

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.

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"General Comments"

It is very interesting article that addresses the role of H₂O₂ in sulfate and SOA formation, which is an important topic in terms of atmospheric chemistry and earth's climate. It is also interesting to see various kinds of organic hydroperoxides detected in the study region. This manuscript could profit from more elaborate discussion about organic hydroperoxide as well as hydrogen peroxide using available measurements made during the experiment. Particularly, the distributions of H₂O₂ described in section 3.1~3.3 should be reanalyzed in relation with primary pollutants such as NO_x and

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SO₂, and its source such as isoprene. Also, to confirm the involvement of hydroperoxide in heterogeneous reaction leading to sulfate and SOA formation needs more evidence other than that shown in Figure 7 and 8. Please see detailed comments as follows.

"Specific Comments"

Experimental

1. Measurement site and meteorological conditions

The measurement site needs to be more fully described in terms of both geographical and meteorological settings. It was identified as a rural area, but close enough to be affected by urban emissions from Guanzhou. Therefore, meteorological conditions would be very important to determine the level of anthropogenic gases and aerosols in measurement site. Meteorological factors were discussed briefly in later section only to emphasize the role of local photochemistry in determining hydroperoxide levels, though. Then, what about primary pollutants including NO_x, CO, and SO₂ that control peroxide level? Their concentrations were mostly elevated at night under southeasterly wind during July 20~22, which is shown in Figure 4.

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 NO_x, SO₂, and CO seem to be higher during July 19~22. 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?

The main results of this paper were obtained during two periods: July 19~22 and July 24~26, when meteorological conditions seemed to be very different. Thus, they need to be clarified before any further discussion.

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2. Hydroperoxide measurement

2.1. Collection solution The pH of collection solution was adjusted to 3.5. Considering the high SO₂ level (up to 60 ppbv), the interference of SO₂ could be significant and should be determined. Although SO₂ levels were mostly high at night when peroxide was not measured, its level remained high in the morning when the measurement started and was also elevated during the day. Moreover, SO₂ variation was just opposite to that of H₂O₂, which is clearly seen in Figure 4 and 7, in which H₂O₂ concentrations started to increase with decrease in SO₂ (and NO_x). There could be other factor such as NO_x inhibiting H₂O₂ formation, but SO₂ interference should be clarified before considering its role in sulfate formation through heterogeneous reaction.

2.2. Detection limit of MHP What was analytical blank that was used to define detection limits of hydroperoxides? Was it collection solution or Milli-Q water? The detection limit of MHP was defined the same way as that of H₂O₂? MHP is rarely detected in either of two solutions. Then, from where was the MHP detection limit of less than 20 pptv obtained.

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

Results and discussion

1. Organic peroxide It is interesting that PAA and BHMP were often detected (Line 16 Page 10493) and HMHP was detected in few samples (Line 12 Page 10494). While BHMP was observed on the 24th (section 3.4), PAA was detected during 19-21 (Line 4 Page 10499). 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.. Therefore, a more elaborate discussion about organic peroxide is needed, in addition to textbook type discussion given in section 3.4.

2. Supplementary measurements A major drawback of this manuscript is that discus-

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sion was not fully supported by supplementary measurements that were obtained in the experiment but not shown in the manuscript. - relative humidity and temperature - SO₂ and NO_x during July 27-31 - NO_y or NO_x/NO_y ratio - Toluene and benzene or their ratio - Alkene, Isoprene (5 ppbv isoprene at night!) Particularly, alkene and isoprene were pointed out as a major source of organic hydroperoxide. It would be much better to present measurements results of isoprene together with organic hydroperoxide, instead of mentioning supportive results from previous studies which can found in papers or textbooks.

3. NO_x diurnal variation and vertical mixing Was NO_x really zero during the day? In addition to NO_x, primary pollutants such as CO and SO₂ were low during daytime. There was no statement about SO₂ or CO variation. For NO_x, however, vertical mixing during the day was suggested as a main reason for the unique diel variation of NO_x (Line 5 Page 10496; Line 15 Page 10499). NO_x concentrations were enhanced at night and dropped down to zero (or close to zero) during the day (Figure 4). Vertical mixing can play a role in reducing the level of NO_x during the day, but the difference was too much to be explained by mixing only. As mentioned above, meteorological condition (change in wind direction) seems to have more significant influence on variations of primary pollutants. At the same time, chemistry should be taken into account. Since concentrations of HO_x radicals were high in the study region, NO could be fast converted to HNO₃, which would be in turn taken up in the aerosol. NO_x variation should be thoroughly examined because NO_x is important in controlling hydroperoxide level.

4. Equations 1-8 and the following discussion (Page 10498) Equations are not really required. The following discussion is not clear. There appears no flaw in previous studies cited here. About 100 pptv of NO can be obtained from a simple calculation using HO₂ average concentration of ~108 molecules/cm³. If HO₂ concentration is higher than that at low NO environment, it is not to mention that the formation of hydroperoxide would be boosted. The NO concentration at Backgarden during daytime (280 pptv) was definitely not high enough to be called “polluted”. This section should be

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removed or reworded completely.

5. Rapid drop of H₂O₂ shown in Figure 5 Two possibilities were suggested in the manuscript: the loss of H₂O₂ due to high relative humidity and dry deposition. They are general removal pathways of H₂O₂ and their effects could not be changed rapidly for a short time. Instead, it may result from SO₂ interference. In Figure 4, SO₂ concentration was enhanced in the afternoon of July 21, which was coincident with a rapid decrease in H₂O₂. On July 20, a similar trend was observed in the afternoon, too. It is difficult to tell if gaseous H₂O₂ was reduced by high SO₂ or H₂O₂ was lost during collection. It should be clarified.

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?

6. Hydroperoxide contribution to aerosols

Most of equations (13)-(23) are not necessary in this section. They can be found in the textbook.

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. 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.

Sulfate production rate from measured sulfate concentration was larger than the estimated by an order of magnitude. 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. In fact, the pH of aerosol around 3~4 would not be unreasonable. Therefore, this approach may not strongly back up the idea that observed sulfate production was too high to be explained by known mechanisms.

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In addition, the negative relation between H₂O₂ and SO₄ (Figure 7) doesn't necessarily result from H₂O₂ consumption by SO₂ in sulfate formation. It is obvious that H₂O₂ is photochemically produced in the atmosphere and thus its concentrations used to start increasing in the morning, reach to maximum in the afternoon, and decrease in the evening. Because their lifetime is about a day against photolysis, its concentration hardly goes down to zero right away at night. 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 couldn't be raised again at night. This relationship between H₂O₂ and SO₂ could be possible, if gaseous H₂O₂ was destroyed during collection.

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 10481, 2008.

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