

1 **The impact of aerosols on photolysis frequencies and ozone**
2 **production in urban Beijing during the four-year period**
3 **2012–2015**

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23 **Abstract**

24 During the period 2012-2015, the photolysis frequencies were measured at the
25 Peking University site (PKUERS), a representative site of urban Beijing. We present a
26 study of the effects of aerosols on two key photolysis frequencies, $j(O^1D)$ and $j(NO_2)$.
27 Both $j(O^1D)$ and $j(NO_2)$ display significant dependence on AOD (380nm) with a
28 nonlinear negative correlation. With the increase in AOD, the slopes of photolysis
29 frequencies vs AOD decrease, which indicates that the capacity of aerosols to reduce
30 the actinic flux decreases with AOD. The absolute values of slopes are equal to
31 $4.2\text{-}6.9 \cdot 10^{-6} \text{ s}^{-1}$ and $3.4\text{-}10^{-3} \text{ s}^{-1}$ per AOD unit for $j(O^1D)$ and $j(NO_2)$ respectively at
32 SZA of 60° and AOD smaller than 0.7, both of which are larger than those observed
33 in a similar, previous study in the Mediterranean. This indicates that the aerosols in
34 urban Beijing have a stronger extinction effect on actinic flux than absorptive dust
35 aerosols in the Mediterranean. Since the photolysis frequencies strongly depended on
36 the AOD and the solar zenith angle (SZA), we established a parametric equation to
37 quantitatively evaluate the effect of aerosols on photolysis frequencies in Beijing.
38 According to the parametric equation, aerosols lead to a decrease in seasonal mean
39 $j(NO_2)$ by 24% and 30% for summer and winter, respectively, and the corresponding
40 decrease in seasonal mean $j(O^1D)$ by 27% and 33% respectively, compared to an
41 aerosol-free atmosphere ($AOD = 0$). Based on an observation campaign in August
42 2012, we used the photochemical box model to simulate the ozone production rate
43 ($P(O_3)$). The simulation results shows that the monthly mean daytime net ozone
44 production rate is reduced by up to 25% due to the light extinction of aerosols.

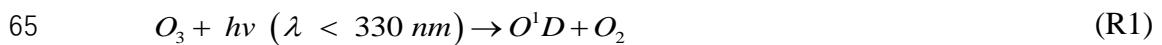
45 Through further in-depth analysis, it was found that particulate matter concentrations
46 maintain high level under the condition of high concentrations of ozone precursors
47 (VOCs and NO_x), which inhibits the production of ozone to a large extent. This
48 phenomenon implies a negative feedback mechanism in the atmospheric environment
49 of urban Beijing.

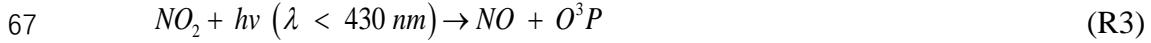
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52 **1. Introduction**

53 Solar radiation plays an important role in atmospheric photochemistry, driving
54 the photolysis of many key species. The photolysis of ozone (O₃), gaseous nitrous
55 acid (HONO), and carbonyl species, which contributes to the primary production of
56 HO_x (Volkamer et al., 2010). The photolysis of ozone produces O¹D, which then
57 reacts with H₂O to form OH radicals; these radicals are the main source of OH
58 radicals in the troposphere, as shown by reactions R1 and R2. The strong dependence
59 of OH concentration on j(O¹D) was found in a number of field measurements (Ehhalt
60 et al., 2000; Rohrer et al., 2014; Stone et al., 2012). In addition, the photolysis of NO₂
61 produces O³P, and then O³P reacts with O₂ to produce O₃, as shown by reactions R3
62 and R4, which is the only significant chemical source of ozone in the troposphere
63 (Finlayson-Pitts et al., 2000). The photolysis frequencies of R1 and R3 are j(O¹D) and
64 j(NO₂), respectively.





69 The photolysis frequencies are calculated by the following formula:

70 $j = \int_{\lambda_1}^{\lambda_2} F(\lambda) \sigma(\lambda, T) \varphi(\lambda, T) d\lambda$ (E1)

71 $F(\lambda)$ is the actinic flux dependent on wavelength. Since the photolysis rates are
72 proportional to the actinic flux and not all stations acquire a 2π spectroradiometer or
73 chemical actinometers for J measurements, several methods have been developed to
74 determine actinic flux and photolysis frequencies from ground based measurements of
75 irradiance (Kylling et al 2003, Kazadzis et al. 2000, 2004, Topaloglou et al. 2005,
76 Trebs et al. 2009). $\sigma(\lambda, T)$ is the absorption cross section of the species that absorbs in
77 the wavelength range λ_1 - λ_2 . $\varphi(\lambda, T)$ is the quantum yield of the photodissociation
78 reaction product. λ , and T represent wavelength, species and temperature,
79 respectively.

80 The effect of aerosols on photolysis frequencies depends on the aerosol optical
81 properties, SZA and altitude (Liao et al., 1999). The aerosol optical depth (AOD)
82 characterizes the integral of the extinction coefficient of aerosols in the vertical
83 direction. The light extinction of aerosols includes scattering and absorption, which
84 have different effects on the actinic flux. Previous studies showed that scattering
85 aerosols can enhance the actinic flux throughout the troposphere, while absorptive
86 aerosols reduce the actinic flux throughout the boundary layer (Jacobson, 1998;
87 Dickerson et al., 1997; Castro et al., 2001; Flynn et al., 2010). To distinguish between

these two components, single scattering albedo (SSA) is defined as the ratio of the scattering coefficient to the total extinction coefficient. In areas with severe aerosol pollution, aerosols can significantly affect photolysis frequencies and ozone production. Studies in Los Angeles (Jacobson, 1998), Mexico City (Castro et al., 2001; Raga et al., 2001; Li et al., 2011), São Paulo (de Miranda et al., 2005), Huston (Flynn et al., 2010), Europe (Real et al., 2011) and Russia (Pere et al., 2015) have found that aerosols reduce ozone concentration by 5-30% by attenuating photolysis frequencies. Studies in the eastern United States have shown that scattering aerosols increase ozone concentration by 5-60% by increasing the photolysis frequencies (Dickerson et al., 1997; He and Carmichael, 1999). Therefore, it is necessary to quantitatively evaluate the effect of aerosols on photolysis frequencies for a better understanding of ozone formation under highly polluted conditions.

Currently, the methods for quantitatively evaluating the influence of aerosols on photolysis frequencies mainly include radiative transfer model and parameterization method (Madronich et al., 1993). Radiative transfer model is based on an algorithm for calculating solar radiation and photolysis frequencies (Madronich et al., 1999). The observed data of related influential factors of the photolysis frequencies are taken as the model's input to calculate the photolysis frequencies. This method comprehensively considers the influence of aerosol optical properties on the photolysis frequencies, but it does not necessarily reflect the true quantitative relationship in the atmosphere due to complicated environmental conditions and thus the simulated results don't necessarily reproduce observed values well (Lefer et al.,

110 2003; Shetter et al., 2003; Hofzumahaus et al., 2004). For example, the simulated
111 slope of $j(O^1D)$ vs AOD by Fast-JX algorithm within the CHIMERE model was
112 significantly smaller than the observed slope, particularly for the high SZA values
113 (Mailler et al., 2016). The parameterization method is based on the observation data
114 taken from a certain region and is used to establish the parameterized relationship
115 between the photolysis frequencies and optical properties of aerosols (such as AOD).
116 The method can reflect the actual atmospheric environment conditions; it also
117 considers less influential factors and thus is easy to apply (Casasanta et al., 2011;
118 Gerasopoulos et al., 2012). The disadvantage of this method is that the established
119 parametric equations apply only to a specific region and cannot be extended to other
120 regions.

121 With rapid economic development and urbanization in past decades, China's
122 atmospheric pollution has become more and more severe, characterized by high
123 concentrations of particulate matter and ozone. Satellite observations indicates that
124 both the particulate matter and the ozone of eastern China are at higher levels
125 compared with other locations in the globe (Verstraeten et al., 2015; Ma et al., 2014).
126 Levels of pollution in the Beijing–Tianjin–Hebei are even more severe (Chang et al.,
127 2009; Che et al., 2008; Zhang et al., 2014, Zhang et al., 2016). Therefore, it is
128 necessary to study the effects of aerosols on photolysis frequencies and ozone
129 production in the urban areas of China.

130 Previous model studies have shown that aerosols in China can affect ozone
131 production by changing the photolysis frequencies. Tang et al. (2004) used a sulfur

132 transmission–emission model (STEM) to discover that ozone concentration in
133 northeastern China was reduced by 0.1–0.8% in the sandstorm due to the change in
134 photolysis frequencies . Tie et al. (2005) used a global aerosol–chemical model to
135 show that aerosols caused $j(O^1D)$ and $j(NO_2)$ to decrease in winter by 20%-30% and
136 10%-30%, respectively, and in summer by 5%-20% and 1%-10%, respectively,
137 resulting in 2%-5% and 2% reductions in ozone concentration in winter and summer,
138 respectively. Li et al. (2011) used an air quality model to estimate the changes in the
139 photolysis frequencies caused by sulfate, nitrate, ammonium, and mineral dust
140 aerosols in the central and eastern regions of China from June 1 to June 12, 2006. This
141 study showed that the daily average $j(O^1D)$ in the troposphere at the altitude of 1 km,
142 3 km, and 10 km from the ground was reduced by 53%, 37-%, and 21%, respectively,
143 resulting in a decrease in the ozone concentration by 5.4%, 3.8%, and 0.10% in the
144 three layers. Lou et al (2014) found that with aerosols, annual mean photolysis
145 frequencies , $j(O^1D))$ and $j(NO_2)$, were simulated to be reduced by 6-18% in polluted
146 eastern China, leading to reductions in O_3 of up to 0.5 ppbv in those regions in spring
147 and summer by using the global chemical transport model (GEOS-Chem). However,
148 all of these studies base their results on model simulations. Research using long-term
149 observational data to evaluate the effects of aerosols on photolysis frequencies and
150 ozone production in China has not yet been published.

151 Our overall goal is to quantitatively evaluate the effect of aerosols in urban
152 Beijing on photolysis frequencies and thus on ozone production. First, the relationship
153 between $PM_{2.5}$ and AOD was investigated. Second, based on long-term observations

154 (2012-2015) of photolysis frequencies, we discussed the impact of AOD on photolysis
155 frequencies ($j(O^1D)$ and $j(NO_2)$) in urban Beijing in detail. The relationship between
156 photolysis frequencies and AOD is adequately compared with previous study in the
157 Mediterranean (Casasanta et al., 2011; Gerasopoulos et al., 2012). Then, the
158 quantitative relationship between photolysis frequencies, AOD, and SZA was
159 acquired by the parameterization method, which could be used to quantitatively
160 evaluate the effect of AOD on photolysis frequencies in Beijing. Finally, a
161 photochemistry box model was used to evaluate the effect of aerosols on ozone
162 production.

163 **2. Methodology**

164 **2.1. Measurement**

165
166 From August 2012 to December 2015, $j(O^1D)$ and $j(NO_2)$ were measured
167 continuously at PKUERS site. The data of the period during October 2012 to March
168 2013 and August 2015 are missed due to instrument maintenance and other
169 measurement campaigns. The site ($39.99^\circ N$, $116.31^\circ E$) is located on the sixth floor of
170 a campus building at the Peking University, 20 km northwest of Tiananmen Square.
171 The height from the ground is about 30 m. The sampling point is surrounded by
172 classroom buildings. Concentration level and composition of air pollutants were
173 thought to be similar to the downtown so as to be representative for the whole of
174 Beijing (Wang et al., 2010; Xu et al., 2011; Zhang et al., 2012; Zhang et al., 2014).

175 The actinic flux was measured using a spectroradiometer and the photolysis
176 frequencies were calculated from the absorption cross section and quantum yield of
177 each species (Shetter and Müller, 1999). The spectroradiometer consisted of a single
178 monochromator with a fixed grating (CARL ZEISS), an entrance optic with a 2π
179 steradian (sr) solid angle quartz diffusor and a 2048×64 -pixel photodiode array
180 detector. The spectral measurements were performed with a wavelength resolution of
181 2 nm, covering a wavelength range of 290-650 nm (Hofzumahaus et al., 1999). A
182 1000 W National Institute of Standard and Technology (NIST) traceable lamp was
183 used for calibration under laboratory conditions (Bohn et al., 2008). The measured
184 spectra were corrected for dark signal and stray light. For $j(O^1D)$, the quantum yields
185 used were taken from Matsumi et al.(2002), while the ozone cross section was derived
186 from Daumont et al. (1992) and Malicet et al. (1995). Measured temperatures were
187 used to retrieve ozone absorption cross section and quantum yield. For $j(NO_2)$, the
188 quantum yields used were taken from Bass et al. (1976) and Davenport et al. (1978),
189 while the cross section was derived from Jones and Bayes (1973), Harker et al. (1977)
190 and Davenport (1978). The calculated photolysis frequencies had a time resolution of
191 10 s and an accuracy of $\pm 10\%$ including uncertainties associated with the quartz
192 receiver and stray-light effects (Edwards and Monks, 2003).

193 The optical properties of aerosols were measured by a CIMEL solar photometer
194 (AERONET level 2 data collection, <http://aeronet.gsfc.nasa.gov/>) and the site selected
195 is the Beijing-CAMS site ($39.93^\circ N$, $116.32^\circ E$), which is 6.4km from the PKUERS
196 site. The CIMEL solar photometer is an automatic solar-sky scanning radiometer that

uses selected spectral channels. The instrumentation, data acquisition, retrieval algorithms, and calibration procedure conform to the standards of the AERONET global network and have been described in detail by Fotiadi et al. (2006). The solar extinction measurement was performed every 3 minutes in the spectral range 340–1020 nm for the calculation of AOD at wavelengths 340, 380, 440, 500, 675, 870, 970, and 1020 nm. Under cloudless conditions, the overall uncertainty of AOD data is \pm 0.01 at $\lambda > 440$ nm and \pm 0.02 at shorter wavelengths. In this study, AOD at the wavelength of 380 nm was chosen for analysis. This wavelength was selected as it is more representative of $j(\text{NO}_2)$. Additionally, at this wavelength we can better compare with the results of Gerasopoulos et al. (2012). The daytime clear-sky conditions were identified according to the presence of AOD data of AERONET since AOD data are unavailable under cloudy conditions. AE and SSA (440nm) were also acquired from ARONET. In addition, the SSA (525nm) data were derived from a field campaign undertaken in August 2012. The absorption and scattering coefficients were measured with an Aethalometer (AE-31, Magee) and a Single Wavelength Integrating Nephelometer (Aurora-1000), respectively, with a time resolution of 1 minute. As aerosol particles were dried by decreasing relative humidity (RH) to $<40\%$ when SSA was measured, we used the measured hygroscopic factor (Liu et al., 2009) and measured RH to correct the SSA. Five-minute averages of AOD, SSA, and photolysis frequencies were analyzed in this study. The total ozone column was obtained by OMI (Ozone Monitoring Instrument) for the year 2012-2015, using overpass data (<http://www.temis.nl/protocols/O3global.html>) (Henk et al., 2003). In addition,

219 meteorological parameters such as temperature, relative humidity, and pressure were
220 simultaneously observed at this site. Table 1 presents total O₃ column, temperature,
221 relative humidity, daytime clear-sky fraction and respective standard deviation for
222 different seasons.

223 The analysis of the effects of aerosols on ozone production (Section 3.4) was
224 based on the field campaign undertaken in August 2012. The relevant contents and
225 methods of observation are shown in Table 2. Since the time resolution of VOCs is 1
226 hour, all data analyzed in Section 3.4 was processed as 1-hour average values. In this
227 study, we focused on the effects of aerosols on photolysis frequencies and ozone
228 production under cloudless conditions.

229 **2.2 Radiative Transfer Model Description**

230 We use the Tropospheric Ultraviolet and Visible (TUV) radiation model (version
231 5.3) provided by Sasha Madronich (Madronich, 1993). In order to solve the radiative
232 transfer equation, TUV uses the discrete-ordinates algorithm (DISORT) with 4
233 streams and calculates the actinic flux spectra with wavelength range of 280-420 nm
234 in 1 nm steps and resolution. Measured temperatures were used to calculate the
235 absorption cross sections and quantum yields. The key aerosol optical properties
236 including AOD, SSA and AE were input into the model to test the effect of aerosols
237 on photolysis frequencies. AE(380/550nm) is taken from AERONET and the mean
238 value of 1.2 during June 2012 - December 2015 is used in TUV model.

239

240 **2.3 Photochemical box model**

241 The photochemical box model used in this study is based on a regional
242 atmospheric chemical mechanism (RACM2) described by Goliff et al. (2013). The
243 mechanism includes 17 stable inorganic compounds, 4 intermediate inorganic
244 compounds, 55 stable organic compounds, and 43 intermediate organic compounds.
245 Compounds not specifically treated in RACM are incorporated into species with
246 similar functional groups. The isoprene-related mechanism used in this model is LIM
247 mechanism proposed by Peeters et al. (2009). In this study, the observed NO₂, CO,
248 SO₂, C₂–C₁₂ NMHCs, HCHO, photolysis frequencies, temperature, pressure, and
249 relative humidity were used as constraints to simulate the concentrations of reactive
250 radicals (RO₂, HO₂, and OH), intermediate species, and associated reaction rate
251 constants. HONO wasn't measured during the period and was calculated according to
252 the concentration of NO₂ and the observed ratio of HONO to NO₂ at an urban site in
253 Beijing, which had a marked diurnal cycle, a maximum in the early morning (ratio
254 values up to ~0.05–0.08 in summer) and a decrease during daytime to values around
255 0.01–0.02 (Hendrick et al., 2014). The model was spun up for two days once it started
256 running in order to ensure that the simulation was stable. It was assumed that the
257 lifetime of simulated species removed by dry deposit was 24 hours. The lifetime
258 corresponds to the assumed deposit rate of 1.2 cm s⁻¹ and a well-mixed boundary
259 layer height of about 1 km (Lu et al., 2012). Net ozone production is equal to the
260 reaction rate between peroxy radicals (RO₂ and HO₂) and NO minus the loss rate of
261 NO₂ and O₃ as shown in E2, E3, and E4 as derived by Mihelcic et al. (2003). The

262 ozone production rate ($P(O_3)$), the ozone loss rate ($D(O_3)$), and the net $P(O_3)$ were
263 calculated from the simulation results.

264

265
$$P(O_3) = k_{HO_2+NO} [HO_2][NO] + \sum (k^i_{RO_2+NO} [RO_2^i][NO]) \quad (E2)$$

266

267
$$D(O_3) = (\theta j(O^1D) + k_{OH+O_3}[OH] + k_{HO_2+O_3}[HO_2] + \sum (k^j_{alkene+O_3} [alkene^j]))[O_3] + k_{OH+NO_2}[OH][NO_2] \quad (E3)$$

268

269
$$net P(O_3) = P(O_3) - D(O_3) \quad (E4)$$

270 where θ is the fraction of O^1D from ozone photolysis that reacts with water vapor. i
271 and j represent the number of species of RO_2 and alkenes, respectively.

272

273 **3. Results and discussion**

274

275 **3.1 The correlation between PM_{2.5} and AOD**

276 Compared with AOD, PM_{2.5} is a more common proxy to evaluate the level of
277 particulate matter pollution in spite that AOD is a more closely related parameter of
278 photolysis frequencies. As a result, we attempted to analyze the quantitative
279 relationship between PM_{2.5} and AOD to evaluate the influence of PM_{2.5} on AOD and
280 thus on photolysis frequencies. The factors that affect this relationship include aerosol
281 type, aerosol size distribution, aerosol distribution in the vertical direction, relative
282 humidity (RH) and planetary boundary layer height (PBLH) (van Donkelaar et al.,

283 2010). Figure 1 shows the correlation between AOD and PM_{2.5} in four different
284 seasons. The determination coefficient (r^2) is 0.53, 0.58, 0.62 and 0.59 for spring
285 (March, April and May), summer (June, July and August), autumn (September,
286 October and November) and winter (December, January and February), respectively.
287 Meanwhile, the correlation exhibits significant seasonal differences, having relatively
288 smaller slope (23.56) in summer and relatively larger slope (73.76) in winter. This
289 implies that PM_{2.5} in summer has stronger light extinction capacity than in winter.
290 One reason for the seasonal differences is the variation in RH among different seasons
291 (Table 1). There is higher RH in summer (57.2% on average) than in winter (30.4%
292 on average), leading to stronger hygroscopic growth of aerosol particles, and thus
293 resulting in higher scattering ability of aerosol particles. According to another study in
294 urban Beijing, the higher the RH, the smaller the slope, and the higher the PBLH, the
295 smaller the slope (Zheng, C. W et al., 2017). In addition, the slope was smaller for
296 scattering-dominant aerosols than for absorbing-dominant aerosols, and smaller for
297 coarse mode aerosols than for fine mode aerosols (Zheng, C. W et al., 2017). The
298 slopes of the correlation between AOD (at 550nm) and PM_{2.5} in this study in summer
299 and winter are equal to 42.2 $\mu\text{g m}^{-3}$ and 119.2 $\mu\text{g m}^{-3}$, respectively, close to that from
300 Ma et al. (2016) (54.9 $\mu\text{g m}^{-3}$ and 110.5 $\mu\text{g m}^{-3}$) and Xin et al. (2016) (55.2 $\mu\text{g m}^{-3}$ and
301 93.4 $\mu\text{g m}^{-3}$), but smaller significantly than that from Zheng et al. (2017) (65~74 $\mu\text{g m}^{-3}$
302 and 143~158 $\mu\text{g m}^{-3}$). The differences mainly depend on the aerosol composition and
303 size distribution at different observational sites in Beijing. Compared with other cities
304 in North China (Tianjin, Shijiazhuang and Baoding) (Ma et al., 2016), the slope in

305 Beijing for winter is significantly higher. Consequently, using PM_{2.5} to estimate AOD
306 has a large uncertainty due to multiple interference factors.

307

308

309 **3.2 Seasonal and diurnal variability of AOD and photolysis frequencies**

310 The diurnal cycles of AOD are shown in Figure 2. AOD displays obvious diurnal
311 variation, with relatively high level at noon and low level at dawn and evening. The
312 diurnal variation of PM_{2.5} is significantly different from AOD. In addition, AOD has
313 obvious seasonal differences, with the highest AOD in summer and the lowest AOD
314 in winter. Conversely, PM_{2.5} in winter ($42\mu\text{g m}^{-3}$) is significantly higher than in
315 summer ($35\mu\text{g m}^{-3}$). In spite of lower PM_{2.5} in summer, AOD in summer is higher due
316 to stronger extinction capacity of PM_{2.5} as discussed in 3.1. Figure 3 shows the diurnal
317 variation of the photolysis frequencies under cloudless conditions for each season.
318 $j(\text{O}^1\text{D})$ and $j(\text{NO}_2)$ are both highest in summer, followed by spring and autumn, and
319 lowest in winter. This seasonal difference is mainly determined by the difference in
320 SZA for the four seasons.

321 The observed mean daily maxima of photolysis frequencies at this site are lower
322 than that observed in the eastern Mediterranean (Crete, Greece, $35^\circ20'\text{N}$, $25^\circ40'\text{E}$)
323 (Gerasopoulos et al., 2012) by $7.8 \times 10^{-6} \pm 5.5 \times 10^{-6} \text{ s}^{-1}$ and $5.5 \times 10^{-6} \pm 1.8 \times 10^{-6} \text{ s}^{-1}$
324 for $j(\text{O}^1\text{D})$, and $1.9 \times 10^{-3} \pm 1.2 \times 10^{-3} \text{ s}^{-1}$ and $3.3 \times 10^{-3} \pm 1.0 \times 10^{-3} \text{ s}^{-1}$ for $j(\text{NO}_2)$, in
325 summer and winter respectively. The corresponding lower photolysis frequencies of
326 Beijing than the eastern Mediterranean due to SZA difference is $1.7 \times 10^{-6} \text{ s}^{-1}$ and $3.0 \times$

327 10^{-6} s⁻¹ for $j(O^1D)$, and 8.0×10^{-5} s⁻¹ and 6.6×10^{-4} s⁻¹ for $j(NO_2)$ according to TUV
328 model under aerosol-free conditions, which are significantly lower than observed
329 decreased magnitudes. Additionally, we know that the temperature is lower in Beijing
330 during the winter compared to conditions in Crete. The measured mean temperature in
331 Beijing during winter is equal to 0.53 ± 4.2 °C (Table 1). When we consider the
332 temperature in Crete is 10 °C higher than in Beijing, the lower $j(O^1D)$ of Beijing than
333 Crete is 5.5×10^{-7} s⁻¹, which is also not able to compensate the $j(O^1D)$ gap between the
334 two sites during winter. Taking into account the similar levels of ozone column
335 concentration in the two sites, the large gap of photolysis frequencies in the two sites
336 is mainly attributed to the higher AOD in Beijing (0.76 ± 0.75) than in the eastern
337 Mediterranean (0.27 ± 0.13).

338 It can be seen from Figure 3 that the difference between winter and summer for
339 $j(O^1D)$ is significantly larger than that for $j(NO_2)$, where the summer midday averages
340 of $j(O^1D)$ and $j(NO_2)$ are 5 times and 2 times those of winter, respectively. There are
341 two reasons for this phenomenon. One, compared with $j(NO_2)$, $j(O^1D)$ is more
342 sensitive to the change in SZA and the same change in SZA results in a larger change
343 in $j(O^1D)$ than $j(NO_2)$. Two, the main influential factors of $j(NO_2)$ under cloudless
344 conditions are SZA and AOD, and the influence of ozone column concentration and
345 temperature on $j(NO_2)$ is negligible. However, $j(O^1D)$ is affected significantly by the
346 ozone column concentration and temperature, in addition to SZA and AOD. The
347 higher ozone column concentration and lower temperature in winter than in summer
348 lead to the difference in $j(O^1D)$ further increasing (Table 1).

349 **3.3 The correlation between photolysis frequencies and AOD**

350 **3.3.1 The correlation between $j(O^1D)$ and AOD**

351 In order to rule out the effect of SZA on photolysis frequencies, we chose SZA
352 equal to 30° and 60° ($\pm 1^\circ$) for analysis. Figure 4 presents the dependence of $j(O^1D)$
353 on AOD at different levels of ozone column concentration at SZA of 30° and 60° (\pm
354 1°). The ozone column concentration has a classification width of 30 DU. This
355 relatively large classification width is chosen to make sure that there are enough
356 points to fit the relationship between $j(O^1D)$ and AOD. $j(O^1D)$ exhibits a clear
357 dependence on AOD, with a nonlinear negative correlation. The scatter of these points
358 is mainly due to variations in ozone column and temperature. As AOD increased, the
359 slope of $j(O^1D)$ -AOD gradually decreases, indicating that the ability of aerosols to
360 reduce $j(O^1D)$ gradually decreases with AOD. This result differs from that found in
361 Mediterranean, where $j(O^1D)$ was linearly negatively correlated with AOD (Casasanta
362 et al., 2011; Gerasopoulos., 2012). A larger variation range of AOD in Beijing (0-3)
363 compared with Mediterranean (0-0.6) is one reason for the difference.

364 For further analysis, the observed relation between $j(O^1D)$ and AOD was
365 compared with TUV-simulated results. Panels a and b of Figure 5 present the
366 comparison between observed and TUV-simulated $j(O^1D)$ against AOD at a SZA of
367 30° and 60° respectively and ozone column concentration of 330-360 DU. The
368 observed $j(O^1D)$ was at ozone column of 330-360DU and were scaled to the
369 temperature of 298K. $AE(380/550\text{nm}) = 1.2$, ozone column = 345 and Temperature =

370 298K were used in TUV model for all simulations. Mean Earth-Sun distance was used
371 in the calculations of TUV model and measured j-values were scaled to the mean
372 Earth-Sun distance. At low AOD level (< 0.8), the observed slope of $j(O^1D)$ vs AOD
373 is significantly larger than the simulated slope at SSA of 0.95, and slightly larger than
374 the simulated slope at SSA of 0.85. With AOD increasing, the observed slope
375 decreases rapidly to the level smaller than the simulated slopes.

376 The rapid change of the slope with AOD can be related to the variation of SSA at
377 different AOD level. Figure 6 presents the relationship between SSA and AOD. Figure
378 6 (a) presents the relationship between AERONET based SSA (440nm) and AOD
379 during 2012-2015. The result suggests a significant positive correlation between SSA
380 and AOD. Additionally, Figure 6 (b) also presents a significant positive correlation
381 between near-ground SSA (525nm) from measurement campaign in August 2012 and
382 AOD. With the increase in AOD, SSA is elevated; meanwhile, the slope of SSA vs
383 AOD is gradually reduced. Similar results in other regions have been obtained by Bais
384 et al., 2005, Krotkov et al., 2005 and Kazadzis et al., 2012. SSA characterizes the ratio
385 of the scattering extinction coefficient to the total extinction coefficient (scattering
386 extinction coefficient plus absorptive extinction coefficient) of aerosols. The smaller
387 the SSA, the higher the absorptive component and lower the scattering component of
388 the aerosol, and the stronger the ability of the aerosol to reduce the actinic flux
389 (Dickerson et al., 1997). Figure 6 indicates that aerosols in Beijing under low AOD
390 conditions had a higher proportion of absorptive aerosol components than under high
391 AOD conditions, and, as a result, had a stronger ability to reduce the photolysis

392 frequencies, which contributed to the rapidly reduced slope of $j(O^1D)$ vs AOD with
393 AOD. However, due to absence of more SSA data of the period 2012-2015, we can't
394 give more sufficient evidence for the dependence of SSA on AOD. For another
395 perspective, Owing to the biomass burning and soot emission generated from heating,
396 the fine mode heavily-absorbing aerosol percentage is higher in winter than in
397 summer (Zheng et al., 2017; Liu et al., 2016; Zhang et al., 2013), and thus aerosols in
398 winter have stronger ability to reduce the photolysis frequencies. Table S1 indicates
399 that SSA in summer is higher significantly than in winter. High AOD levels often
400 appeared in summer and low AOD levels occurred mostly in winter (Figure 2 and
401 Table S1), another fact that may also explains the rapidly reduced slope of $j(O^1D)$ vs
402 AOD with AOD.

403 It worth noting that the mean near-ground SSA (525nm) in August 2012
404 (0.88 ± 0.08) is significantly lower than the mean AERONET based SSA (440nm) in
405 the same period (0.94 ± 0.02) and in summer (0.94 ± 0.02). The different wavelength
406 plays a minor role in the different SSA according to the wavelength dependence of
407 AERONET based SSA in the range of 440-1020 nm (Figure S3). This difference is
408 mainly because that the AERONET based SSA represents the column and in situ SSA
409 happens near the ground. The effect of the difference in SSA (0.88 vs 0.94) results in
410 photolysis frequencies changing by 11%-16% according to TUV model. It means that
411 due to the in situ SSA use, the photolysis frequencies tend to be underestimated.
412 Krotkov et al. (2005) and Corr et al. (2009) pointed out that SSA in the UV can be
413 lower than the visible. So in general this 11-16% could be less. The AERONET based

414 SSA generally reproduces well the slope of $j(O^1D)$ versus AOD in spite that it
415 significantly underestimates the absolute value of the slope at low AOD range
416 (AOD<0.7), which is probably due to the uncertainty of AERONET based SSA in low
417 AOD range. In addition to the uncertainty of SSA, both of SSA at 440nm and at
418 525nm differ from the 305-315nm wavelength range of $j(O^1D)$, which is likely to lead
419 to some uncertainties for the analysis of the relationship between $j(O^1D)$ and AOD.

420 Comparing panels a and b of Figure 4, we see that at AOD smaller than 1, the
421 slope of $j(O^1D)$ vs AOD exhibits a significant dependence on SZA and the slope at 30°
422 of SZA is about 1.5-2.0 times larger than that at 60° of SZA. This result is similar to
423 that of the observations made in the central Mediterranean (Casasanta et al., 2011).
424 For the purpose of comparison with the study in the Mediterranean, the slope of $j(O^1D)$
425 vs AOD was calculated at AOD smaller than 0.7.

426 Table 3 presents slope, intercept and the determination coefficient (r^2) of linear
427 fits of correlation between $j(O^1D)$ and AOD for each ozone column class at AOD
428 smaller than 0.7. At SZA of 60° and O₃ column concentration of 300-330 DU, the
429 respective slope of the linear regression indicates a reduction of $j(O^1D)$ by $4.2 \cdot 10^{-6} s^{-1}$
430 per AOD unit. Gerasopoulos et al. (2012) reported that the observed slope in the
431 eastern Mediterranean was equal to $2.4 \cdot 10^{-6} s^{-1}$ at O₃ column of 300-320 DU.

432 Casasanta et al. (2011) reported that the observed slope in the central Mediterranean
433 varied from $2.7 \cdot 10^{-6} s^{-1}$ to $3.9 \cdot 10^{-6} s^{-1}$ at O₃ column of 300-330 DU. All of these results
434 are smaller than the value of the present study, indicating that aerosols in urban
435 Beijing had a stronger extinction capacity on $j(O^1D)$ than those in the Mediterranean

436 that was influenced by both natural absorptive aerosols and anthropogenic aerosols.
437 Previous study indicated that SSA in Beijing ranged from 0.80 to 0.86 (Garland et al.,
438 2009; Han et al., 2015b; Han et al., 2017; Tian et al., 2015). The relatively low SSA in
439 Beijing could be an important reason for the stronger extinction capacity.

440

441

442 **3.3.2 The correlation between $j(\text{NO}_2)$ and AOD**

443 Unlike $j(\text{O}^1\text{D})$, $j(\text{NO}_2)$ is negligibly affected by ozone column concentration and
444 depends mainly on AOD and SZA under cloudless conditions. Figure 7 presents the
445 dependence of $j(\text{NO}_2)$ on AOD at different SZA levels under cloudless conditions.
446 The cosine of SZA ($\cos(\text{SZA})$) is categorized according to a width of 0.2. In the same
447 category of $\cos(\text{SZA})$, $j(\text{NO}_2)$ displays a strong dependence on AOD. The scatter of
448 these points is due to the relatively large classification width of SZA to a large extent.
449 When $\cos(\text{SZA})$ is at its maximum level (0.8-1), the correlation between $j(\text{NO}_2)$ and
450 AOD is close to linear. When $\cos(\text{SZA})$ decreases, the correlation tends to be
451 nonlinear. Similar to $j(\text{O}^1\text{D})$, the observed slopes of $j(\text{NO}_2)$ vs AOD are also larger
452 than TUV-simulated slope at SSA of 0.95 and 0.85 when AOD is smaller than 0.8,
453 and decreased rapidly with increasing AOD (panels c and d of Figure 5). The reason
454 for this result is the same with that for $j(\text{O}^1\text{D})$ as explained above.

455 Table 4 presents the slope, intercept and the determination coefficient (r^2) of
456 linear fits of correlation between $j(\text{NO}_2)$ and AOD for each ozone column class at

457 AOD smaller than 0.7. The slope of $j(\text{NO}_2)$ vs AOD also displays a significant
458 dependence on $\cos(\text{SZA})$. The slope increases as $\cos(\text{SZA})$ increases from 0 to 0.5
459 and then decreases as $\cos(\text{SZA})$ increases from 0.5 to 1. At SZA of $60^\circ \pm 1$
460 ($\cos(\text{SZA})=0.5 \pm 0.015$), the respective slope of the linear regression indicates a
461 reduction of $j(\text{NO}_2)$ by $3.4 \cdot 10^{-3} \text{ s}^{-1}$ per AOD unit. This result is larger than the value
462 for non-dust aerosols ($2.2 \cdot 10^{-3} \text{ s}^{-1}$) and close to the value for dust aerosols ($3.1 \cdot 10^{-3} \text{ s}^{-1}$)
463 in the eastern Mediterranean reported by Gerasopoulos et al. (2012).

464

465 **3.4 The parameterization relationship between photolysis frequencies, AOD, and**
466 **SZA**

467

468 As analyzed above, the photolysis frequencies ($j(\text{O}^1\text{D})$ and $j(\text{NO}_2)$) strongly
469 depended on AOD and $\cos(\text{SZA})$ and could be fit into expression E5 using a quadratic
470 polynomial form. The fitting parametric equations for $j(\text{NO}_2)$ is shown in Table 5. For
471 $j(\text{O}^1\text{D})$, both of O_3 column and temperature affect $j(\text{O}^1\text{D})$ significantly. Figure S1
472 presents the dependence of $j(\text{O}^1\text{D})$ on ozone column at low AOD level (AOD<0.3)
473 and SZA of (a) $30^\circ \pm 1^\circ$ and (b) $60^\circ \pm 1^\circ$, respectively. Ozone column ranging from 270
474 to 400 DU leads to $j(\text{O}^1\text{D})$ reducing about 50%. In order to evaluate the impact of
475 temperature on $j(\text{O}^1\text{D})$, we calculated the ratio of $j(\text{O}^1\text{D})$ at measured temperature to
476 $j(\text{O}^1\text{D})$ at temperature = 298K ($j(\text{O}^1\text{D})/ j(\text{O}^1\text{D})_{T=298\text{K}}$) (Figure S2). $j(\text{O}^1\text{D})/j(\text{O}^1\text{D})_{T=298\text{K}}$
477 varied from 0.82 to 1.03 indicating that temperature changed $j(\text{O}^1\text{D})$ by no more than

478 21%. Therefore, temperature played a minor role in changing $j(O^1D)$ compared with
479 ozone column. As a result, when we fitted the relationship among $j(O^1D)$, AOD and
480 $\cos(SZA)$, the effect of ozone column is considered but the effect of temperature is
481 not considered. By fitting the relationship at different ozone classes (classification
482 width=30DU), we found that ozone column increasing by 30DU results in $j(O^1D)$ at a
483 constant SZA and AOD decreasing by 18%. Therefore, the parametric equation for
484 $j(O^1D)$ is transformed into the form E6, which reflects the influence of ozone column.

485 The parameters a_1-a_6 correspond to ozone column range = 300-330 DU, thus we use
486 315 DU as the weighted standard of ozone column. The fitting parameters a_1-a_6 for
487 $j(O^1D)$ is shown in Table 6.

488
$$j(NO_2) = a_1 + a_2 AOD + a_3 \cos(SZA) + a_4 (AOD)^2 + a_5 AOD \cos(SZA) + a_6 (\cos(SZA))^2$$

489 E5

490
$$j(O^1D) = [a_1 + a_2 AOD + a_3 \cos(SZA) + a_4 (AOD)^2 + a_5 AOD \cos(SZA) + a_6 (\cos(SZA))^2] \\ \times [1 + (315 - O_3 \text{ column}) \times 0.006]$$

491 E6

492 The coefficients of determination of the fitting equations are greater than 0.95 for
493 $j(NO_2)$ and $j(O^1D)$ at a certain O_3 column, indicating that both of the photolysis

494 frequencies strongly depended on AOD and $\cos(SZA)$, and the effect of other factors
495 such as SSA and AE are integrated into the constant term in the parametric equation.

496 Since the ozone column concentration has greater influence on $j(O^1D)$ than on $j(NO_2)$,
497 the parameters of fitting equations for $j(NO_2)$ are similar, but the parameters of fitting
498 equations for $j(O^1D)$ have a large fluctuation at different O_3 column ranges (especially
499 a_1 and a_2). The parametric equations can be used to quantitatively evaluate the effect

500 of AOD on photolysis frequencies in Beijing. According to the parametric equations,
501 aerosols lead to a decrease in seasonal mean $j(\text{NO}_2)$ by 24% and 30% and a decrease
502 in seasonal mean $j(\text{O}^1\text{D})$ by 27% and 33% in summer and winter under clear-sky
503 conditions, respectively, compared to an aerosol-free atmosphere. The decreasing
504 ratio of the photolysis frequencies in winter is higher than in summer mainly due to
505 the higher SZA in winter.

506

507 The effect of aerosols on photolysis frequencies in Beijing is compared with
508 other studies. Real and Sartelet (2011) reported a reduction in $j(\text{NO}_2)$ and $j(\text{O}^1\text{D})$ of
509 13%-14% due to aerosols by using the radiative transfer code Fast-J during summer
510 2001 over European regions. Flynn et al (2010) reported that aerosols reduced $j(\text{NO}_2)$
511 by 3% in Huston during 2006 by using TUV model. Gerasopoulos et al (2012)
512 reported that aerosols reduced $j(\text{NO}_2)$ and $j(\text{O}^1\text{D})$ by 5%-15% with 5-yr mean AOD at
513 380nm equal to 0.27. All of these results are lower than the reduction ratio of this
514 study mainly due to higher aerosol level in Beijing (4-yr mean AOD equal to $0.76 \pm$
515 0.75). Hodzic et al. (2007) simulated a 15–30% $j(\text{NO}_2)$ photolysis reduction during
516 the 2003 European summer heatwave in the case of absorbing biomass burning
517 aerosols with AOD at 550 nm equal to 0.7-0.8 and SSA at 532 nm equal to 0.83-0.87.

518 The result of Hodzic et al. (2007) is comparable with the reduction ratio of this study
519 possibly due to the equivalent levels of AOD and SSA. In addition, Péré et al (2015)
520 simulated a higher reduction (20–50%) in $j(\text{NO}_2)$ and $j(\text{O}^1\text{D})$ along the transport of
521 the aerosol plume during the 2010 Russian summer wildfires episode. The higher

522 reduction is due to the higher level of AOD (peak value of AOD at 400nm reached
523 2-4), even though SSA is very high (0.97).

524

525 **3.5 The influence of AOD on ozone production**

526

527 In order to explain the effect of aerosol light extinction on ozone production, we
528 used the data from the field observation campaign undertaken in August 2012. Ozone
529 production depends on its precursors (NOx and VOCs), meteorological factors, and
530 solar radiation. Solar radiation is the driving force for tropospheric photochemical
531 reactions, in which $j(O^1D)$ and $j(NO_2)$ are both important for ozone production. On
532 the one hand, the increase in $j(NO_2)$ promotes the photolysis of NO_2 , thereby
533 accelerating the formation of ozone. On the other hand, the increase in $j(O^1D)$
534 accelerates the photolysis of ozone. In addition, the increase in the photolysis
535 frequencies will accelerate the photolysis of OVOC (especially formaldehyde and
536 acetaldehyde), HONO, and H_2O_2 , resulting in increases in OH and HO_2 , which will
537 promote the reaction between OH and VOCs and thus produce more RO_2 . As a result,
538 more ozone is produced by increasing the reaction rate between RO_2 (or HO_2) and NO.
539 However, the increase in OH and HO_2 also consumes ozone and NO_2 , which
540 contributes to the increase in $D(O_3)$. In brief, the overall effect of changes in
541 photolysis frequencies on sources and sinks of ozone determines the change in the net
542 ozone production rate.

543 Ozone production ($\text{HO}_2 + \text{NO}$, $\text{RO}_2 + \text{NO}$), ozone loss ($\text{O}^1\text{D} + \text{H}_2\text{O}$, $\text{HO}_2 + \text{O}_3$,
544 $\text{O}_3 + \text{OH}$, $\text{NO}_2 + \text{OH}$, and $\text{O}_3 + \text{alkenes}$), and net ozone production rate during August
545 2012 were calculated by using the box model. We used the observed photolysis
546 frequencies (i.e. j_{obs}) and the calculated photolysis frequencies by parametric
547 equation under the condition of AOD equal to 0 (i.e. $j_{\text{AOD}=0}$), were used to
548 constrain the box model. The difference of simulated results in the two scenarios can
549 be attributed to the effect of aerosol light extinction. As a result, the presence of
550 aerosols causes a decrease in both ozone production rate and loss rate, as is shown in
551 Figure 8. Since the decreasing amplitude of the daytime ozone production rate is far
552 larger than that of the daytime ozone loss rate, the mean daytime net production rate
553 of ozone is reduced by 25%. This reduction is comparable with the results of the study
554 in Mexico City, where aerosols caused a 20% reduction in the ozone concentrations
555 (Castro et al., 2001). Studies in Houston and Crete have shown that aerosols cause
556 ozone production rates to decrease by about 4% and 12%, respectively, which are
557 lower than that found in this study (Flynn et al., 2010; Gerasopoulos et al., 2012).

558 The ratio of the observed photolysis frequencies to the photolysis frequencies at
559 AOD equal to 0 is defined as JIF (Flynn et al., 2010). A JIF of less than 1 indicates
560 that the aerosols cause a decrease in the photolysis frequencies. Figure 9 shows the
561 relation between $P(\text{O}_3)_{j_{\text{obs}}}/P(\text{O}_3)_{j_{\text{AOD}=0}}$ (or $D(\text{O}_3)_{j_{\text{obs}}}/D(\text{O}_3)_{j_{\text{AOD}=0}}$) and JIF. The
562 majority of JIF values were less than 1, with an average of 0.72, indicating that
563 aerosols greatly attenuated photolysis frequencies due to high levels of AOD (average
564 of 1.07) during the observation period. $P(\text{O}_3)_{j_{\text{obs}}}/P(\text{O}_3)_{j_{\text{AOD}=0}}$ and

565 $D(O_3)_{j_obs}/D(O_3)_{j_AOD=0}$ are both linearly positively correlated with JIF and the scatters
566 are mostly above the 1:1 line. As can be seen from the figure 9, a 30% reduction in
567 photolysis frequencies ($JIF = 0.7$) due to the presence of aerosols results in a decrease
568 in ozone production rate and loss rate by about 26% and 15%, respectively. The
569 decreasing amplitude in the ozone production rate is greater than the decrease in the
570 ozone loss rate because the corresponding processes of ozone production are all
571 light-driven, but the corresponding processes of ozone loss are not all light-driven
572 because the reaction of O_3 with alkenes does not depend on solar radiation. According
573 to the simulated results, the reaction of ozone with alkenes during this campaign
574 accounts for 17% of total ozone loss.

575 The diurnal profile of the mean ozone production and loss rate is shown in
576 Figure 10. $P(O_3)$ peak midday in the 12:00-14:00 local hours at 31 ppb/h without
577 aerosol impact and 23 ppb/h with aerosol impact. The maximum $D(O_3)$ also occurs
578 between 12:00 and 14:00 at 4.2 ppb/h without aerosol impact and 3.5 ppb/h with
579 aerosol impact. There is little difference between aerosol-impact and aerosol-free
580 $P(O_3)$ (or $D(O_3)$) in the hours of 6:00-11:00, but the difference in the afternoon
581 (12:00-18:00) is large, indicating that the reduction effect of aerosol on ozone
582 production mainly occurs during the afternoon.

583 The above analysis focuses on the effect of aerosol on the ozone production due
584 to aerosol light extinction. However, it does not consider the close relationship
585 between aerosol and ozone's gaseous precursors in the actual atmosphere. To explain
586 this problem, we chose two adjacent days (small SZA effect) with obviously different

587 AOD levels: a clean day (A day: August 21, 2012; AOD = 0.21, $\text{PM}_{2.5}=21.6 \mu\text{g m}^{-3}$)
588 and a day with high aerosol pollution (B day; August 26, 2012; AOD = 3.2,
589 $\text{PM}_{2.5}=125.0 \mu\text{g m}^{-3}$) (Table 7). The difference in AOD between the two days can be
590 taken to represent the maximum daytime gap of AOD for this month. The ozone
591 column concentrations for these two days were 302 DU and 301 DU, respectively, of
592 which the effect on $j(\text{O}^1\text{D})$ is negligible. Under these conditions, the $j(\text{O}^1\text{D})$ value at
593 noon time decreases from $3.23 \times 10^5 \text{ s}^{-1}$ on A day to $1.29 \times 10^5 \text{ s}^{-1}$ on B day (i.e., a 60%
594 reduction) and the $j(\text{NO}_2)$ value at noon time decreases from $8.26 \times 10^{-3} \text{ s}^{-1}$ on A day
595 to $4.19 \times 10^{-3} \text{ s}^{-1}$ on B day (i.e., a 49.2% reduction). As shown in Table 7, B day has
596 higher AOD and higher concentrations of gaseous pollutants. The concentrations of
597 CO , NO_2 , HCHO and the OH reactivity of VOCs in B day are much higher than in A
598 day, with the ratio of 3.6, 2.3, and 2.0, respectively. The simultaneous increases of
599 gaseous pollutants and AOD are due to the fact that gaseous pollutants (NO_x , SO_2 ,
600 and VOCs) emitted by major pollution sources in Beijing, including traffic and
601 industry, have undergone the processes of gas-phase oxidation and nucleation to
602 generate secondary particulate matter that contributes to aerosol light extinction.
603 Previous studies have reported that secondary particulate matter has accounted for
604 more than 60% of total particulate matter during severe smog pollution in Beijing
605 summers (Han et al., 2015a; Guo et al., 2014). In addition, several studies have shown
606 that secondary components in particulate matter (especially secondary organics and
607 ammonium sulfate) have dominated the aerosol light extinction (Han et al., 2014; Han
608 et al., 2017; Wang et al., 2015). Observations made in Beijing during the summer of

609 2006 showed that ammonium sulfate and ammonium nitrate contributed 44.6% and
610 22.3%, respectively, to the total extinction coefficient during a severe period of smog
611 (Han et al., 2014); in the summer of 2014 in Beijing, ammonium sulfate, secondary
612 organic aerosols, and ammonium nitrate contributed 30%, 22%, and 18%, respectively,
613 to the total extinction coefficient (Han et al., 2017).

614 As shown in Figure 11, the simulation results indicate that the net $P(O_3)$ of B day
615 is 36.2% higher than that of A day due to higher concentrations of ozone precursors
616 on B day. This result is consistent with the observed ozone concentrations, of which
617 the observed ozone concentration in B day is 2.2 times higher than that of A day. If we
618 adjust the photolysis frequencies level of B day to the level of A day, the net $P(O_3)$
619 increases by 70.0%, which indicates that the high level of particulate matter in B day
620 greatly inhibits ozone production. This result means that the system is under negative
621 feedback, thus keeping O_3 at a relatively stable level. Table 8 summarizes the average
622 levels of gaseous pollutants and photolysis frequencies for AOD less than 1 and
623 greater than 1, as measured during August 2012. It shows that, the concentrations of
624 ozone's precursors are higher and the photolysis frequencies are lower at high AOD
625 levels ($AOD > 1$) than those at low AOD level ($AOD < 1$). This result means that the
626 negative feedback mechanism is prevalent throughout the whole campaign period.
627 Therefore, the prevention and control measures of air pollution in Beijing need to
628 incorporate this coupling mechanism between particulate matter and ozone to achieve
629 effective control of these two main pollutants.

630 **4. Conclusion**

631 Photolysis reactions are important driving forces for tropospheric photochemical
632 oxidation processes and ozone production. In this study, we explored in detail the
633 effects of aerosols on photolysis frequencies and ozone production in Beijing, based
634 on a long observation period of 4 years. We have found that:

635 (1) There is a strong correlation between PM_{2.5} and AOD, and the slope in
636 summer is smaller significantly than in winter, which indicates that aerosols
637 in summer have a more efficient extinction capacity than in winter.

638 (2) As AOD increased, the extinction effect of aerosol on photolysis frequencies
639 was decreased; this result was probably related to a higher proportion of
640 scattering aerosols under high AOD conditions than under low AOD
641 conditions. The slope of the correlation between photolysis frequencies and
642 AOD indicates that the aerosols in urban Beijing have a stronger extinction
643 on actinic flux than absorptive dust aerosols in the Mediterranean.

644 (3) The influence of AOD on photolysis frequencies was evaluated quantitatively
645 by establishing parametric equations. According to the parametric equation,
646 aerosols lead to a decrease in seasonal mean $j(\text{NO}_2)$ by 24% and 30% for
647 summer and winter, respectively, and the corresponding decrease in seasonal
648 mean $j(\text{O}^1\text{D})$ by 27% and 33% respectively, compared to an aerosol-free
649 atmosphere.

650 (4) In order to evaluate the effects of aerosols on ozone production rate, we
651 carried out an observation campaign in August 2012. The results show that

652 aerosols reduced the net ozone production rate by 25% by reducing the
653 photolysis frequencies. High concentrations of ozone gaseous precursors
654 were often accompanied by high concentrations of particulate matter, which,
655 to a large extent, inhibited excessive levels of ozone generation and reflected
656 the negative feedback effect of the atmospheric system. Therefore, the
657 influence of aerosol on photolysis frequencies and thus on the rate of
658 oxidation of VOCs and NOx to ozone and secondary aerosol is important for
659 determining the atmospheric effects of controlling the precursor emissions of
660 these two important air pollutants (aerosols and ozone).

661

662 **Author contribution**

Author	Contribution
Wenjie Wang	acquisition of data; analysis and interpretation of data; drafting the article and revising it critically
Min Shao	substantial contributions to conception and design; revising the article critically
Xin Li	substantial contributions to conception and design; revising the article critically
Min Hu	collection of data
Limin Zeng	collection of data
Yusheng Wu	collection of data
Tianyi Tan	collection of data

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1040 Table 1. O₃ column concentration, temperature, relative humidity, daytime clear-sky
 1041 fraction and respective standard deviation for different seasons (spring: March, April
 1042 and May; summer: June, July and August; autumn: September, October and
 1043 November; winter: December, January and February).

Season	O ₃ column (Du)	Temperature (°C)	Relative humidity (%)	Clear-sky fraction(%)
Spring	355±37	16±7.8	33±18	41
Summer	310±24	28±4.2	57±18	36
Autumn	304±23	16±7.4	46±21	42
Winter	347±28	0.53±4.2	30±18	41

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1065 Table 2. Instruments deployed in the field campaign undertaken in August 2012 and
 1066 used for data analysis.

Parameters	Measurement technique	Time resolution	Detection limit	Accuracy
j(O ¹ D) and j(NO ₂)	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%
VOCs	GC-FID/MS	1 h	20-300 pptv	± 15~20%

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1085 Table 3. Slope, intercept and the square of correlation coefficient (r^2) of linear fits of

1086 correlation between $j(O^1D)$ and AOD for each ozone column class at AOD smaller

1087 than 0.7.

O_3 column (DU)	SZA=30°			SZA=60°		
	Slope ($10^{-6}s^{-1}$)	Intercept ($10^{-6}s^{-1}$)	r^2	Slope ($10^{-6}s^{-1}$)	Intercept ($10^{-6}s^{-1}$)	r^2
300-330	-6.2±1.5	26±1	0.34	-4.2±0.4	7.7±0.3	0.41
330-360	-6.5±1.4	23±1	0.40	-5.0±0.3	7.1±0.2	0.52
360-390	-9.5±1.6	21±1	0.52	-6.9±0.6	7.6±0.3	0.66

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1101
1102 Table 4. Slope, intercept and the square of correlation coefficient (r^2) of linear fits of
1103 correlation between $j(\text{NO}_2)$ and AOD for each ozone column class at AOD smaller
1104 than 0.7.

cos(SZA)	Slope (10^{-3} s^{-1})	Intercept (10^{-3} s^{-1})	r^2
0-0.2	-1.3±0.1	1.5±0.0	0.52
0.2-0.4	-2.4±0.1	3.4±0.0	0.41
0.4-0.6	-3.2±0.1	5.5±0.0	0.49
0.6-0.8	-2.1±0.1	7.2±0.1	0.38
0.8-1.0	-1.8±0.1	8.1±0.1	0.26

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1123 Table 5. The fitting parameters a_1-a_6 and determination coefficients of E5 for $j(\text{NO}_2)$.

a_1	a_2	a_3	a_4	a_5	a_6	r^2
$\times 10^{-3}$						
-0.46 ± 0.05	-2.0 ± 0.03	13 ± 0.2	0.22 ± 0.01	0.32 ± 0.05	-4.0 ± 0.1	0.96

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1128 Table 6. The fitting parameters a_1-a_6 and determination coefficients of E6 for $j(\text{O}^1\text{D})$

1129 at ozone column range = 300-330 DU.

a_1	a_2	a_3	a_4	a_5	a_6	r^2
$\times 10^{-6}$						
1.1 ± 0.3	0.58 ± 0.17	-8.7 ± 0.9	0.63 ± 0.05	-7.5 ± 0.3	43 ± 1	0.96

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1140 **Table 7.** Mean and standard deviation of observed data during daytime (6:00–18:00)

1141 for A day and B day.

Observed data	A day: August 21, 2012	B day: August 26, 2012
AOD	0.21 ± 0.05	3.2 ± 0.4
PM _{2.5} ($\mu\text{g m}^{-3}$)	22 ± 9	125 ± 16
O ₃ column (Du)	302 ± 3	301 ± 3
Temperature($^{\circ}\text{C}$)	28 ± 3	28 ± 3
Relative humidity (%)	48 ± 10	55 ± 12
j(O ¹ D)(s^{-1})	$1.6 \times 10^{-5} \pm 1.2 \times 10^{-5}$	$6.9 \times 10^{-6} \pm 5.2 \times 10^{-6}$
j(NO ₂)(s^{-1})	$5.4 \times 10^{-3} \pm 2.9 \times 10^{-3}$	$2.9 \times 10^{-3} \pm 1.7 \times 10^{-3}$
O ₃ (ppb)	40 ± 17	87 ± 53
NO ₂ (ppb)	11 ± 5	25 ± 10
CO (ppm)	0.24 ± 0.05	0.85 ± 0.14
VOC reactivity (s^{-1})	3.0 ± 0.7	6.4 ± 1.7
HCHO (ppb)	2.7 ± 1.1	7.4 ± 1.9

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1150 Table 8. Monthly mean and standard deviation of observed data during daytime

1151 (6:00–18:00) under the condition of AOD less than 1 and larger than 1 in August 2012

Observed data	AOD<1	AOD>1
AOD	0.43 ± 0.24	2.0 ± 0.8
PM _{2.5} ($\mu\text{g m}^{-3}$)	26 ± 12	77 ± 47
O ₃ column (Du)	303 ± 4	302 ± 5
Temperature($^{\circ}\text{C}$)	30 ± 4	29 ± 4
Relative humidity (%)	42 ± 16	57 ± 13
j(O ¹ D)(s^{-1})	$1.6 \times 10^{-5} \pm 1.1 \times 10^{-5}$	$1.0 \times 10^{-5} \pm 0.7 \times 10^{-5}$
j(NO ₂)(s^{-1})	$5.6 \times 10^{-3} \pm 2.4 \times 10^{-3}$	$3.8 \times 10^{-3} \pm 1.7 \times 10^{-3}$
O ₃ (ppb)	52 ± 34	68 ± 46
NO ₂ (ppb)	16 ± 7.8	24 ± 9
CO (ppm)	0.47 ± 0.20	0.95 ± 0.47
VOC reactivity (s^{-1})	4.3 ± 1.7	6.2 ± 2.2
HCHO (ppb)	4.0 ± 1.4	6.5 ± 1.9

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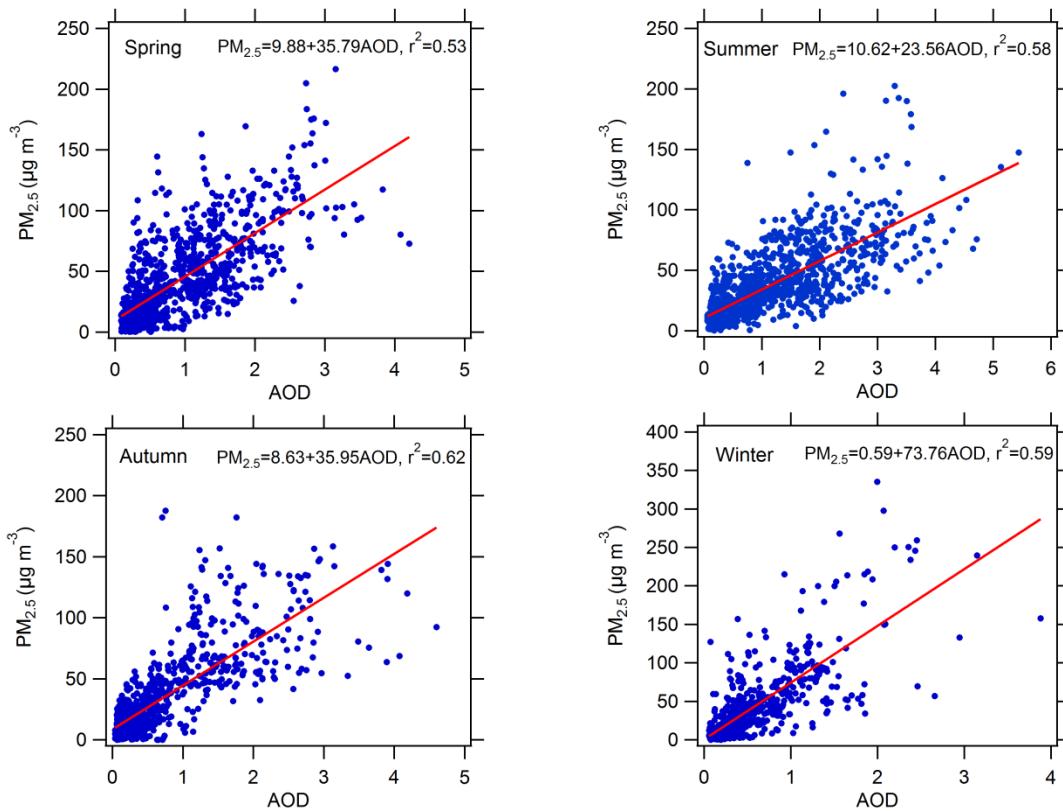
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1162 Figure 1. Scatter plots between AOD at 380nm and $\text{PM}_{2.5}$ in four different seasons.

1163 The slope, intercept and determination coefficient (r^2) were calculated.

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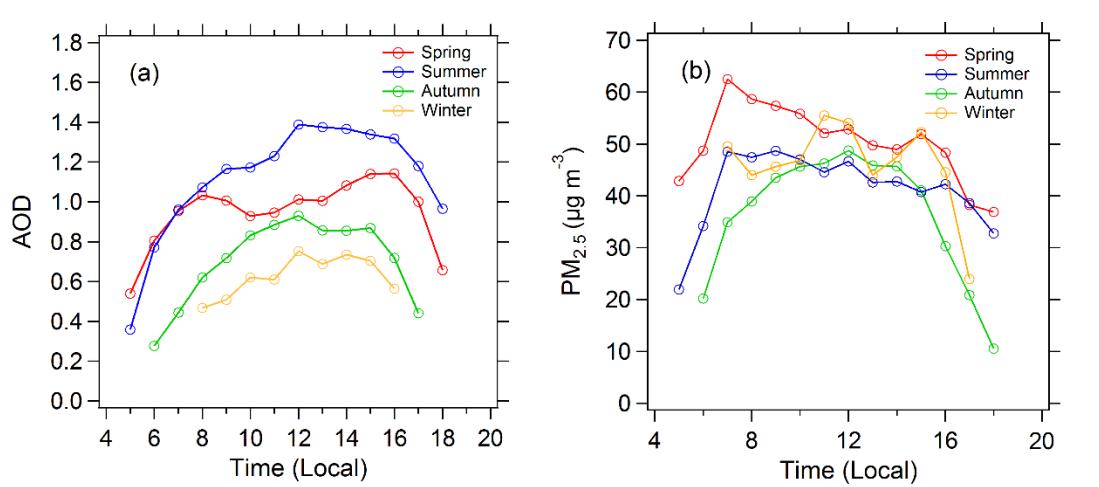
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Figure 2. Diurnal cycles of (a) mean AOD and (b) mean $\text{PM}_{2.5}$ in the four seasons

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under cloudless conditions.

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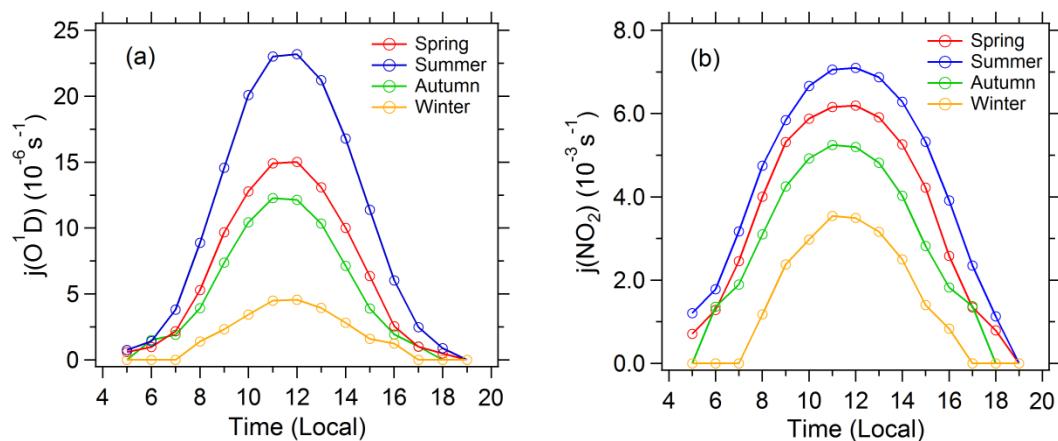
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1200 Figure 3. Diurnal cycles of (a) mean $j(O^1D)$ and (b) mean $j(NO_2)$ in the four seasons

1201 under cloudless conditions.

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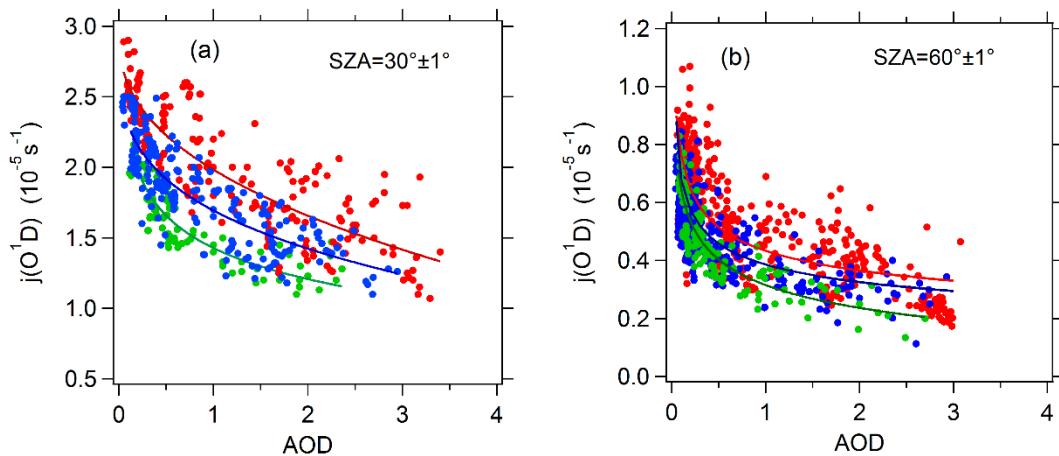
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1224 Figure 4. Dependence of $j(O^1D)$ on AOD (380nm) at SZA of (a) 30° and (b) 60° and
1225 at different classes of ozone column concentration: 300-330 DU (red), 330-360 DU
1226 (blue), and 360-390 DU (green). The full lines are fitted by exponential function.

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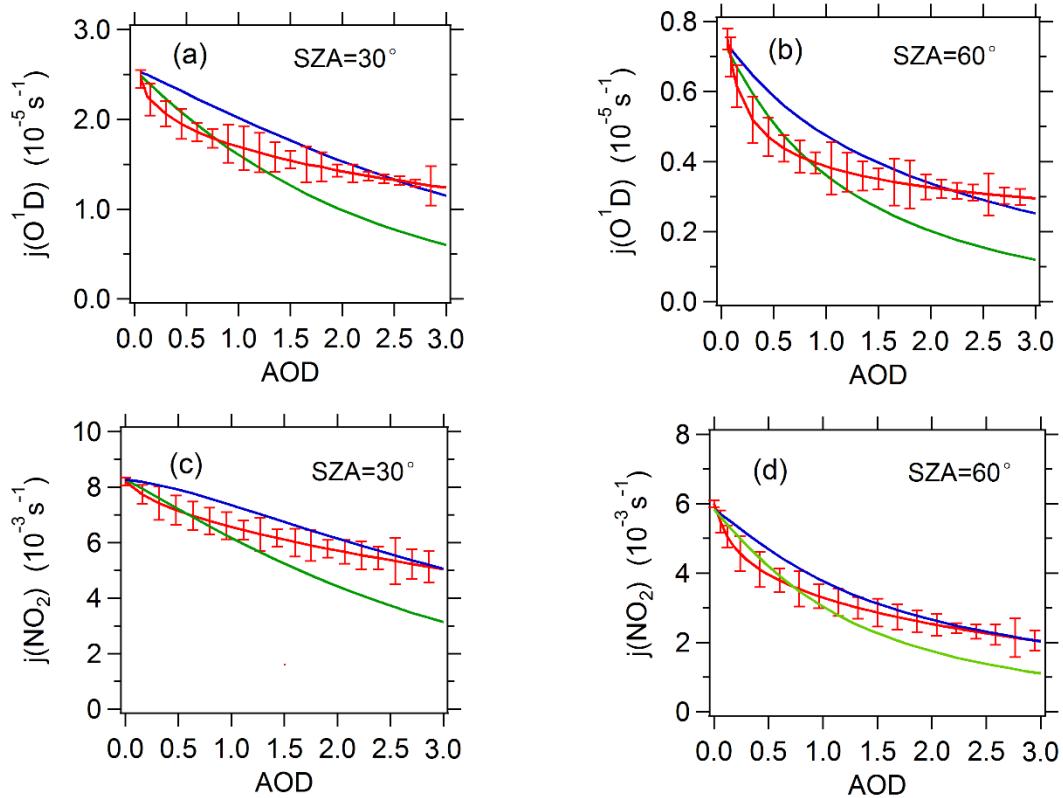
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1244 Figure 5. The relationship between observed or TUV-simulated photolysis
 1245 frequencies and AOD (380nm) at SZA of 30° and 60° . For $j(O^1D)$, total ozone
 1246 column classification of 330-360 DU is chosen. The red line represents observed
 1247 average photolysis frequencies; the blue line and green line represents TUV-simulated
 1248 average photolysis frequencies at SSA of 0.95 and 0.85 respectively.

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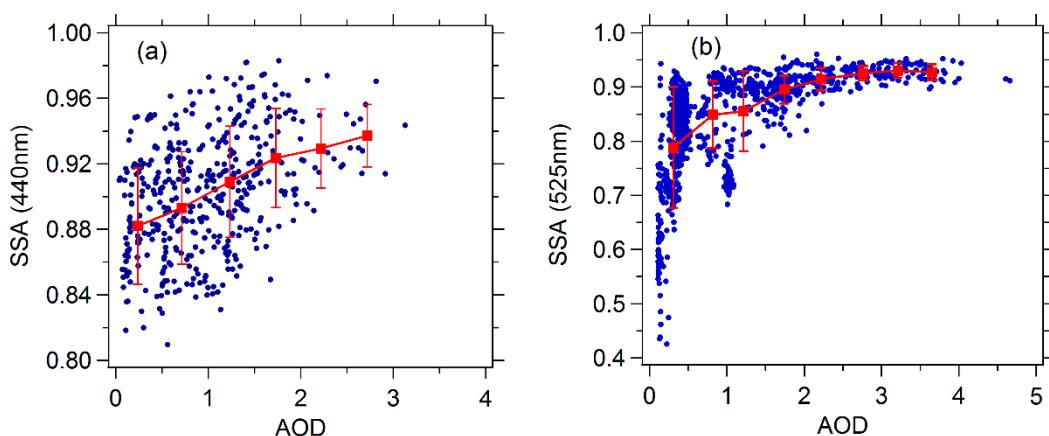
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1262 Figure 6. Correlation between SSA and AOD (380nm). (a) SSA (440nm) is acquired

1263 from AERONET during 2012-2015. (b) SSA (525nm) is acquired from near-ground

1264 measurement campaign in August 2012.

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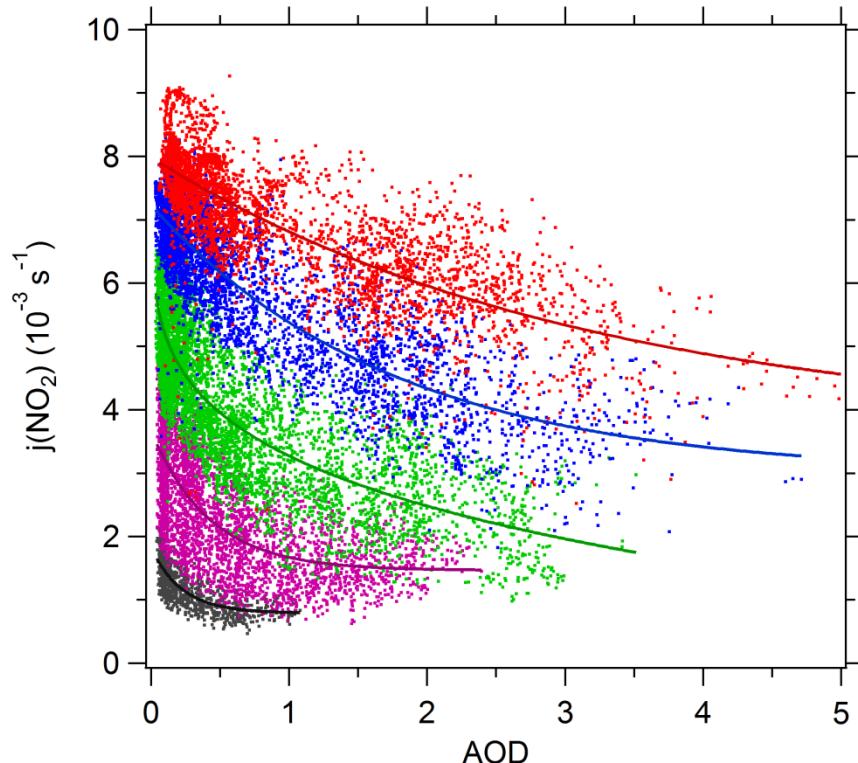
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1278 Figure 7. Dependence of $j(\text{NO}_2)$ on AOD (380nm) at different SZA classes. The
 1279 classes of $\cos(\text{SZA})$ are 0–0.2 (black), 0.2–0.4 (purple), 0.4–0.6 (green), 0.6–0.8
 1280 (blue), and 0.8–1 (red). The full lines are fitted by exponential function.

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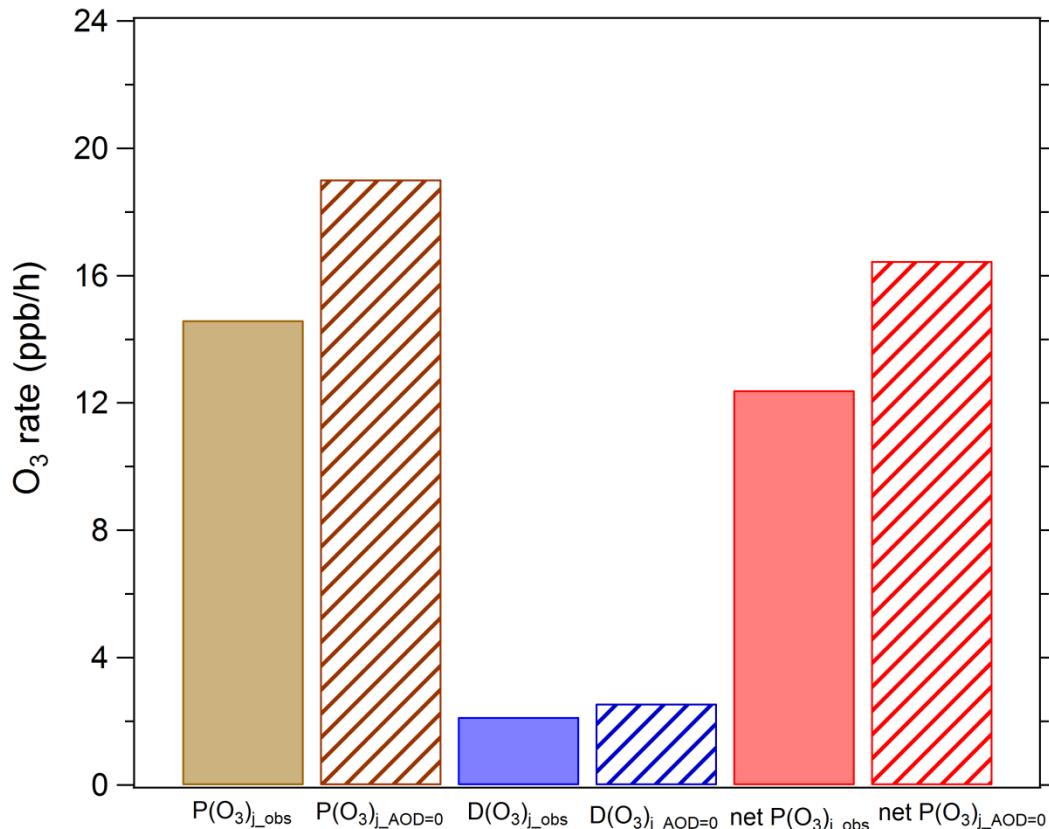
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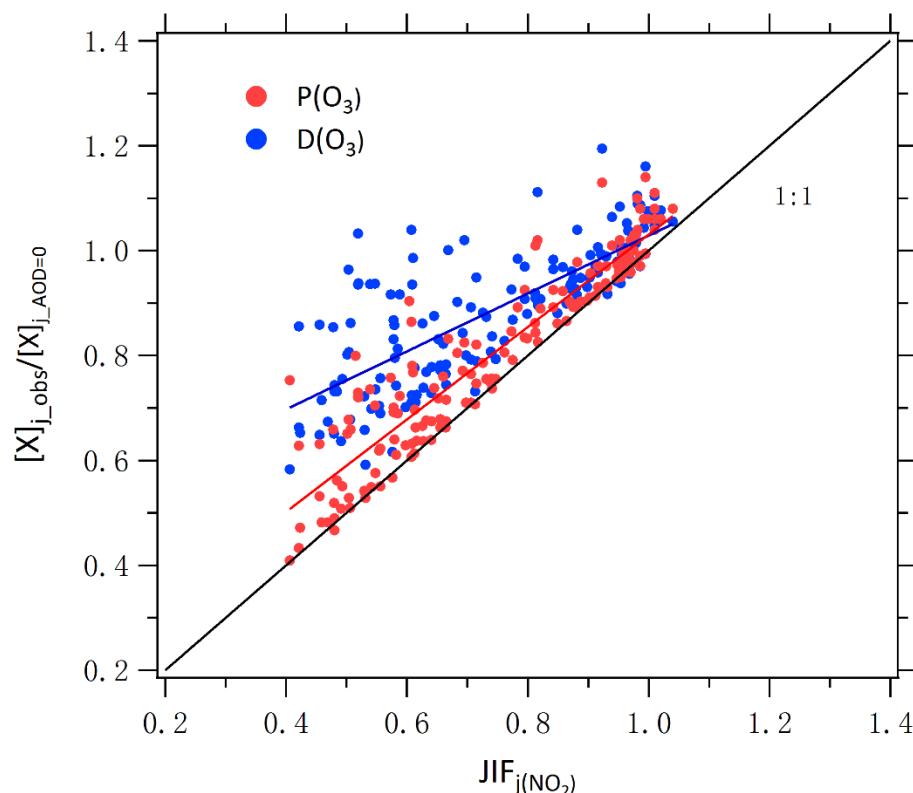
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1296 Figure 8. Mean daytime ozone production and loss terms in August 2012. P(O₃)_j_obs,
1297 D(O₃)_j_obs and net P(O₃)_j_obs represents ozone production rate, ozone loss rate, and net
1298 ozone production rate under observed photolysis frequencies; P(O₃)_j_AOD=0, D(O₃)
1299 j_AOD=0 and net P(O₃)_j_AOD=0 represents ozone production rate, ozone loss rate, and net
1300 ozone production rate under calculated photolysis frequencies when AOD is equal to
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1309 Figure 9. Correlation between $P(O_3)_{j_obs}/P(O_3)_{j_AOD=0}$ (or $D(O_3)_{j_obs}/D(O_3)_{j_AOD=0}$) and
1310 $JIF_{j(\text{NO}_2)}$. Single data point represent daytime hourly mean value.

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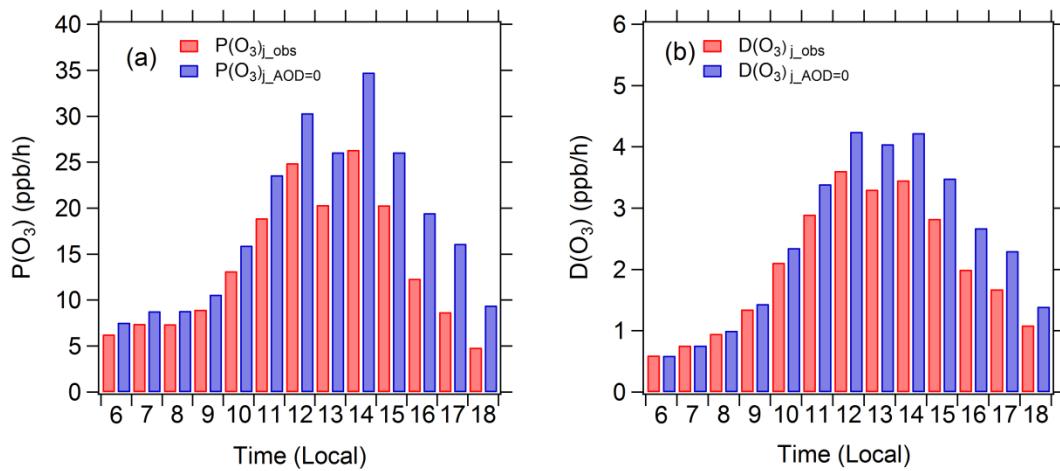
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1328 Figure 10. Diurnal profiles of mean $P(O_3)_{j_obs}$, $P(O_3)_{j,AOD=0}$, $D(O_3)_{j_obs}$, and
1329 $D(O_3)_{j,AOD=0}$ in August 2012 under clear-sky conditions.

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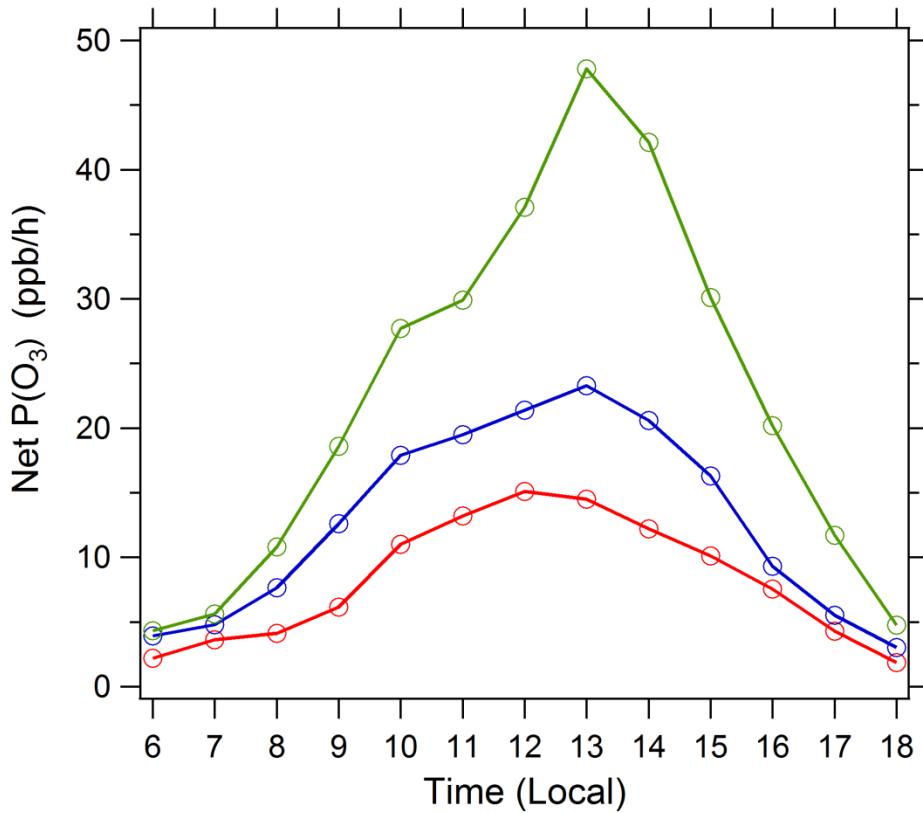
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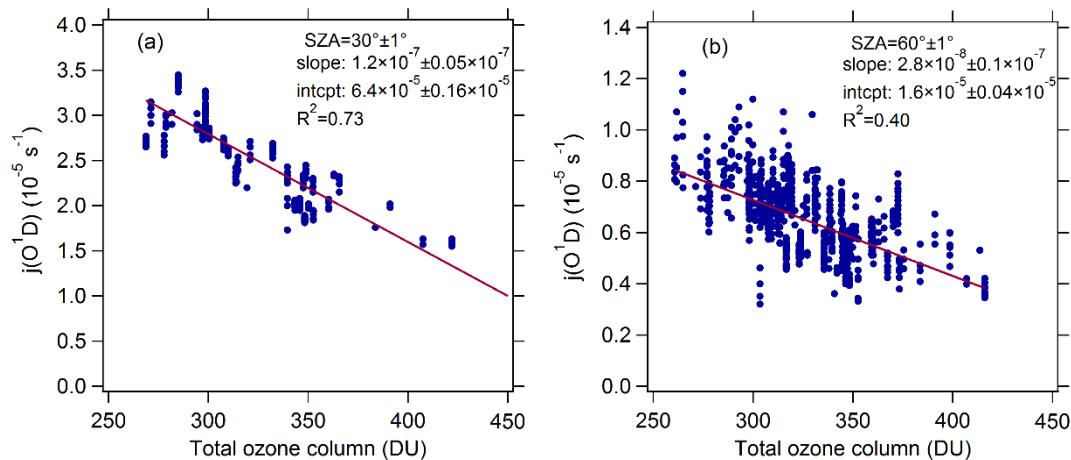


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1351 Figure 11. Diurnal profile of net $P(O_3)$ simulated by the box model. Three cases are
1352 displayed: (1) A day (red circles): August 21, 2012 with low AOD level and high
1353 photolysis frequencies; (2) B day (blue circles): August 26, 2012 with high AOD level
1354 and low photolysis frequencies; and (3) the photolysis frequencies of B day adjusted
1355 to the level of A day with other conditions unchanged (green circles). The specific
1356 conditions of A day and B day are listed in Table 7.

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1362 Supporting information
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1367 Figure S1. Dependence of $j(O^1D)$ on AOD (380nm) at low AOD level ($AOD < 0.3$) and
1368 SZA of (a) $30^\circ \pm 1^\circ$ and (b) $60^\circ \pm 1^\circ$, respectively.
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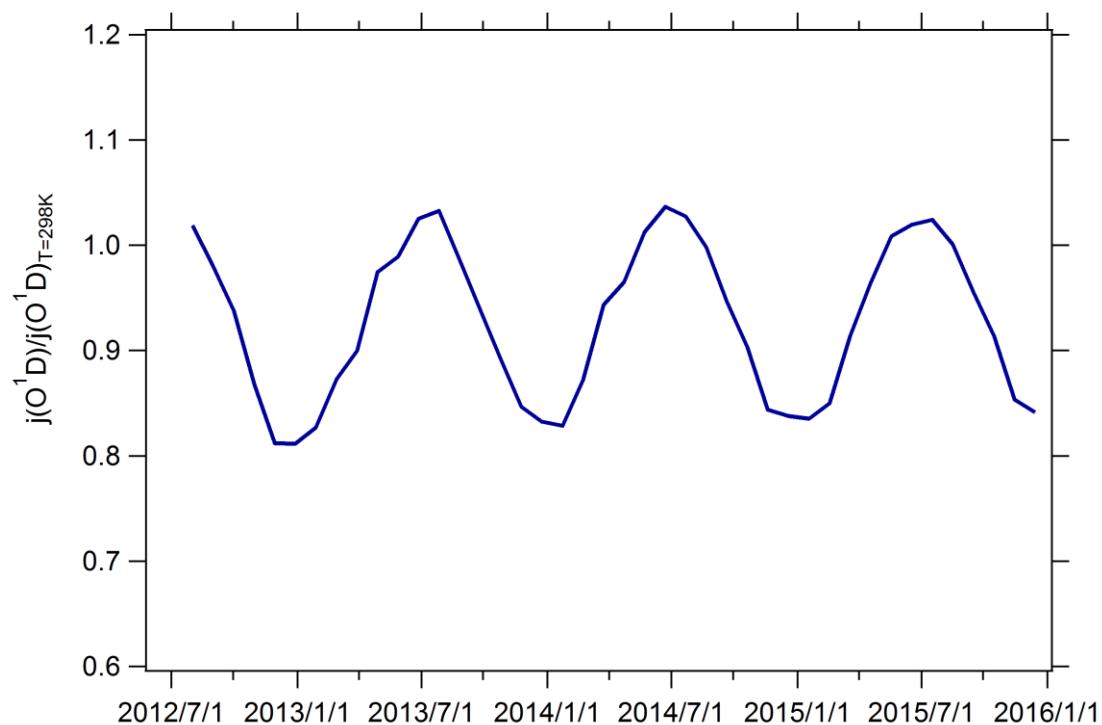
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1389 Figure S2. The time series of the monthly mean ratio of $j(O^1D)$ to $j(O^1D)_{T=298K}$
1390 $(j(O^1D)/j(O^1D)_{T=298K})$ from August 2012 to December 2015.

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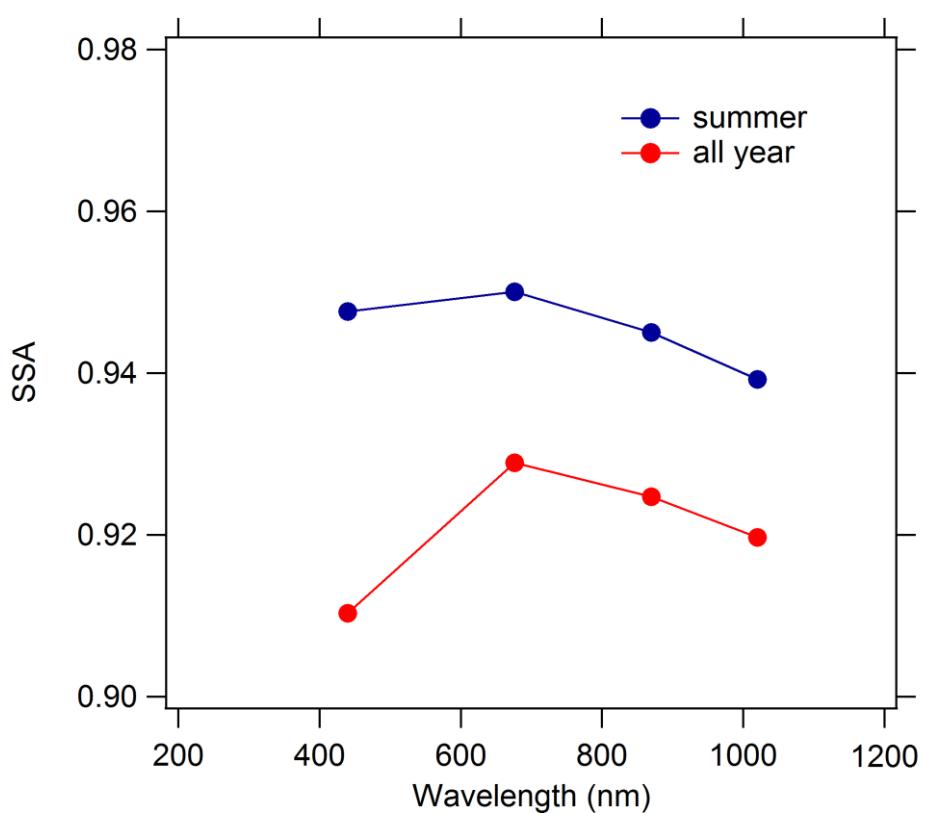
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1410 Figure S3. The dependence of AERONET based SSA on wavelength.
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Table S1. The seasonal mean AOD and SSA of AERONET.

Seasons	Spring	Summer	Autumn	Winter
AOD	0.83 ± 0.72	0.99 ± 0.90	0.59 ± 0.70	0.47 ± 0.47
SSA	0.91 ± 0.03	0.94 ± 0.02	0.91 ± 0.03	0.88 ± 0.03

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