Exploring the drivers of the increased ozone production in Beijing in

summertime during 2005-2016

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Abstract

In the past decade, average PM$_{2.5}$ concentrations decreased rapidly under the strong pollution control measures in major cities in China; however, ozone (O$_3$) pollution emerged as a significant problem. Here we examine a unique (for China) 12-year data set of ground-level O$_3$ and precursor concentrations collected at an urban site in Beijing (PKUERS), where the maximum daily 8 h average (MDA8) O$_3$ concentration and daytime Ox (O$_3$ + NO$_2$) concentration in August increased by 2.3 $\pm$ 1.2 ppbv (+3.3 $\pm$ 1.8%) yr^{-1} and 1.4 $\pm$ 0.6 (+1.9 $\pm$ 0.8%) yr^{-1} respectively from 2005 to 2016. In contrast, daytime concentrations of nitrogen oxides (NOx) and the OH reactivity of volatile organic compounds (VOCs) both decreased significantly. Over this same time, the decrease of particulate matter, and thus the aerosol optical depth, led to enhanced solar radiation and photolysis frequencies, with near-surface j(NO$_2$) increasing at a rate of 3.6 $\pm$ 0.8% yr^{-1}. We use an observation based box model to analyze the combined effect of solar radiation and ozone precursor changes on ozone production rate, P(O$_3$). The results indicate that the ratio of the rates of decrease of VOCs and NOx (about 1.1) is inefficient in reducing ozone production in Beijing. P(O$_3$) increased during the decade due to more rapid atmospheric oxidation caused to a large extent by the decrease of particulate matter. This elevated ozone production was driven primarily by increased actinic flux due to PM$_{2.5}$ decrease and to a lesser extent by reduced heterogeneous uptake of HO$_2$. Therefore, the influence of PM$_{2.5}$ on actinic flux and thus on the rate of oxidation of VOCs and NOx to ozone and to secondary aerosol (i.e., the major contributor to PM$_{2.5}$) is important for determining the atmospheric effects of controlling the emissions of the common precursors of PM$_{2.5}$ and ozone when attempting to control these two important air pollutants.

1 Introduction

Tropospheric ozone (O_3) plays a key role in the oxidizing capacity of the atmosphere and affects the global climate; high concentrations of ground-level ozone are harmful to human health and ecosystems (Monks et al., 2015;Fiore et al., 2009). Ozone is produced rapidly in sun-lit polluted air by photochemical oxidation of volatile organic compounds (VOCs) in the presence of nitrogen oxides ($NO_x \equiv NO + NO_2$) (Atkinson, 2000). In recent years, China has undergone rapid economic development, resulting in higher demand for energy, and greater usage of fossil fuels. As a result, high emissions to the atmosphere produce heavy pollution in eastern China, which now suffers from severe ozone pollution, especially in urban areas, where the daily maximum 8 h average (MDA8) ozone level often exceeds the standard of 80 ppb (Jinfeng et al., 2014;Wang et al., 2011;Zhang et al., 2014;Lu et al., 2018;Li et al., 2019b). A recent study reported that the national warm-season (April−September) fourth highest MDA8 ozone level (86.0 ppb) and the number of days with MDA8 values of > 70 ppb was much higher than regional averages in Japan, South Korea, Europe, or the United States (Lu et al., 2018). Satellite observations found that regional ozone concentrations in eastern China increased by 7% between 2005 and 2010 (Verstraeten et al., 2015). From 2013 to 2017, the O_3 concentrations in 74 cities as a whole showed an upward trend with Beijing-Tianjin-Hebei region being the most serious (Li et al., 2019b;Lu et al., 2018). Better understanding of the causes of elevated ozone in China is important for developing effective emission control strategies to reduce the ozone pollution problem.

Aerosols impact ozone production primarily in two ways: alteration of photolysis rates by aerosol radiative influence and heterogeneous reactions occurring on the aerosol surface. The reduction of photolysis frequencies by the extinction effect of aerosol and thus its influence on ozone production has been explored in the past (Dickerson et al., 1997;Castro et al., 2001;Real and Sartelet, 2011;Gerasopoulos et al., 2012;Wang et al., 2019). Absorbing aerosols reduce photolysis frequencies

83   throughout the boundary layer, and as a result decrease near-surface photochemical

84   ozone production (de Miranda et al., 2005;Jacobson, 1998;Wendisch et al., 1996;Raga

85   et al., 2001). Conversely, scattering aerosols in the boundary layer increase photolysis

86   frequencies throughout the troposphere, and thereby increase ozone production aloft

87   (Jacobson, 1998;Tian et al., 2019;Dickerson et al., 1997). The importance of aerosol

88   heterogeneous reactions in ozone photochemistry in China has been previously

89   investigated in model studies (Lou et al., 2014;Li et al., 2018b;Xu et al., 2012;Li et

90   al., 2019b). The effects of NO_2, NO_3, and N_2O_5 heterogeneous reactions showed

91   opposite O_3 concentration changes in VOC-limited and NOx-limited regions. In a

92   VOC-limited region, NO_2, NO_3, and N_2O_5 heterogeneous reactions lead to ozone

93   concentration increases (Lou et al., 2014;Xu et al., 2012). The heterogeneous reaction

94   of HO_2 decreases ozone production in both VOC-limited and NOx-limited regions by

95   decreasing the reaction rate of HO_2 with NO (Lou et al., 2014;Li et al., 2019b).

96   In the past decade, Eastern China has experienced severe fine particulate matter

97   ($PM_{2.5}$) pollution in winter (Zhang et al., 2016), and this issue has been the main focus

98   of the government's air pollution control strategy. These stringent emission control

99   measures have significantly decreased the concentrations of particulate matter in many

100 Chinese cities. During 2008-2013, ground-level $PM_{2.5}$ estimated from satellite-

101 retrieved aerosol optical depth (AOD) in China declined at a rate of 0.46 μg m^{-3} year^{-1}

102 (Ma et al., 2016b). Another study indicated that the annual average concentration of

103 $PM_{2.5}$ in Beijing decreased by 1.5μg m^{-3} year^{-1} and 27% in total from 2000 to 2015

104 under the implementation of 16 phases' air pollution control measures (Lang et al.,

105 2017). Hu et al (2017) reported that $PM_{2.5}$ in Beijing declined significantly from 2006

106 to 2016, and meanwhile solar radiation increased (Hu et al., 2017). However, despite

107 the reduction in emissions of particulate matter (PM) and ozone precursors, ozone

108 concentrations increased, even while PM concentrations decreased.

109   In Beijing, the second largest city in China, with rapid economic development and

110 urbanization in recent years, ozone pollution is one of the worst among China's cities.

111 Thus, Beijing is a representative city in which to study urban ozone pollution in China.

Despite extensive study of the relationship between ozone and its precursors in Beijing and other mega cities in China (Zhang et al., 2014;Chou et al., 2011;Lu et al., 2019;Liu et al., 2012), there remains a lack of understanding of the cause of the long-term surface ozone concentration increase that accompanied reductions in precursor emissions. In this study, we utilize measurements from a representative urban site in Beijing to explore how the variations in solar radiation and heterogeneous reactions influence the trend of ozone and the coupling effect of aerosol and ozone precursor changes on ozone production. Our overall goal is to determine the extent to which increasing actinic flux caused by the decline in PM contributed to the observed increase in ozone concentrations. This research provides a clearer understanding of how efforts to reduce PM concentrations affect ozone concentrations, and thus informs air quality improvement efforts in China's urban areas.

2 Materials and methods

2.1 Measurements of air pollutants, photolysis frequencies and aerosol surface concentration

Ambient air pollutants and photolysis frequencies were measured at an urban site in Beijing in August between 2005 and 2016. The site (39.99° N, 116.31°E) was located on the roof of a six story building (~20m above the ground level) on the campus of Peking University (PKUERS) near the 4th Ring Road with high density of traffic, but without obvious industrial or agricultural sources (Wehner et al., 2008). Temporal trends of air pollutants and composition of VOCs are thought to be representative for the whole of Beijing (Wang et al., 2010;Xu et al., 2011;Zhang et al., 2012). Measured parameters include O_3, NOx, CO, SO_2, C2 - C10 VOCs, photolysis frequencies and aerosol surface concentration. The measurement techniques are included in the Table 1.

During 2006 and 2008, ambient levels of VOCs were measured using an online GC-FID system built by the Research Center for Environmental Changes (RCEC; Taiwan). A detailed description of this system and QA/QC procedures can be found in

139 Wang et al. (Wang et al., 2004). During August 2007 and 2009, ambient VOCs were

140 measured using a commercial GC-FID/PID system (Syntech Spectra GC955 series

141 600/800 analyzer) (Xie et al., 2008;Zhang et al., 2014). From 2010 to 2016, VOCs were

142 measured using a cryogen-free online GC-MS/FID system developed by Peking

143 University. A detailed description of this system and QA/QC procedures can be found

144 in Yuan et al. and Wang et al. (Yuan et al., 2012;Wang et al., 2014). Formaldehyde

145 (HCHO) concentrations were measured by a Hantzsch fluorimetry.

146 Photolysis frequencies (including $j(O^1D)$, $j(NO_2)$, $j(HONO)$, $j(HCHO)\_M$,

147 $j(HCHO)\_R$, $j(H_2O_2)$) were calculated from solar actinic flux spectra measured by a

148 spectroradiometer as described by Bohn et al. (Bohn et al., 2008). The particle number

149 size distributions were measured by a system consisting of a Nano-SMPS (TSI

150 DMA3085 + CPC3776) and a SMPS (TSI DMA3081 + CPC3775). Aerosol surface

151 concentration (Sa) during 2006-2016 was calculated from the measured particle number

152 size distributions between 3 nm and 700 nm by assuming the particles are spherical in

153 shape.

2.2 Estimate of photolysis frequencies

155 Photolysis frequencies were measured in August 2011-2014 and 2016. The

156 Tropospheric Ultraviolet and Visible (TUV) radiation model (version 5.3) was used to

157 calculate photolysis frequencies in August over the entire 2006-2016 period under

158 clear-sky conditions. TUV uses the discrete-ordinate algorithm (DISORT) with four

159 streams and calculates the actinic flux spectra with a wavelength range of 280 – 420 nm

160 in 1 nm steps and resolution. We used observed aerosol optical properties including

161 AOD, single scattering albedo (SSA) and Ångström exponent (AE), total ozone column

162 to constrain the TUV model (Madronich, 1993). The calculated values agree well with

163 measured results as shown in Figure 1 indicating that the TUV model accurately

164 calculated the photolysis frequencies. Data of photolysis frequencies under cloudless

165 conditions were selected according to the presence of AOD data since AOD

166 measurements were not possible under cloudy conditions.

2.3 Measurements of aerosol optical properties

Aerosol optical properties were measured with a CIMEL Sun photometer (AERONET level 1.5 and level 2.0 data collection, http://aeronet.gsfc.nasa.gov/) at the Beijing-CAMS site (39.933°N, 116.317°E) and at the Beijing site (39.977N,116.381E). The instrumentation, data acquisition, retrieval algorithms and calibration procedure, which conform to the standards of the AERONET global network, are described in detail by Fotiadi et al. (Fotiadi et al., 2006). The solar extinction measurements taken every 3 minutes within the spectral range 340 – 1020 nm were used to compute AOD at 340, 380, 440, 500, 675, 870, 970 and 1020 nm. The overall uncertainty in AOD data under cloud-free conditions was 0.02 at a wavelength of 440 nm (Dubovik and King, 2000). In this study, AOD at the wavelength of 380nm was chosen for analysis. This wavelength was selected as it is more representative of $j(NO_2)$. In addition to AOD, that network also provided single scattering albedo (SSA) and Ångström exponent (AE) data.

Cloud optical thickness (COT) was acquired from Aura satellite measurements with a time resolution of 24 hours. Total ozone column was obtained by OMI (Ozone Monitoring Instrument), using overpass data.

2.4 Trend analysis method

A simple linear regression (the least-squares method) was implemented to investigate temporal trends of ozone, precursors, aerosol optical properties, $PM_{2.5}$ and photolysis frequencies. The null hypothesis is that air pollutants and time have no linear relationship and this was tested using the standard F-statistic test (ratio of the mean-square regression to the mean-square residual). The p value associated with the F-statistic is the probability of mistakenly rejecting the null hypothesis (** $p < 0.01$; * $p < 0.05$). The p values for the trends of different parameters are summarized in Table 2.

2.5 Chemical box model

Ozone production rate, P(O$_3$), is calculated by a chemical box model. This model is based on the compact Regional Atmospheric Chemical Mechanism version 2 (RACM) described by Goliff et al. (Goliff et al., 2013), which includes 17 stable inorganic species, 4 inorganic intermediates, 55 stable organic compounds and 43 intermediate organic compounds. Compounds that are not explicitly treated in the RACM are lumped into species with similar functional groups. The isoprene mechanism includes a more detailed mechanism based on the Leuven Isoprene Mechanism (LIM) proposed by Peeters et al. (Peeters et al., 2009). A detailed description of this model can be found in Tan et al. (Tan et al., 2017).

In this study, the model was constrained by measured hourly average CO, NO$_2$, O$_3$, SO$_2$, NMHCs (56 species), HCHO, photolysis frequencies, temperature, pressure, and relative humidity. HONO was not measured. HONO concentrations are generally underestimated by the gas phase reaction source of HONO (OH + NO → HONO) in urban areas due to the emission of HONO and the heterogeneous reaction of NOx at surfaces to form HONO, both of which are related to NOx concentration. As a result, the HONO concentration was calculated according to the concentration of NO$_2$ and the observed ratio of HONO to NO$_2$ at an urban site in Beijing, which had a marked diurnal cycle (Hendrick et al., 2014). For the model calculation, the ratio of HONO to NO$_2$ is equal to 0.08 at 6:00 and decreases linearly from 0.08 to 0.01 during 6:00 - 10:00 reflecting increasing photolysis of HONO, and maintains the value of 0.01 during 10:00-18:00. In this study, we focused on daytime P(O$_3$) (6:00 - 18:00), thus the nocturnal HONO concentrations were not required.

RO$_2$, HO$_2$, OH were simulated by the box model to calculate the ozone production and loss rates as shown in Equations E1 and E2 as derived by Mihelcic et al. (Mihelcic et al., 2003).

$$P(O_3) = k_{HO2+NO}[HO_2][NO] + \Sigma \left(k^i_{RO2+NO}[RO^i_2][NO] \right) - k_{OH+NO2}[OH][NO_2] - L(O_3) \quad \text{E1}$$

$$L(O_3) = (\theta j(O^1D) + k_{OH+O3}[OH] + k_{HO2+O3}[HO_2] + \Sigma(k^j alkene + O_3[alkene^j])[O_3] \quad \text{E2}$$

221   where θ is the fraction of O^1D from ozone photolysis that reacts with water vapor. i and

222   j represent the number of species of RO_2 and alkenes, respectively.

223   The model runs were performed in a time-dependent mode with two days' spin-

224   up. A 24 h lifetime was introduced for all simulated species, such as secondary species

225   and radicals, to approximately simulate dry deposition and other losses of these

226   species (Lu et al., 2013). This lifetime corresponds to an assumed deposition velocity

227   of 1.2 cm s^{-1} and a well-mixed boundary layer height of about 1 km. Sensitivity tests

228   show that this assumed deposition lifetime has a relatively small influence on the

229   reactivity of modeled oxidation products and ROx radicals.

230   Aerosols can influence O_3 production by heterogeneous reactions such as uptake

231   of HO_2, NO_2, N_2O_5 and NO_3. For these species, the heterogeneous uptake of HO_2 is

232   expected to have the largest effect on rapid ozone production in summertime and VOC-

233   limited conditions (Li et al., 2019b). Thus, the effect of heterogeneous reaction of HO_2

234   on ozone production was simulated in the chemical box model using RH corrected

235   aerosol surface concentration (S_{aw}) and uptake coefficient of HO_2. The rate of change

236   in HO_2 due to irreversible uptake is expressed by E3.

237
$$\frac{dC}{dt} = \frac{\gamma_{HO_2} \times S_{aw} \times v \times C}{4} \qquad \text{E3}$$

238   Where C, v, and γ_{HO_2} are the gas phase concentration, mean molecular velocity, and

239   uptake coefficient, respectively. To derive S_{aw} we used the measured hygroscopic

240   factor (Liu et al., 2009) and measured RH to correct the measurement-derived S_a to

241   ambient conditions. In this study, we chose $\gamma_{HO_2} = 0.2$ provided by laboratory

242   measurements of HO_2 uptake by aerosol particles collected at two mountain sites in

243   eastern China (Taketani et al., 2012). The effects of HO_2 uptake on $P(O_3)$ in Beijing in

244   2006 were simulated assuming that the product of HO_2 uptake by aerosols is either

245   H_2O or H_2O_2. The results indicate that the two scenarios showed no significant

246   difference because the recycling of HOx radicals from H_2O_2 is inefficient (Li et al.,

247   2019b). In the following simulations in this study, the product of HO_2 uptake by

248   aerosols is taken to be H_2O.

249   Heterogeneous uptake of N_2O_5, NO_2 and NO_3 was included in the chemical box

250 model. This includes $\gamma_{N2O5} = 0.007$ for converting N_2O_5 to HNO_3 (Wang et al., 2017),

251 $\gamma_{NO2} = 1 \times 10^{-5}$ for conversion of NO_2 to HONO and HNO_3 (which yields a good

252 simulation of HONO/NO_2 concentration ratios in China (Shah et al., 2020)) and γ_{NO3}

253 $= 1 \times 10^{-3}$ for conversion of NO_3 to HNO_3 (Jacob, 2000).

3 Results and discussion

3.1 Trend of ozone

256 Ozone pollution levels can be characterized by a number of metrics. Table 3 lists

257 10 ozone metrics and their definition summarized by Lu et al. (2018). We classify these

258 indicators into four categories: (1) metrics that characterize general levels of ozone:

259 median value of hourly ozone concentrations (median), daily maximum 8 h average

260 ozone concentration (MDA8) and daytime average ozone concentration (DTAvg); (2)

261 metrics that characterize extreme levels of ozone: daily maximum 1 h average ozone

262 concentration (MDA1), 98th percentile of hourly ozone concentrations (Perc98) and

263 4th highest MDA8 (4MDA8); (3) metrics that characterize ozone exposure: cumulative

264 hourly ozone concentrations of >40 ppb (AOT40) and sum of positive differences

265 between MDA8 and a cutoff concentration of 35 ppb (SOMO35); (4) The metrics that

266 characterize the days when the ozone exceeds the standard: total number of days with

267 MDA8 values of >70 ppb (NDGT70) and number of days with the ozone concentration

268 exceeding the Chinese grade II national air quality standard (Exceedance). Figure 2

269 presents variations in these four categories of ozone metrics at PKUERS site during the

270 study periods. The results show that overall all metrics increased during the 12 year

271 period. However, the percent increase, the p value and the correlation coefficient vary

272 between metrics. The median, DTAvg, and MDA8 indicators, which characterize the

273 general concentration levels of ozone, increased at rates of 2.8% - 5.7% yr^{-1}. The

274 metrics that characterize the extreme concentration levels of ozone increased more

275 slowly (1.2% - 2.7% yr^{-1}). Among them, Perc98 had the smallest rate of increase, only

276 1.2% yr^{-1}, and the correlation is not significant (p = 0.29, r^2 = 0.11). This indicates that

277 increases in the extreme ozone pollution was less significant. In contrast, the increase

278 rates of the ozone exposure metrics AOT40 and SOMO35 are faster, 8.4% yr^{-1} and 8.3%

279 yr^{-1}, respectively, than the metrics that characterize ozone concentrations. The NDGT70

280 and Exceedance metrics, related to the number of days of ozone exceeding the standard,

281 showed the fastest increases, 10% yr^{-1} and 9.8% yr^{-1}, respectively.

282 As shown in Figure 3, from 2005 to 2016 MDA8 O_3 concentrations increased at a

283 rate of 2.3 ± 1.2 ppbv (3.3 ± 1.8 %) yr^{-1} ($r^2 = 0.66$) at the PKUERS site, which

284 corresponds to a total MDA8 ozone concentration increase of 25.3 ppbv. Meanwhile,

285 O_X (O_3+NO_2) concentrations increased at a slower rate of 1.4 ± 0.6 ppbv (1.9 ± 0.8 %)

286 yr^{-1}, due to the decrease in NOx concentrations (Figure 5).

287 Temperature and wind speed, which can directly influence ozone production and

288 concentrations, showed no significant trend during 2005-2016 (Figure 4). The average

289 temperatures in summer were between 26 and 31℃. The temperature in 2005 was the

290 lowest and in 2007 it was the highest. The average wind speeds were less than 2.5 m s^{-1}

291 in all years. The average relative humidity may have decreased slightly (~ 1.5% yr^{-1}).

292 In summary, we believe that meteorological factors did not play more than a minor role

293 in the overall Beijing O_3 trend. Therefore, our discussion focuses on photochemical

294 processes.

295 The ozone concentration observed at a receptor site depends on two

296 contributions: regional background ozone and local photochemical production. We

297 have no direct measurements of the long-term trend of regional background ozone in

298 Beijing, but others have reported measurements of ozone at regional background sites

299 in China. At a baseline Global Atmospheric Watch (GAW) station in the northeastern

300 Tibetan Plateau region (Mt Waliguan, 36.28° N, 100.9° E) the average annual daytime

301 ozone concentration increased at a rate of 0.24 ppb yr^{-1}, over the 1994 to 2013 period,

302 but there was no significant trend in summer (Xu et al., 2018). The measurement at a

303 rural station (Dingling site) in Beijing (116.22° E, 40.29° N, 34 km northwest of the

304 observation site in this study) showed a decrease of ozone at a rate of -0.47 ppb yr^{-1}

305 over the 2004 to 2015 period (Zheng et al., 2016). The MDA8 ozone concentration at

306   the Shangdianzi site, a background station in Beijing, showed an increasing trend of

307   1.1 ppb yr^{-1} during 2004-2014 (Ma et al., 2016a). Additionally, there were very small

308   trends of O$_3$ concentrations at the background site (Dongtan) in Shanghai, located to

309   the south of the North China Plain (Gao et al., 2017). However, these background

310   sites in Beijing and Shanghai may be strongly affected by local emissions. MDA8

311   ozone concentrations at the Changdao site, a background site in the east of the North

312   China Plain that is much less influenced by local emissions, increased slowly (+1.2

313   ppbv yr^{-1}, r^2=0.11), but that rate is not statistically significant (p = 0.25) during 2013-

314   2019 (Figure S1). Based on these reports of smaller and variable trends, we assume

315   that the trend in regional background ozone in the North China Plain made only a

316   minor contribution to the relatively larger ozone trend observed at the PKUERS site

317   (+2.3 ± 1.2 ppbv yr^{-1}, r^2=0.66, p = 0.001). We thus surmise that the increase in O$_3$ at

318   the PKUERS site was mainly due to "local" photochemistry driven by emissions of

319   ozone precursors from the central urban and surrounding suburban areas of Beijing.

320   **3.2 Trend of gaseous precursors**

321   This increase in ozone concentrations is opposite to the decreasing trend of its

322   precursors, including VOCs, CO and NOx (Figure 5). The overall change of the total

323   OH loss rate due to VOCs (VOC reactivity) was -0.36 s^{-1} (-6.0%) yr^{-1}. For

324   anthropogenic VOCs, the highest reactivity was generally contributed by alkene

325   species, with an average value over the eleven years of 2.00 ± 0.43 s^{-1}, followed by

326   aromatics and alkanes, with average reactivities of 1.51 ± 0.74 s^{-1} and 0.92 ± 0.60 s^{-1},

327   respectively. Thus, the alkenes and aromatics are more important for O$_3$ production

328   than are alkanes. The trends for alkenes, aromatics, and alkanes were a decrease of

329   0.14 s^{-1} (7.1%), 0.12 s^{-1} (7.9%), and 0.065s^{-1} (7.0%) yr^{-1}, respectively, indicating that

330   alkenes and aromatics also played the dominant role in the reduction of anthropogenic

331   VOC reactivity. The rate of decrease in VOCs at PKUERS site is similar to that

332   reported for Los Angeles by Warneke et al. and Pollack et al. (7.3-7.5% yr^{-1} over 50

333   years) (Warneke et al., 2012;Pollack et al., 2013). The decrease in anthropogenic

334   VOCs in Los Angeles was predominantly attributed to decreasing emissions from

335   motor vehicles due to increasingly strict emissions standards. Similarly, a previous

336   study at the PKUERS site indicated that the decreasing anthropogenic VOC was

337   mainly attributed to the reduction of gasoline evaporation and vehicular exhaust under

338   the implementation of stricter emissions standards for new vehicles and specific

339   control measures for in-use vehicles (Wang et al., 2015a). For naturally emitted

340   VOCs, mainly isoprene, the OH reactivity had little trend with large fluctuations, as

341   the emissions of plants vary greatly with temperature and light intensity. Therefore,

342   the decrease in total VOCs reactivity was dominated by the decrease in anthropogenic

343   VOCs. Similarly, CO, which is mainly contributed by anthropogenic emissions,

344   decreased rapidly (9.3% yr^{-1}) during 2006–2016.

345   NOx data in 2005 were not available. Therefore, the trend of NOx during 2006-

346   2016 was analyzed. Daytime concentrations of NOx at the PKUER site also decreased

347   significantly from 2006 to 2016 (Figure 5), with a slope (excluding 2008, which had a

348   much lower NOx concentration due to enhanced emission controls implemented during

349   the Olympic Games) of -1.48 ppbv yr^{-1} (−5.5% yr^{-1}, $r^2 = 0.81$). The decrease in NOx

350   was mainly due to the reduction in vehicle exhaust and coal combustion (Zhao et al.,

351   2013). The decrease in NOx was significantly faster than that found in Los Angeles by

352   Pollack et al. (2.6% yr^{-1} over 50 years) (Pollack et al., 2013). In contrast to Beijing, Los

353   Angeles O_3 concentrations have continuously decreased from 1980 to 2010 (Parrish et

354   al., 2016). The ratio of the rates of decrease of VOCs and NOx in Los Angeles (2.9) is

355   significantly greater than unity and larger than that at the PKUER site (1.1), which

356   possibly can be a contributing cause of the opposite trends of ozone in the two regions.

357   It worth noting that the precursor concentrations in 2008, the Olympic Games year,

358   were particularly low, but that ozone was nevertheless on the regression line. The

359   monthly average ratio of VOC reactivity to NOx concentration in 2008 is 0.28 s^{-1} ppbv^{-}

360   ^{1}, higher than the average ratio of VOC reactivity to NOx concentration during 2006-

361   2016 (0.24 s^{-1} ppbv^{-1}). The adverse reduction ratio of VOC to NOx is the main cause of

362   inefficient reduction in O_3 level in 2008, which is consistent with the study of Chou et

363   al. (2011).

364   Since 2013, under the implementation of the Action Plan on Air Pollution

365   Prevention and Control (http://www.gov.cn/zwgk/2013-09/12/content_2486773.htm),

366   more stringent emission control measures were implemented to restrict industrial and

367   vehicle emission. As a result, there are indications that both VOCs and NOx decreased

368   faster over the 2013 to 2016 period: 0.81 s^{-1} yr^{-1} (16% yr^{-1}, $r^2 = 0.71$) and 1.94 ppbv yr^{-1}

369   (9.3% yr^{-1}, $r^2 = 0.78$) for VOC reactivity and NOx, respectively. This could be the

370   cause of the decline in O_3 concentrations from 2014 to 2016.

371   **3.3 Trend of particulate matter**

372   From 2009 to 2016, $PM_{2.5}$ concentrations declined rapidly, achieving the air

373   quality standard of China (35 $\mu g/m^3$) in 2016 (Figure 6). Since 2000, Beijing had

374   implemented 16 phases' air pollution control measures, mainly including the

375   controlling of industry, motor vehicle, coal combustion and fugitive dust pollution,

376   which was effective for the reduction in $PM_{2.5}$ (Lang et al., 2017). Especially the

377   strengthening of the reduction in coal combustion, which was gradually replaced by

378   natural gas since 2004, favored improved visibility in Beijing (Zhao et al., 2011).

379   As shown in Figure 6, from 2006 to 2016 AOD decreased at a rate of 9.3% yr^{-1}.

380   The correlation between AOD and $PM_{2.5}$ can be determined from the observations of

381    $PM_{2.5}$ and AOD in August during 2009-2016 at the PKUERS site (Figure 7). AOD

382   and $PM_{2.5}$ are linearly correlated with a correlation coefficient of +0.74. This result

383   indicates that the decrease in $PM_{2.5}$ was the primary cause of the reduction in AOD. In

384   addition to $PM_{2.5}$, relative humidity also has an important effect on AOD. The

385   decrease in relative humidity during 2006-2016 (Figure 4) would reduce the

386   hygroscopic growth of aerosol, leading to a weakened extinction effect of particulate

387   matter on solar radiation (Qu et al., 2015). It is worth noting that although $PM_{2.5}$ in

388   2011 was lower than that in 2010, AOD in 2011 was higher than that in 2010 (Figure

389   6). For one reason, the relative humidity in 2011 was higher. Additionally, the aerosol

390   type, atmospheric boundary layer height and the vertical structure of aerosol

391   distribution also affects the dependence of AOD on PM$_{2.5}$ (Zheng et al., 2017),

392   probably contributing to the scatter about the AOD versus PM$_{2.5}$ relationship shown in

393   Figure 7.

394   Monthly mean AE (380/550 nm) in August showed no overall trend during 2006-

395   2016 (Figure 8). The monthly AE means were between 0.87 and 1.2, suggesting that

396   the size-distribution of aerosol was generally stable during this period. Monthly mean

397   SSA (440 nm) in August showed an upward trend of +0.004 yr^{-1} (+0.45% yr^{-1}, p =

398   0.001) during 2006-2016 (Figure 8), indicating the proportion of the light-absorbing

399   component of aerosols (e.g. black carbon) has decreased, due to the stringent and

400   effective controls on the burning of biomass/biofuel and coal (Ni et al., 2014;Cheng et

401   al., 2013). This result is consistent with the studies of Lang et al. and Wang et al.,

402   which indicated that black carbon in China's mega cities has decreased rapidly over

403   the past decade (Wang et al., 2016b;Lang et al., 2017).

3.4 Trend of photolysis frequencies

405   The influence of solar radiation on O$_3$ photochemistry can be described by

406   actinic flux (or photolysis frequencies). We chose j(NO$_2$) as a representative

407   photolysis frequency to analyze the trend of actinic flux. Wang et al (2019) studied the

408   quantitative relationship between j(NO$_2$) and AOD at the PKUERS site, and found

409   that j(NO$_2$) and AOD showed a clear nonlinear negative correlation at a given SZA,

410   with slopes ranging from -1.3 to -3.2 × 10^{-3} s^{-1} at AOD < 0.7, indicating a significant

411   extinction effect of AOD on actinic flux near the ground.

412   The j(NO$_2$) calculated by the TUV model under clear-sky conditions shows an

413   upward trend of 3.6% yr^{-1} from 2005 to 2016 and agrees well with the 5 years of

414   observed values from 2011 to 2016 (Figure 6). According to sensitivity analysis of

415   TUV, the decrease in AOD plays a dominant role in the j(NO$_2$) increase, contributing

416   about 80% of the total. Additionally, the increase in SSA also contributes significantly

417   to j(NO$_2$) increase, contributing about 17%.

418   In addition to aerosol optical properties, the photolysis frequency in the planetary

419 boundary layer is affected by other factors, including cloud extinction, ground

420 reflection, absorption by gases such as O_3, and Rayleigh scattering by gases. The

421 ground reflection is relatively stable for different years in the same city with stable

422 ground covering. The change in Rayleigh scattering of gases and absorption of NO_2,

423 SO_2 and HCHO plays a negligible role in the variation in photolysis frequencies

424 according to sensitivity analysis of TUV model. This is consistent with the results of

425 Barnard et al. (Barnard et al., 2004). As shown in Figure 9, the total ozone column

426 fluctuated between 285-307 DU without a significant overall trend. The magnitude of

427 total ozone column variation (22 DU) can change $j(O^1D)$ by about 10%, but plays a

428 negligible role in changing other photolysis frequencies according to sensitivity

429 analysis using the TUV model. The cloud optical thickness (COT) for most years was

430 relatively stable, ranging from 6 to 8, but in 2005, 2012 and 2015 COT was

431 significantly larger (Figure 9). As there was no significant trend of COT, we surmised

432 that the light-extinction effect of clouds did not play a key role in determining the

433 trend of photolysis frequencies.

434 **3.5 Combined effect of changes in ozone precursors and aerosols on ozone**

435 **production**

436 We investigated the overall effect of the changes in VOCs, NOx, photolysis

437 frequency, and aerosol uptake of HO_2 on ozone production rate using the chemical

438 box model. We focus on the period during 2006-2016 due to the lack of NOx data in

439 2005. By testing the response of $P(O_3)$ as calculated from Equation E1 to the changes

440 of VOCs and NOx concentrations (Figure 10), we concluded that photochemical

441 environment of the PKUERS site was, on average, in the VOC-limited regime. This

442 result is consistent with previous studies (Zhang et al., 2014;Chou et al., 2011). Under

443 this condition, the long-term decrease in VOCs in Beijing has contributed to a

444 decrease in $P(O_3)$, while the decrease in NOx has tended to increase $P(O_3)$. As shown

445 in Figure 11, when the increase in photolysis frequencies and aerosol uptake of HO_2

446 were not included in the calculation, the simulated daytime average $P(O_3)$ decreased

447 slightly at a rate of 1.1% yr^{-1}. This indicates that the ratio of the rates of decrease of

448 VOCs and NOx (about 1.1) is nearly inefficient in reducing ozone production in

449 Beijing. However, when the increase in photolysis frequencies was included in the

450 model calculation, the calculated daytime average P(O$_3$) showed an increasing trend

451 of 2.2% yr^{-1}. This result indicates that the increase in photolysis frequencies more

452 than compensated for the downward trend of O$_3$ production driven by decreased

453 VOCs and NOx, leading to increasing O$_3$ production through the decade. The

454 photochemical box model calculations indicate that the increase in photolysis

455 frequencies has two major impacts on P(O$_3$) - an increase in primary production of

456 OH through accelerated photolysis of O$_3$, HONO, HCHO and other carbonyl

457 compounds, and an accelerated radical recycling of OH as VOCs are oxidized. As

458 particulate matter has decreased and photolysis frequencies correspondingly have

459 increased, a more rapidly decreasing rate of the VOC to NOx ratio is required to

460 achieve a significant reduction in O$_3$ in the future.

461 The simulated P(O$_3$) in the afternoon hour (12:00-15:00) when ozone production

462 is active and HOx levels are high increased at a rate of 1.3% yr^{-1}, which is lower than

463 the increasing rate of daytime average P(O$_3$) (2.2% yr^{-1}) (Figure S2). Hollaway et al.

464 (2019) show that the impacts of aerosols on the summertime photolysis of NO$_2$ and

465 ozone at surface in Beijing are important before 11:00 am and after 3:00 pm but very

466 limited in afternoon hours due to smaller SZA and lower light absorption of aerosol

467 (i.e. higher SSA) in the afternoon. However, the diurnal variation of simulated P(O$_3$)

468 in this study indicates that the influence of aerosols on P(O$_3$) is still significant in the

469 afternoon, leading to average P(O$_3$) decreased by ~18% (Figure S3), which is slightly

470 lower than the mean daytime decrease (26%). This is because the average AOD in the

471 afternoon (1.4) is significantly higher than that before 11:00 am (0.94) and after 3:00

472 pm (1.1) despite the smaller SZA and higher SSA.

473

474 When we include heterogeneous uptake of HO$_2$ in the model, the calculated

475 P(O$_3$) increases at a faster rate of 2.9% yr^{-1} due to the overall reduced aerosol surface

476 concentration (S_a), which reduces heterogeneous uptake of HO_2 (Figure 11). This

477 result indicates that the effect of heterogeneous uptake of HO_2 contributed roughly

478 0.7% yr^{-1} to the $P(O_3)$ increase. Hence, our result indicates that the increase in

479 photolysis rates due to PM decrease plays a more important role than the decrease in

480 heterogeneous uptake of HO_2 by aerosols in accelerating ozone production in Beijing.

481 Previous measurements indicate that the uptake coefficient varies widely from 0.003

482 to 0.5 with a strong dependence on the aerosol concentration of transition metal ions

483 such as Cu(II) (Zou et al., 2019;Taketani et al., 2008;Lakey et al., 2015;Matthews et

484 al., 2014;Lakey et al., 2016). This strong dependence on aerosol composition implies

485 that a single assumed value for $\gamma_{HO2} = 0.2$ has large uncertainty. $\gamma_{HO2} = 0.2$ used in our

486 simulation is likely an overestimate of the effect of heterogeneous uptake of HO_2 on

487 ozone production rate at PKUERS site.

488 A few heterogeneous chemical reactions of nitrogen oxides are thought to be

489 potential influential factors of ozone production. For example, the heterogeneous

490 uptake of NO_2 to produce HNO_3 and HONO, and the heterogeneous uptake of NO_3

491 and N_2O_5 to produce HNO_3. Our simulation indicates that the reduced heterogeneous

492 uptake of NOx caused $P(O_3)$ to increase by only ~2.2 % during 2006-2016. Li et al.

493 (2019a) also reported that the effect of heterogeneous uptake of nitrogen oxides on

494 ozone is very small under VOC-limited and summertime conditions in North China

495 Plain. Our simulated result in summertime Beijing, where VOC-limited

496 photochemistry dominates, is consistent with the result of Li et al. (2019a).

497 In summertime, PM in the Beijing urban area is mainly formed by the secondary

498 conversion of gaseous precursors (Han et al., 2015;Guo et al., 2014), indicating that

499 VOCs and NOx are not only the precursors of ozone, but also the main precursors of

500 PM in this urban area. In addition, observations in Beijing have shown that the

501 secondary components of PM, including secondary organic matter, ammonium sulfate

502 and ammonium nitrate, dominate the light extinction of PM (Han et al., 2014;Han et al.,

503 2017;Wang et al., 2015b). As a result, reductions of VOCs and NOx are expected to

504 lead to a decrease in secondary PM formation, and thus to further enhancement in solar

radiation (or actinic flux). Therefore, in order to reduce ozone effectively, the contribution of VOCs and NOx to secondary PM formation and their effect on solar radiation must be comprehensively considered. However, the summertime formation of PM is quite complex; the conversion efficiency of gaseous precursors to aerosols and the resulting influence on ozone production is a research area that requires further study.

3.6 Additional considerations

One limitation of this study is that the photochemical box model is constrained by surface observations, and hence may not accurately represent some aspects of the photochemistry through the full depth of the planetary boundary layer over Beijing. Here we briefly consider several of these aspects: (1) The treatment of ozone and VOC and NOx precursor concentrations likely are accurately represented, because rapid daytime vertical mixing ensures that there is only a small vertical gradient in the concentrations of these relatively long-lived species. (2) In daytime, the HONO lifetime is so short that it may be largely confined to near the surface, where it has surface sources (heterogeneous reaction of H_2O and NO_2 and emissions on surfaces). Therefore, the estimated HONO based on near-surface NO_2 concentrations may overestimate average boundary layer HONO concentrations; however, in this study the influence of HONO on the calculation is relatively small, so this is not a large source of error. (3) The model is constrained by surface measurements of photolysis frequencies, but these surface measurements do not accurately quantify the actinic flux throughout the boundary layer. Figure 12 presents the vertical profiles of $j(NO_2)$ simulated by the TUV model for aerosol properties representative of Beijing. A thick layer of aerosol effectively reduces radiation at the bottom of the layer, but not at the top, where radiation may be enhanced due to upward scattering from the aerosol below (Dickerson et al., 1997;Jacobson, 1998). Overall, vertical average $j(NO_2)$ increased by 32% from 2006 to 2016, which is comparable to the surface increase (36%). These simulations indicate that the increased trend of $j(NO_2)$ derived from surface observations do approximate the trend through the entire boundary layer.

However, there is a shift in the vertical profile of $j(NO_2)$ that is important. The crossing point between $j(NO_2)$ profile of 2006 and zero AOD profile is above PBL, while in 2016 the $j(NO_2)$ profile crosses the zero AOD profile within the PBL. This means that as the AOD is reduced further, changes in the vertical average $j(NO_2)$ will be limited, since increases in $j(NO_2)$ near the top of the PBL will compensate for decreases near the surface. Additionally, this also denotes that the role of $PM_{2.5}$ may be more important under condition like 2006, but will be limited under condition like 2016 when there is offsetting effect for PBL ozone by vertical mixing caused by larger ozone vertical gradient (Gao et al., 2020).

Quantitative studies suggested that, the impact of aerosols via affecting photolysis rates on net ozone production (Cai, 2013;Wang et al., 2019;Castro et al., 2001) is more than on surface ozone concentrations (Jacobson, 1998;Li et al., 2011a;Li et al., 2011b;Wang et al., 2016a). Moreover, several different transport model studies (Xing et al., 2017;Li et al., 2018a;Li et al., 2019c) also show that the impact of $PM_{2.5}$ on summer surface ozone concentrations is not important, which is different from the relatively large change of net ozone production in this study. There are several possible causes of this difference: (1) The net ozone production characterizes the local ozone production level but can't completely represent ozone concentrations that are also influenced by regional transport of ozone (Streets et al., 2007;Wang et al., 2020;Moghani et al., 2018). (2) The light-extinction effect of aerosols lead to ozone at the top of PBL being entrained by turbulence to the surface to partly counteract the reduction in surface ozone photochemical production induced by aerosols (Gao et al., 2020). (3) AOD decreased by 58% in Beijing in this study, which is higher than that of regional AOD decrease in eastern China (20%) (Li et al., 2019b). (4) The photolysis rates in this study are determined using the observed AOD SSA, and confirmed by ground-level measurements of photolysis frequencies, while photolysis rates are determined using online algorithm in other transport model studies. The different calculation procedures also contribute to the different results between our study and other transport model studies.

4 Conclusion

During the past decade, China has devoted very substantial resources to improving the environment. These efforts have improved atmospheric particulate matter loading, but ambient ozone levels have continued to increase. Based on the long-term measurements at a representative site in Beijing, we explored the factors driving the increase in ozone production. Consistent with the implementation of stringent emission control measures, concentrations of $PM_{2.5}$ and ozone precursors (VOCs and NOx) decreased rapidly, but in contrast surface O_3 and Ox concentrations increased. This investigation finds that the primary cause of the O_3 increase is that decreasing PM concentrations led to an increase in actinic flux, which in turn increased the photochemical production of ozone. This result indicates that the influence of aerosol on ozone production is important for determining the full manifold of atmospheric effects that result from reducing the emissions of the O_3 and PM precursors.

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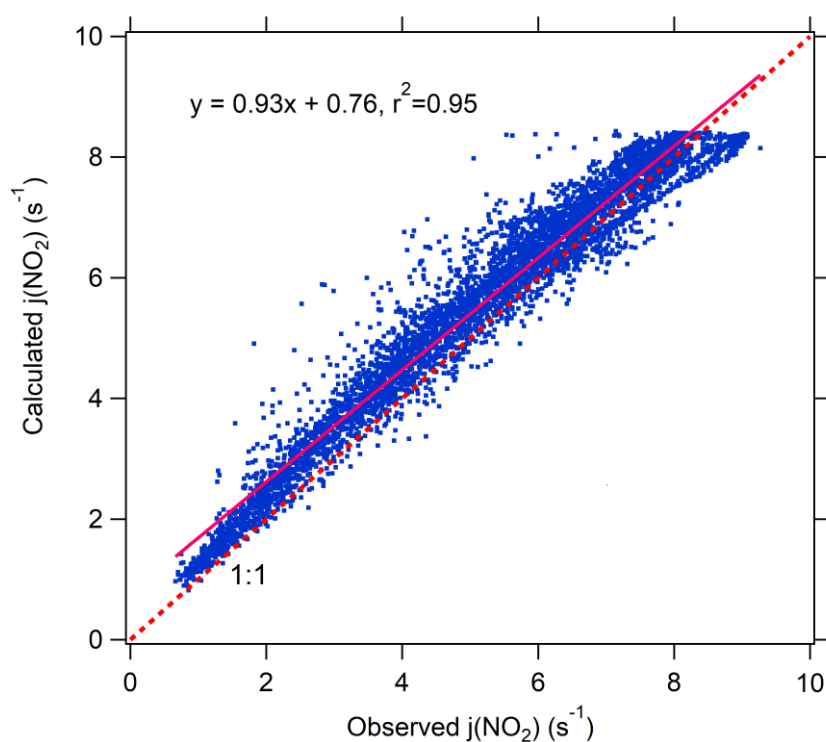
582   Figure 1. Correlation between Observed and calculated j(NO₂) by TUV model in

583   Beijing in summer time during 2012 - 2015.

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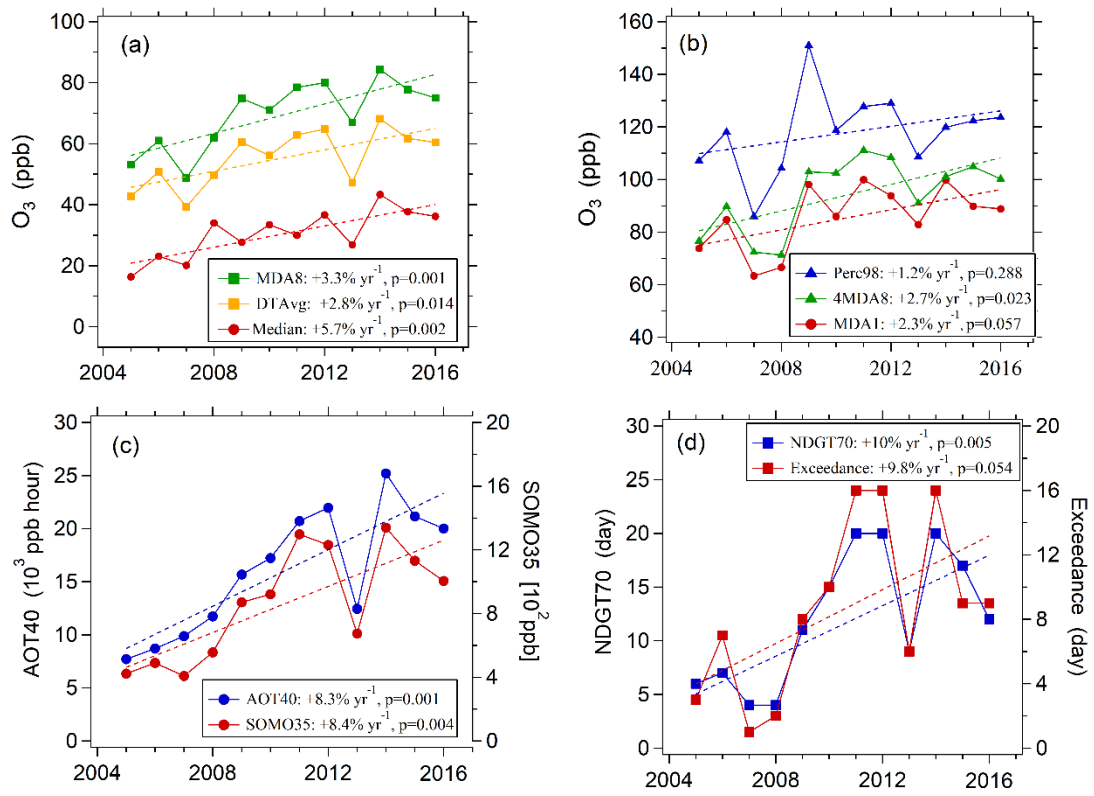
586
587 Figure 2. Variations in multiple O₃ metrics at the PKUERS site in Beijing in August
588 between 2005 and 2016.
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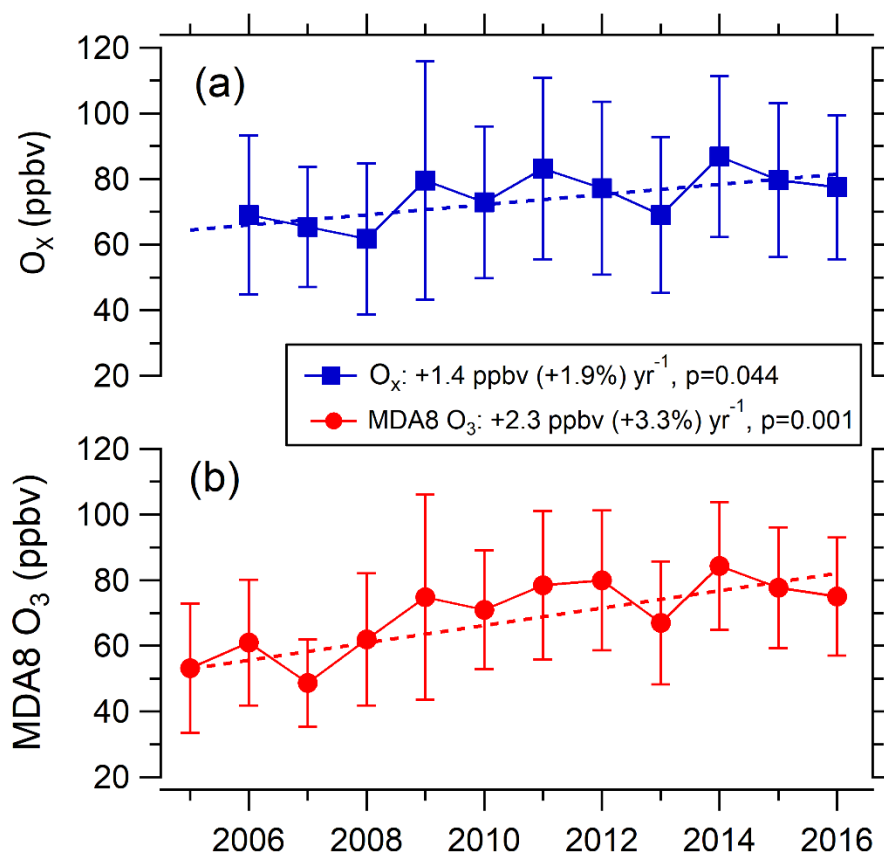
Figure 3. Variations in average MDA8 O_3 and daytime (7:00-19:00) average Ox in

Beijing, August between 2005 and 2016.

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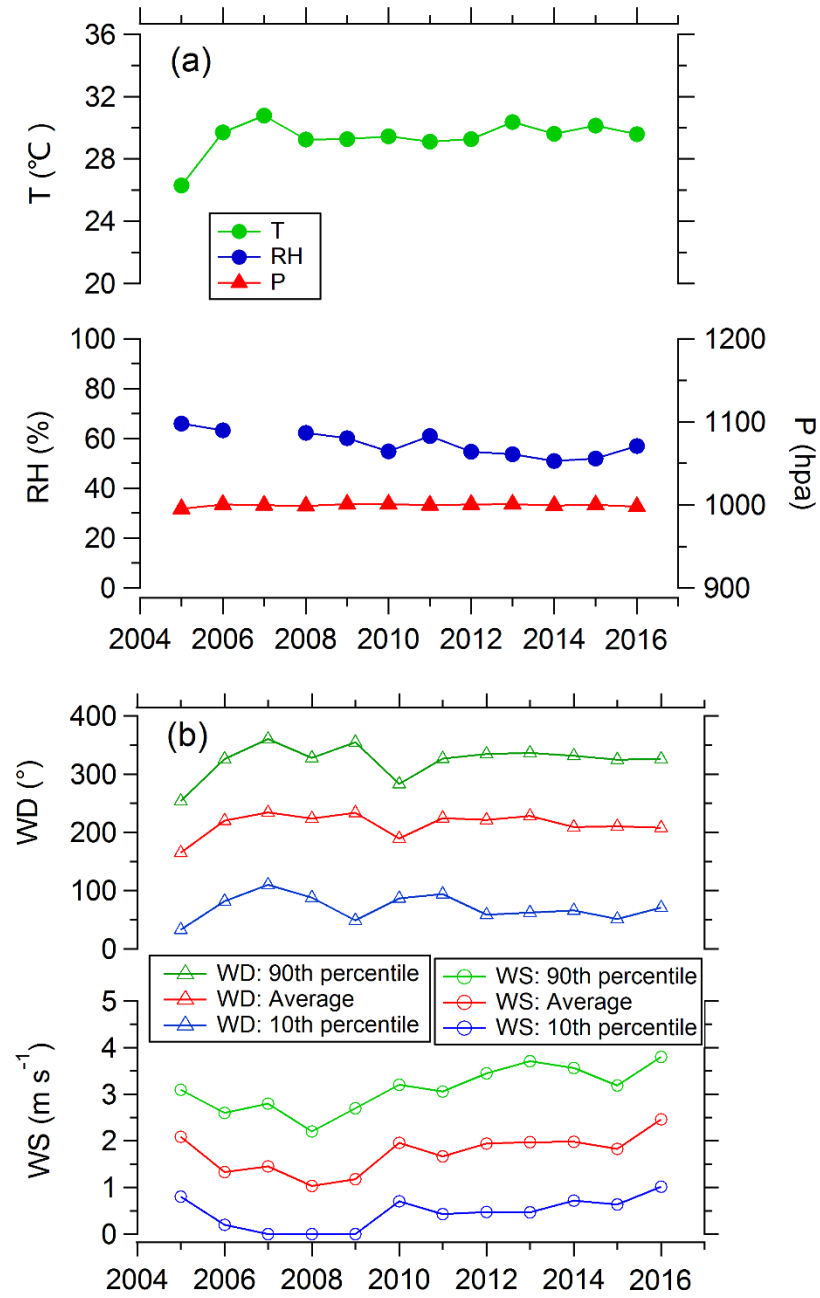
Figure 4. Variations in daytime (7:00-19:00) averages of meteorological conditions

including temperature (T), relative humidity (RH), wind direction (WD) and wind

speed (WS) in Beijing, August during 2005 - 2016.

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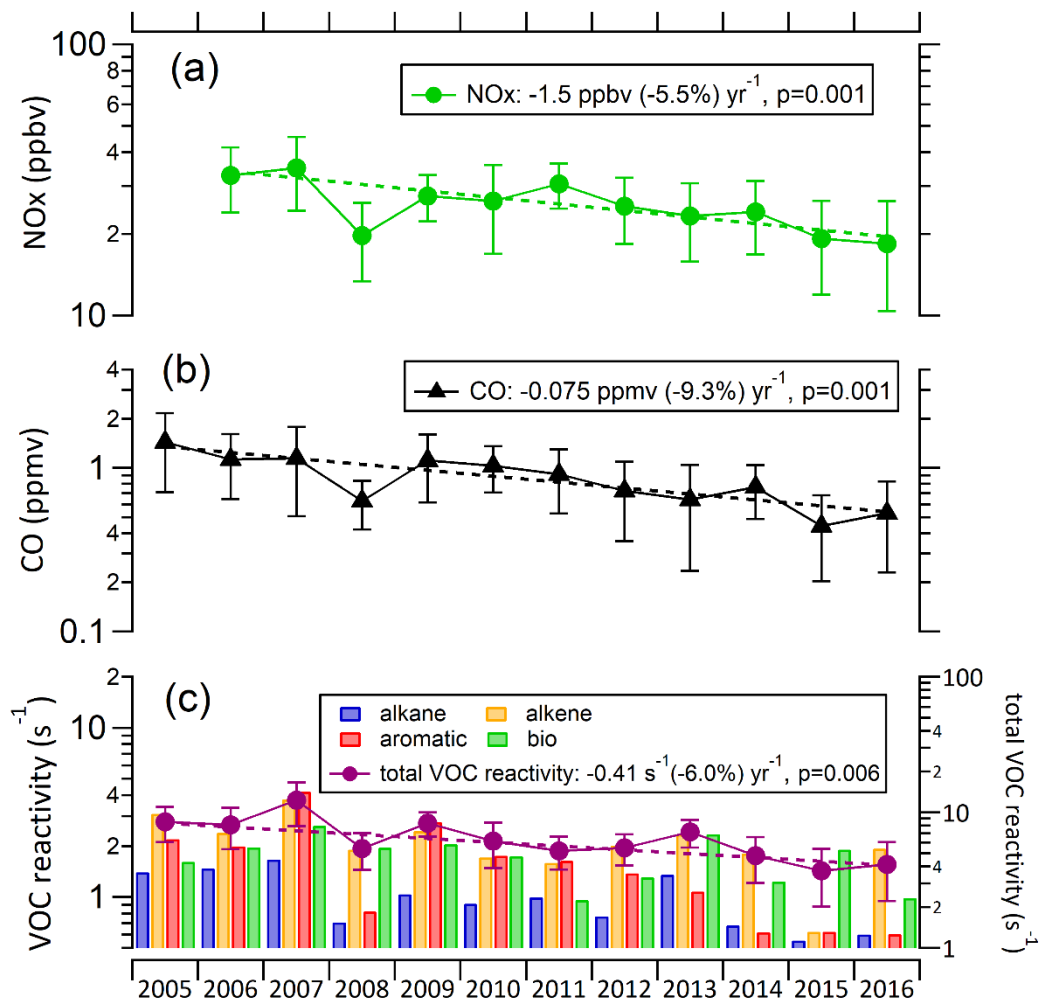
Figure 5. Variations in geometric mean of daytime NOx, CO and VOCs reactivity in

Beijing, August between 2005 and 2016. VOCs reactivity is depicted by reactivity of

each species (left axis) and total VOC reactivity (right axis). On the y-axes, a log-

scale is used.

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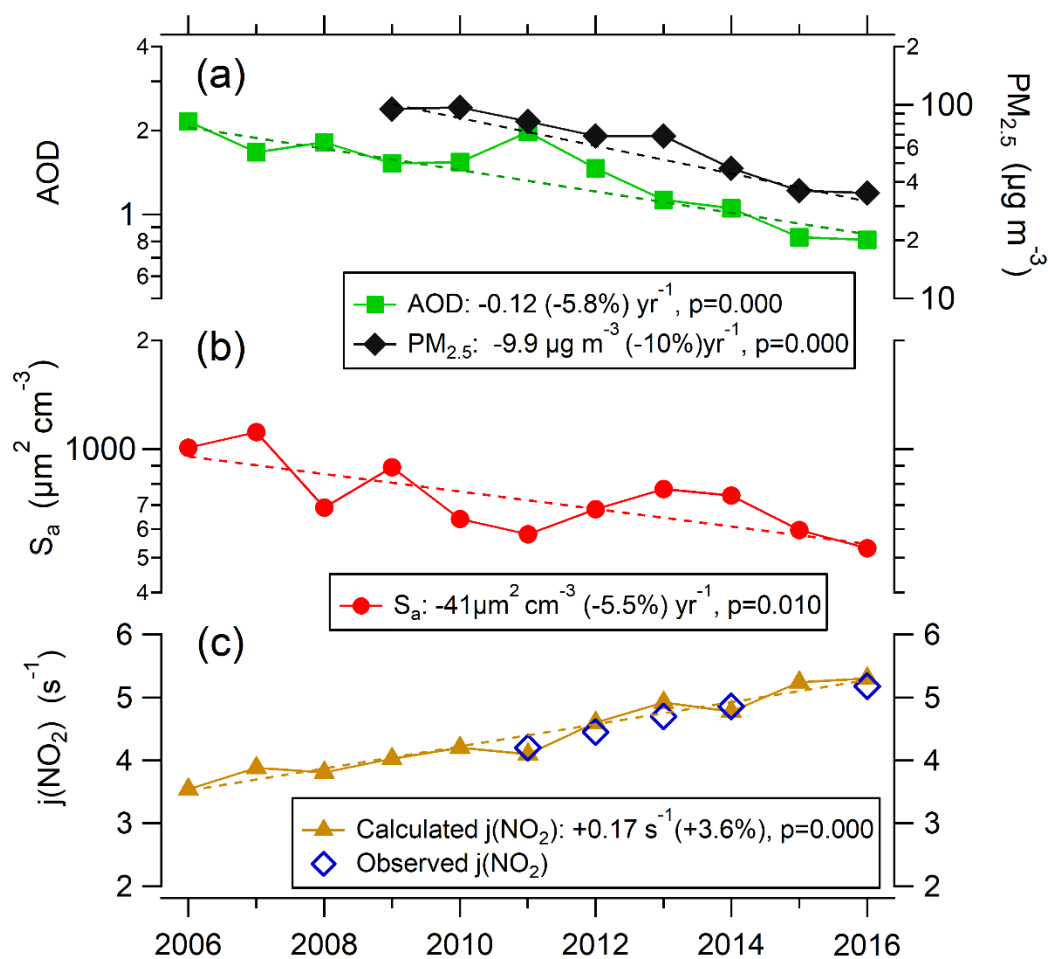
611 Figure 6. Variations in daytime (7:00-19:00) averages of AOD (380 nm), $PM_{2.5}$, S_a,

612 $j(NO_2)$ Calculated $j(NO_2)$ by TUV in Beijing, August between 2006 and 2016. AOD

613 and $j(NO_2)$ are both corresponding to cloudless weather. On the y-axes, a log-scale is

614 used for $PM_{2.5}$, AOD and S_a and a linear scale is used for $j(NO_2)$.

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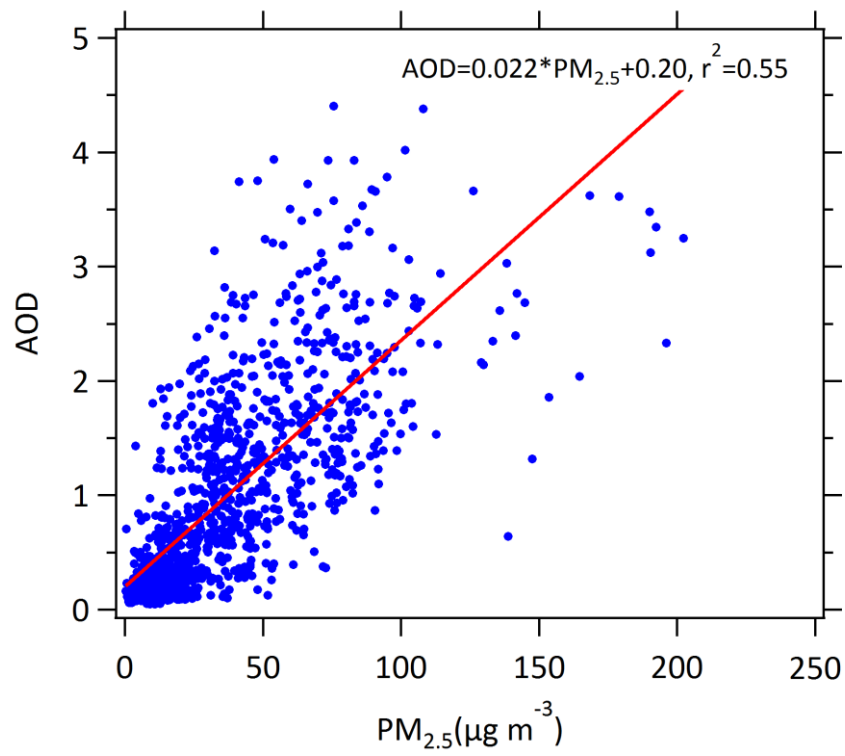
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618   Figure 7. Correlation between AOD and PM2.5 in Beijing, summertime during 2009 -

619   2016.

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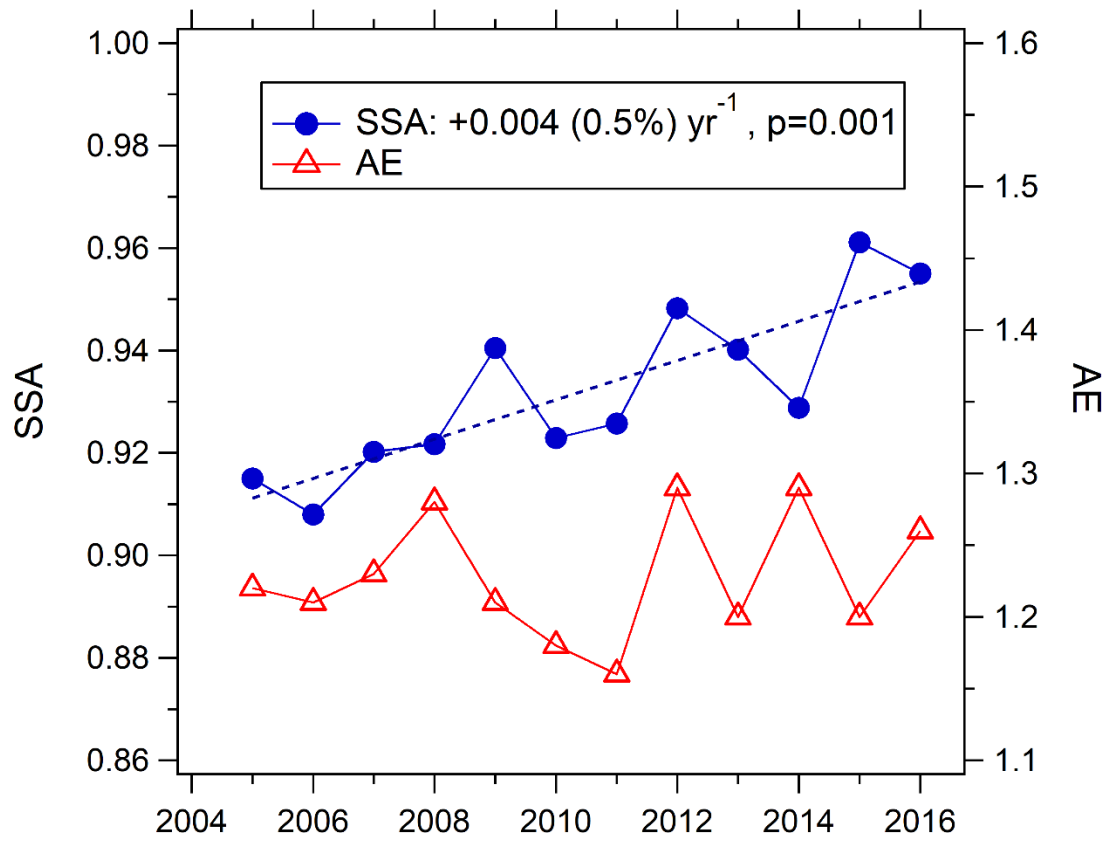
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622 Figure 8. Variation in monthly mean single scattering albedo (SSA) and Ångström
623 exponent (AE) in Beijing for the month of August during 2005 - 2016.
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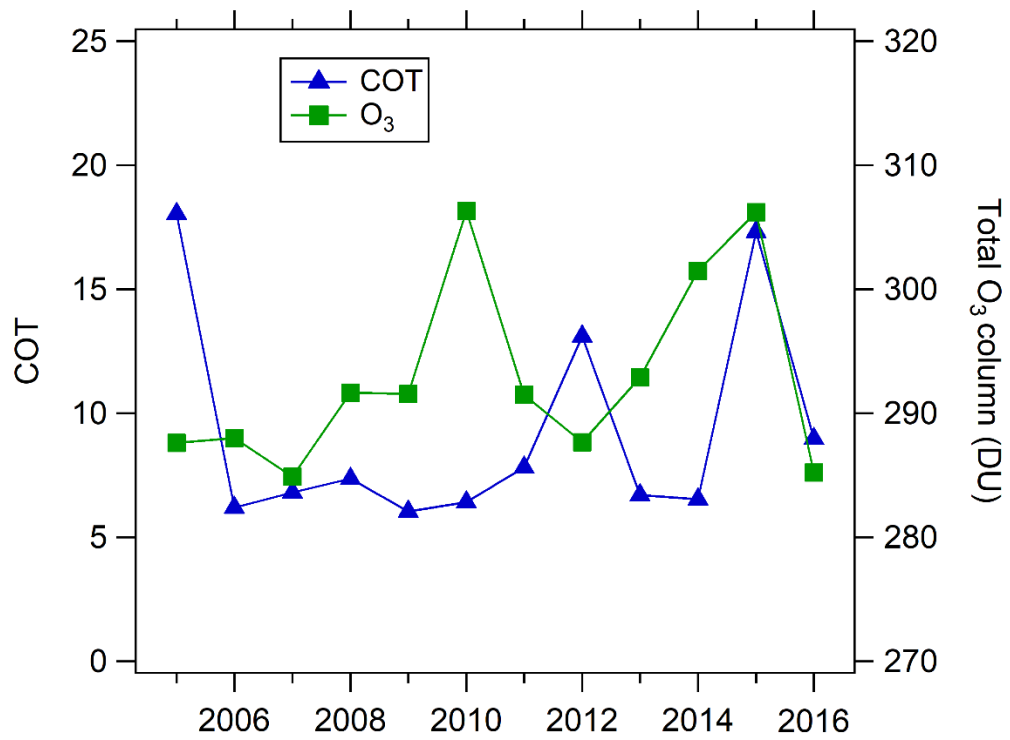
628   Figure 9. Variations in mean total ozone column and cloud optical thickness (COT) in

629   Beijing for the month of August during 2005 - 2016.

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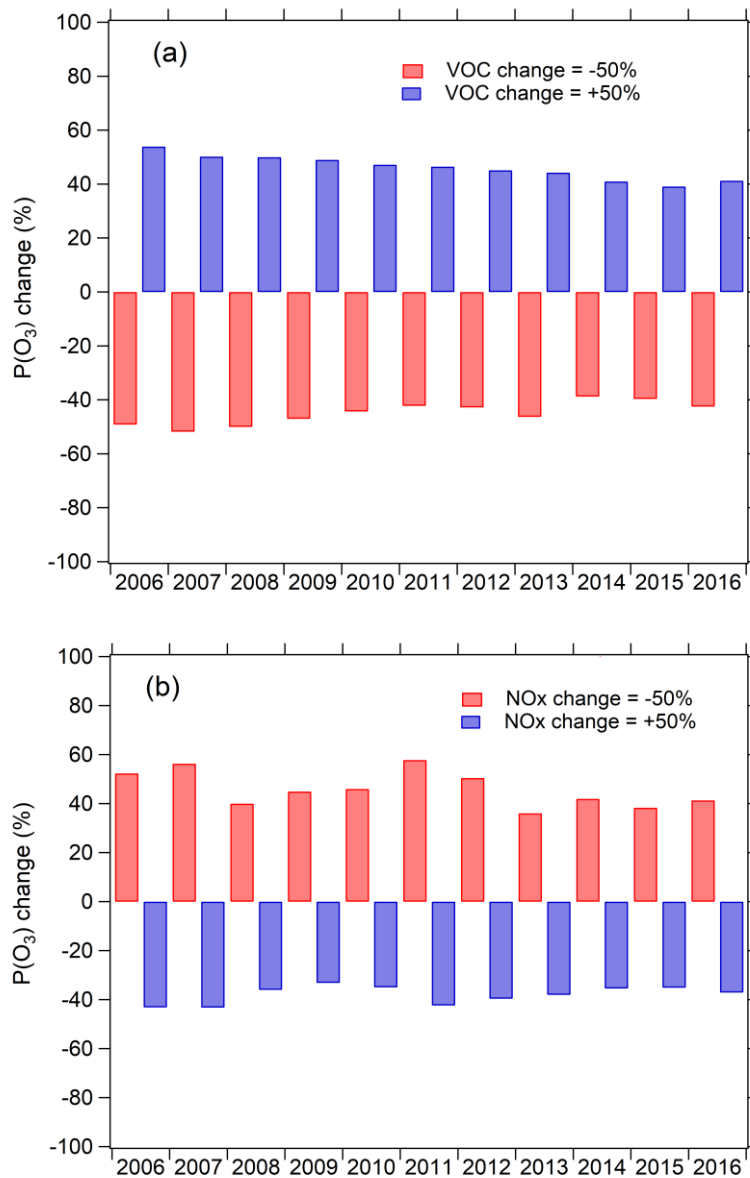
Figure 10. Sensitivity of monthly daytime mean P(O₃) to VOCs and NOx simulated by box model during 2006 - 2016. VOCs and NOx is increased by 50% or decreased by 50% to test the fractional change of monthly daytime mean P(O₃).

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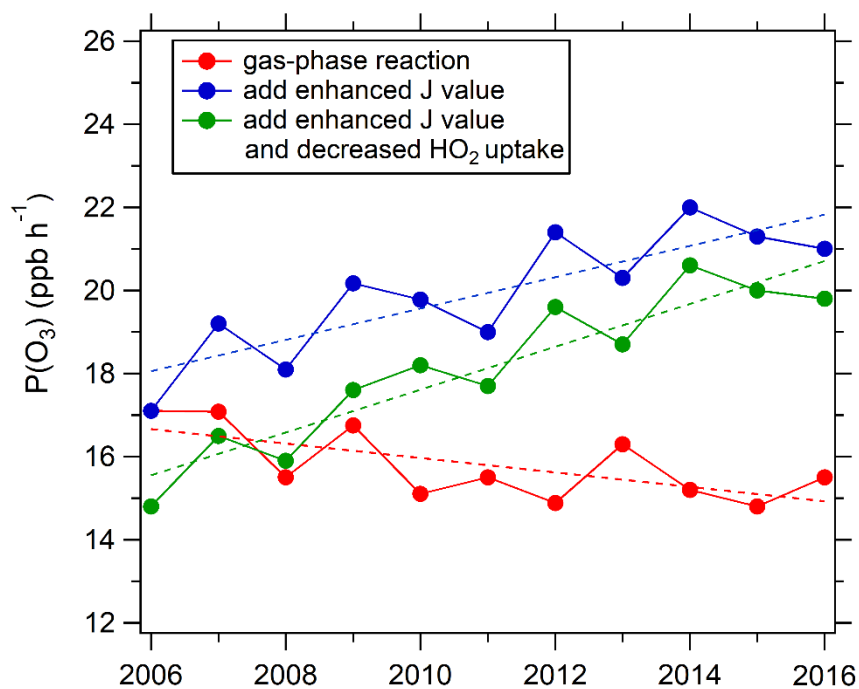
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640 Figure 11. Trend of monthly daytime mean P(O₃) simulated by the chemical box

641 model. Red dots: Only the gas-phase reactions are considered in the box model

642 constrained by observed photolysis frequencies from 2006 for all eleven years. Blue

643 dots: the box model as above, but constrained by the photolysis frequencies derived

644 for each year. Green dots: the box model constrained by the photolysis frequencies

645 derived for each year with the changing aerosol uptake of HO₂ also considered.

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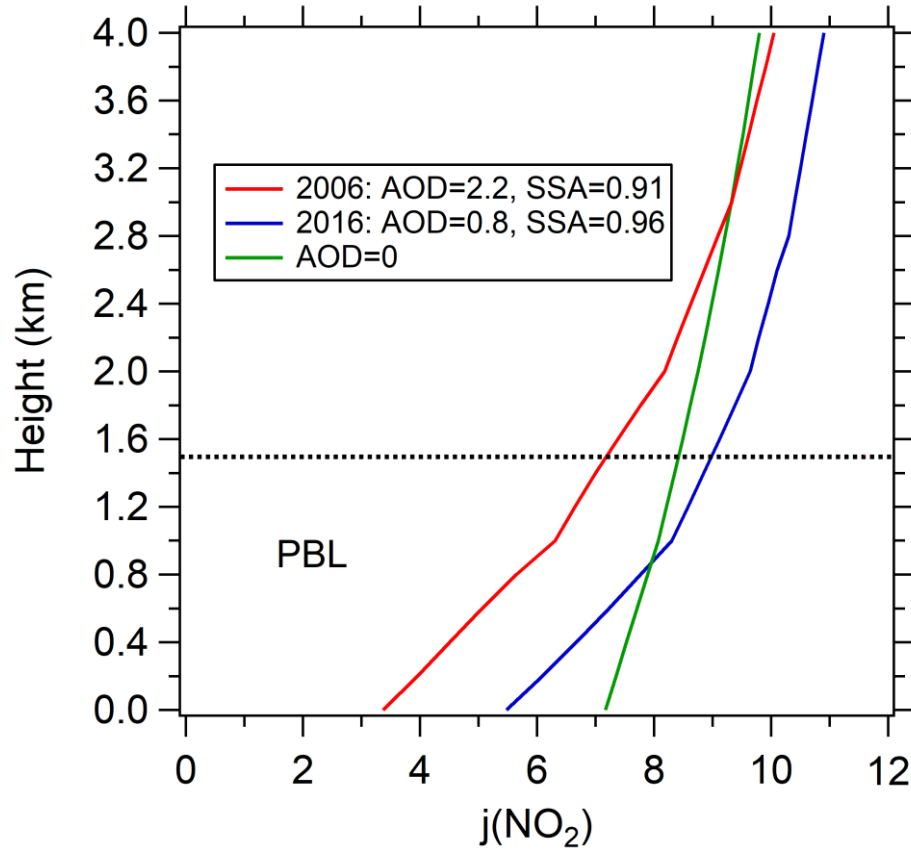
Figure 12. Vertical profiles of j(NO$_2$) simulated by the TUV model in Beijing. Three scenarios are simulated: The model parameters are: (1) AOD=2.2, SSA=0.91 in August 2006; (2) AOD=0.8, SSA=0.96 in August 2016; (3) AOD=0. The daytime average SZA=53°is used for all simulations. Dotted line represent the top of boundary layer.

654   Table 1. Instruments deployed in the measurement undertaken in August during 2005 -

655   2016 and used for data analysis.

Parameters	Measurement technique	Time resolution	Detection limit	Accuracy
Photolysis frequencies	Spectroradiometer	10 s	/	± 10%
O_3	UV photometry	60 s	0.5 ppbv	± 5%
NO	Chemiluminescence	60 s	60 pptv	± 20%
NO_2	Chemiluminescence	60 s	300 pptv	± 20%
CO	IR photometry	60 s	4 ppb	± 5%
SO_2	Pulsed UV fluorescence	60 s	0.1 ppbv	± 5%
HCHO	Hantzsch fluorimetry	60 s	25 pptv	± 5%
C2-C10VOCs	GC-FID/MS	1 h	20-300 pptv	± 15~20%
$PM_{2.5}$	TH-2000	60s	1μg m^{-3}	± 5%
S_a	SMPS	60s	/	±3%
AOD, SSA, AE	CIMEL Sun photometer	5min	0.01	±5%

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658 Table 2. p value of temporal trends for different parameters.

Parameter	Period	r^2	p value	P value <0.01?	P value <0.05?
median	2005-2016	0.63	0.002	yes	yes
perc98	2005-2016	0.11	0.288	no	no
DTAvg	2005-2016	0.47	0.014	no	yes
MDA1	2005-2016	0.32	0.057	no	no
MDA8	2005-2016	0.66	0.001	yes	yes
4MDA8	2005-2016	0.42	0.023	no	yes
AOT40	2005-2016	0.67	0.001	yes	yes
NDGT70	2005-2016	0.56	0.005	yes	yes
SOMO35	2005-2016	0.57	0.004	yes	yes
exceedance	2005-2016	0.32	0.054	no	no
Ox	2005-2016	0.38	0.044	no	yes
CO	2005-2016	0.87	0.001	yes	yes
VOC reactivity	2005-2016	0.52	0.006	yes	yes
NO_X	2006-2016	0.81	0.001	yes	yes
Calculated $j(NO_2)$	2006-2016	0.94	0.000	yes	yes
AOD (380 nm)	2006-2016	0.78	0.000	yes	yes
$PM_{2.5}$	2009-2016	0.93	0.000	yes	yes
Sa	2006-2016	0.51	0.010	yes	yes
SSA	2005-2016	0.70	0.001	yes	yes
AE	2005-2016	0.03	0.593	no	no
COT	2005-2016	0.003	0.875	no	no
Total O_3 column	2005-2016	0.15	0.215	no	no

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671 Table 3. Description of Ozone Metrics used in this study.

categories	metric	definition
general level	median (ppb)	50th percentile of hourly concentrations
	MDA8 (ppb)	daily maximum 8 h average; the mean MDA8 O_3 in August of each year is used in this study.
	DTAvg (ppb)	daytime average ozone is the average of hourly ozone concentrations for the 12 h period from 07:00 to 19:00 local time
extreme level	MDA1 (ppb)	daily maximum 1 h average; the mean MDA1 O_3 in August of each year is used in this study.
	Perc98 (ppb)	98th percentile of hourly concentrations
	4MDA8 (ppb)	4th highest MDA8
ozone exposure	AOT40 (ppb h)	cumulative hourly ozone concentrations of >40 ppb
	SOMO35 (ppb day)	sum of positive differences between MDA8 and a cutoff concentration of 35 ppb
Exceedance days	NDGT70 (day)	total number of days with MDA8 values of >70 ppb
	Exceedance (day)	number of days with the ozone concentration exceeding the Chinese grade II national air quality standard, defined as MDA8 > 160 $\mu g\ m^{-3}$

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Supplementary Information
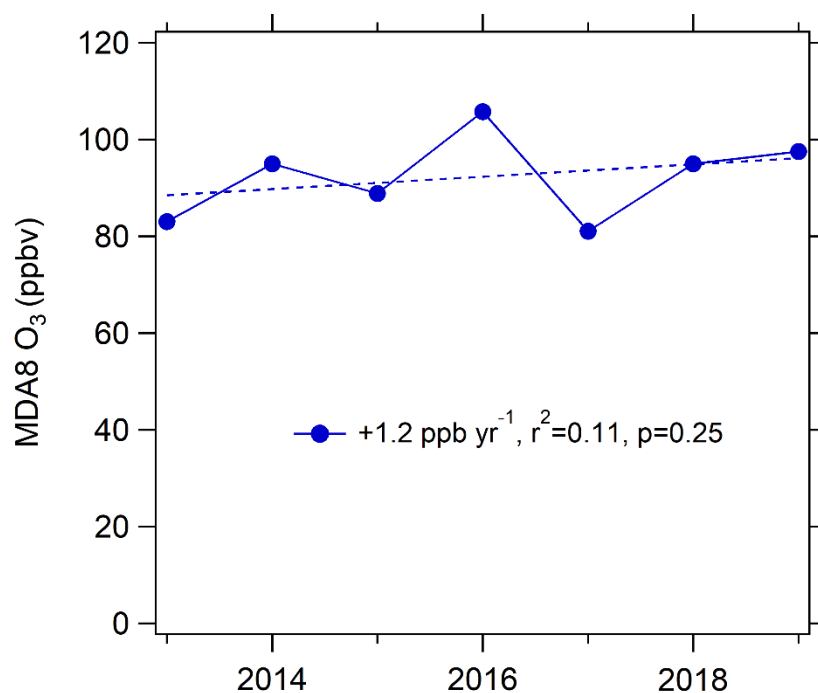
Figure S1. The trend of average MDA8 ozone in Changdao during 2013-2019. These data are acquired from "Blue book on prevention and control of atmospheric ozone pollution in China (in Chinese)" reported by Chinese Society of Environmental Sciences in 2020 (http://www.ep-serve.com/forepart/zxnr_index.do?oid=51478637&tid=26378242).

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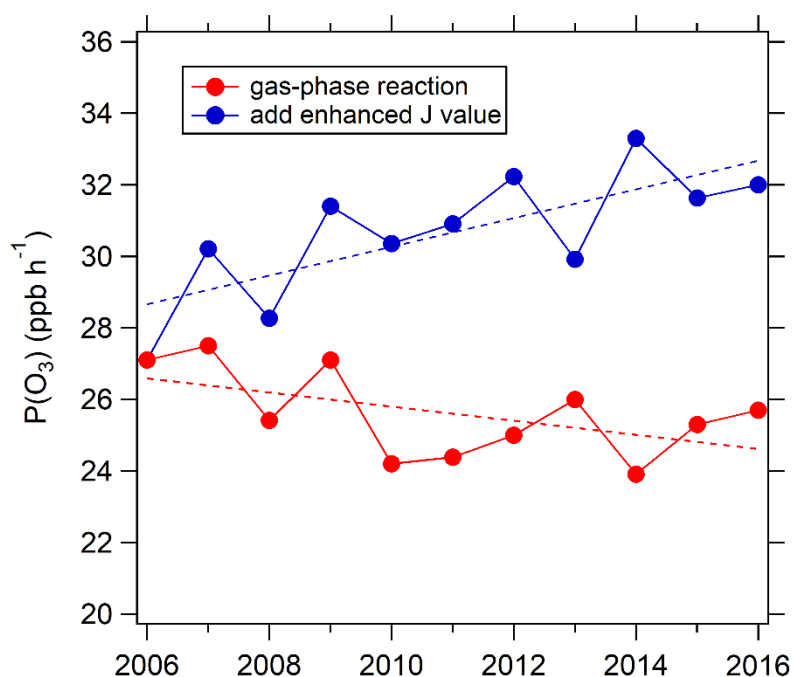
1052 Figure S2. Trend of monthly afternoon (12:00-15:00) mean $P(O_3)$ simulated by the
1053 chemical box model. Red dots: Only the gas-phase reactions are considered in the box
1054 model constrained by observed photolysis frequencies from 2006 for all eleven years.
1055 Blue dots: the box model as above, but constrained by the photolysis frequencies
1056 derived for each year without the changing aerosol uptake of HO_2 considered.

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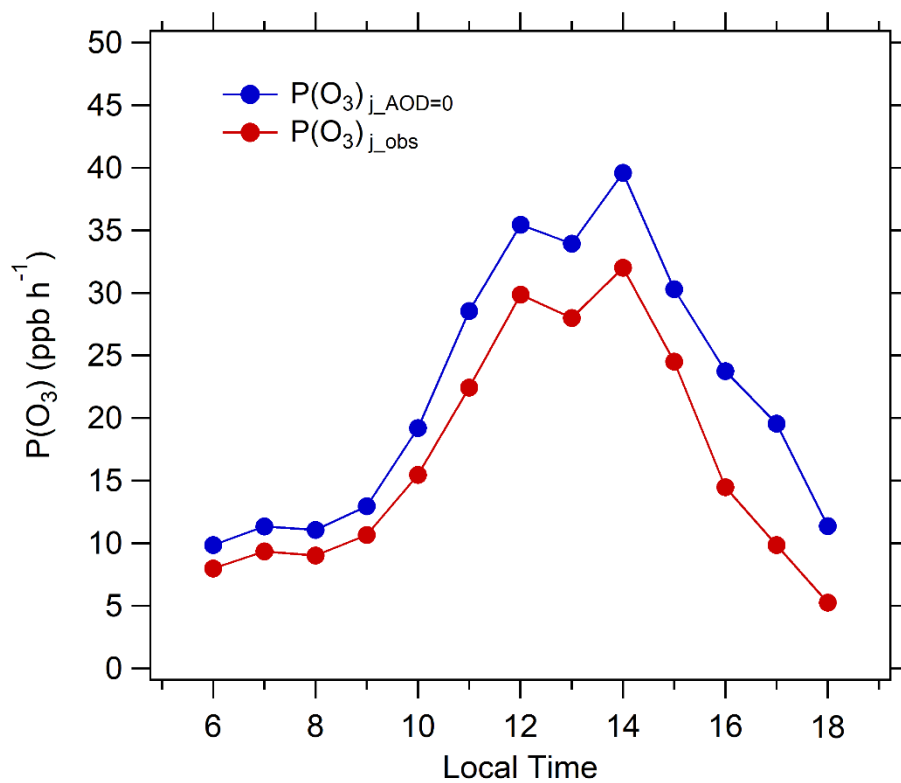
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Figure S3. Diurnal variation of simulated P(O₃) in Beijing in August during 2006-

2016. $P(O_3)_{j\_obs}$ represents ozone production rate under observed photolysis

frequencies; $P(O_3)_{j\_AOD=0}$ represents ozone production rate under calculated

photolysis frequencies when AOD is equal to 0.

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