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1 **Characterization of peroxyacetyl nitrate (PAN) under different PM_{2.5}** 2 **concentration in wintertime at a North China rural site**

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13 **Abstract**

14 As a secondary pollutant of photochemical pollution, peroxyacetyl nitrate (PAN) has attracted a
15 close attention. A four-month campaign was conducted at a rural site in North China Plain (NCP)
16 including the measurement of PAN, O₃, NO_x, PM_{2.5}, oxygenated volatile organic compounds
17 (OVOCs), photolysis rate constants of NO₂ and O₃ and meteorological parameters to investigate the
18 wintertime characterization of photochemistry from November 2018 to February 2019. The results
19 showed that the maximum and mean values of PAN were 4.38 and 0.93 ± 0.67 ppbv during the
20 campaign, respectively. The PAN under different PM_{2.5} concentrations from below 75 µg/m³ up to
21 250 µg/m³, showed different diurnal variation and formation rate. In the PM_{2.5} concentration range
22 of above 250 µg/m³, PAN had the largest daily mean value of 0.64 ppbv and the fastest production
23 rate of 0.33 ppbv/hr. From the perspective of PAN's production mechanism, the light intensity and
24 precursors concentrations under different PM_{2.5} pollution levels indicated that there were sufficient
25 light intensity and high volatile organic compounds (VOCs) and NO_x precursors concentration even
26 under severe pollution level to generate a large amount of PAN. Moreover, the bimodal staggering
27 phenomenon of PAN and PM_{2.5} provided a basis that PAN might aggravate haze through secondary
28 organic aerosols (SOA) formation.

29 **Keywords:**

30 Peroxyacetyl nitrate

31 PM_{2.5}

32 Wintertime

33 North China

34 Rural site

35 -----

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37 **Introduction**

38 Peroxyacetyl nitrate (PAN) is an important photochemical oxidation product, which exists
39 widely in the tropospheric atmosphere. PAN was first discovered in the photochemical smog of Los
40 Angeles in 1956 by Stephens et al. (1956). Related studies have pointed out that PAN can cause
41 severe irritation to human eyes and may even cause skin mutations. PAN is approximately two times
42 more irritating than formaldehyde. In addition, it can produce injury on plant leaves such as tomato
43 plants (Altshuller, 1978; Carter et al., 1981; Taylor, 1969).

44 PAN has no natural source and can be produced exclusively by the reactions of volatile organic
45 compounds (VOCs) and NO₂ (Aikin et al., 1982; LaFranchi et al., 2010). Acetaldehyde is the main
46 precursor of PAN (Kondo et al., 2008). In addition, acetone, methacrolein (MACR), methylglyoxal
47 (MGLY), methyl ethyl ketone (MEK), methyl vinyl ketone (MVK), biacetyl are also the precursors
48 of PAN. Most of these compounds are second-generation precursors. Among the first-generation
49 precursors that produce OVOCs, aromatics and isoprene are the most contributors (Xue et al., 2014).
50 These VOCs can generate peroxyacetyl (PA) radicals through photolysis or oxidation by OH or NO₃
51 and then PA radicals react with NO₂ to produce PAN. Thermal decomposition accounts for a large
52 fraction degradation of PAN. The lifetime of PAN is only 35 min at 298 K, but at 247 K, it can be
53 as long as 5 years (Atkinson et al., 1997; Atkinson et al., 1992). Through thermal degradation, PAN
54 can release PA radicals and NO₂, therefore PAN is considered as a reservoir of NO_x. Meanwhile
55 PAN becomes a precursor for formaldehyde and free radicals (Orlando et al., 1992; Singh et al.,
56 1986). With low temperature stability, PAN can be transported to distant places in winter or at the
57 top of troposphere thereby affecting regional atmospheric chemistry (Honrath et al., 1996; Roberts
58 et al., 2004). Besides, PAN can also be removed by photolysis, reaction with OH radicals, and wet

59 or dry deposition.

60 In recent years, a large number of PAN observations experiments have continued to be carried
61 out over the world. Observation sites have covered large cities, suburbs, rural areas, seaside areas,
62 and even polar regions (Singh and Salas, 1983). The observed PAN concentrations ranged from a
63 few pptv in inaccessible places to 30 ppbv in megacities (Gaffney et al., 1999; Jacobi et al., 1999;
64 Mills et al., 2007). The atmospheric environment of different sites determined the pollution
65 characteristics of PAN, which provided data basis for comparison and analysis between different
66 regions. Photochemical pollution in China has also received more and more attention, and PAN has
67 been measured in some places of China such as Beijing, Lanzhou (Zhang et al., 2014, 2009). Blanks
68 about characteristics of PAN in more regions need to be filled. Many literatures have focused on the
69 relationship of PAN and O₃. The correlation analysis of PAN and O₃ also has obvious differences in
70 seasons or regions. In general, there is a positive correlation between PAN and O₃. However, there
71 are less research that focus on the relationship between PAN and PM_{2.5}. Unlike what is known in
72 theory, high concentrations of PM_{2.5} are usually accompanied by an increase in PAN concentrations.
73 Many studies have noted positive correlation between PAN and PM_{2.5}, but correlation analysis can
74 provide weak evidence. Zhao et al. (2017) simulated the heterogeneous reaction of PAN on soot
75 surface, which suggested the link between PAN and particulate matter (PM). Especially in winter,
76 the relationship between severe haze pollution and the formation and sink mechanism of PAN
77 become more complicated. Laboratory research has also constantly been conducted on the
78 heterogeneous reactions of PAN i.e., liquid phase reaction, particle surface reaction (Frenzel et al.,
79 2000; Langer et al., 1992). However, the complex atmospheric environment makes the research
80 between PAN and PM_{2.5} difficult.

81 In this study, we conducted measurements of PAN, PM_{2.5}, trace gas, meteorological data and
82 photolysis rate constants from Nov. 2018 to Feb. 2019 in Wangdu of Hebei Province to provide
83 better understanding photochemical pollution in our country's rural areas. This observation filled
84 the scarcity of PAN in rural areas. We analyzed the characterization of PAN under different pollution
85 conditions characterized by concentrations of PM_{2.5}. From the perspective of PAN-producing
86 precursors, the reasons for the elevation in PAN concentrations in severe pollution periods were
87 analyzed. Additionally, the effect of PAN on PM_{2.5} was studied during the periods when the PAN

88 concentrations exceeded 2 ppbv.

89 **1. Material and methods**

90 **1.1. Measurement site**

91 Field measurement was carried out from November 2018 to February 2019 in Wangdu (115.12°
92 E, 38.40°N), which located in the central area of the Beijing-Tianjin-Shijiazhuang region. Wangdu
93 County is ~90 km south to Shijiazhuang, ~35 km north to Baoding, and ~180 km north to Beijing.
94 There is 230,000 agricultural population. Our site is ~1 km northwest to a 8-lane highway (G4) and
95 surrounded by farmland and villages. As a heavily polluted rural area, Wangdu observation is
96 necessary and significant.

97 **1.2. Measurement techniques**

98 PAN concentrations were detected by online system using a gas chromatograph equipped with
99 an electron capture detector (GC-ECD, PANs-1000, Focused Photonics Inc., Hangzhou, China).
100 The working principle of the system was as follows: when start sampling, the sample entered the
101 quantitative loop after being filtered through the polytetrafluoroethylene (PTFE) microporous filter
102 membrane. After that, the sample was separated in chromatographic column. The separated
103 components were brought into the electron capture detector (ECD) for detection, and the output
104 electrical signal was recorded. The detection limit of analyzer (PANs-100, Focused Photonics Inc.,
105 Hangzhou, China) was 50 pptv. The uncertainty and precision were up to 10% and 3%, respectively.
106 The calibration system (PANs-200, Focused Photonics Inc., Hangzhou, China) consisted of a flow
107 control unit, a synthesis reaction unit, and a dilution mixing unit. The flow control unit controlled
108 the flow of NO, acetone and zero air to achieve precise control of reactant gas. The synthesis
109 reaction unit was composed of a reaction chamber, an ultraviolet lamp and a radiator fan. After
110 acetone (20 ppmv) and NO (1 ppmv) standard gas were mixed, the ultraviolet light penetrated the
111 wall of the reaction chamber to irradiate mixed gas for photochemical synthesis reaction. The
112 dilution mixing unit diluted the PAN synthesized by acetone and NO through zero air to obtain the
113 target concentration. In addition to diluting the PAN standard gas, zero air also provided a PAN-free
114 baseline. The multi-point calibration was conducted once a month, and the single-point calibration
115 was conducted once a week.

116 A series of supporting information including NO_x/NO/NO₂, CO, O₃ were measured by

117 monitors (42i, 48i, 49i, Thermo Scientific Inc., MA, USA). The calibration was performed by the
118 gaseous analyzer every 5 days. Meteorological parameters (wind speed, wind direction) were
119 obtained by an automatic weather station (Vaisala, Helsinki, Finland). The concentrations of PM_{2.5}
120 were gained by using the Synchronized Hybrid Ambient Real-time Particulate Monitor (Sharp
121 Model 5030i, Thermo Scientific Inc., MA, USA), with a time resolution of 1 hr.

122 Online oxygenated VOCs (OVOCs) measurement was obtained by using gas chromatography–
123 mass spectrometry detector (GC–MS, ZF-PKU-VOC1007, Pengyuchangya Inc., Beijing, China)
124 with a time resolution of 1 hr. A total of 13 OVOCs were identified and quantified. The air samples
125 were first enriched in a capillary column (15 cm × 0.53 mm inner diameter (ID)), and then
126 transferred into the GC-MS channel to be measured with a DB-624 column (60 m × 0.25 mm ID).
127 The detection limit of OVOCs varied from 0.001 to 0.015 ppbv. The photolysis rate constants of
128 NO₂, O₃ were detected by photolysis spectrometer (PFS-100, Focused Photonics Inc., Hangzhou,
129 China) which mainly used quartz receiver to collect solar radiation from all directions, then the
130 signal scanned by the spectrometer was converted into photochemical flux (F_{λ}) to calculate
131 photolysis rate constants. The instrument had simple structure and fast response speed, and could
132 obtain the photolysis rate of important substances and free radicals in the atmosphere in real time.

133 1.3. Net formation rate

134 The net formation rate for PAN, O_x is defined in Eq. (1)

$$135 \text{ Net formation rate (ppbv/hr)} = \frac{C_{t+1} - C_t}{1 \text{ hour}} \quad (1)$$

136 where C represents the concentrations of PAN or O_x at a certain moment, and t is the time. To
137 exclude the effect of mixing layer height, we use CO-scaled rate to further illustrate the chemical
138 processes.

139 The calculation is as follows:

$$140 \text{ Net CO-scaled formation rate (ppbv/hr)} = \frac{(C/\text{CO})_{t+1} - (C/\text{CO})_t}{1 \text{ hour}} \quad (2)$$

141 where C/CO represents the concentrations of PAN or O_x divided by CO.

142 2. Results and discussion

143 2.1. Time series and overviews of PAN

144 We conducted observations of PAN, PM_{2.5}, O₃, NO, NO₂, VOCs and meteorological

145 parameters from November 2018 to February 2019 at Wangdu. The time series of above pollutants
146 are showed in Fig. 1. The mass concentrations of PM_{2.5} ranged from 0.93 to 823 µg/m³ with an
147 average of 184.13 ± 138.32 µg/m³, which reflected the severe haze pollution level in rural areas of
148 the North China Plain (NCP). High concentrations of particulate matter (PM) in the NCP were often
149 reported (Liu et al., 2017; Xu et al., 2019). The maximum and mean values of PAN were 4.38 and
150 0.93 ± 0.67 ppbv. Table 1 presents previous observation data of PAN for comparison. Compared
151 with observations values of other sites during winter, the values of PAN in Wangdu were at a higher
152 level. They were higher than those such as in Beijing (maximum: 1.46 ppbv, mean: 0.31 ppbv)
153 during November 2012 - January 2013, in Ziyang (maximum: 1.61 ppbv, mean: 0.55 ppbv) during
154 Dec. 2012, in Xiamen (maximum: 4.19 ppbv, mean: 0.64 ppbv) during December 2016 - January
155 2017. Of course, higher concentrations of PAN have been reported in the literature. Liu et al. (2018)
156 reported quite high values of PAN during winter in Jinan (maximum: 9.61 ppbv, mean: 1.89±1.42
157 ppbv) due to high local formation. In history, the highest record of PAN concentration was in Mexico
158 in 1997, which reached 34 ppbv.

159 Generally, the concentrations of PAN are higher in summer than in winter which is because
160 stronger photochemical reaction in summer can produce a large amount of PAN. However, the
161 concentrations of PAN during winter in Wangdu even were at a comparable level in summer in some
162 places. Judging from the location of the sites, the PAN concentrations in urban areas are usually
163 higher than in rural areas due to more anthropogenic emission sources in urban areas. However,
164 located in rural areas, the concentrations of PAN in Wangdu are at a higher level than other rural
165 sites, and even higher than that in some urban areas, indicating that Wangdu had serious
166 photochemical pollution in winter.

167 **2.2. Characteristics of PAN under different concentrations of PM_{2.5}**

168 **2.2.1. Diurnal variation**

169 According to the second-grade Chinese National Ambient Air Quality Standard (CNAAQs),
170 the concentrations of PM_{2.5} were divided into four levels. In order to illustrate the differences in
171 characteristics of pollutants under different pollution conditions, we classified the measurement
172 days into four categories (<75 µg/m³, 75-150 µg/m³, 150-250 µg/m³, and > 250 µg/m³) according
173 to different PM_{2.5} concentrations. In order from low to high, these four levels represented clean
174 periods, light haze pollution, moderate haze pollution, and severe haze pollution. The days in these

175 four ranges respectively accounted for 14.3%, 25%, 37.5%, 23.2% of the total observation days
176 which illustrated severe haze pollution. Note that all values were under stable weather (wind speed
177 < 2 m/sec). The mean diurnal profiles of PAN, O₃, O_x, NO, NO₂ which were calibrated with CO
178 are illustrated in Fig. 2. CO is hard to react with other pollutants in atmosphere due to its inertness
179 and CO concentrations mainly controlled by meteorological factor. To understand the influence of
180 chemical processes to pollution concentrations, CO ratios method is always used to exclude dilution
181 effects and calculate the chemical growth rate (Kuang et al., 2020; Liu et al., 2019). Zhang et al.
182 (2015) considered CO as a tracer and used the ratios of SO₂/CO, NO_x/CO, and O₃/CO.

183 Generally, the early morning rise in CO-scaled PAN concentrations happened from 8:00 local
184 time (LT) which were consistent with the beginning of acute photochemical reactions. CO-scaled
185 PAN reached its maximum value at 15:00 LT under the PM_{2.5} concentrations range of 75-150, 150-
186 250, and above 250 $\mu\text{g}/\text{m}^3$, one hour later than the periods of below 75 $\mu\text{g}/\text{m}^3$. Different haze
187 pollution levels had a relatively small impact on the time for CO-scaled PAN to appear its maximum
188 value. As the pollution level increased, the daily average maximum values of CO-scaled PAN
189 presented a trend of increasing first, then decreasing and then increasing. During the periods of 75-
190 150 $\mu\text{g}/\text{m}^3$, the daily maximum of CO-scaled PAN was the highest with the value of 1.52 ppbv.
191 When the concentrations of PM_{2.5} exceeded 250 $\mu\text{g}/\text{m}^3$, the average CO-scaled PAN concentration
192 increased continuously from 0.23 ppbv at 8:00 LT to 1.39 ppbv at 15:00 LT. And during the daytime,
193 the concentrations of PAN were the highest during some periods. Overall PAN had the largest daily
194 mean value of 0.64 ppbv when PM_{2.5} concentrations exceeded 250 $\mu\text{g}/\text{m}^3$. Compared with clean
195 periods, PAN concentrations in the haze periods were significantly higher. O₃ and PAN were both
196 products of photochemical reactions, so their diurnal changes were similar. Generally CO-scaled O₃
197 presented unimodal change, which increased from 8:00 LT to 15:00 LT when PM_{2.5} exceeded 75
198 $\mu\text{g}/\text{m}^3$. For below 75 $\mu\text{g}/\text{m}^3$ concentrations, CO-scaled O₃ peaked at 14:00 LT. Different from CO-
199 scaled PAN, the maximum values of CO-scaled O₃ gradually decreased with the aggravation of
200 pollution, which showed that formation and accumulation of O₃ was suppressed in highly polluted
201 condition. Considering the titration of NO, we further researched on the diurnal variation of odd
202 oxygen (O_x = O₃ + NO₂). The time for O_x to reach its maximum values was the same as that of O₃.
203 The difference was that although the concentrations of CO-scaled O_x showed downward trend as
204 pollution worsened, when PM_{2.5} exceeded 250 $\mu\text{g}/\text{m}^3$, it increased, implying that atmospheric
205 oxidizing ability during heavy haze periods enhanced. CO-scaled NO presented unique bimodal
206 change, which accumulated to peak at midnight and decreased before dawn, then due to motor

207 vehicle exhaust emissions reached the peak at 8:00 LT. As the photochemical precursors, NO rapidly
208 participated in the photochemical reaction under strong solar radiation which led to decline after
209 8:00 LT and then increased from 16:00 LT. When $PM_{2.5}$ concentrations were between 75 and 150
210 $\mu\text{g}/\text{m}^3$, concentrations of CO-scaled NO were the lowest, which might be the reason for the highest
211 daily maximum of PAN during this period. As competitive reaction of PAN formation, NO could
212 react with peroxyacetyl (PA) radicals which led to generate fewer PAN. In general, there was little
213 difference in NO concentrations during the daytime. Due to the conversion of NO, the
214 concentrations of CO-scaled NO_2 began to rise from 8:00 LT, and arrived maximum values between
215 15:00 LT and 17:00 LT. When $PM_{2.5}$ concentrations were between 75 and 150 $\mu\text{g}/\text{m}^3$, the daily
216 maximum of NO_2 was the largest. As the pollution worsened, although the maximum daily value
217 decreased, other daytime hours were not much different or even the concentrations increased.

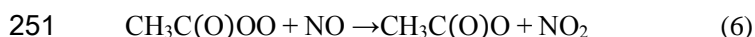
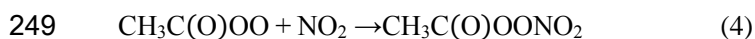
218 **2.2.2. Formation rate**

219 To further analyze the behaviors of PAN under different $PM_{2.5}$ concentrations, net formation
220 rate of PAN and CO-scaled PAN, O_x were illustrated in Fig. 3. The divergence in the formation rate
221 of PAN before and after correction was obvious, indicating boundary layer had a certain influence
222 on the concentrations. Except periods of severe pollution ($>250 \mu\text{g}/\text{m}^3$), net formation rate of CO-
223 scaled PAN all appeared in the afternoon (13:00 LT or 14:00 LT). During heavy pollution periods,
224 the peak of net CO-scaled formation rate advanced to 10:00 LT with maximum value of 0.33 ppbv/hr.
225 The atmospheric environment at that time determined net formation rate of CO-scaled PAN. The
226 reason for the maximum generation rate time point in advance during conditions of above $250 \mu\text{g}/\text{m}^3$
227 requires more relevant data to explain in the future. As the pollution level deepened, the net CO-
228 scaled formation rate of PAN presented a trend of rising first, then falling, and then rising again.
229 When concentrations of $PM_{2.5}$ exceeded $250 \mu\text{g}/\text{m}^3$, net formation rate of CO-scaled PAN during
230 the daytime was significantly accelerated. PAN still kept a rapid formation rate during the heavy
231 pollution periods. According to the daily variation and net formation rate of PAN under different
232 levels of $PM_{2.5}$, we can speculate that during severe haze periods, it is favorable for the formation
233 of PAN which will be explored in detail in next section. For lower $PM_{2.5}$ concentrations, net
234 formation rate of CO-scaled O_x was the highest with average daily maximum of 39.29 ppbv/hr.
235 When $PM_{2.5}$ concentrations were below $250 \mu\text{g}/\text{m}^3$, maximum value also appeared at 14:00 LT.
236 When $PM_{2.5}$ concentrations exceeded $250 \mu\text{g}/\text{m}^3$, maximum values appeared before noon. The high

237 PM_{2.5} concentrations inhibited the formation rate of CO-scaled O_x to a certain extent. During heavy
238 haze periods, PAN and O_x presented different growth characteristics. In summary, diurnal profile
239 and considerable formation rate of PAN and O_x indicated higher photochemical reaction intensity
240 under high PM_{2.5} concentrations.

241 2.3. PAN and its precursors

242 The reaction process indicates the formation of PAN is affected by the concentrates of
243 precursors (VOCs, NO_x), solar intensity and temperature. PAN is formed through the reaction of
244 VOCs and NO₂. VOCs are oxidized by OH radicals or photodegraded to generate PA radicals. And
245 then, PA radicals react with NO₂ to produce PAN. PAN can be removed through thermal degradation
246 to release PA radicals and NO₂. In addition to reacting with NO₂, PA radicals can also be reduced to
247 acetoxy by NO. The reaction formula is as follows:



252 where $h\nu$ is irradiation with light.

253 As shown in Reaction (5), thermal decomposition is a prominent removal pathway of PAN, which
254 is mainly affected by temperature. Compared with summer, the lifetime of PAN in winter increase
255 significantly. Considering only thermal decomposition, the lifetime of PAN in winter can be
256 calculated with the following formula:

$$257 \quad \tau (\text{PAN}) = \frac{1}{k_3} \left(1 + \frac{k_2[\text{NO}_2]}{k_4[\text{NO}]} \right) \quad (7)$$

258 where τ (PAN) (sec) represents the lifetime of PAN; k_2 (cm³/(molecule·sec)) is the rate constant
259 for Reaction (4); k_3 (sec⁻¹) is the rate constant for Reaction (5); and k_4 (cm³/(molecule·sec)) is the
260 rate constant for Reaction (6).

261 According to the formula, the lifetime of PAN was related to temperature and the ratio of NO₂
262 to NO, so we calculated the lifetime of PAN for three conditions distinguished by PM_{2.5}
263 concentrations: clean days (<75 μg/m³), moderate haze days (75-250 μg/m³), severe haze days
264 (>250 μg/m³). Table 2 shows the lifetime of PAN in three conditions. The temperature and ratio of
265 NO₂ to NO involved in the calculation were calculated using average values. In winter, the

266 temperature was around 273 K on average in Wangdu, which was in favor of the accumulation of
267 PAN. There was a big difference in the ratio of NO₂ to NO. The lifetime of PAN in the three
268 conditions was 80, 10, and 5 days respectively. There was lower lifetime of PAN during severe haze
269 episodes due to lower ratio of NO₂ to NO. The significantly reduced lifetime of PAN in the haze
270 period indicated that compared with clean episodes, there was faster photochemical reaction rate in
271 haze episodes, especially in severe haze episodes. This phenomenon was consistent with the above
272 findings.

273 Theoretically, high concentrations of PM will weaken the solar light and inhibit the generation
274 of PAN. Contrary to theory, elevated PAN concentrations are frequently accompanied with
275 increasing levels of PM_{2.5} during winter in this study. According to the formation mechanism we
276 used the photolysis rate constants of NO₂ and O₃ (JNO₂ and JO¹D) to reflect the solar radiation
277 intensity near the ground. The photolysis reaction of O₃ is mainly affected by wavelengths below
278 330 nm (Casasanta et al., 2011), while NO₂ is mainly affected by wavelengths shorter than 410 nm
279 (Atkinson et al., 2004). Moreover, the formation of PAN need oxidants which can be generated by
280 the photolysis of O₃. The photolysis of NO₂ can influence atmospheric oxidation and photochemical
281 pollution process. Therefore, the combination of JNO₂ and JO¹D can better reflect the light radiation
282 intensity of the wave involved in the photochemical reaction. Fig. 4 shows diurnal variation in the
283 photolysis rate constants of NO₂ and O₃ divided according to different concentrations of PM_{2.5}. For
284 JNO₂, high particle concentrations didn't obviously have an unfavorable effect on the intensity of
285 photolysis rate constants. Even under extremely high PM_{2.5} concentrations, JNO₂ exceeded that of
286 clean episodes for a few days, which probably resulted from the different interference ability of
287 diverse particle sizes to different wavelengths of light. For JO¹D, when PM_{2.5} exceeded 75 μg/m³,
288 photolysis rate constants decreased significantly. High concentrations of PM_{2.5} inhibited the
289 photolysis of O₃, consistent with the fact that photolysis of O₃ under haze periods was not the main
290 way to produce OH radicals (Fuchs et al., 2017; Lu et al., 2013). Combined with the variation of
291 JNO₂ and JO¹D, we inferred there was still moderate light radiation intensity in high PM_{2.5}
292 concentrations, which was very likely to be one of the reasons for elevated photochemical reaction
293 rate to generate PAN at Wangdu during severe haze pollution periods.

294 Although the photolysis rate of O_3 decreased during high $PM_{2.5}$ concentrations, studies have
295 shown that HONO is the main source of OH radicals during haze pollution period in winter (Bao et
296 al., 2018). Regrettably, we lacked the data of HONO in this observation. Liu et al. (2014) found that
297 aerosols played an important role on daytime heterogeneous HONO formation. And Zhang et al.
298 (2019) measured that the formation rate of OH radicals through the photolysis of HONO and the
299 loss rate of OH radicals through reaction with VOCs were enhanced on haze days compared with
300 non-haze days at Wangdu site over winter observation campaign in 2017. It could be seen that
301 HONO produced enough OH radicals to participate in the photochemical reaction at Wangdu during
302 winter.

303 It has become a recognized fact that the concentrations of VOCs increase during pollution
304 periods (Liu et al., 2017; Sun et al., 2016). Primary emitted VOCs are transformed to OVOCs by
305 OH radicals, so we mainly focus on OVOCs in this study. The 3D scatter plot of precursors (OVOCs,
306 NO_2) and PAN divided according to $PM_{2.5}$ concentrations is shown in Fig. 5a. In order to show more
307 clearly, the PAN and precursors concentrations in the four grade ranges are also shown in the four
308 graphs. In general, the concentrations of CO-scaled OVOCs and NO_2 were lower when $PM_{2.5}$
309 concentrations were below $75 \mu g/m^3$, which was consistent with less PAN in clean periods. Under
310 clean periods, when the concentrations of CO-scaled NO_2 were between 10 and 30 ppbv, as the
311 concentrations of CO-scaled OVOCs increased, the concentrations of CO-scaled PAN gradually
312 increased. And when CO-scaled OVOCs concentrations were fixed, as the concentrations of CO-
313 scaled NO_2 increased, PAN did not change significantly. The concentrations of precursors increased
314 largely, which led to the increase of PAN concentrations when $PM_{2.5}$ concentrations elevated. When
315 concentrations of $PM_{2.5}$ were between 75 and $150 \mu g/m^3$, the concentrations of CO-scaled NO_2 were
316 mainly concentrated in the range of 10-40 ppbv. As the concentrations of CO-scaled OVOCs
317 gradually increased to 15 ppbv, the concentrations of PAN also increased. In addition, there were
318 high concentrations of precursors, which explained the highest daily maximum values and fast
319 generation rate of PAN during this period. Under periods of $PM_{2.5}$ concentrations were between 150
320 and $250 \mu g/m^3$, the concentrations of CO-scaled NO_2 mainly changed between 10 ppbv and 60 ppbv.
321 When it was between 10 and 40 ppbv, in the process of the concentrations of CO-scaled OVOCs

322 rose to 10 ppbv, PAN concentrations also increased. When PM_{2.5} concentrations exceeded 250
323 $\mu\text{g}/\text{m}^3$, the concentrations of CO-scaled NO₂ decreased, but the concentrations of CO-scaled OVOCs
324 were close. When the CO-scaled NO₂ concentrations were between 10 and 40 ppbv, the PAN
325 concentrations changed significantly with the fluctuation of CO-scaled OVOCs. In particular CO-
326 scaled OVOCs increased from 5 to 10 ppbv, PAN concentrations increased obviously. Apparently,
327 the positive correlation between PAN and precursors concentrations during severe haze period was
328 more obvious. In terms of PAN's relative dependence on its precursors, OVOCs had a greater impact
329 on PAN than NO₂ concentrations did. Especially when the concentrations of NO₂ were between 10
330 and 40 ppbv, as the concentrations of OVOCs increased, and the concentrations of PAN increased
331 significantly. These results suggested that VOCs emissions made a great contribution to the
332 formation of PAN. Therefore, to reduce PAN pollution, efforts must be made to control VOCs
333 emissions in Wangdu. The sensitivity of PAN to NO₂ enhanced under severely polluted weather
334 which meant the importance of NO₂ control during heavy haze periods.

335 According to the formation mechanism of PAN, we have discussed solar light intensity and
336 precursors concentrations under different PM_{2.5} concentrations. The results showed that the
337 appropriate light intensity and elevated precursors concentrations generated high concentrations of
338 PAN during haze pollution periods. During haze pollution period, the light intensity and the highest
339 precursors concentrations supported the generation of PAN, especially OVOCs dominated the
340 generation of PAN. In the severe haze pollution periods, the contribution of NO₂ to PAN increased
341 which led to high PAN value and fast formation rate.

342 **2.4. SOA and PM_{2.5}**

343 Wangdu experienced severe haze pollution in winter from 2018 to 2019. Measurements at our
344 site showed that the daily average concentrations of PM_{2.5} exceeding 75 $\mu\text{g}/\text{m}^3$ accounted for 85%,
345 with daily maximum breaking through 800 $\mu\text{g}/\text{m}^3$. There are many factors that drive haze pollution,
346 such as traffic emissions, biomass combustion, coal combustion, and secondary aerosols formation.
347 Huang et al. (2014) found that secondary aerosols, i.e., secondary inorganic aerosols (SIA) and
348 secondary organic aerosols (SOA) accounted for 30%-77% for PM_{2.5}. Among them, the source
349 apportionment of secondary organic aerosols (SOA) formed from oxidation of VOCs was up to 25%.
350 Especially during heavy pollution periods, PM_{2.5} was mainly composed of secondary components.

351 Strong secondary generation and regional transmission have been reported to contribute to the
352 increase in PM_{2.5} concentrations (Sun et al., 2019). In order to explore whether active photochemical
353 reaction represented by high concentrations of PAN and the secondary pollutants had an impact on
354 the aggravation of PM_{2.5} concentrations, we selected some periods when the PAN concentrations
355 exceeded 2 ppbv and combined with concentrations of O₃, O_x to conduct detailed analysis.
356 Excluding the explosive growth of PM_{2.5} at nighttime which was considered to be the result of
357 primary emission (Wei et al., 2020), we finally chose four periods (case A:25-27 November; case
358 B: 30 November-3 December; case C: 2-3 January; case D: 4-5 February) To reflect concentration
359 changes controlled by atmospheric chemical process, all data was corrected with CO. The pollutants
360 showed same change patterns in these periods. As shown in the black dashed box in the Fig. 6,
361 during the daytime when photochemical reactions occurred, PAN, O_x, O₃ often started to increase
362 earlier than PM_{2.5}. The phenomenon of bimodal interleaving could be observed, which meant that a
363 few hours after the PAN peak appeared, the PM_{2.5} concentration also reached its peak. This
364 phenomenon was in line with the change characteristics that the secondary products of
365 photochemical reactions promoted or initiated the growth of PM_{2.5}. At present, laboratory
366 simulation experiments showed that there were heterogeneous reactions on the surface of soot (30-
367 50 nm) which generated CH₃COO⁻, HCOO⁻, NO₃⁻, NO₂⁻. As the reaction time increased, the
368 proportion of C=O bonds gradually increased which suggested soot was oxidized (Zhao et al., 2017).
369 Kames et al. 1991 noted the hydrolysis mechanism of PAN in water surface. PAN was hydrolyzed
370 to generate organic acids, NO₃⁻, NO₂⁻. Although the liquid phase reaction of PAN is limited. The
371 real atmospheric environment is complicated, so the liquid phase reaction and particle phase
372 reaction of PAN need more field observations to prove it.

373 Previous studies have reported several mechanisms of particle growth, including condensation,
374 gas-to-particle partitioning and heterogeneous reaction (Kroll and Seinfeld, 2008; Zhang et al.,
375 2012). Combining previous laboratory simulation results and field observations, it is speculated that
376 PAN may aggravate the haze during the development of the haze. PAN can enter into smaller
377 particles through gas-particle partitioning or condensation and further react to form SOA to promote
378 the growth of PM and aggravate haze pollution. Moreover, the increase of water content in the air
379 during the haze period complicated the PAN heterogeneous reactions. PAN's promotion to PM

380 concentrations needs more field observations and simulation experiments to support.

381 **3. Conclusions**

382 The study performed continuous field measurements of PAN concentrations combined with
383 supplementary data of PM_{2.5}, O₃, O_x, NO, NO₂, photolysis rate constants of NO₂ and O₃ from
384 November 2018 to February 2019 in the rural Wangdu site. The maximum and mean values of PAN
385 concentrations were 4.38 and 0.93±0.67 ppbv in winter, which were at a higher level. In addition to
386 photochemical pollution, Wangdu also experienced severe haze pollution in winter. We focused on
387 the pollution characteristics of PAN, O₃, O_x, NO, NO₂ under different levels of PM_{2.5}. Compared
388 with the clean periods, the concentrations of PAN increased significantly during haze periods.
389 Diurnal variation and net formation rate indicated there was the highest daily mean value of 0.64
390 ppbv and the fastest formation rate of 0.33 ppbv/hr under PM_{2.5} concentrations range of above 250
391 µg/m³. In order to further explain the reasons for the differences under different pollution conditions,
392 we discussed the formation mechanism of PAN. The low temperature contributed to the
393 accumulation of PAN in winter. The photolysis rate constants of NO₂, O₃ showed that the light
394 intensity was not significantly inhibited as PM_{2.5} increased, which was very likely to be the cause
395 of the faster photochemical reaction rate in the haze periods. From the perspective of precursors,
396 the concentrations of OVOCs and NO₂ in the haze period increased obviously. And compared with
397 NO₂, PAN seemed to be more sensitive to changes in OVOCs concentrations, especially when it
398 was low. During the severe haze periods, moderate light intensity and elevated precursors
399 concentrations contributed to the formation of PAN. However, the reason for the different
400 performance of PAN under different PM_{2.5} concentrations during the haze periods which required
401 more field data to explore in the future. In addition, we selected the dates when the PAN exceeded
402 2 ppbv to analyze the characteristics of PAN, O₃, O_x and PM_{2.5} in detail. As the products of
403 photochemical reactions, PAN, O₃, O_x and PM_{2.5} existed the phenomenon of double peaks staggered.
404 Combining observational data and previous studies on PAN's heterogeneous reactions, we speculate
405 that high concentrations of PAN can aggravate haze pollution by participating in the formation of
406 SOA.

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546

Table 1 Summary of PAN concentrations in other studies.

Location	Site description	Monitoring time	PAN (ppbv)		References
			Maximum values	Mean values	
Wangdu, China	Rural	November 2018-March 2019	4.48	0.78±0.66	This study
Ziyang, China	Urban	December 2012	1.61	0.55	Zhu et al., 2018
Jinan, China	Urban	November 2015-January 2016	9.61	1.89±1.42	Liu et al., 2018
Beijing, China	Urban	November 2012-January 2013	1.46	0.31	Zhang et al., 2020
Xiamen, China	Urban	December 2017-February 2018	4.19	0.64	Hu et al., 2020
Hong Kong, China	Suburban	October-December 2016	7.30	0.63±0.05	Zeng et al., 2019
Beijing, China	Urban	July-August 2008	9.34		Xue et al., 2014
Chongqing, China	Urban	August-September 2015	12.17	2.05±0.94	Sun et al., 2020
Pearl River Delta Region, China	Suburban	November-December 2011	2.80	0.69±0.46	Wang et al., 2010
Tibetan Plateau, China	Rural	August 2011	0.76	0.36	Xu et al., 2018
		May-July 2012	0.99	0.44	
Seoul, Korea	Urban	Winter 2011	5.03	0.64±0.49	Lee et al., 2013
Jeju Island, Korea	Rural	October-November 2010	2.40	0.60	Han et al., 2017
Azusa, USA	Rural	July-October 1997	4.84	0.88±0.74	Grosjean et al., 2001
Simi Valley, USA	Rural	June-October 1997	2.99	0.61±0.43	
Mexico, USA	Urban	February-March 1997	34		Gaffney et al., 1999

Table 2 Lifetime and reaction rate (k) of PAN under different conditions.

Condition	$k_2 (\times 10^{-11}$ $\text{cm}^3/(\text{molecule}\cdot\text{sec}))$	$k_3 (\times 10^{-6} \text{ sec}^{-1})$	$k_4 (\times 10^{-11}$ $\text{cm}^3/(\text{molecule}\cdot\text{sec}))$	Temperature (K)	NO_2/NO	Lifetime (days)
Clean days	1.32	4.42	2.21	269	50.04	80
Moderate haze days	1.30	7.72	2.18	272	10.31	10
Severe haze days	1.30	9.27	2.17	273	4.49	5

Reaction rate constants for Reactions (4, 5, 6) (k_2 , k_3 , k_4) refer to the references Atkinson et al., 1997; Villalta and Howard, 1996

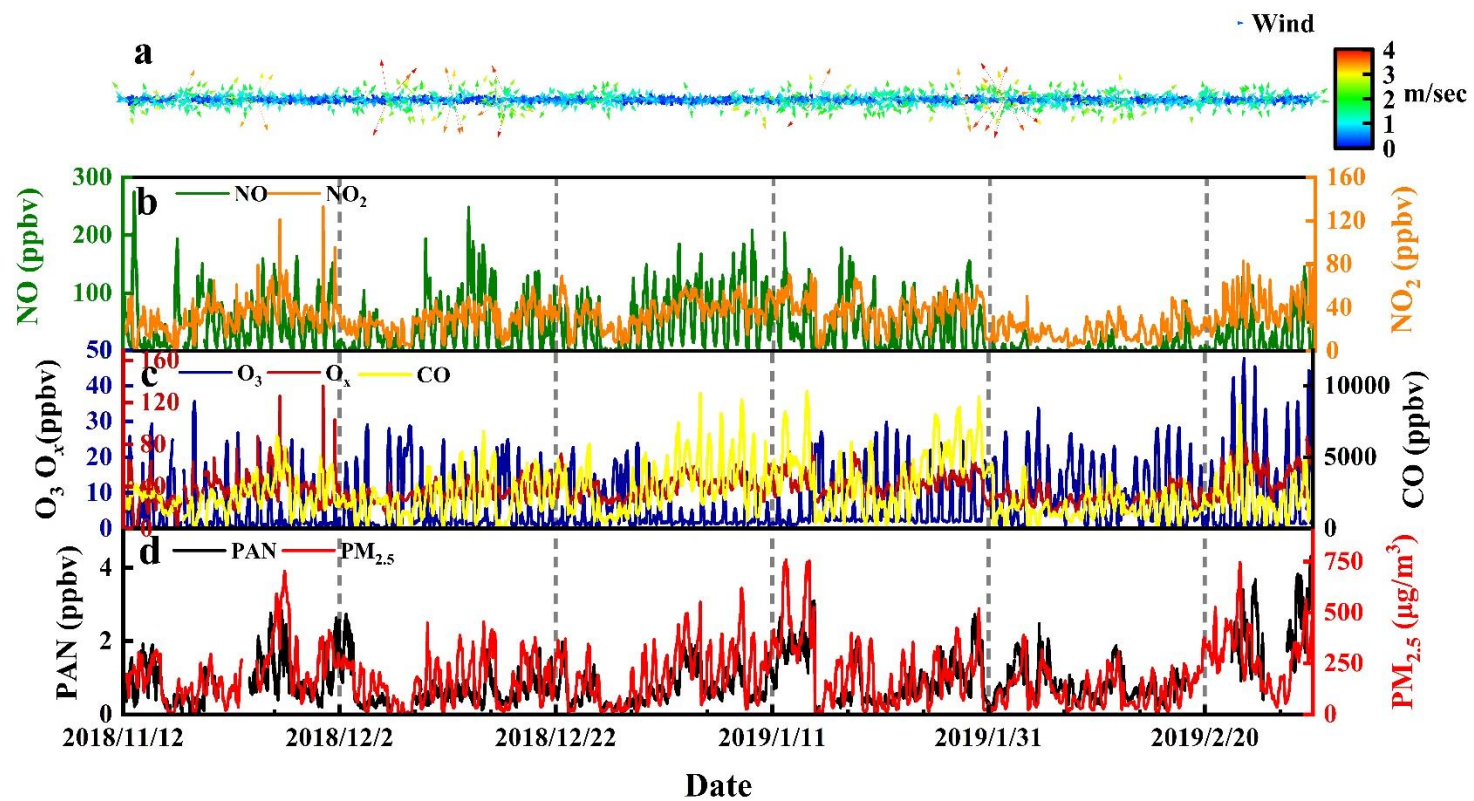


Fig. 1 Time series of pollutants and meteorological parameters in Wangdu between November 2018 and February 2019. (a) wind direction and wind speed; (b) NO, NO₂; (c) O₃, O_x, CO; (d) peroxyacetyl nitrate (PAN), PM_{2.5}.

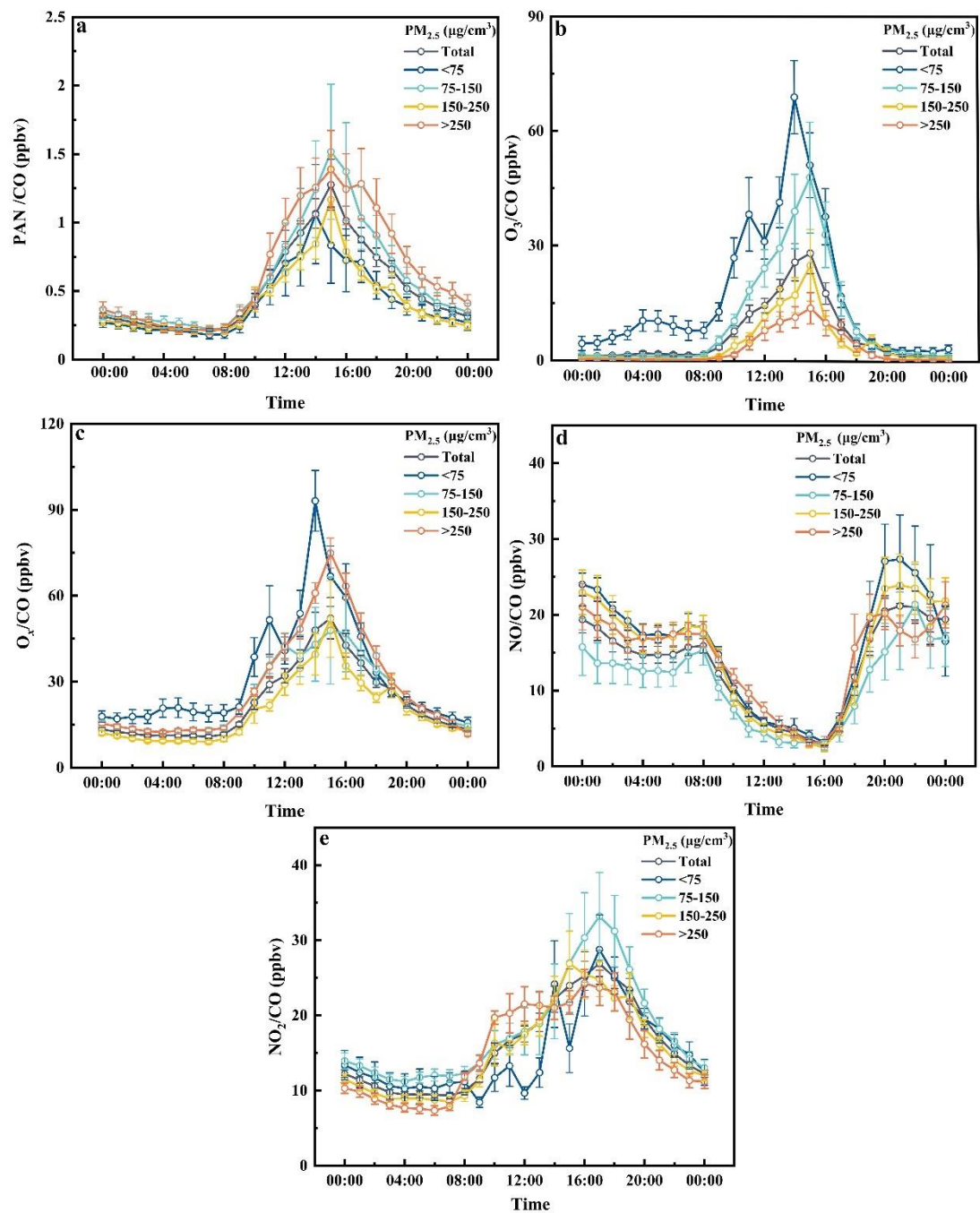


Fig. 2 Diurnal variation of (a) PAN, (b) O_3 , (c) O_3 , (d) NO, and (e) NO_2 under different concentrations of $PM_{2.5}$. Error bars are standard errors.

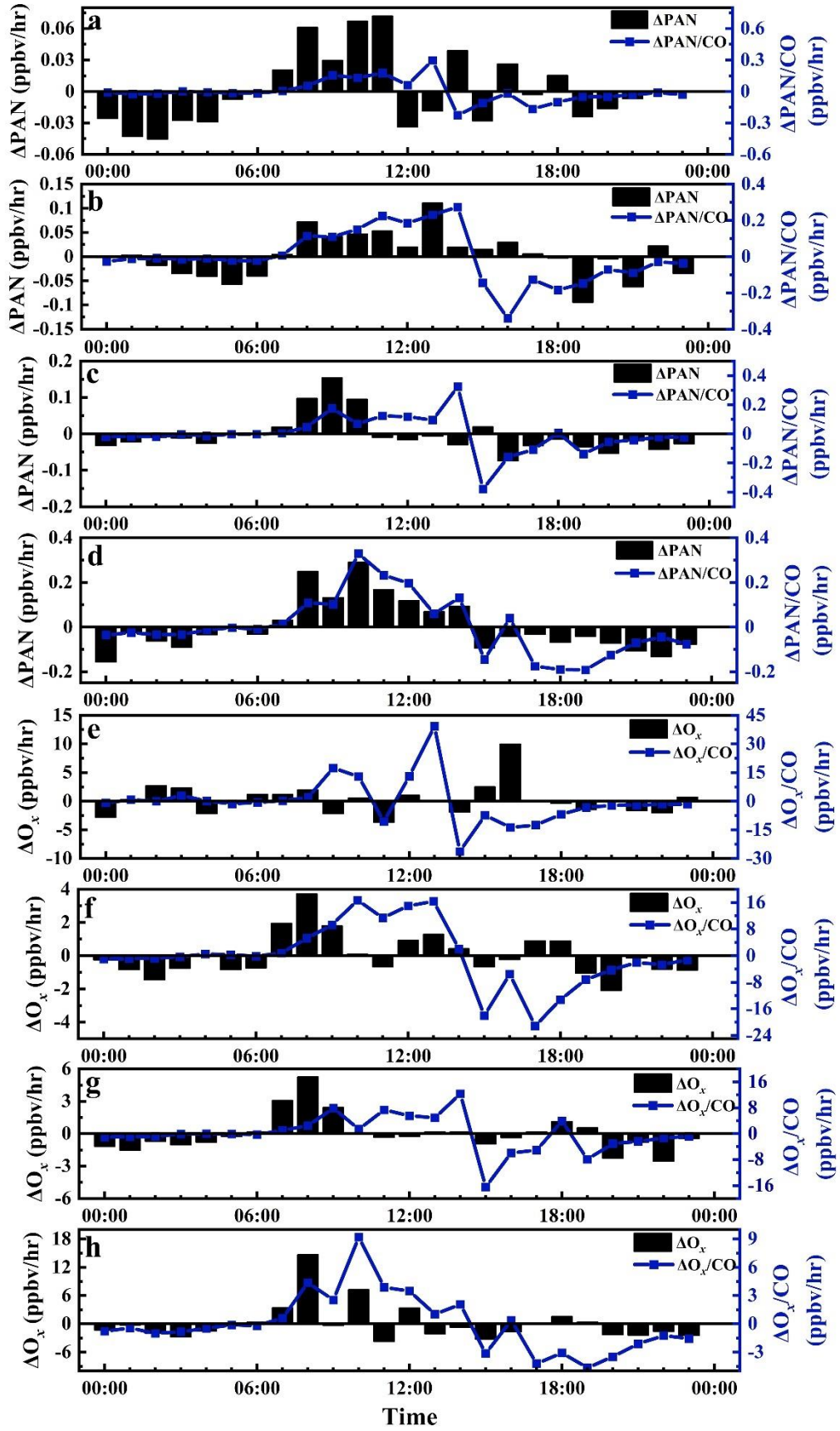


Fig. 3 Generation rate of PAN and O_x (Δ PAN and ΔO_x) under different concentrations of $PM_{2.5}$:

(a,e) $<75 \mu\text{g}/\text{cm}^3$, (b,f) $75\text{-}150 \mu\text{g}/\text{cm}^3$, (c,g) $150\text{-}250 \mu\text{g}/\text{cm}^3$ and (d,h) $>250 \mu\text{g}/\text{cm}^3$.

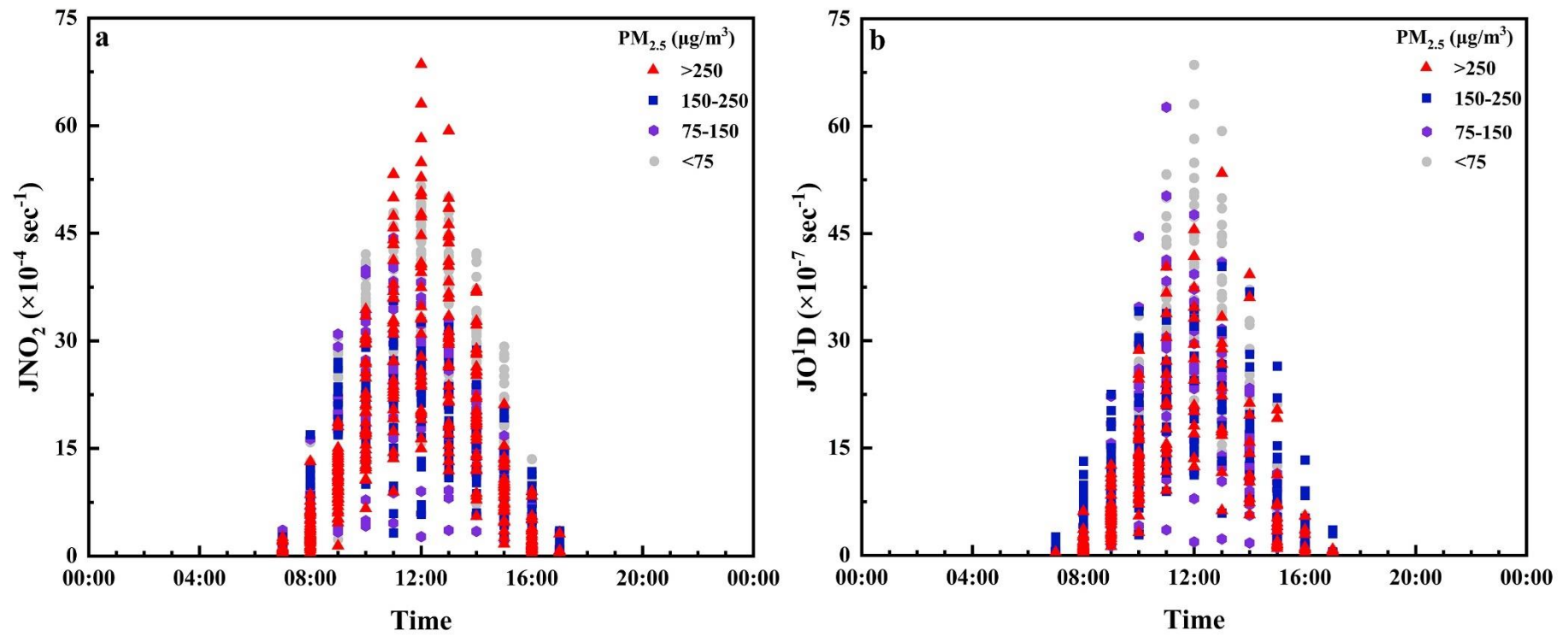


Fig. 4 Diurnal variation in the photolysis rate constants of NO₂ (J(NO₂)) and O₃ (J(O¹D)) color-coded by different concentrations of PM_{2.5}

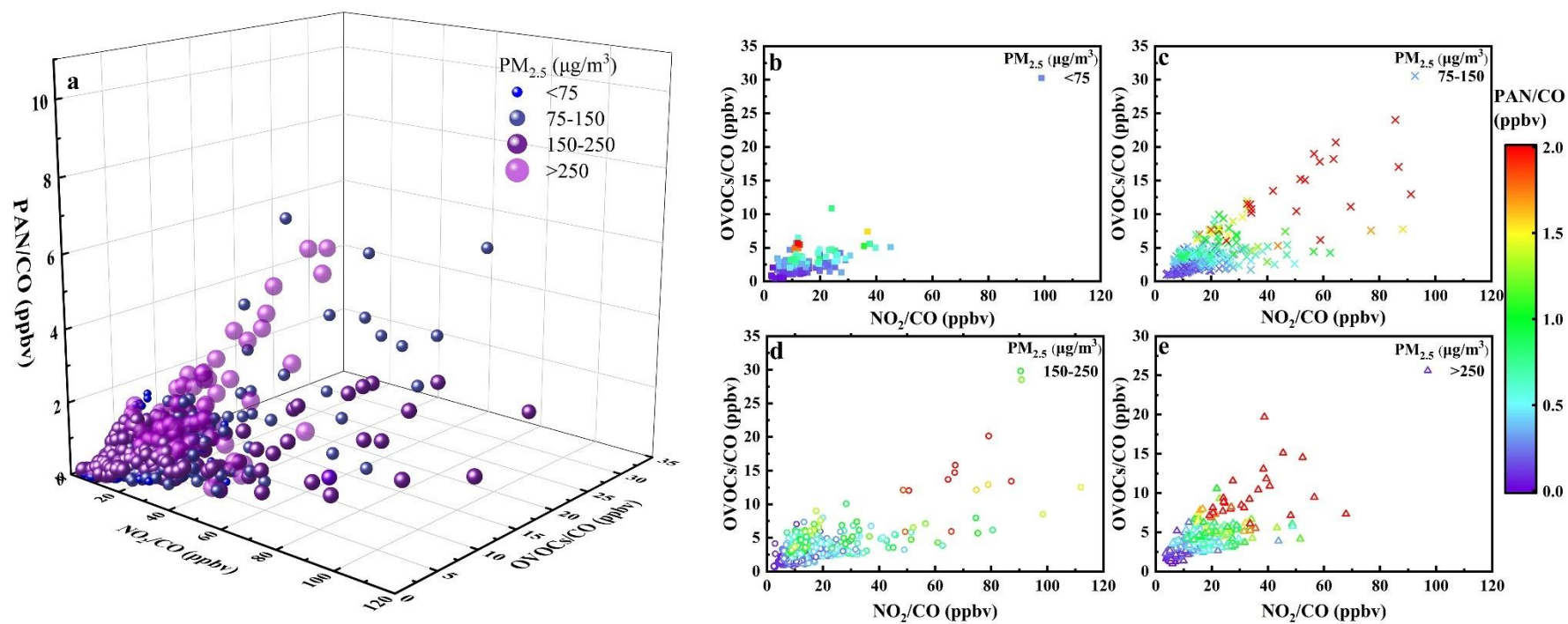


Fig. 5 Relationship of PAN and its precursors NO₂, oxygenated volatile organic compounds (OVOCs) under different concentrations of PAN: (a) overall 3D scatter plot, (b) < 75 μg/cm³, (c) 75-150 μg/cm³, (d) 150-250 μg/cm³ and (e) >250 μg/cm³.

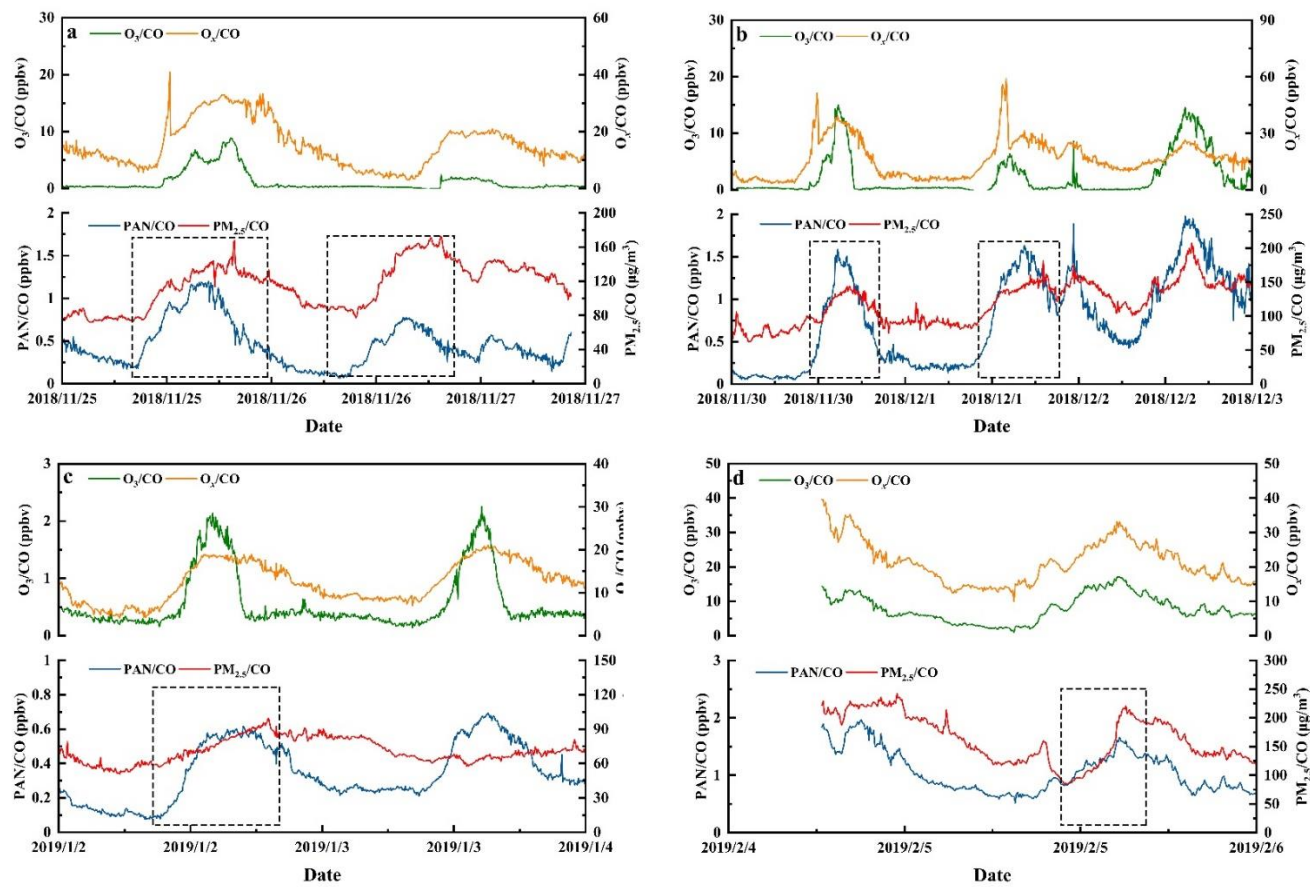


Fig. 6 Diurnal cycles of PAN, $PM_{2.5}$, O_3 , and O_x on case (a) 25-27 November, 2018, (b) 30 November, 2018-2 December, 2018, (c) 2-3 January, 2019; (d) 4-5 February, 2019.