Strong impacts of biomass burning, nitrogen fertilization, and fine particles on gas-phase hydrogen peroxide (H2O2)

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Strong Impacts of Biomass Burning, Nitrogen Fertilization, and Fine Particles on Gas-phase Hydrogen Peroxide (H_2O_2)

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Abstract. Gas-phase hydrogen peroxide (H_2O_2) plays an important role in atmospheric chemistry as an indicator of the atmospheric oxidizing capacity. It is also a vital oxidant of sulfur dioxide (SO_2) in the aqueous phase, resulting in the formation of acid precipitation and sulfate aerosol. However, sources of H_2O_2 are not fully understood especially in polluted areas affected by human activities. In this study, we reported some high H_2O_2 cases observed during one summer and two winter campaigns conducted at a polluted rural site in the North China Plain. Our results showed that agricultural fires led to high H_2O_2 concentrations up to 9 ppb, indicating biomass burning events contributed substantially to primary H_2O_2 emission. In addition, elevated H_2O_2 and O_3 concentrations were measured after

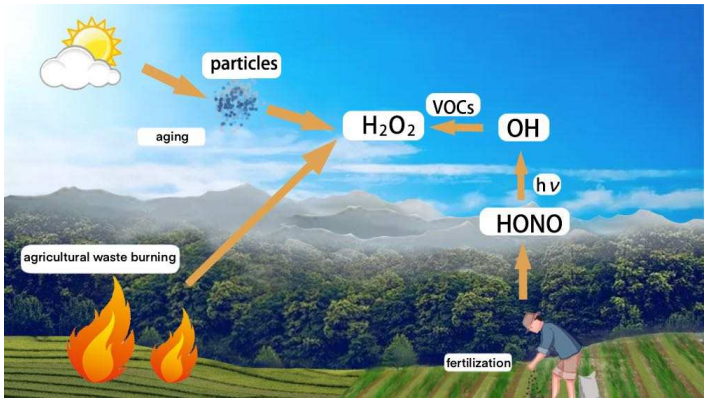
fertilization as a consequence of the enhanced atmospheric oxidizing capacity by soil HONO emission. Furthermore, H_2O_2 exhibited unexpectedly high concentration under high NO_x conditions in winter, which are closely related to multiphase reactions in particles involving organic chromophores. Our findings suggest that these special factors (biomass burning, fertilization, and ambient particles), which are not well considered in current models, are significant contributors to H_2O_2 production, thereby affecting the regional atmospheric oxidizing capacity and the global sulfate aerosol formation.

Key words: H_2O_2, biomass burning, fertilization, particles, organic chromophores

Highlights

- Biomass burning events led to high H_2O_2 concentrations up to 9 ppb observed.
- H_2O_2 and O_3 were greatly enhanced after fertilization events due to HONO emission by fertilized soil.
- Particle-phase reactions involving organic chromophores contributed to H_2O_2 production.

Graphical abstract



1 Introduction

Atmospheric hydrogen peroxide (H_2O_2) acts as a temporary reservoir of HO_x ($OH+HO_2$) radicals and hence an indicator of the oxidizing capacity of the atmosphere. Besides, H_2O_2 itself is one of the most important oxidants in the atmosphere and can oxidize SO_2 in clouds, droplets, and deliquesced particles (Penkett et al., 1979; Calvert and Stockwell, 1983), with the formation of sulfate, an important component of fine particulate matter that impacts air quality, climate, and human health (Grantz et al., 2003; Nel, 2005; Fuzzi et al., 2015). Furthermore, H_2O_2/HNO_3 was suggested as a robust indicator to determine whether ozone production is more sensitive to NO_x or VOCs (Sillman, 1995; Sillman et al., 1998). Vermeuel et al. (2019) evaluated the sensitivity of O_3 to VOCs and NO_x alongside the Lake Michigan Coastline utilizing the modeled ratio of H_2O_2 and HNO_3 production rates. Results indicated that the O_3 production was strongly VOC-limited in the urban areas and became more NO_x-limited as the plume advected North. As O_3 pollution is becoming a big concern with increase of NO_x and VOCs emissions (Tan et al., 2018; Yu et al., 2020), H_2O_2 has drawn more attention in both urban and rural areas.

$$HO_2 + HO_2 \rightarrow H_2O_2 \quad \text{R1}$$

$k_{R1}=1.5\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K

$$HO_2 + NO \rightarrow NO_2 + OH \quad \text{R2}$$

$k_{R2}=8.9\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K

Based on the current understanding, H_2O_2 is mainly produced by the self-reaction of two hydroperoxy radicals (HO_2) (R1), which are produced from the oxidation of hydrocarbons by OH radicals or the photolysis of formaldehyde. R1 largely depends on ambient NO_x levels. With high NO_x levels, R2 would dominate relative to R1 due to more rapid HO_2 consumption through R2. For example, with typical noontime NO concentration of 1 ppb and HO_2 concentration of 4×10^7 molecules cm^{-3} observed or modelled in the winter NCP (Ma et al., 2019; Slater et al., 2020; Xue et al., 2020), HO_2 loss rate through R2 (8.4×10^6 molecules cm^{-3} s^{-1}) is 3 orders of magnitude faster than that of R1 (2.6×10^3 molecules cm^{-3} s^{-1}). Field measurements also supported that under the condition of NO concentrations exceeding 1

ppb, H_2O_2 production through R1 will be substantially suppressed (Walker et al., 2006; He et al., 2010; Watanabe et al., 2018). Besides the H_2O_2 formation channel through R1, ozonolysis of alkenes also contributes to H_2O_2 production, which could proceed without sunlight (Becker et al., 1990; Hua et al., 2008). The main sinks of H_2O_2 include photolysis, dry deposition, reaction with OH radicals, and reaction with SO_2 in the liquid phase. The typical photolysis rate of H_2O_2 daily maximum value is 6.0×10^{-6} s^{-1} in the northern midlatitude (Stockwell et al., 1997), corresponding to τ_{photo}=46 h (lifetime against photolysis). As for the reaction of H_2O_2 with OH radicals, the rate constant is 1.7×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K (Atkinson et al., 2004), and the temperature influence on the rate constant is small. τ_{H2O2} (lifetime with respect to OH reaction) is estimated to be around 32 h if OH concentration is assumed to be 5×10^6 molecule cm^{-3}. Assuming the dry deposition velocity of H_2O_2 is about 2 cm s^{-1} (Liang et al., 2013), the lifetime of H_2O_2 with respect to dry deposition is 7 h with a boundary height of 1 km. Therefore, dry deposition loss was a dominant factor influencing the lifetime of H_2O_2 in the atmosphere.

H_2O_2 formation does not only depend on NO_x levels, which was discussed earlier but also as a function of many other chemical and physical parameters. First of all, H_2O_2 concentrations are affected by precursors concentrations like VOCs. High VOC to NO_x ratio leads to more HO_2 production, in favor of the production of H_2O_2 (Lee et al., 2008; Crowley et al., 2018). O_3 and HONO, which are important contributors to OH radicals in the lower troposphere, also have crucial effect on H_2O_2 formation under certain atmospheric conditions. For instance, in a clean environment, OH radicals mainly come from O_3 photolysis followed by the reaction of $O(^1D)$ with water vapor. In polluted areas (like urban sites), HONO appeared to be an important source of OH radicals (Elshorbany et al., 2010; Xue et al., 2020). In addition, since H_2O_2 is very soluble with high Henry's law constant of 1.07×10^5 M atm^{-1} at 298 K (Lee et al., 2000; Reeves and Penkett, 2003), H_2O_2 can be readily consumed via reaction with SO_2 in the atmospheric aqueous phase (Penkett et al., 1979; Hoffmann and Edwards, 1975). Hence, high SO_2 concentrations are usually associated with low H_2O_2 concentrations (Watanabe et al., 2016; Guo et al., 2014). Moreover, solar radiation has a significant impact on H_2O_2 concentrations. Model simulations by Kleinman et al. showed that a 60% decrease in solar radiation intensity could lead to a 65% decrease in H_2O_2 concentrations (Kleinman, 1986), which highlights the important role of solar

radiation in the formation of H_2O_2. The absolute humidity is an important factor for H_2O_2 formation as high humidity may lead to an increase in OH radical and hence more H_2O_2 production (Hamilton Jr and Lii, 1977; Fischer et al., 2019). Also, higher temperature promotes the rate of photochemical reactions, resulting in more radical production and hence more H_2O_2 production (Das and Aneja, 1994; Nunnermacker et al., 2008; Zhang et al., 2018). These factors are well understood and all considered in the box model and regional transport models. However, it was reported that H_2O_2 was still underestimated during polluted periods, indicating that some extra factors affecting H_2O_2 concentrations may be neglected (Qin et al., 2018; Ye et al., 2018). Moreover, there is still a gap between modeled and measured sulfate concentrations during haze events, suggesting sulfate formation is not completed in current mechanisms (Wang et al., 2014; Zheng et al., 2015). Hence, it is essential to incorporate all processes related to H_2O_2 formation into regional models for better predictions. However, there is a relatively small body of literature that is concerned with gas-phase H_2O_2 measurements in China (Wang et al., 2016; Qin et al., 2018; Ye et al., 2018; Zhang et al., 2018), especially in the North China Plain (NCP) where it is encountering serious air pollution.

In order to more accurately predict H_2O_2 concentrations and evaluate its role in the oxidizing capacity of the atmosphere, a comprehensive investigation of factors controlling gaseous H_2O_2 should be conducted. In this study, H_2O_2 and other relevant pollutants were simultaneously measured at a polluted rural site in the NCP in summertime (31 May to 8 July 2017) and wintertime (1 November to 31 December 2017, 1 to 15 December 2018). Time series of H_2O_2 and related parameters in the three field campaigns were shown in Figure S1. In addition to the factors mentioned above, some special factors were also found to profoundly affect atmospheric H_2O_2 concentrations in our study, which might be overlooked by the current understanding. The following will be some cases observed in our field measurements to reveal these special factors.

2 Experiments

2.1 Measurement site

The measurements were conducted at a rural site (SRE-CAS, 38.66°N, 115.25°E) located in Wangdu County (Liu et al., 2017; Xue et al., 2020), in Hebei province, which is 150 km southwest of Beijing city in the NCP. This site was surrounded by vast areas of farmlands and impacted by coal combustion in winter and agricultural activities such as biomass burning and fertilization in summer. A high-speed way was located 2 km southwest of the site. There are no industries around the sampling site. All instruments were placed into a container with the sampling inlet about 3.4 m above the ground.

2.2 Measurement methods

A Germany commercial H_2O_2 monitor (AEROLASER AL-2021) based on a wet chemical technique was employed to measure gas-phase H_2O_2. Firstly, soluble peroxides, including H_2O_2 and organic peroxides, were sampled by a stripping coil with a buffered solution. In order to distinguish H_2O_2 and organic peroxides, the stripping solution was divided into two channels. In the first channel, the peroxides in the stripping solution react with p-hydroxyphenyl acetic acid (POPHA) under the catalysis of peroxidase, resulting in the formation of fluorescent dye. After excitation at 326 nm, the fluorescence could be detected at 400-420 nm. In the second channel, before peroxides reaction with POPHA, enzyme catalase was added to selectively destroy H_2O_2. Then H_2O_2 was determined as the difference between the two channels. Liquid calibration was performed every two days. The detection limit of the instrument was <50 ppt. Detailed information can be found in our previous study (Ye et al., 2018).

HONO was measured by a commercial long path absorption photometer instrument (LOPAP, Model-03, QUMA) (Heland et al., 2001). Briefly, ambient air was sampled by using two same stripping coils connected in series. Because HONO is highly soluble, almost all the ambient HONO was absorbed by the absorption solution in the first stripping coil, while possibly interfering species were sampled in the first as well as the second stripping coil. Thus, the signal

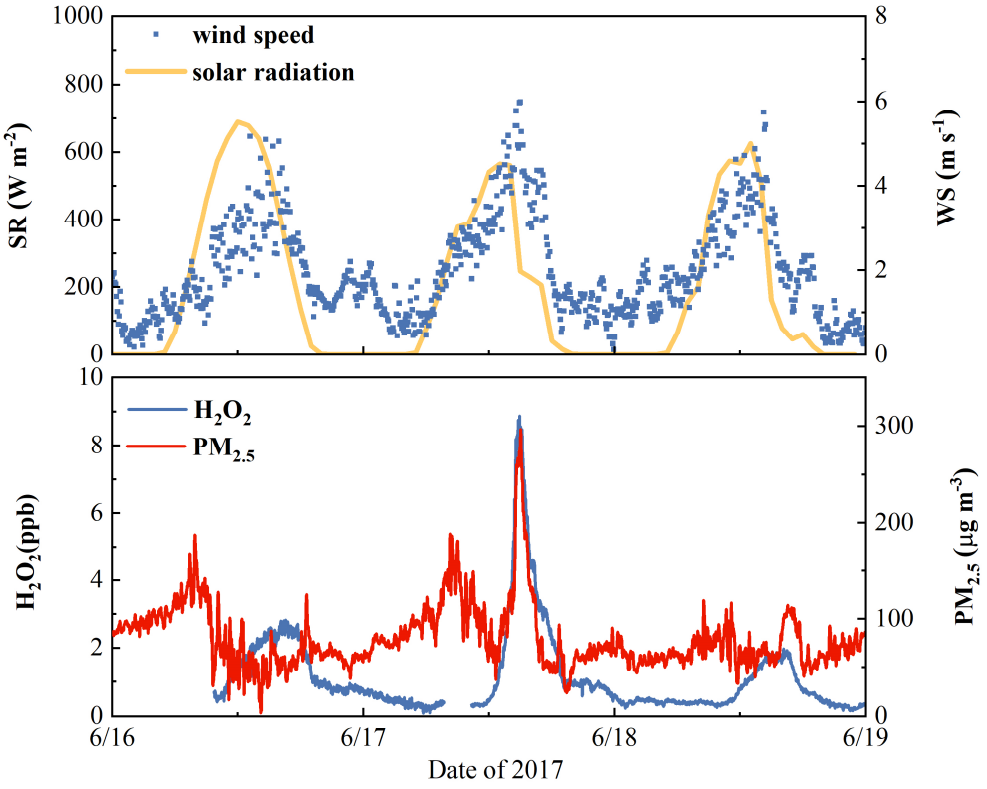
difference between the two channels can largely eliminate the possible influence of the interfering species on the HONO measurement. Instrument background was conducted by sampling ultrapure nitrogen twice per day. The instrument has a detection limit of <5 ppt on 5 min average.

NO and NO_2 were measured with a chemiluminescence analyzer (Thermo Environmental Instruments (TEI), Model 42i) equipped with a photolytic converter. Ozone (O_3) was measured by a commercial UV photometric analyzer (TEI Model 49i). SO_2 was measured by a pulsed fluorescence SO_2 analyzer (Model 43i). The analyzers of NO_x (NO/NO_2), O_3 and SO_2 were regularly calibrated once per week. $PM_{2.5}$ levels were measured by a standard Tapered Element Oscillating Microbalance system (TEOM 1400A, Thermo Scientific). Organic carbon (OC) and elemental carbon (EC) were measured by using an online organic/elemental carbon analyzer (TR20N9, CECEP Talroad Technology Co., Ltd., China). Meteorological measurements (temperature, pressure, wind speed and direction, relative humidity, and solar radiation) were achieved by a potable weather station (Model WXT520, Vaisala, Finland).

3 Results and discussion

3.1 Influence of biomass burning events on H_2O_2 chemistry

Figure 1 depicts the time series of H_2O_2, $PM_{2.5}$, and some meteorological parameters from 16 to 19 June 2017. H_2O_2 exhibited a typical diurnal pattern with a maximum in the early afternoon and low concentrations during the night and in the morning. For instance, on 16 June, H_2O_2 reached a maximum value of ~2.5 ppb around 15:00 LST (Local Standard Time). However, at 13:00 LST on the following day, H_2O_2 increased remarkably from ~1 to ~9 ppb in two hours. Notably, $PM_{2.5}$ also increased concurrently with H_2O_2 from ~50 to ~300 μg m^{-3}.



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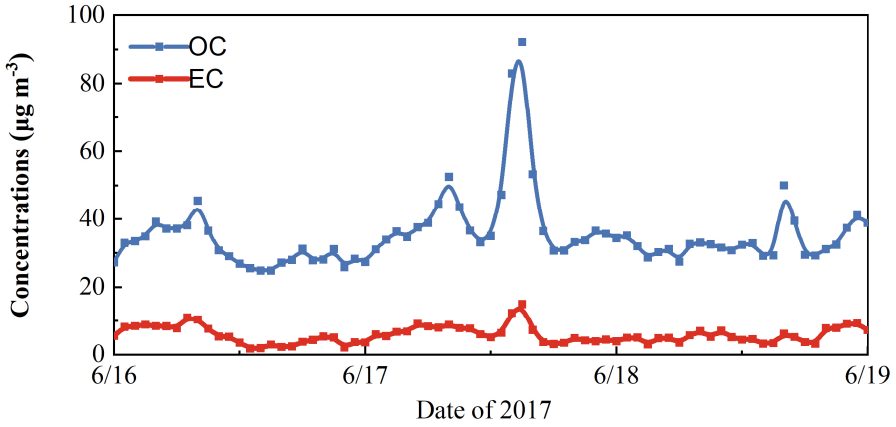
146 **Figure 1: Time series of H_2O_2, $PM_{2.5}$, solar radiation, and wind speed from 16 to 19 June 2017 in the summer**
147 **campaign. H_2O_2 and $PM_{2.5}$ were shown in minute-average data.**

148 The significantly positive correlation between H_2O_2 and $PM_{2.5}$ from 13:00 to 18:00 during the event (r^2=0.97)
149 indicated the same reason for their increases. However, the wind speed was high during the elevation period (~4-6 m s^{-1}),
150 and there wasn't a significant difference in the solar radiation with regard to other days, indicating photochemical
151 reactions alone couldn't explain the sharp increase of H_2O_2 in such a short period. Considering the high wind speed
152 when the high H_2O_2 event was observed, the exceptionally high H_2O_2 might be ascribed to the regional transport of
153 H_2O_2 from the emission source. In addition, the OC (organic carbon) to EC (elemental carbon) ratio at 15:00 LST
154 being higher than 5 (Figure 2) suggested a biomass burning event encountered here (Watson et al., 2001). The well-
155 defined shape and narrow width of the observed H_2O_2 within the plume indicated that the plume had not experienced

156 significant dispersion and mixing since it was emitted, suggesting that the sampling site is not far from the emission
157 source.



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159 **Figure 2: Time series of OC and EC from 16 to 19 June 2017 in the summer campaign.**

160 Given the short lifetime of H_2O_2 in the atmosphere (typically less than one day), we calculated 1-day back trajectory
161 with the HYSPLIT model (https://www.ready.noaa.gov/HYSPLIT.php, last access: 15 April 2022) and found the
162 sampling site was influenced by the plume coming from the southern areas (Figure 3a). The fire spot data on 16 June
163 and 17 June showed that south areas were filled with dense fire spots (Figure 3b), indicative of large areas of
164 agricultural (wheat straw) fires. Large areas of biomass burning in farmland contributed to the primary H_2O_2 emission,
165 resulting in the high H_2O_2 concentrations measured at the downwind site. Lee et al. (1997) observed H_2O_2
166 concentrations up to 10 ppb and attributed this to the direct production of H_2O_2 within biomass burning plumes. Some
167 studies also found an underestimation of modelled H_2O_2 concentration compared with observations during biomass
168 burning events (Wang et al., 2016; Crowley et al., 2018). H_2O_2 concentrations at our sampling site increased by a
169 factor of ~5 (from ~2 ppb to ~9 ppb), which is larger than the value (1.2-3.6) observed in biomass burning plumes by a
170 recent study (Allen et al., 2022). The difference may be explained by the different photochemical age of the air mass
171 sampled. In addition to primary emission, H_2O_2 concentrations will also increase with the photoaging of the biomass
172 burning plume as a consequence of abundant precursors contributing to secondary H_2O_2 production (Yokelson et al.,
173 2009). Moreover, low NO_x levels at the rural areas are conducive for secondary H_2O_2 production. Unfortunately, we

are unable to distinguish primary emission from secondary production during the plume transport. Our results provided direct field evidence that biomass burning events significantly affect H_2O_2 concentrations, despite the polluted plume was already aged or diluted. The primary and secondary H_2O_2 produced from biomass burning contributes to odd-hydrogen radicals, thereby affecting the oxidizing capacity of the atmosphere. Given that wildfire is increasing globally and agricultural fires can be commonly seen during harvesting seasons worldwide (Andreae et al., 2019; Liu et al., 2015), they are expected to make great contributions to H_2O_2 production. To better evaluate the global consequence of the biomass burning-related H_2O_2 production, the emission factor and the production mechanism need to be critically determined.

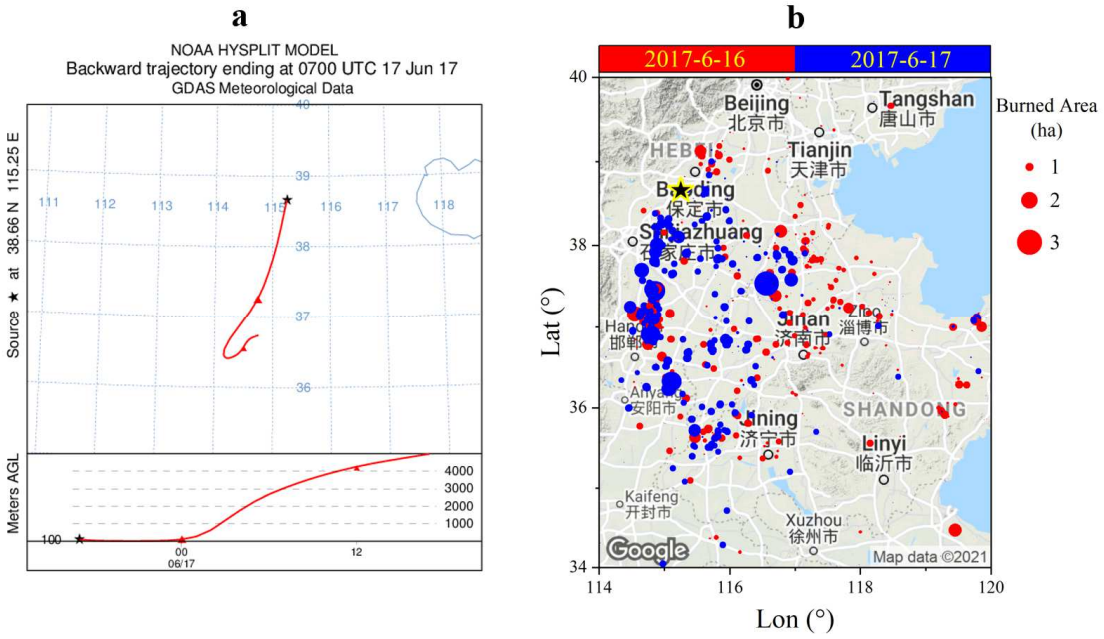


Figure 3. (a) 24 h-trajectory arriving at SRE-CAS site at 15:00 (UTC+8), 17 July 2017 when the peak H_2O_2 occurred. (b) Fire spots map on 16 and 17 June 2017 UTC time obtained from the FINN biomass burning inventory (Wiedinmyer et al., 2011). The sampling site is represented by a black triangle. Map copyright: GoogleMap.

3.2 Influence of nitrogen fertilization on the H_2O_2 chemistry

The summer campaign covered the important agricultural activities period like fertilization. The fertilization process for the agricultural fields around our station was conducted on 13 June, 2017. Details about the fertilization event can be found in our recent study, in which HONO emissions from the fertilized fields were discussed and its potential impacts on O_3 and H_2O_2 were preliminarily mentioned (Xue et al., 2021). Figure 4 exhibited the time series of H_2O_2, O_3 and solar radiation before (6-14 June) and after (14-21 June) the fertilization event. H_2O_2 and O_3 showed pronounced diurnal patterns that were similar to those observed for solar radiation. After fertilization, both H_2O_2 and O_3 diurnal peak values evidently increased (Figure 4 and Figure 5).

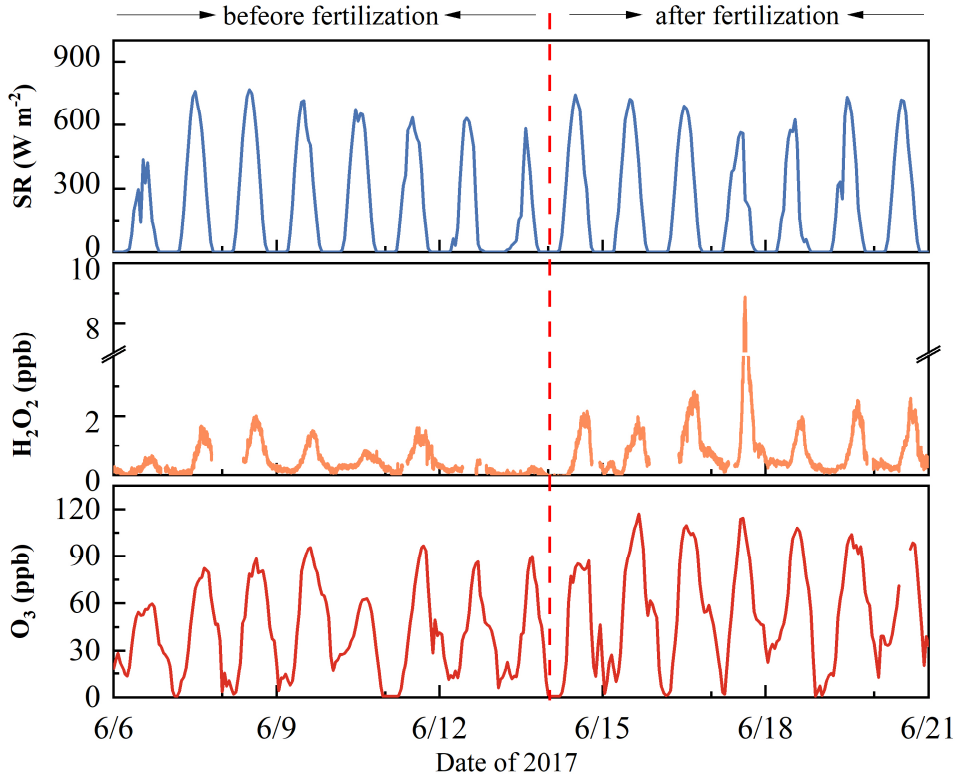


Figure 4: Time series of H_2O_2, O_3 and solar radiation intensity before (6-14 June) and after (14-21 June) the fertilization. The red line indicates the time when the fertilization event around the site began.

To more accurately elaborate on the influence of fertilization events on H_2O_2, the H_2O_2 concentrations on 17 June, which were mainly affected by biomass burning events as discussed in Section 3.1, were not taken into consideration. The averaged concentrations of H_2O_2 and O_3 were a factor of 1.32 and 1.31 higher than the levels observed before the fertilization events (Figure 5), but the solar radiation didn't show a significant change, indicating that fertilization may promote the formation of H_2O_2 and O_3. Previous laboratory studies have reported that fertilized soil could be a source of HONO with the use of nitrogen fertilizer (Su et al., 2011; Donaldson et al., 2014). Our previous work also provided field evidence for soil HONO emission after fertilization at this site (Xue et al., 2019). Therefore, one can expect that HONO concentrations may increase after the fertilization and subsequent HONO photolysis could release more OH radicals compared to the period before fertilization, thereby accelerating the photochemical production of H_2O_2 and O_3. Further analysis confirmed that after fertilization events the enhancements of H_2O_2 and O_3 were consistent with the rising ambient HONO levels (Figure 5). Additionally, the significant increase in H_2O_2 (ΔH_2O_2) and O_3 (ΔO_3) appeared around noontime, coincident with the HONO enhancement (ΔHONO) (Figure 5) and inferred soil HONO emission flux in Xue et al. (2021). It is worth mentioning that Tan et al. (2017) reported high OH concentrations up to 3×10^7 cm^{-3} at the same rural site during a summer campaign in 2014, which was ascribed to local HONO emission from the fertilized agricultural fields (Liu et al., 2019). Therefore, agricultural activities may strongly influence the atmospheric oxidizing capacity and hence the concentrations of H_2O_2, which should be better constrained in atmospheric chemical transport models to assess the impacts of H_2O_2 on regional air quality and global climate.

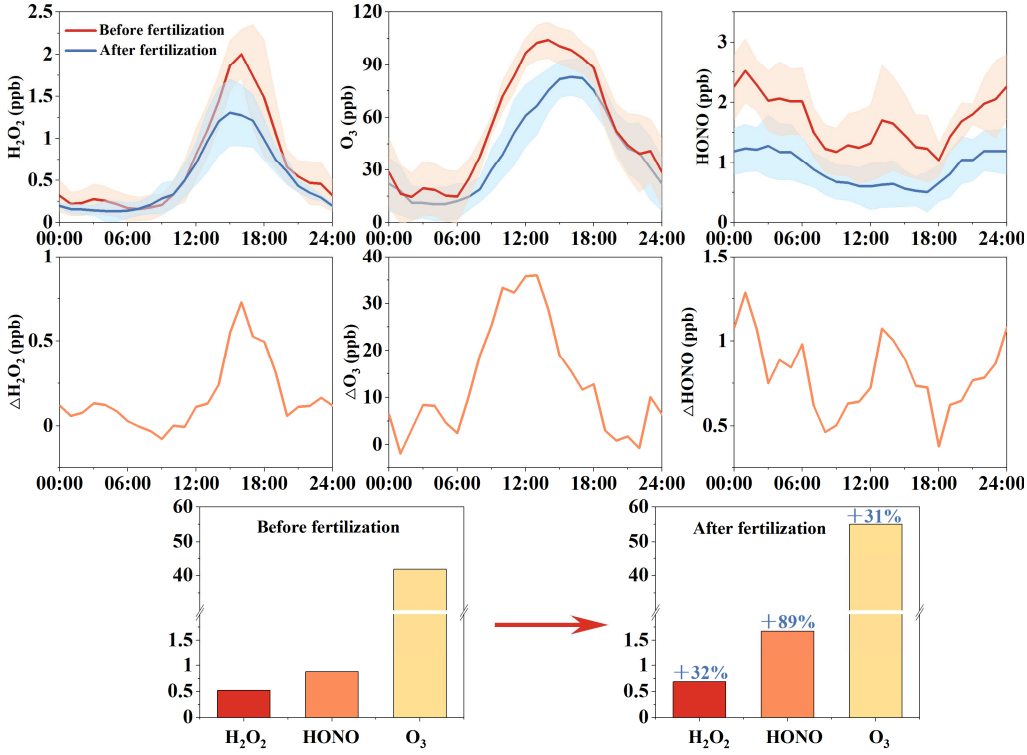
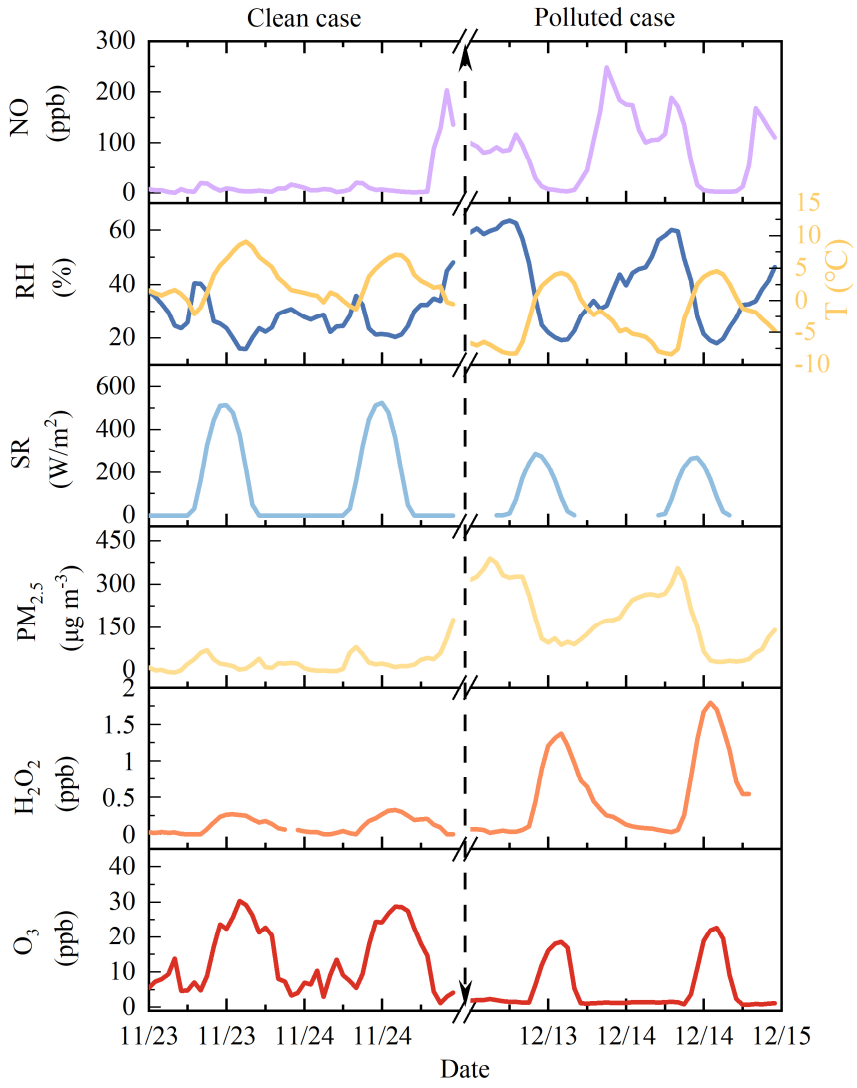


Figure 5: Average concentrations of H_2O_2, HONO and O_3 before (6-14 June) and after (14-21 June) the fertilization in June 2017.

3.3 Influence of particles on H_2O_2 chemistry

To investigate H_2O_2 production on clean and polluted days in the wintertime, representative cases were selected based on $PM_{2.5}$ levels. Figure 6 shows H_2O_2 and other related chemical species and meteorological parameters measured during the winter campaign. In winter, the photochemical generation of OH radicals is weak as a consequence of significantly reduced solar radiation intensity, water vapor and ozone concentrations. Thus, the concentrations of secondary oxidants like H_2O_2 levels are typically believed to be low (Xue et al., 2016). On 23 and 24 November 2017 during our field measurements (the clean case in Figure 6), the maximum solar radiation intensity was lower than 500 W m^{-2} and O_3 concentrations were less than 30 ppb, indicative of the low photochemical activity compared to summer seasons. The corresponding observed H_2O_2 concentrations were less than 0.35 ppb in the clean case.



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228 **Figure 6: H_2O_2, NO, $PM_{2.5}$, O_3, solar radiation intensity (Sa), relative humidity (RH) and temperature (T)**
229 **measured in winter. Left panel: clean case (daily-averaged $PM_{2.5}$ concentrations lower than 75 μg m^{-3}) from 23**
230 **to 25 November 2017; Right panel: polluted case (daily-averaged $PM_{2.5}$ concentrations higher than 75 μg m^{-3})**
231 **from 13 to 15 December 2018.**

232 In contrast, during the polluted case, the maximum solar radiation intensity (~300 W m^{-2}) and O_3 concentrations (~25
233 ppb) were lower than that in the clean case, while the maximum H_2O_2 concentrations (> 1.5 ppb) in the polluted case

(Figure 6) were four times higher than that in the clean case. Contrary to our conventional thought, measured H_2O_2 concentrations during the polluted periods were unexpectedly high, which were even similar to summer levels.

It should be noted that the periods when H_2O_2 grew rapidly coincided with high NO levels exceeding several tens ppb (Figure 6). As discussed in the introduction section, the reaction rate of R2 was more than three orders of magnitude higher than R1 under the condition of 1 ppb NO. Therefore, gas-phase recombination of HO_2 radicals couldn't explain the high H_2O_2 levels observed. The peak value of H_2O_2 average diurnal pattern during polluted days (daily-averaged $PM_{2.5}$> 75 μg m^{-3}) was evidently higher than that during clean days (daily-averaged $PM_{2.5}$< 75 μg m^{-3}), indicating particles promoting H_2O_2 production (Figure S2). Moreover, H_2O_2 exhibited a pronounced diurnal pattern following the track of solar radiation, which implied that H_2O_2 was possibly photochemically produced. Taking all these hints into account, in-particle photochemical reactions are likely to produce the gas-phase H_2O_2. Some other typical cases (two clean and two polluted cases) were also identified and summarized in Table 1. These polluted cases with high H_2O_2 levels were observed in different years and should therefore be representative to reveal the promotion effect of particles on H_2O_2 production.

Table 1. **Summary of the clean and polluted cases**

Case type	Date	Average $PM_{2.5}$ (μg m^{-3})	H_2O_2 maximum increase rate[a] (ppb h^{-1})	Maximum H_2O_2 (ppb)
Clean	8 December 2017	14	0.05	0.36
	4 December 2018	32	0.04	0.21
Polluted	21 December 2017	135	0.266	1.16
	22 December 2017	216	0.267	1.19

[a]H_2O_2 increase rate was calculated as $(C_{t+1}-C_t)/1$ h. C_t represents the hourly-averaged H_2O_2 concentrations at time t.

Previous studies have reported the photochemical production of H_2O_2 free of NO suppression effect in the atmospheric aqueous phase like in clouds and fog water (Faust et al., 1993; Anastasio et al., 1994; Zuo and Hoigné, 1993; Anastasio et al., 1997). The observation is also consistent to our recent chamber and flow tube studies which revealed

253 that photochemical aging of particles involving organic chromophores could produce gas-phase H_2O_2 (Ye et al., 2021;
254 Liu et al., 2021). Organic chromophores have long been identified as important contributors to the aqueous photo-
255 production of H_2O_2 (Faust et al., 1993; Anastasio et al., 1997; Arellanes et al., 2006; Fang et al., 2019). The filter
256 sample analysis showed that particles at our sampling site in winter contained a significant concentration of light-
257 absorbing chromophores (Wang et al., 2020). Considering the photoactivity and abundance of organic chromophores
258 in particles (Poschl and Shiraiwa, 2015; Herrmann et al., 2015), particles may have a crucial effect on the
259 photochemical production of gas-phase H_2O_2. In winter, especially under the conditions of high NO presence, this
260 multiphase reaction channel for H_2O_2 formation, which is less sensitive to NO concentration, may play a more
261 important role than the classical self-reaction of HO_2 radicals, thereby contributing to more sulfate formation. The
262 enhanced photochemical release of H_2O_2 and subsequent oxidation of SO_2 could also shed light on the discrepancy
263 between observed and modeled sulfate concentrations during polluted periods.
264 A recent study found evident O_2^- and sulfate production on Beijing urban $PM_{2.5}$ filter samples under simulated UV
265 radiation (Zhang et al., 2020). This study also indicated that H_2O_2 might be produced in the aging process of $PM_{2.5}$ and
266 subsequent H_2O_2-oxidation leads to the formation of sulfate, which is in agreement with our findings based on field
267 measurements. Further work is needed to fully understand this unique H_2O_2-production pathway and assess its impacts
268 on the global H_2O_2 abundance and sulfate budget.

269 **4 Conclusions and implications**

270 Several field campaigns with measurements on atmospheric H_2O_2 and related parameters were conducted in the rural
271 NCP during different seasons. It allows a determination of special factors (biomass burning, fertilization, and ambient
272 particles) influencing gas-phase H_2O_2 concentrations in this region. First, biomass burning plumes with high H_2O_2
273 concentrations up to 9 ppb were observed during a summer campaign. The measured H_2O_2 rapidly increased from 1
274 ppb to 9 ppb in two hours. Such a high H_2O_2 level and rapid increase can't be solely explained by photochemical
275 production. Along with the analysis of back-trajectory and fire spots data, high H_2O_2 level was mainly attributed to

primary emission by large areas of biomass burning event. Second, a significant H_2O_2 increase was observed after the agricultural nitrogen fertilization event in the summer. We found concurrent elevation of HONO levels compared to that before the fertilization events. The enhanced HONO levels, caused by the soil HONO emission from the fertilized agricultural fields, promoted the atmospheric oxidizing capacity and accelerated the production of secondary oxidants like H_2O_2 and O_3. Third, high H_2O_2 concentrations exceeding 1.5 ppb, were observed under the presence of several tens ppb NO during pollution episodes in the winter campaigns. Under such high NO conditions, the traditional gas-phase channel for H_2O_2 formation would be greatly suppressed so that it was far to explained the measured H_2O_2. High H_2O_2 cases were typically accompanied by high $PM_{2.5}$ levels, suggesting the potential role of particles in H_2O_2 production. Analogous to the aqueous H_2O_2 production in the atmospheric aqueous phase like clouds by organic chromophores, high H_2O_2 during winter polluted periods might be produced by chromophores in the particle phase considering the prevalence of chromophores in particles at this site.

Very limited measurements on atmospheric H_2O_2 in China, especially in polluted regions, are currently available despite its important role in the atmospheric oxidizing capacity and sulfate aerosol formation. This study provides a unique dataset (one summer and two winter campaigns) of H_2O_2 measurements in the NCP, which will benefit the assessment of model performance in the prediction of H_2O_2 concentrations and its potential regional and global impacts. Our results also highlight the important roles of the special factors (biomass burning, fertilization, and ambient particles) in enhancing the concentrations of gas-phase H_2O_2. The enhanced H_2O_2 production influenced by these special factors will contribute to the oxidizing capacity of the atmosphere and hence more sulfate aerosol formation, which has a crucial effect on air quality and direct forcing of the earth's climate. Additionally, particle-bound H_2O_2 will further produce OH radical by photolysis and Fenton reaction, which will contribute to the aerosol aging and oxidizing organics within particles. Furthermore, reactive oxygen species (e.g., H_2O_2, OH, O_2^-) are at least partly responsible for the particle-related adverse health effect. The in-particle production of H_2O_2 may constitute a public risk to human health. However, these special factors influencing H_2O_2 concentrations are not well considered in model estimates of H_2O_2 and may limit the accurate prediction of the H_2O_2 budget in the atmosphere and its associated

climate and health effects. Hence, further research on the factors in controlling H_2O_2 concentrations and model improvements in H_2O_2 simulations are greatly warranted.

Data availability. Observation data are available at https://zenodo.org/record/4456345#.YAp7DzMufX8

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

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