



1 **Ozone formation under low solar radiation in eastern China**

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24 Abstract

25 $PM_{2.5}$, a particulate matter with a diameter of 2.5 micrometers or less, is one of the
26 major components of the air pollution in eastern China. In the past few years, China's
27 government made strong efforts to reduce the $PM_{2.5}$ pollutions. However, another
28 important pollutant (ozone) becomes an important problem in eastern China. Ozone
29 (O_3) is produced by photochemistry, which requires solar radiation for the formation
30 of O_3 . Under heavy $PM_{2.5}$ pollution, the solar radiation is often depressed, and the
31 photochemical production of O_3 is prohibited. This study shows that during fall in
32 eastern China, under heavy $PM_{2.5}$ pollutions, there were often strong O_3
33 photochemical productions, causing a co-occurrence of high $PM_{2.5}$ and O_3
34 concentrations. This co-occurrence of high $PM_{2.5}$ and O_3 is un-usual and is the main
35 focus of this study. Recent measurements show that there were often high HONO
36 surface concentrations in major Chinese mega cities, especially during daytime, with
37 maximum concentrations ranging from 0.5 to 2 ppbv. It is also interesting to note that
38 the high HONO concentrations were occurred during high aerosol concentration
39 periods, suggesting that there were additional HONO surface sources in eastern China.
40 Under the high daytime HONO concentrations, HONO can be photo-dissociated to be
41 OH radicals, which enhance the photochemical production of O_3 . In order to study the
42 above scientific issues, a radiative transfer model (TUV; Tropospheric
43 Ultraviolet-Visible) is used in this study, and a chemical steady state model is
44 established to calculate OH radical concentrations. The calculations show that by
45 including the OH production of the photo-dissociated of HONO, the calculated OH
46 concentrations are significantly higher than the values without including this
47 production. For example, by including HONO production, the maximum of OH
48 concentration under the high aerosol condition (AOD=2.5) is similar to the value
49 under low aerosol condition (AOD=0.25) in the no-HONO case. This result suggests
50 that even under the high aerosol condition, the chemical oxidizing process for O_3
51 production can occurred, which explain the co-occurrence of high $PM_{2.5}$ and high O_3
52 in fall season in eastern China. However, the O_3 concentrations were not significantly



53 affected by the appearance of HONO in winter. This study shows that the seasonal
54 variation of solar radiation plays important roles for controlling the OH production in
55 winter. When the solar radiation is in a very low level in winter, it reaches the
56 threshold level to prevent the OH chemical production, even by including the HONO
57 production of OH. This study provides some important scientific highlights to better
58 understand the O₃ pollutions in eastern China.

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60 **Keywords; High PM_{2.5} and O₃, eastern China, HONO photolysis**

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67 1. Introduction

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69 Currently, China is undergoing a rapid economic development, resulting in a higher
70 demand for energy and greater use of fossil fuels. As a result, the high emissions of
71 pollutants produce heavy pollutions in mega cities of eastern China, such as Beijing
72 and Shanghai. For example, in the city of Shanghai (a largest mega city in China), the
73 urban and economical developments of the city are very rapid. During 1990 to 2015,
74 the population increased from 13.3 to 24.1 million. The number of automobiles
75 increased from 0.2 million (1993) to 2.0 million (2011). The rapid growing population
76 and energy usage caused a rapid increase in the emissions of pollutants, leading to
77 severe air pollution problems in these mega cities (Zhang et al., 2006; Geng et al.,
78 2007; Deng et al., 2008).

79

80 Measurements, such as satellite observations have revealed much higher aerosol
81 pollution in eastern China than in eastern US (Tie et al., 2006). The high aerosol
82 pollution causes a wide range of environmental consequences. According to a study
83 by Tie et al. (2009a), exposure to extremely high particle concentrations leads to a
84 great increase of lung cancer cases. High PM (particular matter) concentrations also
85 significantly reduce the range of visibility in China's mega cities (Deng et al., 2008).
86 According to a recent study, the high aerosol pollution causes important effects on the
87 crop (rice and wheat) production in eastern China (Tie et al., 2016).

88

89 In the troposphere, ozone formation is resulted from a complicated chemical process,
90 and requires ozone precursors, such as VOCs (volatile organic carbons) and $\text{NO}_x =$
91 $\text{NO} + \text{NO}_2$ (nitrogen oxides) (Sillman, 1995). As the increase in industrial activity and
92 number of automobiles, the precursors of ozone (O_3) and the global budget of
93 oxidization are also significantly increased (Huang et al., 2017; Huang et al., 2018).
94 As a result, O_3 pollutions are becomes a serous pollution problem in Shanghai and
95 other Chinese mega cities (Geng et al., 2010; Tie 2009b; Tie et al., 2015). The effects
96 on O_3 production rate can be characterized as either NO_x -sensitive or VOC-sensitive
97 conditions (Sillman, 1995; Zhang et al., 2003; Lei et al., 2004; Tie et al., 2013). Thus,
98 better understanding the trends of O_3 precursors (VOCs, NO_x) is important to



99 determine the O₃ trends in Shanghai (as well as many large cities in China).

100 In the past few years, China's government made strong efforts to reduce the PM_{2.5}
101 pollutions. However, another important pollutant (O₃) becomes an important problem
102 in eastern China. Several studies regarding the O₃ formation are previously studied in
103 Shanghai. For example, Geng et al. (2007; 2008) study the relationship between O₃
104 precursors (NO_x and VOCs) for the ozone formation in Shanghai. Tie et al. (2009)
105 study the short-term variability of O₃ in Shanghai. Their study suggested that in
106 addition to the ozone precursors, meteorological conditions, such as regional transport,
107 have also strong impacts on the ozone concentrations. During September 2009, a
108 major field experiment (the MIRAGE-Shanghai) was conducted in Shanghai, and
109 multiply chemical species were measured during the experiment. The summary of the
110 measurements by Tie et al (2013) suggests that the ozone formation in Shanghai is
111 under VOC-sensitive condition. However, if the emission ration of NO_x/VOCs
112 reduces to a lower value (0.1-0.2), the ozone formation in Shanghai will switch from
113 VOC-sensitive condition to NO_x-sensitive condition.

114 Despite of some progresses have been made for the ozone formation in mega cities in
115 China, it is still lack of study of ozone development in large cities of China. For
116 example, this study shows that during fall in eastern China, under heavy PM_{2.5}
117 pollutions, there were often strong O₃ chemical productions, causing the
118 co-occurrence of high PM_{2.5} and O₃ concentrations. Under heavy aerosol condition,
119 the solar radiation is depressed, significantly reducing the photochemical production
120 of O₃. This co-occurrence of high PM_{2.5} and O₃ is an unusual and is the focus of this
121 study. Recent measurements show that there were often high HONO concentrations in
122 major Chinese mega cities, especially during daytime, with maximum concentrations
123 ranging from 0.5 to 2 ppbv (Huang et al., 2017). It is also interesting to note that the
124 high HONO surface concentrations were occurred during high aerosol concentration
125 periods, suggesting that there are additional HONO surface sources in eastern China.
126 Under the high daytime HONO concentrations, HONO can be photo-dissociated to be
127 OH radicals, which enhance the photochemical production of O₃.



128

129 The paper is organized as follows: in Section 2, we describe the measurement of O₃
130 and PM_{2.5}. In Section 3, we describe the calculation of photo-dissociated rate of
131 HONO and a steady state model for the calculation of OH, and the causes of high O₃
132 production under the heavy aerosol condition. Section 4 shows a brief conclusion of
133 the results.

134

135 **2. Measurements of O₃ and PM_{2.5}**

136

137 There are long-term measurements in Eastern China by Chinese Environment
138 Protection Agency (CEPA) for monitoring the air quality in China. In eastern China,
139 especially in the capital city of China (Beijing), there are often heavy air pollutions,
140 especially for fine particulate matter (PM_{2.5} – the radius of particle being less than 2.5
141 μm). Figure 1 shows the measurement sites in Beijing, in which the measured
142 concentrations of PM_{2.5} and O₃ are used to the analysis. In the region, the air
143 pollutions were very heavy, especially in winter (Long et al., 2016; Tie et al., 2017).
144 The previous studies suggested that the both aerosol and O₃ pollutions became the
145 major pollutants in the region (Li et al., 2017).

146

147 Figure 2 shows the daily averaged concentrations of PM_{2.5} and O₃ in the Beijing
148 region in 2015. The daily averaged concentrations show that there were strong daily
149 and seasonal variations for both the concentrations of PM_{2.5} and O₃. Despite the daily
150 variation, the concentrations of PM_{2.5} existed a strong seasonal variation. For example,
151 there were very high concentrations during winter, with maximum of ~300 μg/m³.
152 While in summer, the maximum concentrations reduced to ~150 μg/m³. The seasonal
153 variability of O₃ concentrations were opposite with the PM_{2.5} concentrations, with
154 lower concentrations in winter (< 50 μg/m³) and higher concentrations in summer (>
155 150 μg/m³). These seasonal variations of PM_{2.5} and O₃ have been studied by previous
156 studies (Tie and Cao, 2017; Li et al., 2017). Their results suggest that the winter high



157 PM_{2.5} concentrations were resulted from the combination of both the high emissions
158 (heating season in the Beijing region), and poor meteorological ventilation conditions,
159 such as lower PBL (Planetary Boundary Layer) height (Quan et al., 2013; Tie et al.
160 2015). According to the photochemical theory of O₃ formation, the summer high and
161 winter low O₃ concentrations are mainly due to seasonal variation of the solar
162 radiation (Seinfeld, J. H. and Pandis, 2006).

163

164 In addition to the seasonal variation of solar radiation, the heavy aerosol
165 concentrations play important roles to reduce solar radiation, causing the reduction of
166 solar radiation and O₃ formation (Bian et al., 2007). As we show in Fig. 3a, during
167 wintertime, the O₃ concentrations were strong anti-correlated with the PM_{2.5}
168 concentrations, suggesting that the reduction of solar radiation by aerosol particles
169 have important impact on the reduction of O₃ concentrations. Figure 3a also shows
170 that the relationship between O₃ and PM_{2.5} was not linearly related. For example,
171 when the concentrations of PM_{2.5} were less than 100 μg/m³, O₃ concentrations rapidly
172 decreased with the increase of PM_{2.5} concentrations. In contrast, when the
173 concentrations of PM_{2.5} were greater than 100 μg/m³, O₃ concentrations slowly
174 decreased with the increase of PM_{2.5} concentrations. This is consistent with the result
175 of Bian et al (2007).

176

177 It is interesting to note that during late spring, summer, and early fall periods, the
178 correlation between PM_{2.5} and O₃ concentrations was positive relationship compared
179 to the negative relationship in winter (see Fig. 3b). This result suggests that O₃
180 production was high during the heavy haze period, despite the solar radiation was
181 greatly depressed. In order to clearly display this unusual event, we illustrate diurnal
182 variations of PM_{2.5} and O₃, and NO₂ during a fall period (from Oct.5 to Oc. 6, 2015).
183 Figure 4 shows that during this period, the PM_{2.5} concentrations were very high,
184 ranging from 150 to 320 μg/m³. Under such high aerosol condition, the solar radiation
185 should be significantly reduced, and O₃ photochemical production would be reduced.
186 However, the diurnal variation of O₃ was unexpectedly strong, with high noontime



187 concentration of $>220 \mu\text{g}/\text{m}^3$ and very low nighttime concentration of $\sim 25 \mu\text{g}/\text{m}^3$. This
188 strong diurnal variation was due to the photochemical activity, which suggested that
189 during relatively low solar conditions, the photochemical activities of O_3 production
190 was high. According to the theory of the O_3 chemical production, the high O_3
191 production is related to high oxidant of OH (Seinfeld and Pandis, 2006), which should
192 not be occurred during lower solar radiation. This result brings important issue for air
193 pollution control strategy, because the both air pollutants (high $\text{PM}_{2.5}$ and O_3) were
194 important air pollution problems in eastern China.

195

196 2. Method

197

198 In order to better understand the O_3 chemical production occurred in heavy aerosol
199 condition in eastern China, the possible O_3 production in such condition is discussed.
200 Ozone photochemical production ($\text{P}[\text{O}_3]$) is strongly related to the amount of OH
201 radicals (OH) (Chameides et al., 1999). According to the traditional theory, the
202 amount of surface OH radicals is proportional to the surface of solar radiation, which
203 is represented by

204

$$205 \quad [\text{OH}] = \text{P}[\text{HOx}]/\text{L}[\text{HOx}]^* \quad (\text{R-1})$$

206

207 Where $[\text{OH}]$ represents the concentration of hydroxyl radicals ($\#/\text{cm}^3$); HOx
208 represents the concentration of $\text{HO}_2 + \text{OH}$ ($\#/\text{cm}^3$); $\text{P}[\text{HOx}]$ represents the
209 photochemical production of HOx ($\#/\text{cm}^3/\text{s}$); and $\text{L}[\text{HOx}]^*$ (1/s) represents the
210 photochemical destruction of HOx, which is normalized by the concentrations of OH.

211

212 The major process for the photochemical production of $\text{P}[\text{HOx}]$ is through the O_3
213 photolysis and follows by the reaction with atmospheric water vapor. It can express
214 by

$$215 \quad \text{P}[\text{HOx}] = \text{J}_1[\text{O}_3]/(k_1 \times \text{am}) \times 2.0 \times k_2[\text{H}_2\text{O}] = \text{P}_1[\text{HOx}] \quad (\text{R-2})$$

216



217 Where J_1 represents the photolysis of $O_3 + h\nu \rightarrow O^1D$; k_1 represents the reaction rate
218 of $O^1D + am \rightarrow O^3P$; and k_2 represents the reaction rate of $O^1D + H_2O \rightarrow 2OH$. As
219 we can see, this HOx production is proportional to the magnitude of solar radiation
220 (J_1), and J_1 is the O_3 photolysis with the solar radiation. Figure 5 shows the
221 relationship between the values of J_1 and aerosol concentrations in October at
222 middle-latitude calculated by the TUV model Madronich and Flocke (1999). This
223 result suggests that under the high aerosol concentrations ($AOD = 2.5$), the J_1 value is
224 strongly depressed, resulting in significant reduction of OH concentrations and O_3
225 production. For example, the maximum J_1 value is about 2.7×10^{-5} (1/s) with lower
226 aerosol values ($AOD = 0.25$). According to the previous study, the surface $PM_{2.5}$
227 concentrations were generally smaller than $50 \mu g/m^3$ with this AOD value (Tie et al.,
228 2017). However, when the AOD value increase to 2.5 (the $PM_{2.5}$ concentrations are
229 generally $>100 \mu g/m^3$), the maximum J_1 value rapidly decreases to about 6×10^{-6} (1/s),
230 which is about 450% reduction compared to the value with $AOD=0.25$. This study
231 suggests that under high $PM_{2.5}$ concentrations ($>100 \mu g/m^3$), the photochemical
232 production of OH (P[HOx]) is rapidly decreased, leading to low OH concentrations,
233 which cannot initiate the high oxidation of O_3 production. As a result, the high O_3
234 production shown in Fig. 4 cannot be explained. Other sources for O_3 oxidation are
235 needed to explain this result.

236

237 Recent studies show that the HONO concentrations are high in eastern China (Huang
238 et al., 2017). Because under high solar radiation, the photolysis rate of HONO is very
239 high, resulting in very low HONO concentrations in daytime (Seinfeld and Pandis,
240 2006). These measured high HONO concentrations are explained by their studies.
241 One of the explanations is that there are high surface HONO sources during daytime,
242 which produces high HONO concentrations (Huang et al., 2017).

243

244 Figure 6 shows the measured HONO concentrations in two large cities in China
245 (Shanghai and Xi'an) during fall time. It shows that the measured HONO
246 concentrations were high, with a maximum concentration of 2.3 ppbv during morning,



247 and about 0.5-1.0 ppbv in daytime. It is also interesting to note that the high HONO
248 concentrations were occurred during high aerosol concentration periods. Figure 7
249 illustrates that when the PM_{2.5} concentrations increased to 70-80 $\mu\text{g}/\text{m}^3$, and the
250 HONO concentrations enhanced to 1.4-18 ppbv during September in Shanghai. This
251 measured high HONO concentrations were significantly higher than the calculated
252 concentrations (shown in Fig. 6), suggesting that some additional sources of HONO
253 are needed. This result is consistent with the HONO measurements in other Chinese
254 cities (Huang et al. 2017).

255

256 Under the high HONO concentrations in daytime, HONO can be photolyzed to be OH,
257 and become another important process to produce OH. As a result, the OH production
258 rate (P[HOx]) can be written to the following reactions.

259

$$260 \quad P_2[\text{HOx}] = J_2 \times [\text{HONO}] \quad (\text{R-3})$$

$$261 \quad P[\text{HOx}] = P_1[\text{HOx}] + P_2[\text{HOx}]$$

$$262 \quad = J_1[\text{O}_3]/(k_1 \times \text{am}) \times 2.0 \times k_2[\text{H}_2\text{O}] + J_2 \times [\text{HONO}] \quad (\text{R-4})$$

263

264 Because the chemical lifetime of OH is less than second, OH concentrations can be
265 calculated according to equilibrium of chemical production and chemical loss. With
266 the both OH chemical production processes, the OH concentrations can be calculated
267 by the following equation (Seinfeld and Pandis, 2006).

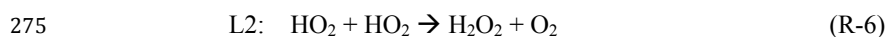
268

$$269 \quad P_1 + P_2 = L_1 + L_2$$

270

271 Where P1 and P2 are the major chemical productions, expressed in R-4, and L1 and
272 L2 are the major chemical loss of OH, and represent by

273



276



277 Under high NO_x condition, such as in the Shanghai region, NO_x concentrations were
278 often higher to 50 ppbv (shown in Fig. 3), the L1 term is larger than L2. The OH
279 concentrations can be approximately expressed by

280

$$281 \quad [\text{HO}] = \frac{\{J_1[\text{O}_3]/(k_1 \times \text{am}) \times 2.0 \times k_2[\text{H}_2\text{O}] + J_2 \times [\text{HONO}]\}}{282 \quad k_3[\text{NO}_2]} \quad (\text{R-5})$$

283

284 Where k_3 is the reaction coefficient of $\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3$.

285

286 **3. Result and analysis**

287

288 **3.1. OH productions in different HONO conditions**

289

290 In order to quantify the individual effects of these two OH production terms (P1 and
291 P2) on the OH concentrations, the P1 and P2 are calculated under different daytime
292 HONO conditions (calculated low HONO and measured high HONO concentrations).
293 Figure 8 shows that under the low HONO condition, the P1 is significantly higher
294 than P2, and P2 has only minor contribution to the OH values. For example, the
295 maximum of P1 occurred at 13 pm, with a value of $65 \times 10^6 \text{ \#/cm}^3/\text{s}$. In contrast, the
296 maximum of P1 occurred at 10 am, with a value of $15 \times 10^6 \text{ \#/cm}^3/\text{s}$. However,
297 under high HONO condition, the P2 plays very important roles for the OH production.
298 The maximum of P1 occurred at 11 am, with a value of $350 \times 10^6 \text{ \#/cm}^3/\text{s}$, which is
299 about 500% higher than the P1 value. It is important to note that this calculation is
300 based on the high aerosol condition (AOD = 2.5) in September. This result can
301 explain the high O₃ chemical production in Fig. 4.

302

303 **3.2. OH in different aerosol conditions**

304

305 In order to understand the effect of aerosol conditions, especially high aerosol
306 conditions, on the OH concentrations. Figure 9 shows the OH concentrations with and
307 without HONO production of OH. With including the HONO production (i.e.,



308 including P1 and P2), the calculated OH concentrations are significantly higher than
309 without including this production (i.e., only including P1). The both calculated OH
310 concentrations are rapidly changed with different levels of aerosol conditions. For
311 example, without HONO production, the maximum OH concentration is about
312 $7.5 \times 10^5 \text{ #/cm}^3$ under low aerosol condition (AOD=0.25). In contrast, the maximum
313 OH concentration rapidly reduced to $1.5 \times 10^5 \text{ #/cm}^3$ under high aerosol condition
314 (AOD=2.5), and further decreased to $1.0 \times 10^5 \text{ #/cm}^3$ with the AOD value of 3.5. In
315 contrast, with including HONO production, the OH concentrations significantly
316 increased. Under higher aerosol condition (AOD=2.5), the maximum of OH
317 concentration is about $7.5 \times 10^5 \text{ #/cm}^3$, which is the same value under low aerosol
318 condition in the no-HONO case. This result suggests that the measured high O₃
319 production occurred in the high aerosol condition is likely due to the high HONO
320 concentrations in Shanghai.

321

322 **3.3. OH in winter**

323

324 The measurement of O₃ also shows that the concentrations in winter were always low
325 (see Fig. 2), suggesting that the O₃ concentrations were not significantly affected by
326 the appearance of HONO. Figure 10 shows the OH concentrations in September and
327 December. It shows that under different aerosol conditions, OH concentrations in
328 December were very low compared with the values in September. Both the calculated
329 OH concentrations include the HONO production term. For example, under the
330 condition of AOD=2.5, the maximum OH is about $7.5 \times 10^5 \text{ #/cm}^3$ in September, while
331 it rapidly reduces to $1.5 \times 10^5 \text{ #/cm}^3$ in December. Under the condition of AOD=3.5,
332 the maximum OH is still maintaining to a relative high level ($4.5 \times 10^5 \text{ #/cm}^3$) in
333 September. However, the maximum OH values are extremely low in December, with
334 maximum value of $0.5 \times 10^5 \text{ #/cm}^3$ in December. Because both the OH chemical
335 productions (P1 and P2) are strongly dependent upon solar radiation (see equation
336 R-4), the seasonal variation of solar radiation plays important roles for controlling the
337 OH production in winter. When the solar radiation is in a very low level in winter, it



338 reaches a threshold level to prevent the OH chemical production, even by including
339 the HONO production term.

340

341 **Summary**

342

343 Currently, China is undergoing a rapid economic development, resulting in a high
344 demand for energy, greater use of fossil fuels. As a result, the high emissions of
345 pollutants produce heavy aerosol pollutions ($PM_{2.5}$) in eastern China, such as in the
346 mega city of Beijing. The long-term measurements show that in addition to the heavy
347 aerosol pollution, the O_3 pollution becomes another major pollutants in the Beijing
348 region. The measured results show that there were very strong seasonal variation in
349 the concentrations of both $PM_{2.5}$ and O_3 in the region. During winter, the seasonal
350 variability of O_3 concentrations were anti-correlated with the $PM_{2.5}$ concentrations.
351 However, during late spring and fall periods, the correlation between $PM_{2.5}$ and O_3
352 concentrations was positive compared to the negative in winter. This result suggests
353 that during heavy aerosol condition (the solar radiation was depressed), the O_3
354 chemical production was still high, appearing a double peak of $PM_{2.5}$ and O_3 during
355 fall period. This co-occurrence of high $PM_{2.5}$ and O_3 is the focus of this study. The
356 results are highlighted as follows;

357

358 (1) There are high daytime HONO concentrations in major Chinese mega cities, such
359 as in Beijing and Shanghai. It is also interesting to note that the high HONO
360 concentrations were occurred during high aerosol concentration periods. Under
361 the high daytime HONO concentrations, HONO can be photo-dissociated to be
362 OH radicals, and becomes an important process to produce OH.

363 (2) With including the OH production of measured HONO concentrations, the
364 calculated OH concentrations are significantly higher than without including this
365 production. For example, without HONO production, the maximum OH
366 concentration is about $7.5 \times 10^5 \text{ \#/cm}^3$ under low aerosol condition ($AOD=0.25$),



367 and rapidly reduced to $1.5 \times 10^5 \text{ \#/cm}^3$ under high aerosol condition (AOD=2.5) in
368 September. In contrast, by including HONO production, the OH concentrations
369 significantly increased. For example, under higher aerosol condition (AOD=2.5),
370 the maximum of OH concentration is about $7.5 \times 10^5 \text{ \#/cm}^3$, which is similar to the
371 value under low aerosol condition in the no-HONO case. This result suggests that
372 even under the high aerosol conditions, the chemical oxidizing process for O₃
373 production can be active. This result is likely for explaining the co-occurrence of
374 high PM_{2.5} and high O₃ in fall season in eastern China.

375 (3) The measurement of O₃ also shows that the concentrations in winter were always
376 low, suggesting that the O₃ concentrations were not significantly affected by the
377 appearance of HONO. The calculated result shows that the seasonal variation of
378 solar radiation plays important roles for controlling the OH production in winter.
379 When the solar radiation is a very low level in winter, it reaches a threshold level
380 to prevent the OH chemical production, even by including the HONO production
381 term.

382 Because in recent years, the PM_{2.5} pollutions are reduced due to the large control
383 efforts by the Chinese government, the O₃ pollutions become another severe pollution
384 problem in eastern China. This study is important, because it provides some important
385 scientific highlights to better understand the O₃ pollutions in eastern China.

386

387 **Author contributions.** XT came up with the original idea of investigating the
388 scientific issue. XT and JX designed the analysis method. XL, GL and SZ provided
389 the observational data and helped in discussion. XT prepared the manuscript with
390 contributions from all co-authors.

391

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485 **Figure Caption**

486

487 **Fig. 1.** The geographic locations of the measurement sites in Beijing, in which the
488 measured concentrations of PM_{2.5} and O₃ are used to the analysis.

489

490 **Fig. 2.** The daily averaged concentrations of PM_{2.5} and O₃ in the Beijing region in
491 2015. The concentrations are averaged over all sites shown in Fig. 1. The blue lines
492 represent the PM_{2.5} concentrations (µg/m³), and the red bars represent the O₃
493 concentrations (µg/m³). The rectangles show some typical events during winter
494 (green), spring and fall (orange), and summer (red).

495

496 **Fig. 3.** The correlation between O₃ and PM_{2.5} concentrations during winter (upper
497 panel) and during late spring and fall (lower panel). During winter, O₃ concentrations
498 were strong anti-correlated with the PM_{2.5} concentrations. During late spring and fall,
499 O₃ concentrations were correlated with the PM_{2.5} concentrations.

500

501 **Fig. 4.** The diurnal variations of PM_{2.5} (blue line) and O₃ (red line), and NO₂ (green
502 line) during a fall period (from Oct.5 to Oc. 6, 2015). It shows that with high PM_{2.5}
503 condition, there was a strong O₃ diurnal variation.

504

505 **Fig. 5.** The effect of aerosol levels with AOD = 0.25 (black line), AOD = 2.5 (red
506 line), AOD = 3.5 (blue line), and AOD = 4.0 (green line) on the O₃ photolysis
507 calculated by the TUV model in October at middle-latitude.

508

509 **Fig. 6.** The measured HONO concentrations (ppbv) in two large cities in China. The
510 red line was measured in Xi'an from 24 July to August 6, 2015. The blue line was
511 measure in Shanghai from 9 to 18 September, 2009. The green line is calculated by
512 the WRF-Chem model. The measurement in fall of Shanghai is applied to the
513 calculation for the OH production of HONO.

514

515 **Fig. 7.** The measured HONO (upper panel) and PM_{2.5} concentrations (lower panel) in
516 fall in Shanghai. It illustrates that the high HONO concentrations were corresponded
517 with high PM_{2.5} concentrations.

518

519 **Fig. 8.** The calculated OH production P(HOx) (#/cm³/s) by using the model calculated
520 HONO (low concentrations) (in the upper panel) and by using the measured HONO
521 (high concentrations) (in the lower panel). The red bars represent the calculation of
522 the P1 term, and the red bars represent the calculation of the P2 term (OH
523 production from HONO).

524

525 **Fig. 9.** The calculated OH concentrations (#/cm³) with (upper panel) and without
526 (lower panel) HONO production of OH, under different aerosol levels. Dark red
527 (AOD=0.25), red (AOD=2.5), red (AOD=3.5), and red (AOD=4.0).



528 **Fig. 10.** The calculated OH concentrations in September (blue bars) and December
529 (dark red bars), under different aerosol levels.

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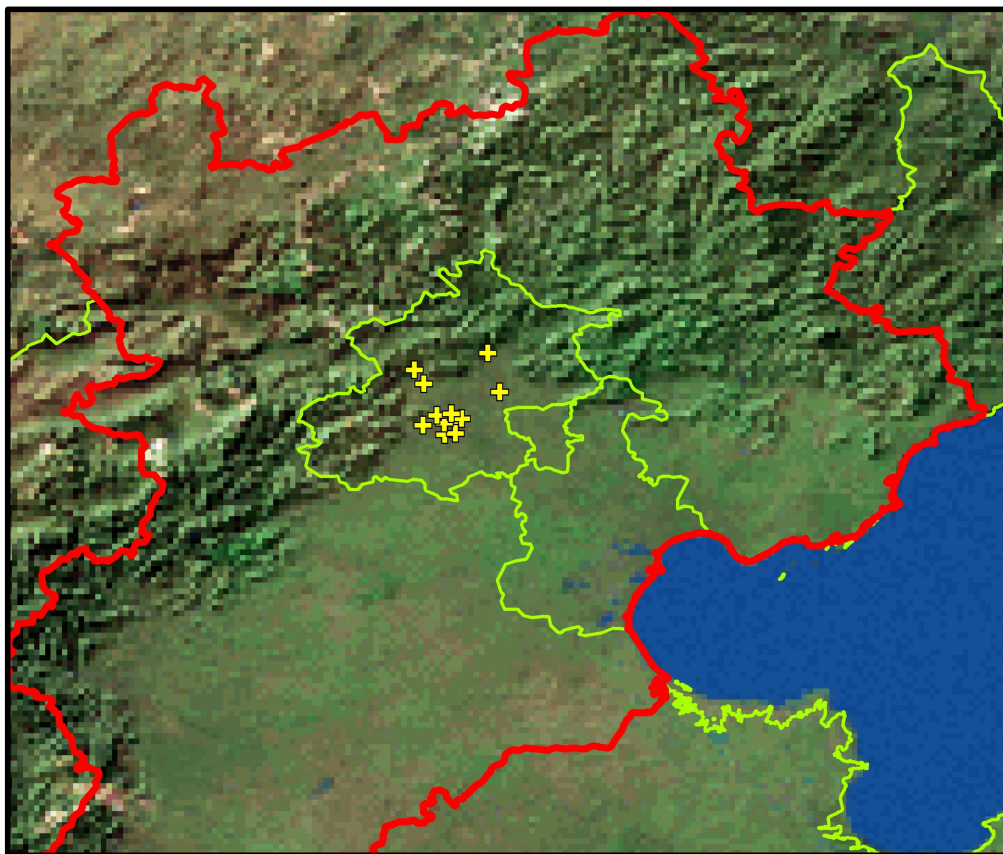
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Figures

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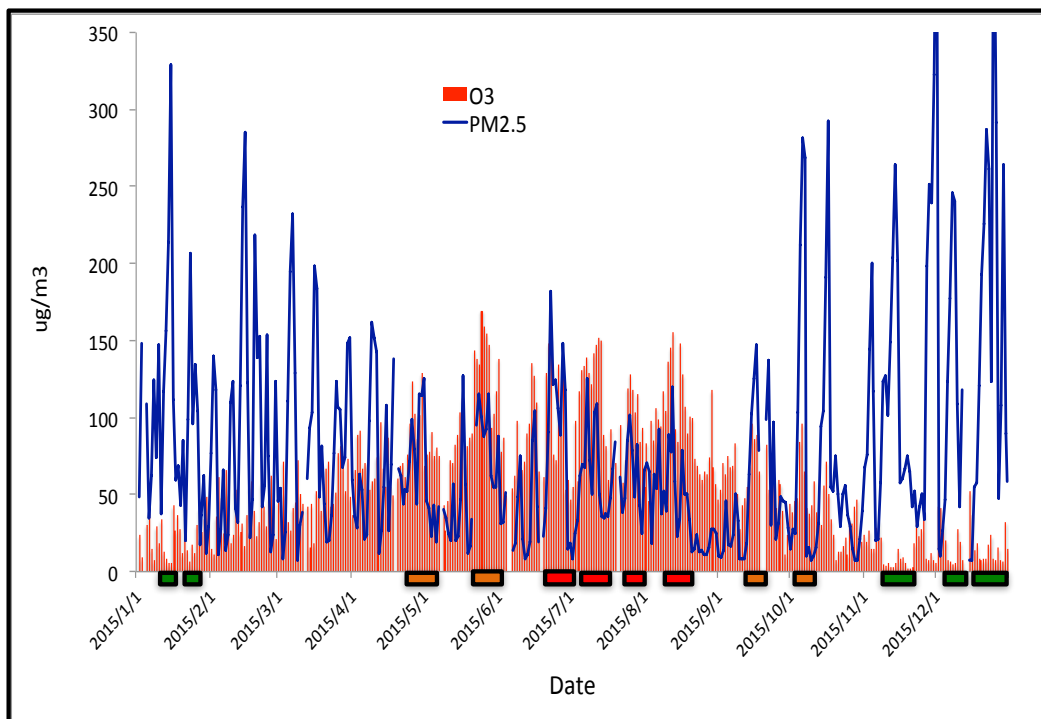


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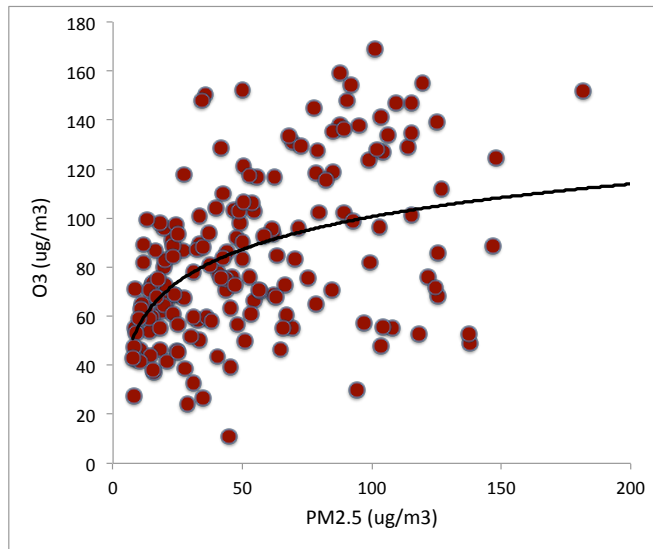
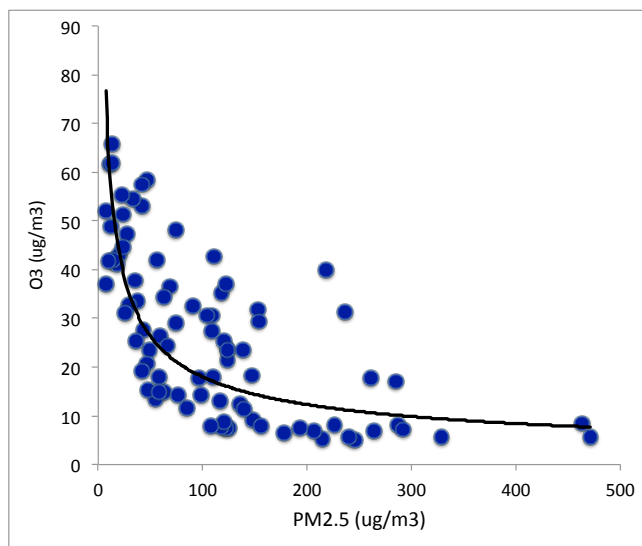
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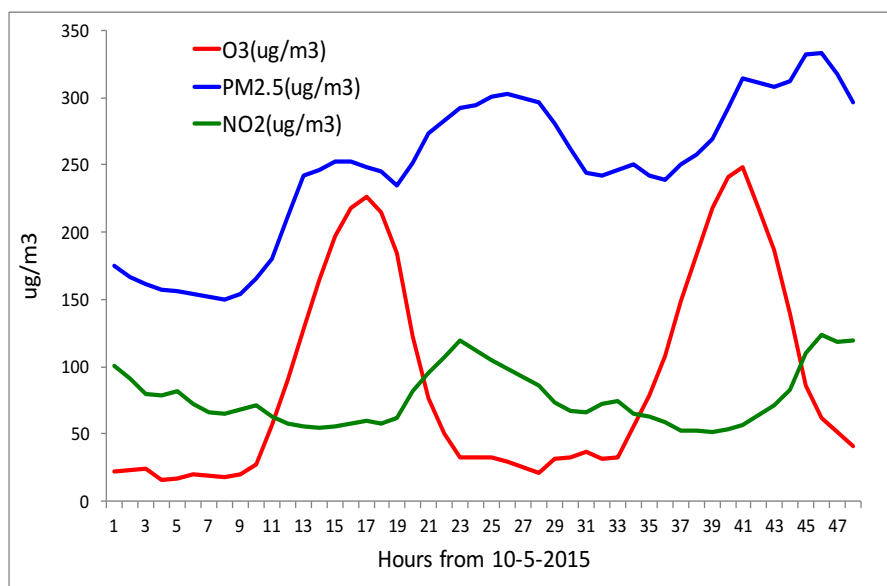
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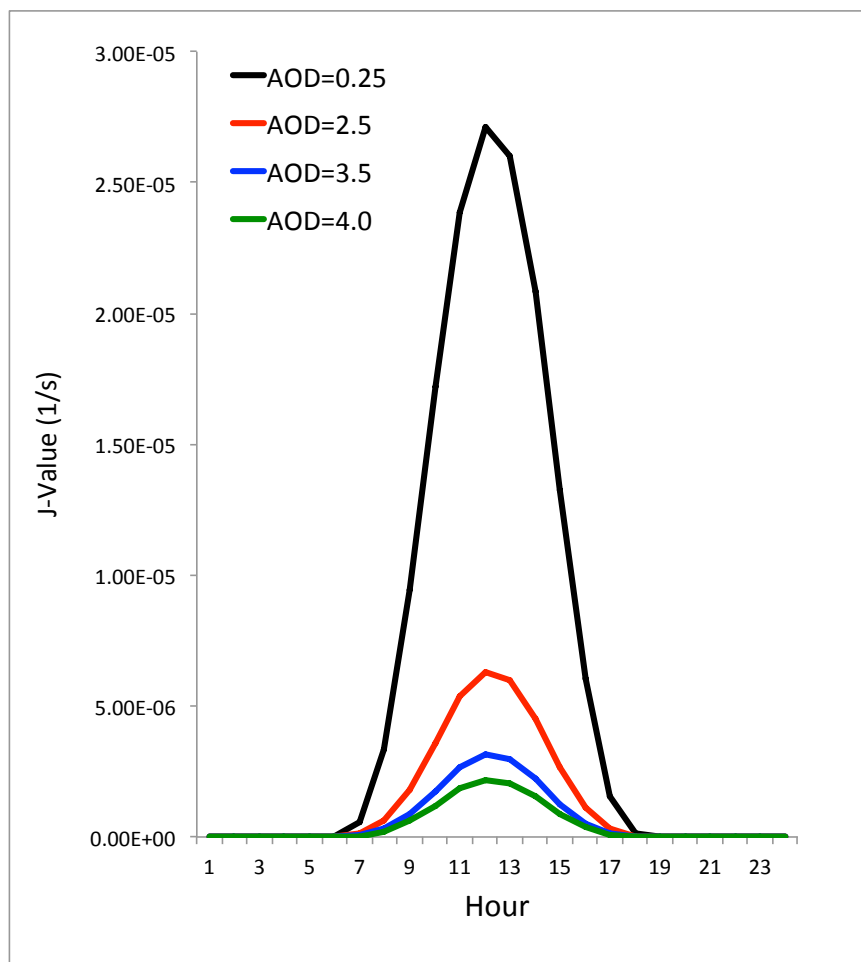
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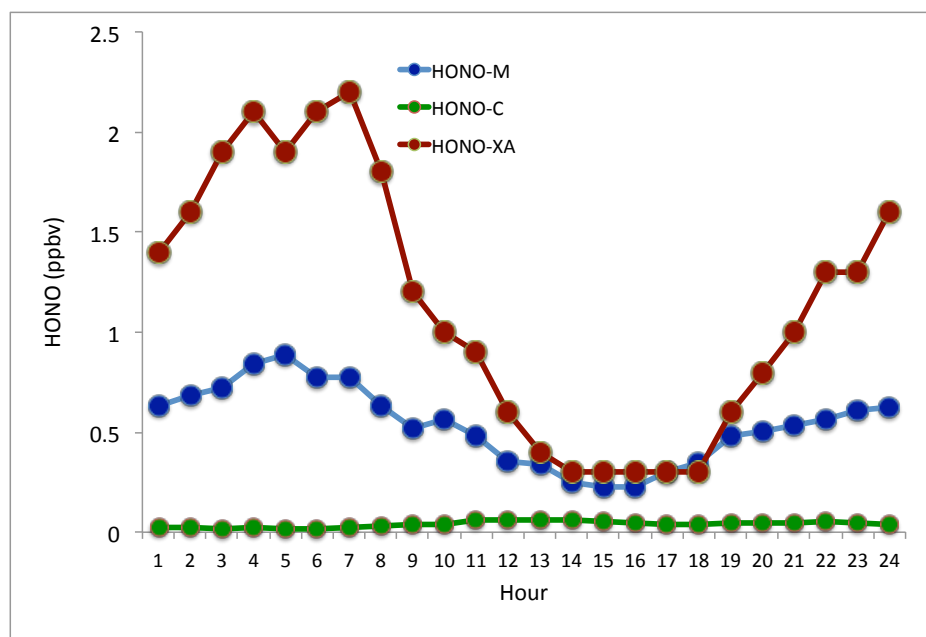
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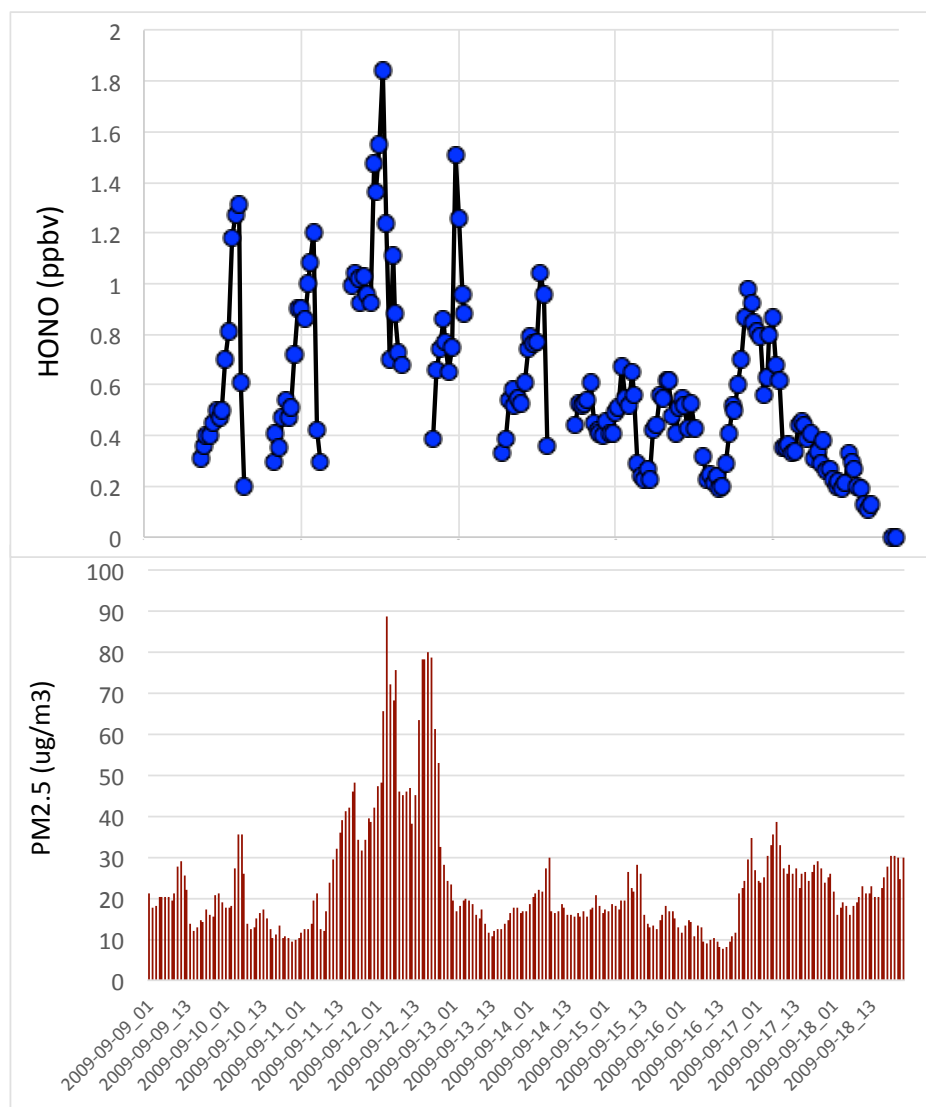
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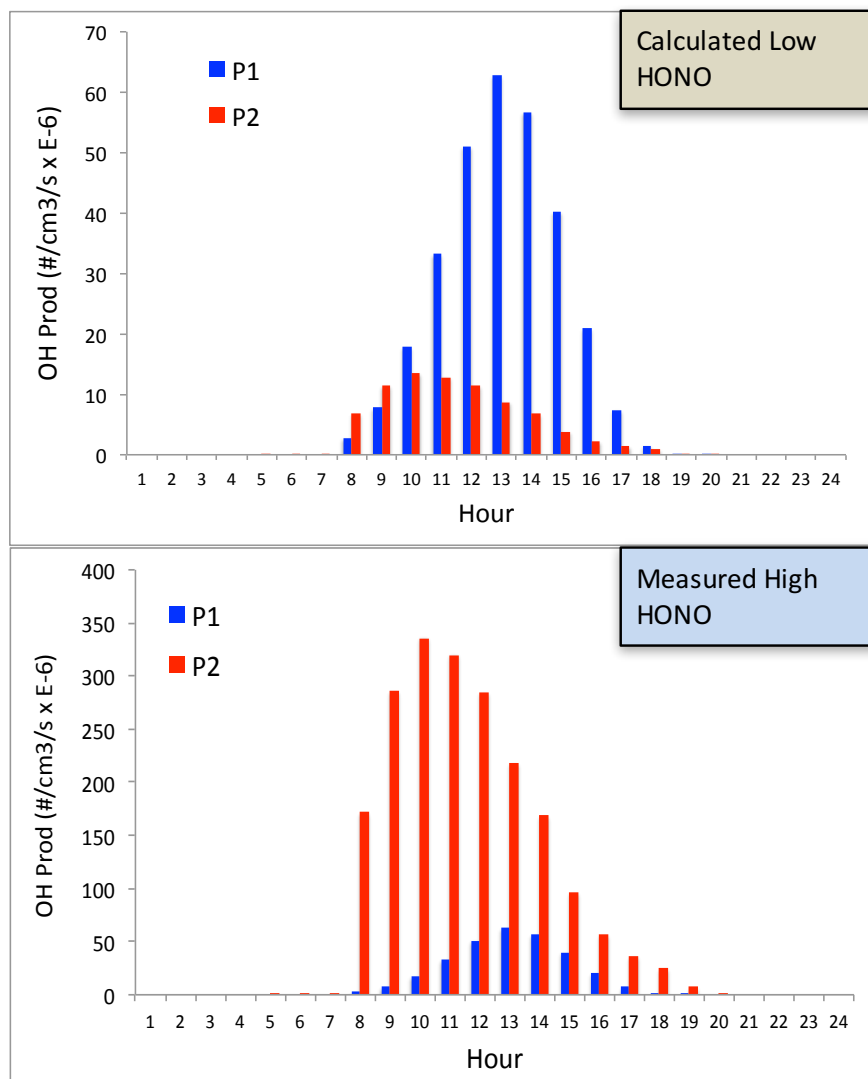
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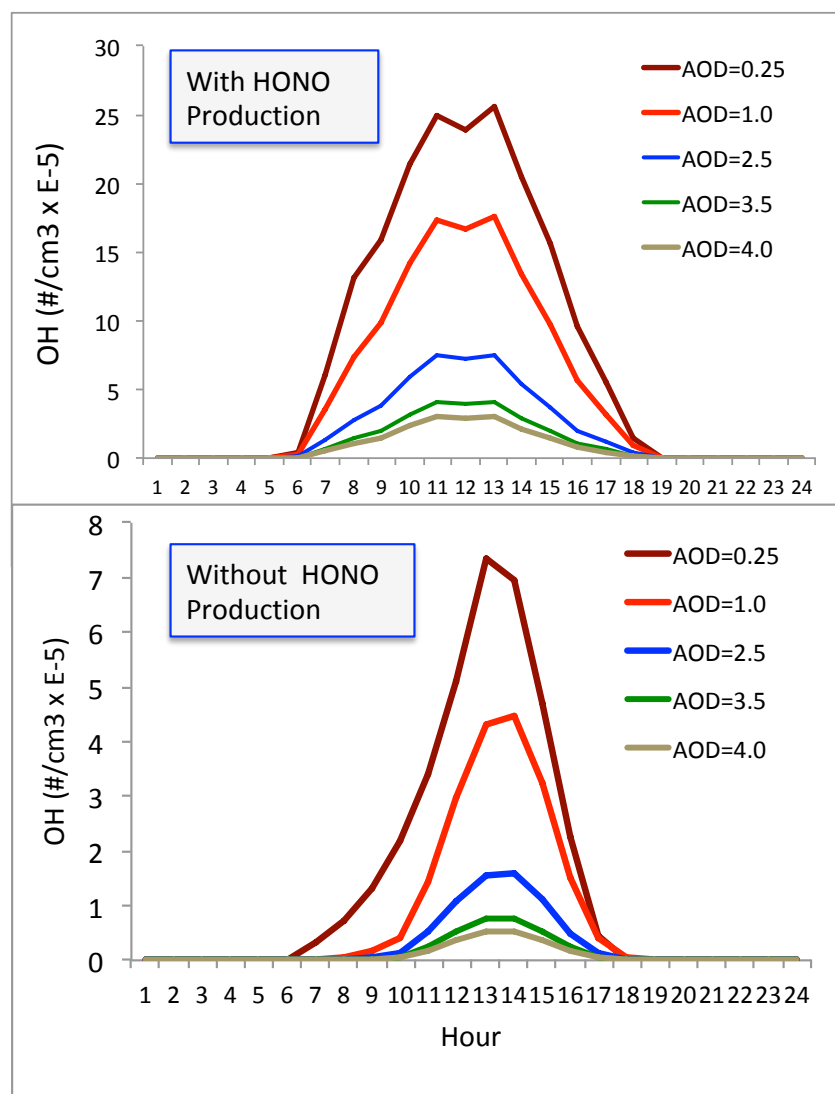
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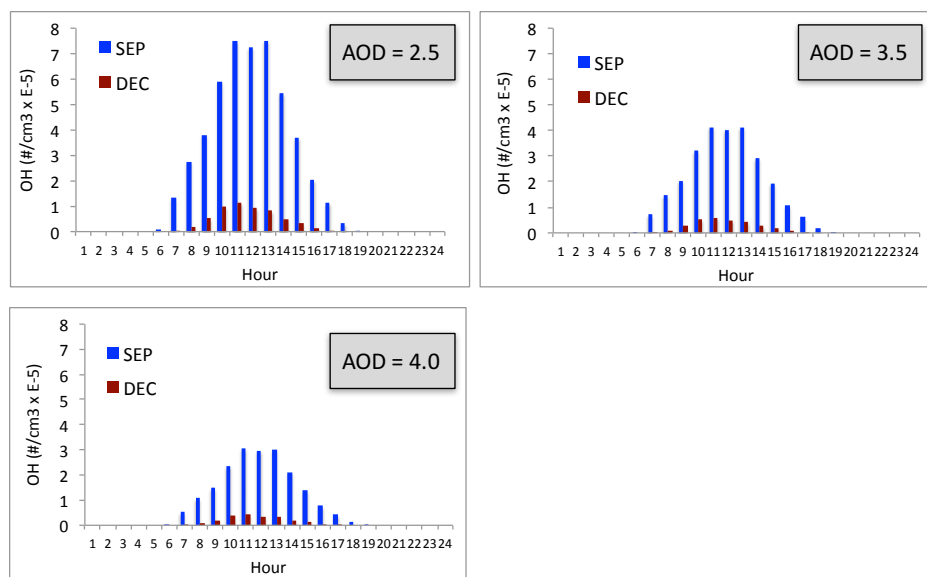
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