from the significant O_3 increases detected at XJH and other rural sites reported

515 in previous studies, the observed mean O_3 concentrations at SSI exhibited statistically

516 insignificant increasing changes (1.12 ppbv yr^{-1}, α>0.10) during the observation period

517 and insignificant decreasing changes (-0.72 ppbv yr^{-1}, α>0.10) in September and October

518 when the transport of city pollutants had minimum impacts on the island. Due to fewer

519   impacts of anthropogenic emissions, most of the observed changes in O_3 at SSI could be

520   attributed to the changes of meteorological conditions. Observed wind speed exhibited

521   significant increases (0.21 m s^{-1} yr^{-1}, α<0.05) in September and October during the

522   observation period, suggesting that enhanced diffusion conditions could be an important

523   meteorological factor in determining the decreases in O_3 concentrations during the

524   observation period.

525   The impacts of urban plumes on O_3 levels in oceanic air at SSI are evaluated by

526   studying the relationships between observed O_3 and NO_x under different wind conditions.

527   The SW and W winds usually carried air masses with higher NO_x concentrations in both

528   daytime and nighttime to the island. Generally, observed daytime and nighttime O_3

529   concentration decreased as NO_x concentration increases in SW and W winds, exhibiting

530   typical VOC-limited characteristics of O_3 formation. The pattern was more typical in SON

531   and DJF, with R values of -0.72 and -0.75, respectively between O_3 and NO_x

532   concentrations. In MAM and JJA, the daytime O_3-NO_x variations presented kind of

533   positive relationships under SW and W wind conditions, suggesting continuous O_3

534   production in aged city plumes from Shanghai. As reported in previous studies during the

535   MIRAGE-Shanghai campaign, enhanced OVOCs oxidation should be the most important

536   driver of the observed O_3 enhancements in the city plumes transported by the SW and W

537   winds.

538   The influence of the oceanic O_3 air inflows on urban O_3 air quality in Shanghai are

539   quantified during an easterly wind dominant episode (September 1–30, 2014). Numerical

540   experiments are conducted with chemical BCs of O_3 assigned according to different inflow

541   conditions using the WRF-Chem model. Model results suggest that increases of O_3 in the

542   easterly oceanic air inflows will lead to gradient increases from the ocean to the continent.

543   With every 10 ppbv O_3 increases, the calculated surface mean O_3 concentrations can

544   increase by 3–6 ppbv in the land and 4–7 ppbv in the offshore region. Compared to those

545   in surrounding regions, O_3 in central city of Shanghai exhibited lower enhancements in

546   response to the O_3 increases in oceanic air inflows due to strong O_3 depression processes.

547   Even so, the impacts of the oceanic air inflows can still lead to 20–30% increases in urban

548   O_3 concentrations which should be crucially considered in dealing with O_3 pollution in

549   large coastal cities like Shanghai.

550

551   *Data availability.* The data used in this paper can be provided upon request from Dr.

552   Jianming Xu (metxujm@163.com).

553

554   *Author contribution.* YG and JX came up with the original idea, designed the analysis

555   methods, developed the model code, and performed the simulations. WG provided the

556   observational data. YG and YQ conducted the analysis of the observations and model

557   results. YG prepared the manuscript with contributions from all co-authors.

558

559   *Competing interest.* The authors declare that they have no conflict of interest.

560

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Yue, X. and Unger, N.: Ozone vegetation damage effects on gross primary productivity in the United States, Atmos. Chem. Phys., 14, 9137–9153, 2014.

727   Table 1 Mean CO mixing ratios (ppmv) under north (N), northeast (NE), east (E),

728   southeast (SE), south (S), southwest (SW), west (W), northwest (NW) and calm (C) wind

729   conditions at Dongtan (DT) site, a remote rural site near the Sheshan Island (SSI) during

730   2012 to 2017.

	N	NE	E	SE	S	SW	W	NW	C
CO	0.31	0.27	0.25	0.23	0.27	**0.44**	**0.56**	0.38	0.34

731   Table 2 Monthly mean wind speeds (m s^{-1}) and occurrence frequencies (%) of the

732   southwest (SW) and west (W) winds at Dongtan (DT) site, a remote rural site near the

733   Sheshan Island (SSI) during 2012 to 2017.

	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.
SW+W	11.5	9.2	11.9	13.2	12.7	9.8	17.7	10.8	**6.1**	**5.2**	11.9	15.1
Wind speed	2.70	2.93	2.98	3.04	2.86	2.51	2.65	2.77	**2.49**	**2.50**	2.55	2.54

734 Table 3 Statistical results of the Mann-Kendall test and Theil-Sen trend estimate for daily

735 mean values of NO_x, CO mixing ratios, temperature (T), and wind speed (WS) in

736 September and October at Dongtan (DT) site, a remote rural site near Sheshan Island

737 (SSI) site during the 2012–2017 period. The units of the calculated slopes are ppbv yr^{-1} for

738 NO_x and CO, $°C\ yr^{-1}$ for T, and $m\ s^{-1}\ yr^{-1}$ for WS.

	NO_x	CO	T	WS
Slope Estimate	0.48*	2.67$^\Delta$	0.15$^\Delta$	0.21*

739 *The result is significant at the 95% confidence level.

740 $^\Delta$The result cannot pass the Mann-Kendall trend test at the 90% confidence level.

741 Table 4 Statistical results of the comparisons between the simulated and observed

742 surface O_3 concentrations at Sheshan (SS), Xujiahua (XJH), Pudong (PD), DT (Dongtan)

743 and Sheshan Island (SSI) sites during September 2014. The calculated O_3 levels are

744 obtained from BC_40, BC_50 and BC_60 simulations, respectively. Values of the average

745 surface O_3 concentrations (Mean) and normalized mean bias (NMB) are displayed. The

746 NMB is defined as NMB=$\frac{\sum_{i=1}^{n}(P_i-O_i)}{\sum_{i=1}^{n}O_i}$, where P_i and O_i are predicted and observed ozone

747 mixing ratios for sample i, n is the number of total samples (numbers in parentheses).

	Cases	SS (681)	XJH (641)	PD (690)	DT (690)	SSI (720)
	Observation	39.7	30.4	40.3	46.4	57.7
Mean	BC_40	36.0	22.0	29.5	35.3	36.9
(ppbv)	BC_50	39.1	25.1	33.3	39.6	41.8
	BC_60	43.1	29.0	37.9	45.0	47.3
	BC_40	-9.4	-27.6	-26.7	-23.9	-36.1
NMB(%)	BC_50	-1.5	-17.5	-17.2	-14.5	-27.5
	BC_60	8.6	-4.6	-5.9	-3.0	-18.1

748 **Figure Captions**

749 **Figure 1** Land cover of Shanghai and corresponding locations and landscapes of Xujiahui

750 (XJH, urban), Dongtan (DT, rural) and Sheshan Island (SSI, remote and oceanic) stations.

751 **Figure 2** Monthly wind rose diagrams averaged over the period of 2012 to 2017 at

752 Dongtan (DT) site, a remote rural site near the Sheshan Island (SSI).

753 **Figure 3** Monthly mean CO mixing ratios under north (N), northeast (NE), east (E),

754 southeast (SE), south (S), southwest (SW), west (W), northwest (NW) and calm (C) wind

755 conditions at Dongtan (DT) site, a remote rural site near the Sheshan Island (SSI) during

756 2012 to 2017.

757 **Figure 4** Monthly and year-round mean diurnal variations of O_3 (ppbv) at Sheshan Island

758 (SSI, remote and oceanic) and Xujiahui (XJH, urban) sites during 2012 to 2017.

759 **Figure 5** Calculated monthly mean ratios of daily maximum O_3 concentrations (O_{3-max}) to

760 minimum O_3 concentrations (O_{3-min}) at Sheshan Island (SSI, remote and oceanic) and

761 Xujiahui (XJH, urban) sites, respectively during 2012 to 2017.

762 **Figure 6** Variations of (a) monthly mean O_3 concentrations at Sheshan Island (SSI,

763 remote and oceanic) and Xujiahui (XJH, urban) sites during the period 2012–2017, (c)

764 corresponding variations of daily mean O_3 concentrations at SSI and XJH in September

765 and October, and (c) variations of mean O_3 concentrations during daytime (10:00-16:00

766 LST) and nighttime (23:00-04:00 LST) at SSI.

767 **Figure 7** Daytime and nighttime mean O_3 mixing ratios (ppbv) at Sheshan Island (SSI)

768 and NO_x mixing ratios (ppbv) at Dongtan (DT) site, a remote rural site near SSI under

769 north (N), northeast (NE), east (E), southeast (SE), south (S), southwest (SW), west (W),

770   and northwest (NW) wind conditions in MAM (March–May), JJA (June–August), SON

771   (September–November), and DJF (December–February), respectively during 2012 to

772   2017.

773   **Figure 8** Calculated distributions of monthly mean O_3 concentrations (shades, ppbv) from

774   BC_40, BC_50 and BC_60 simulations, respectively in September 2014. Model results

775   are compared with observed mean O_3 concentrations (circles, ppbv) obtained from

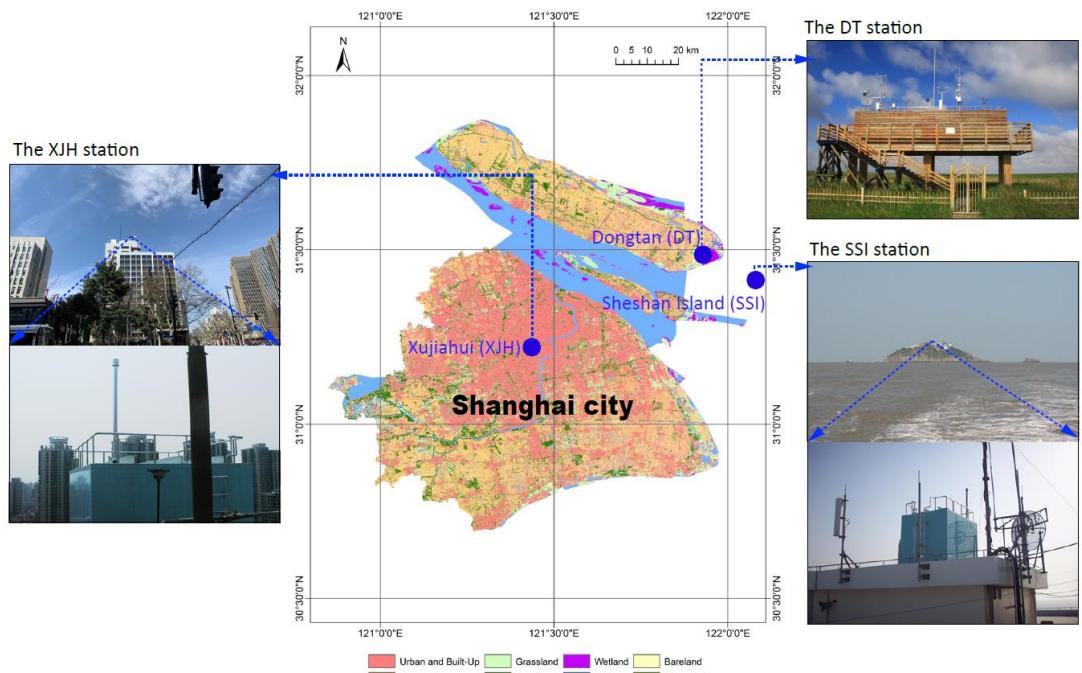
776   Sheshan (SS), Xujiahua (XJH), Pudong (PD), DT (Dongtan) and Sheshan Island (SSI)

777   sites. Also shown is the calculated wind field (m s^{-1}) averaged over the same period.

778   **Figure 9** Mean differences in surface O_3 concentrations (ppbv) simulated with different

779   chemical boundaries: (a) BC_50 minus BC_40, (b) BC_60 minus BC_40, and (c) BC_60

780   minus BC_50 in September 2014. Also shown is the calculated wind field (m s^{-1}) averaged

781   over the simulation period.

782

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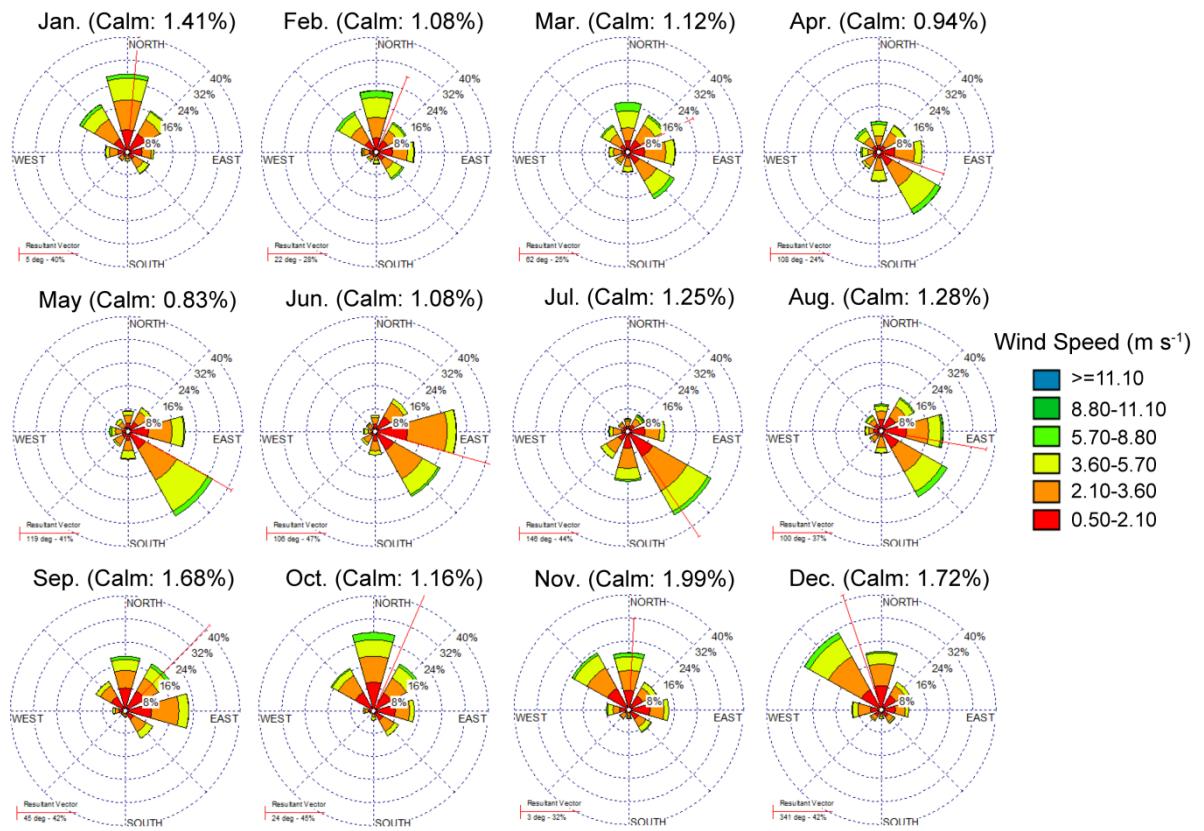
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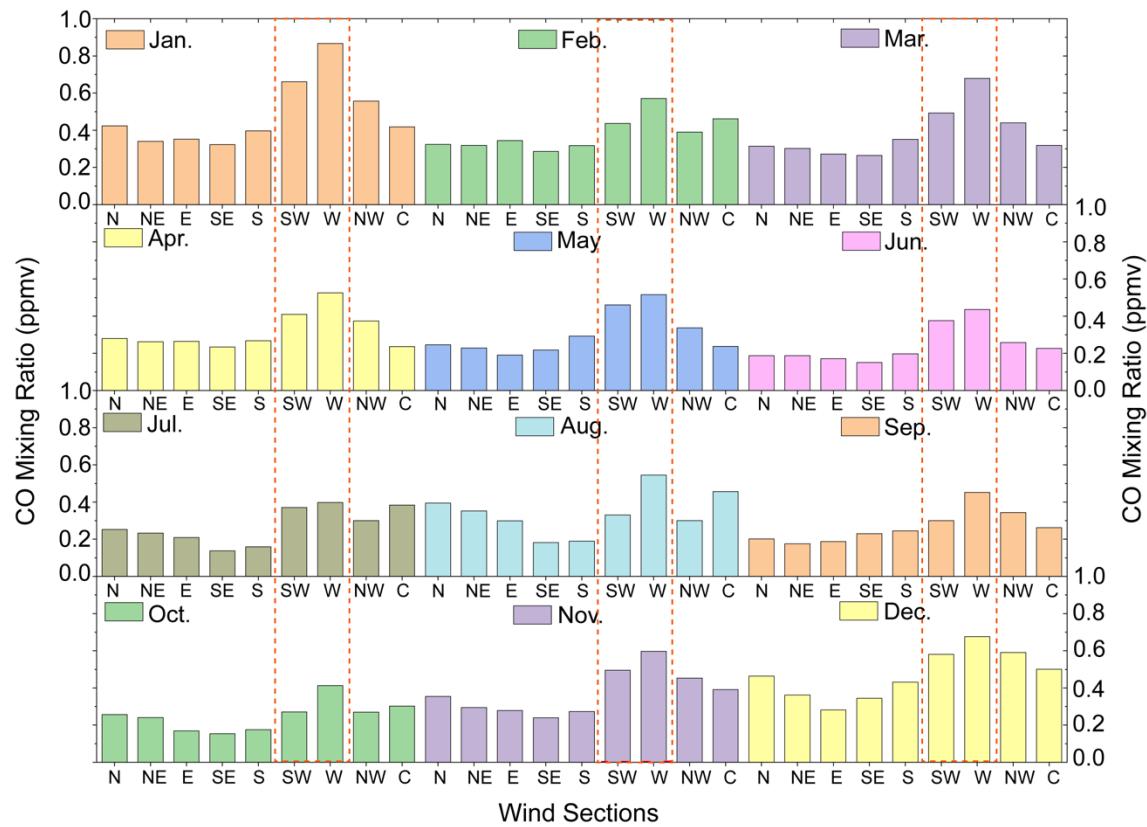
Figure 2 Monthly wind rose diagrams averaged over the period of 2012 to 2017 at

Dongtan (DT) site, a remote rural site near the Sheshan Island (SSI).

788

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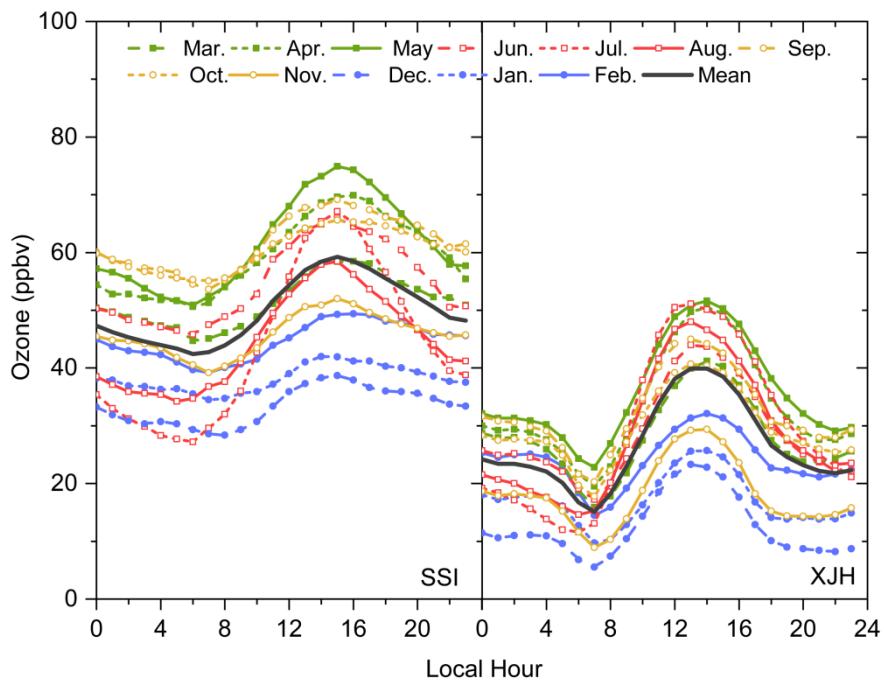
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796

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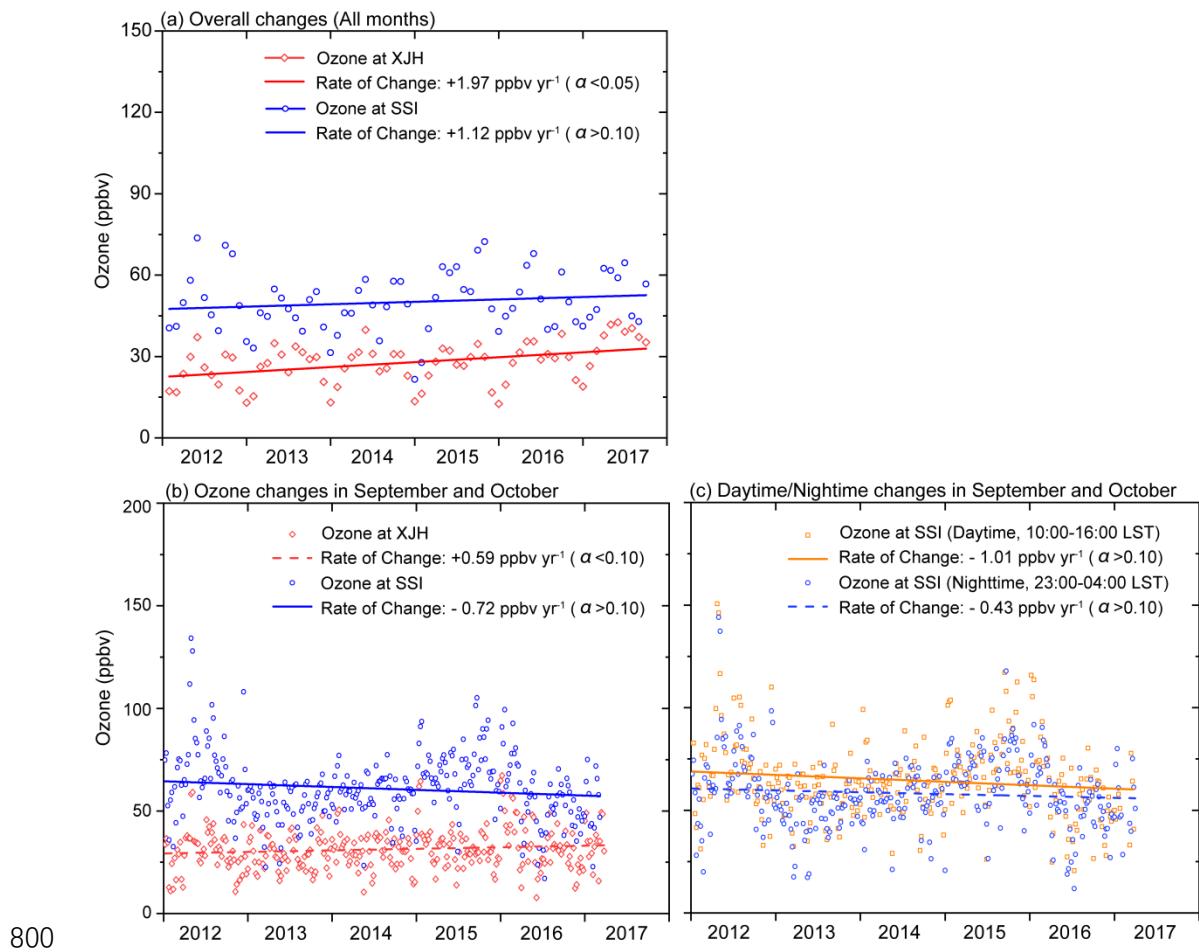
Figure 6 Variations of (a) monthly mean O_3 concentrations at Sheshan Island (SSI, remote and oceanic) and Xujiahui (XJH, urban) sites during the period 2012–2017, (b) corresponding variations of daily mean O_3 concentrations at SSI and XJH in September and October, and (c) variations of mean O_3 concentrations during daytime (10:00-16:00 LST) and nighttime (23:00-04:00 LST) at SSI.

Figure 7 Daytime and nighttime mean O_3 mixing ratios (ppbv) at Sheshan Island (SSI) and

NO$_x$ mixing ratios (ppbv) at Dongtan (DT) site, a remote rural site near SSI under north (N),

northeast (NE), east (E), southeast (SE), south (S), southwest (SW), west (W), and

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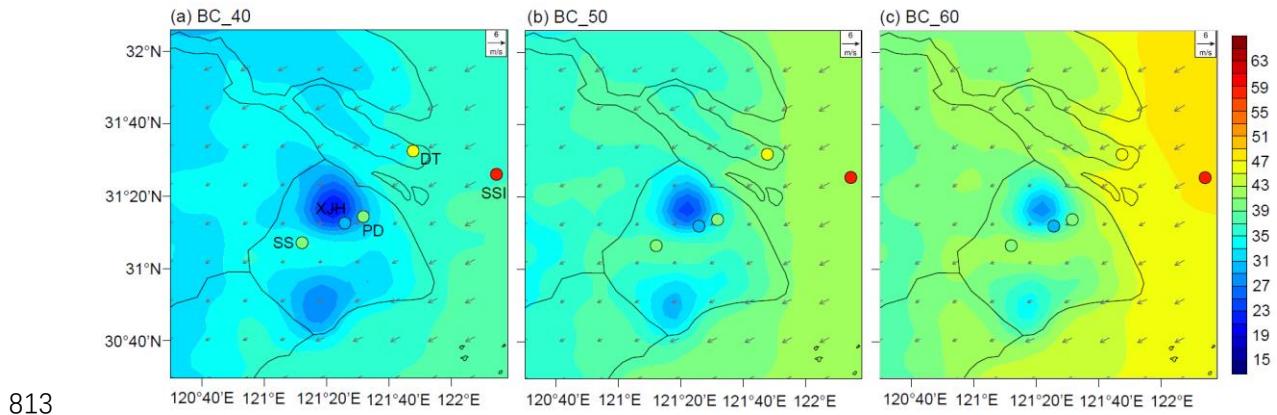
2017.

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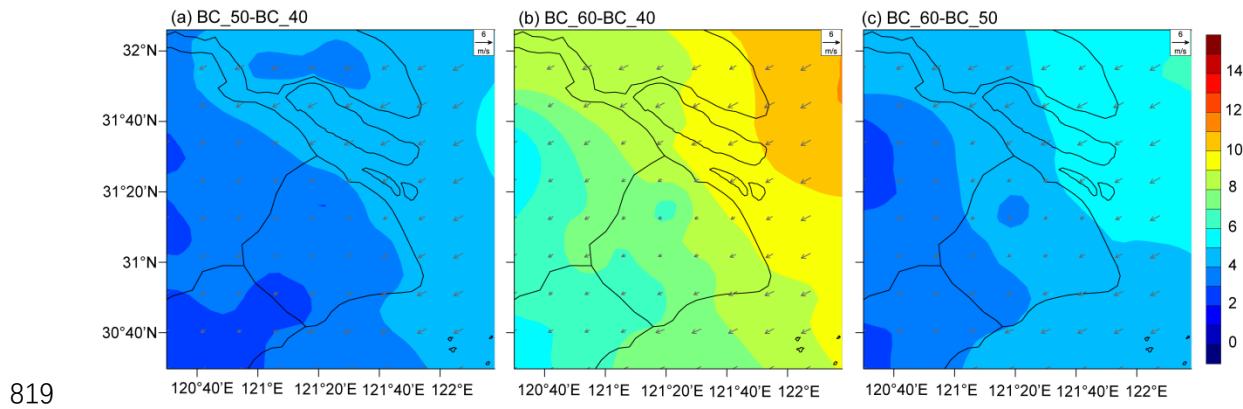
819

820   Figure 9 Mean differences in surface O_3 concentrations (ppbv) simulated with different

821   chemical boundaries: (a) BC_50 minus BC_40, (b) BC_60 minus BC_40, and (c) BC_60

822   minus BC_50 in September 2014. Also shown is the calculated wind field (m s^{-1}) averaged

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