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Atmospheric
Chemistry
and Physics
Discussions

# *Interactive comment on* "Atmospheric hydrogen peroxide and organic hydroperoxides during PRIDE-PRD'06, China: their concentration, formation mechanism and contribution to secondary aerosols" *by* W. Hua et al.

**W. Hua et al.**

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We highly appreciate your constructive comments. Here are our responses to the comments.

Experimental

1. Measurement site and meteorological conditions:

(Q1): The measurement site needs to be more fully described in terms of both geographical and meteorological settings. Then, what about primary pollutants including NOx, CO, and SO2 that control peroxide level?

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(A1): We agree that we should describe the measurement site more fully in terms of both geographical and meteorological settings and describe the primary pollutants including NOx, CO, and SO2, so we have modified the text to read as follows:

’The observations are from the PRIDE-PRD’06 (Program of Regional Integrated Experiments of Pearl River Delta Region) Air Quality Monitoring Campaign that took place from the 3rd to the 30th of July 2006 at Backgarden (23.548°N 113.066°E), a rural site, surrounded by 20 km2 of forest and 2.7 km2 of lake, located north of the central PRD and about 60 km northwest of the mega-city Guangzhou in southeast China, which is the capital city of Guangdong Province. The increase in industry and population impacts the air quality of Guangzhou. Guangzhou is undergoing a complex air pollution composition due to the mixture of coal burning and vehicle emissions. Backgarden is a much less populated area at the outskirts of the densely populated center of the PRD and can be treated as a regional background site. Backgarden does not have significant local vehicle emission, while the biomass burning in the afternoon and burning of cable in the evening might be a source of local emission. The Backgarden site experiences a typical sub-tropical climate and is usually influenced by the monsoon circulation in the July. During the measurement of hydroperoxides, the observation site was mainly influenced by the western pacific subtropical high and typhoon. When controlled by the western pacific subtropical high, 19-23 July, the days were sunny, and the dominant wind direction at Backgarden was southerly. While the influenced by typhoon from 24th to 25th of July, northerly winds prevailed at the observation site. During the last days of the campaign, 26-30 July, the local weather conditions were cloudy and rainy and the sampled air masses came mainly from the south/southeast. The average meteorological values (arithmetic mean +- standard deviation) for the campaign were: 29.5+-3.4 C ambient temperature, 76.2+-14.4% ambient relative humidity, 1001+-4 hPa ambient pressure, and 1.9+-1.2m/s local wind speed. The meteorological factors are shown in Fig. 4. The primary pollutants including NOx, CO, and SO2 influenced the hydroperoxides level significantly during the campaign. Their concentrations kept relatively low in the daytime, but were elevated at night, particularly under

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southeasterly wind during July 20-22. In addition to the measurement of peroxides, all major trace gases (NOx, NOy, PAN, SO2, CO, O3, biogenic/anthropogenic VOC, etc.), aerosols (mass concentration, number concentration, chemical compositions), free radicals (OH, HO2, RO2) and meteorological parameters (temperature, wind direction, wind speed and relative humidity, pressure, rainfall) were monitored at this site by a number of groups.'

(Q2): It was also mentioned that the study area was under influence of typhoon during July 24-26. On what basis was the air more polluted during that period (Line 3 Page 10495)? The levels of NOx, SO2, and CO seem to be higher during July 19-22.

(A2): We agree that the sentence '...in particular, the central and eastern parts, resulting in more heavily polluted conditions than normal in this region'(Line 1-3 Page 10495) is incorrect. The 'more heavily polluted conditions' we mentioned is the case for the central and eastern parts of PRD, for example, Guangzhou city (another super observation site of the PRIDE-PRD2006 campaign). Because during 23-25 July, the averaged and maximum ozone concentrations at Guangzhou city were about 100 ppbv and $>$140 ppbv respectively in the afternoon. As for Backgarden site, only the ozone concentration of July 23th was higher. To clarify this misleading, we have modified the text as follows:

'The second period, 23-26 July, was influenced by typhoon Kaemi, which came across most of the PRD and resulted in heavily polluted conditions in the central and eastern PRD (Z. B. Yuan, 2007, personal communication). During this period, high levels of hydroperoxides were also observed at Backgarden on the 24 and 25 of July, two sunny days.'

(Q3): In later section, it was also stated that the air was more aged due to the influence of typhoon (Line 20 Page 10500). The two words 'polluted' or 'aged' appears to contradict. The former indicates the air affected by land emissions, while the latter indicates the air came from the ocean?

(A3): We are sorry that we cannot exactly understand the meaning of this question. In 'This indicates that during that time the air at Backgarden influenced by the typhoon front was photochemically aged' (Line 20-23 Page 10500), we mean that the air was aged, rather than more aged, considering the ratio of toluene/benzene of $<$0.5 between 12:00 LT on 24 July to 21:00 LT on 25 July, with a few exceptions in the early morning of 25 July. We have proved that during 13:00-17:00 LT of 19-21 July the air was photochemically aged from the ratio of NOx/NOy and toluene/benzene (Line 13-17 Page 10496). In the Sect. 3.2.3, we introduced that during two sunny periods: July 19-22 and July 24-26, both air masses were photochemically aged, the relatively high levels of hydroperoxides were observed, and the wind speeds were similar, at ˜2 m/s, but the dominant wind directions were just opposite. Thus, much of the variation of hydroperoxide mixing ratios observed at Backgarden on these sunny days can be attributed, to a large extent, to the local photochemical drive.

2. Hydroperoxide measurement

(Q4): 2.1. Collection solution The pH of collection solution..., but SO2 interference should be clarified before considering its role in sulfate formation through heterogeneous reaction.

(A4): Please see the discussion in answer 17 (A17).

(Q5): 2.2. Detection limit of MHP

(A5): There was an error in previous description. The detection limit of MHP was not defined the same way as that of H2O2. So we have corrected the text as follows: The detection limit (d.l.) of H2O2, defined as three times the standard deviation of the analytical blanks of Milli-Q water, was 0.012 uMol/L using a 100 uL sampling loop. The detection limit of MHP, based on three times the standard deviation of the MHP standard solution (7.0E-7 M), was 0.021 uMol/L. These corresponded to d.l. of about 20 pptv for H2O2 and 35 pptv for MHP in the gas phase under these sampling conditions.

(Q6): 3. Aerosol measurements WSOC concentrations are shown in Figure 7, but cutoff size was not given anywhere in the text.

(A6): The cutoff size of WSOC aerosol measurements was 1.0 um. The text has been altered to ’The AMS consists of a particle sampling inlet with cutoff size 1.0 um...’ (Line 20 Page 10492).

Results and discussion

(Q7): 1. Organic peroxide As suggested in the title, it is likely to expect new insight into organic hydroperoxide: what condition was favorable for the formation of organic peroxide and the consequence of their formation, etc..

(A7): The reviewer made a very good sugguestion here. We agree that a more elaborate discussion about organic peroxide is needed, so the following the discussion was added to the end of section 3.4 the (Line 5 Page 10505) as a new paragraph.

’From Fig. 4, we found that relatively high levels of hydroperoxides were also measured in the evening of 20-21 July, which coincided with the increase of C3-C5 alkenes, especially isoprene, in the same time periods. Moreover, BHMP was also observed in the morning and in the afternoon of 25 July in addition to afternoon and night of 24 July. Noticeably, when BHMP was detected, the mixing ratios of C3-C5 alkenes, particularly isoprene, propylene, 1-butene and 1-pentene were higher, as shown in Fig.4. Thus, we suggest that high levels of alkenes, especially isoprene, are favorable for the formation organic hydroperoxides. Besides BHMP, the relatively high level of PAA was often detected on 23-25 July in addition to 20-21 July mentioned in Sect. 3.2.2. The maximum mixing ratio of PAA during the observation was observed in the afternoon on 24 July, on which PAN also exhibited a high level of ˜3 ppbv (B. Wang, 2008, personal communication, Peking University). Hence, we suggest that the high levels of PAN and strong solar radiation in the daytime could favor the formation of PAA. It is noteworthy that PAA was often detected after sunset on 20-21 and 23-25 July, which means that PAA might also be formed in absence of photo-oxidation. However, to our

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best knowledge, PAA has not been reported as a product of the ozonolysis of alkenes, and the relevant mechanism is unclear and need further investigation. The solubility of BHMP is higher than H2O2 (H BHMP=6.0E5 M atm-1, 293K), thus, it could enter into the aqueous phase easily. BHMP could easily decompose and convert to H2O2, and then it might take part in the formation of sulfate and SOA in the form of H2O2. PAA is an important acid in its own right and could decompose into acetic acid and H2O2 under typical tropospheric conditions. As a result, PAA could play a role in acid deposition both as an oxidant and an acid.

(Q8): 2. Supplementary measurements The author state that it would be much better to present measurements results of isoprene together with organic hydroperoxide.

(A8): we agree the reviewer'point, so we modify the Fig. 4. and add relative humidity and temperature, - SO2 and NOx during July 27-31 - NOx/NOy ratio-; Toluene/benzene ratio, isoprene and C3-C5 alkenes into Fig. 4. The discussion about the measurements results of isoprene together with organic hydroperoxide has been mentioned in answer 7 (A7).

(Q9): 3. NOx diurnal variation and vertical mixing Was NOx really zero during the day? In addition to NOx, primary pollutants such as CO and SO2 were low during daytime. There was no statement about SO2 or CO variation.

(A9): In order to clarify this question, we have checked the data carefully and found that the NOx was not really zero during the day but exhibited very low mixing ratios (0.4˜3 ppbv) during the afternoon of 19-21 and 23-25 July. Fig. 4 can not clearly show these low values because of the the coarse scale. Moreover, we find that the specific values of the mixing ratio of NOx in the morning were incorrect because of our data editing error, that is, the 36 ppbv in the (Line 1 Page 10496) and ˜8 ppbv in the (Line 3 Page 10496) should be corrected to 32 ppbv and ˜3 ppbv respectively.

We agree the reviewer's point that the meteorological condition (change in wind direction) seems to have more significant influence on variations of primary pollutants. The

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role of change in wind direction in variations of NOx has been mentioned in the text (Line 6-7 Page 10496). The text in (Line 15 Page 10499) has been modified as follows:

’The sharp increase of H2O2 at about 09:45 (LT) on July 21 coincides with the decrease of the NOx, SO2 and CO mixing ratios, which might be explained by vertical exchange and changes in the wind direction. In the morning, the wind direction turned clockwise via northeast (07:30 LT) to southeast (09:30 LT).’

The reviewer made a good point here and we agree that the chemistry of NOx should be taken into account and variation of SO2 and CO should be stated. Hence, to better discuss these details, the text from (Line 7-10 Page 10496) has been modified as follows:

’and then to south (09:30 LT). Moreover, the chemistry conversion of NOx to HNO3 might also serve as an important sink for the NOx. Since the concentrations of HOx radicals were high in the study region, NO could be fast converted to NO2 and then this NO2 react with OH radicals and form HNO3, which would be in turn taken up in the aerosol. The increase of gas-phase HNO3 in the morning is consistent with the sudden drop of NOx (H. Su, 2008, personal communication, Peking University), and this could be evidence of the chemistry conversion route. In addition to NOx, the concentration of SO2 and CO varied significantly in the morning. The concentrations of SO2 and CO were relatively high at 08:15 LT, with 41 ppbv and 1 ppmv respectively. After 08:15 LT, the concentrations of SO2 and CO decreased rapidly to ˜6 ppbv and ˜0.3 ppmv respectively at 10:30 LT, and remained at this relatively low level until sunset. The mixing ratio of H2O2 began to increase markedly at 08:45 and reached 2.8 ppbv at 10:30 LT, which is consistent with the sudden drop of NOx, SO2 and CO detected, and the hydroperoxides showed a high level during the daytime. A similar diurnal trend of NOx, SO2 and CO was observed during the daytime on 20-21 July.’

(Q10): 4. Equations 1-8 and the following discussion (Page 10498) Equations are not really required. The NO concentration at Backgarden during daytime (280 pptv) was

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definitely not high enough to be called ’polluted’

(A10): We agree that reviewer’s point that the equations 2-8 should be removed and the NO concentration at Backgarden during daytime (280 pptv) was definitely not high enough to be called polluted, so we have modified text from Line 22 Page 10496 to the end of the Sect. 3.2.1 as follows (and the corresponding expression in the abstract and conclusion will be modified accordingly):

’However, the NO reaction with peroxy radicals will compete with the formation of hydroperoxides, since the reactions of NO with peroxy radicals are faster than recombination reactions of peroxy radicals (Lee et al., 2000). At Backgarden, the average NO mixing ratio at 10:30-14:00 LT and 14:00-18:00 LT on July 19 -21 were ˜ 280 pptv and ˜ 80 pptv respectively, and the mixing ratio of HO2 radicals was ˜2E9 molecule/cm3 at noon. Using the HO2 average concentration, it can be obtained from a simple calculation that when the concentration of NO is ˜65 pptv, the reaction rate of NO-HO2 and HO2 -HO2 could be about equal. Hence, high levels of hydroperoxides detected in the daytime may be attributed to the moderate level of NOx and exceptionally high mixing ratio of HO2 radicals produced by oxidation of VOC and CO at Backgarden.’

(Q11): 5. Rapid drop of H2O2 shown in Figure 5

(A11): Please see the discussion in answer 17 (A17).

(Q12): 5. Rain It is very interesting case to detect MHP in rain samples. MHP was also the highest in the first rain sample like H2O2?

(A12): We have checked again the raw data and found that MHP was also the highest in the first rain sample like H2O2.

(Q13): 6. Hydroperoxide contribution to aerosols

(A13): We accept the reviewer’s suggestion and will delete the equations (13)-(16) and (17)-(23).

(Q14): First of all, as aerosols used to contain fair amount of water, it needs to be clarified what is the heterogeneous reaction suggested in this paper that is distinguished from known aqueous reactions leading to sulfate production.

(A14): We would like to clarify the heterogeneous reaction suggested in this paper. The known aqueous reactions mean that both the two reactants stay and react in the aqueous phase; however, the heterogeneous reaction we suggested here is the interfacial reaction occurring on the surface of particles, that is, one reactant stays in the aqueous phase and reacts, via collision, with another reactant from the gas phase, or neither of the two reactants stay in the aqueous phase but both can contact the aqueous phase simultaneously from the gas phase and react at the instant of contact. Chen et al. (2008) have elaborated this kind of heterogeneous reaction on the surface of droplets (or called the interfacial reaction) and suggested that it might be significant for a rapid reaction. With regard to the ubiquity of the nanometer-size water clusters (H2O)n, micrometer-size water droplets and water-soluble layer covered aerosols in the atmosphere, the high solubility of H2O2, and the rapid reaction rate of H2O2 with S(IV), we suggested that the big gap between the estimated sulfate production rate and measured value might be explained by the heterogeneous reaction.

(Q15): If heterogeneous reaction was crucial in sulfate and WSOC formation, there should be any measurements of number or mass concentrations of submicron aerosols, or size distribution that is relevant to indicating surface areas of aerosol.

(A15): We preliminarily estimate the surface areas of aerosol using the size distribution measured by TDMPS instrument and found that that the surface area of aerosol increase obviously between 13:30 and 15:30 LT on 21 July. The increase of surface area of aerosol together with humid weather condition would benefit the occurrence of the heterogeneous reactions and formation of sulfate and WSOC.

(Q16): As the estimation was made with assuming that the pH of aerosol was about 4-5, the observed and calculated could be about equal if pH is lowered by one unit.

(A16): We agree the reviewer's point that the pH of aerosol around 3˜4 would not be unreasonable. However, as mentioned in the (Line 1 Page 10507), the previous study has pointed out that the rate of S(IV) reaction with H2O2 is practically independent of pH over the pH range of atmospheric interest (Schwartz et al., 1984). Additionally, to clarify this question, we use the pH 2˜3 to calculate the reaction rate, and find that the reaction rate is still ˜1.4E-12 mol m-3 s-1 in the aqueous phase when pH is ˜ 3, and it only increase to ˜2.3E-12 mol m-3 s-1 even when pH is ˜ 2. Hence, we think that the observed sulfate production can not be explained only by known mechanisms, and the heterogeneous chemistry on the surface of droplets and aerosols is potentially important for sulfate formation.

(Q17): In addition, the negative relation between H2O2 and SO4 (Figure 7)

(A17): This question is closely related to the question 2.1 'Collection solution' and the question 5 'Rapid drop of H2O2 shown in Figure 5', so we would like to answer this question together with them.

The reviewer's concern about the SO2 interference on H2O2 measurement is correct. We admit that SO2 does influence the H2O2 measurement and agree that SO2 interference should be clarified before considering its role in sulfate formation through heterogeneous reaction. Thus, we answer these questions from two aspects.

On one hand, we would like to clarify these questions by a calculation. At 283K (temperature adopted in our sample collection), the Henry's Law Constants of H2O2 and SO2 are 2.85E5 M atm-1 and 2.32 M atm-1 respectively (Sander et al., 2003). As mentioned in Sect. 3.5.1, the total amount of dissolved S(IV) always exceeds that predicted by Henry's Law for SO2 alone, so we calculate the effective Henry's Law constant of SO2 by the expression given in textbook (Seinfeld and Pandis, 1998), and obtain a value of 98 M atm-1 at pH 3.5. Assuming the mixing ratios of H2O2 and SO2 are 1 ppbv and 10 ppbv respectively in air, and then the equilibrium concentrations of H2O2 and SO2 in collection solution (pH 3.5) are estimated to be 285 uM and 1 uM respectively in solution, on the basis of Henry's Law. Then, we calculate that the reaction rate of the dissolved H2O2 and S(IV) are ˜6.6 uM s-1 at pH 3.5. In the glass coil collector for hydroperoxides collection, the contact time of the sampled air and the collection solution is less than 10 s. After this time, the air is separated from the collected solution, and the collection solution, containing hydroperoxides, is rapidly delivered into the HPLC system and no longer contacts with SO2 in the sampled air again. This means that the SO2 in sampled air can only destroy H2O2 and influence H2O2 measurement within this 10 s (in the coil collector). From the above calculation, we can find that, under the condition of 1 ppbv H2O2 and 10 ppbv SO2, about 66 uM of 285 uM H2O2 will be destroyed during collection, indicating that the mixing ratio of H2O2 will be underestimated by ˜25%. More details regarding the interference of SO2 in H2O2 measurement can be seen from Table 1.

Table 1. The loss of H2O2 during collection (10 s) under different SO2 concentrations (H2O2 is assumed as 1 ppbv)

| SO2 (ppbv) | 2 | 5 | 10 | 15 | 20 | 30 |
|---|---|---|---|---|---|---|
| H2O2 Loss | 5% | 12% | 23% | 35% | 46% | 70% |

We admit that, when the SO2 level remained high in the morning or elevated during the day (>15 ppbv), H2O2 were detected in very low concentrations because of potentially significant interference of SO2. We agree that reviewer's point that, in addition to high relative humidity and dry deposition, the loss of H2O2 by high SO2 during collection could also be a very important reason for the decrease of gaseous H2O2 in the afternoon of July 21, as shown in Figure 5. We will add 'In addition, resulting from the limitation of the collection method, the loss of H2O2 by elevated SO2 during collection could also be an important reason for the decrease of H2O2 in the late afternoon' to the end of (Line 13 Page 10500) in the text. Meanwhile, considering the fact that the loss of H2O2 in the real atmosphere will also be amplified by elevated SO2, we think that the diurnal cycle of H2O2 shown in Figure 4 can reflect the variation trend of H2O2 in the atmosphere to some extent, although the uncertainty of H2O2 quantification occurs.

However, it is noteworthy that when the mixing ratio of SO2 is lower than 10 ppbv, the condition for most of the daytime during the measurement period, the measurement of H2O2 were not significantly influenced, that is, most of our data were not significantly influenced by interference of SO2 and are reliable.

As shown in Figure 7, during the time period (13:30-15:30 LT), in which the role of H2O2 in sulfate formation through heterogeneous reaction was discussed, the averaged and the maximum mixing ratios of SO2 are 6.5 ppbv and 9.9 ppbv respectively, and these SO2 levels could only result in 10˜20% loss of H2O2 during collection; thus, it is reasonable to think that the SO2 interference on measurement of H2O2 was minor and the mixing ratios of H2O2 detected could reflect the situation of the real atmosphere. Therefore, we think that the discussion on the potentially important role of H2O2 in sulfate formation through the heterogeneous reactions is reasonable.

On the other hand, we studied the interference of the SO2 using the Horibe tube in a cold trap (described in the end of Page 10489). We added 1 ml mixing standard solution containing 10-6 M H2O2, MHP and EHP (comparable to hydroperoxides concentrations in the atmosphere) into the Horibe tube before introducing the air flow. Then the air flow containing SO2 flowed into the Horibe tube. We find that the losses of H2O2 are ˜10%, ˜30% and ˜50% respectively when the SO2 concentrations are 10 ppbv, 20 ppbv and 50 ppbv respectively. The losses of organic hydroperoxides were lower than H2O2. This result also supports our point that the interference of SO2 will not be significant under a 15 ppbv level of SO2 and most of our measurement data are reliable. We prepare to publish the specific results in another paper later.

Moreover, the reviewer mentioned 'In Figure 7, H2O2 was close to detection limit during 6˜8 PM with the second maximum of SO2 and then increased a little bit with decrease in SO2. If all H2O2 was used up on aerosol surfaces, H2O2 could not be raised again at night.' We admit the role of SO2 in this decrease of H2O2, but we suggest the increase of H2O2 later might be partly explained by the ozonolysis of alkenes as discussed at the beginning of answer 7 (A7).

(Q18): In Figure 8, it is hard to find any consistent relationship between H2O2 and WSOC. Discussion was almost about results from previous studies without any crucial evidence implying that H2O2 played a role in WSOC formation through heterogeneous reactions aerosol surfaces.

(A18): We would like to clarify that the relationship between H2O2 and WSOC is not consistent. The relationship expressed in the text is that the diurnal trends of the observed hydroperoxides and WSOC have a negative correlation. We admit that, due to the limitation of experimental instrument, we can not provide crucial experimental evidence, for example, the existence of important WSOC indicator species, 2-methyltetrols or 2, 3-dihydroxymethacrylic acid, to support the important role of H2O2 in the WSOC formation through heterogeneous reactions on aerosol surfaces. Because, as described in (Line 10 Page 10492), the measurements of WSOC were made using a particle-into-liquid sampler (PILS) followed by online quantification of TOC every 6 min using a total organic carbon (TOC) analyzer. Moreover, these SOA species also can not be identified by other aerosol measurement methods used in the campaign. Thus, it is difficult for us to give powerful evidence now. However, more and more evidences from laboratory studies show that the role of hydroperoxide in the formation of SOA through heterogeneous reactions is potentially important; we attempt to give a field evidence for this relationship for the first time. Actually, as the reviewer pointed out, our given evidence is still weak, and more field evidences should be provided in the future.

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