Atmos. Chem. Phys. Discuss., 8, S5932–S5938, 2008
www.atmos-chem-phys-discuss.net/8/S5932/2008/

Atmospheric
Chemistry
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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.

Received and published: 13 August 2008

Thanks for your effort and constructive comments. Here are our responses to your comments:

(Q1): General comments.

(A1): We highly appreciate your general comments. The questions you mentioned here are answered in the specific comments.

(Q2): Introduction This section could be significantly reduced. Concentration ranges could be included within directly relevant sections of the article.

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(A2): We agree that we should reduce the concentration ranges description (Line 5-15 Page 10487) from the introduction part, and include within directly relevant sections of the article. And, we rewrite the sentence (Line 24 Page 10493) as follows:

’The mixing ratios of H2O2 and MHP are in agreement with those reported in the literature with H2O2 ranging between 0.5 ppbv and 5 ppbv and MHP ranging between several pptv and 2.7 ppbv worldwide respectively’

In addition, we also rewrite the sentence (Line 22 Page 10501) in the section of rainfall discussion as follows:

’This concentration is within the range from 0.1 uMol/L to 300 uMol/L reported for earlier studies’

(Q3): Measurement site It is difficult to appreciate the geographical setting and the typical meteorology encountered at the measurement site to be able to set the results in context (amounts to only 5 lines at the beginning of this section) and this could be much more descriptive.

(A3): We agree the review’s suggestion, so we rewrite the relevant section 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 burn-

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ing 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 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.’

(Q4): Measurement method for hydroperoxides More detail needs to be given about the location of the sampling inlet (presently states from the uppermost room of a three story building). Was this surrounded by other buildings such that air could not freely circulate or was it in a much more confined location? A map of the measurement site might assist. Was the sample line cleaned in advance in order to minimise loss to the walls? No mention of any line loss experiments, were these carried out? Collection efficiency determined at 10 C, was this the temperature at which the stripping coil was cooled to during the sampling period? If not, have collection efficiencies been carried

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out at the ambient sampling temperature? Were synthesised standards purified in order to determine concentration of hydroperoxides? There is no discussion of any experiments that have been carried out to determine artefact production of peroxides within the sampling set-up.

(A4): These constructive comments help us to make the measurement method clearer. We modify the relevant description for sampling inlet (Line 2-5 Page 10489) as follows:

’A three-story hotel building located next to a 2.7 km2 reservoir in a rural resort was used exclusively to house the measurement campaign, with almost no other buildings within 300 m radius area. The whole resort was surrounded by a large area of farmland and forest. The instrument for determining hydroperoxides was located in an air conditioned room on the top floor, and the sampling inlet was mounted on the rooftop. The space over the rooftop was very open to surroundings, resulting in the air flowing freely. Ambient air was drawn by a vacuum pump through a 6 m Teflon tube (1/4 inch O.D.) extending 1.5 m above the rooftop, so that the air samples were taken about 12 m above the ground.’

The Telfon sample line was cleaned in advance in order to minimize loss to the walls. Moreover, we washed the sampling line using Milli-Q water every day during the campaign. The line loss experiments were not carried out. The air residence time in the inlet tubing was less than 2 s, so we think the loss to the walls might be minor.

During the sampling period, the stripping coil was cooled to 10 C as mentioned in the text (Line 8-9 Page 10489), this temperature is the same as the temperature for collection efficiency measurement.

The standard solutions of MHP and EHP were prepared by dilution of the synthesized pure MHP and EHP respectively. The purity of these two synthesized samples were proved to be higher than 97% using infrared spectrometry. The stock solutions of MHP and EHP (˜ 0.01 M) were prepared by dilution of synthesized pure samples, and then the concentrations of stock solutions were determined using KMnO4 and

KI/Na2S2O3/starch every two weeks. HMHP, BHMP and 1-HEHP could decompose easily and the limited conditions of the campaign, so we could not obtain their steady concentrations of standards in the field. Thus, we only analyze these peroxides in the samples qualitatively rather than quantitatively. We add a sentence to the (Line 22 Page 10491) as follows:

’...Lee, et al., 1995). The purity of the synthesized MHP and EHP were proved to be higher than 97% using infrared spectrometry.’

We have carried out experiments in the laboratory to determine artefact production of peroxides within the sampling set-up. Using the same instrument and sampling set-up as field measurement, when the pure synthetic air was introduced to the sampling inlet instead of the ambient air, we could not find any peroxides in the samples. So we think artefact production of peroxides within the sampling set-up was negligible. We add a sentence to the end of the (Line 10 Page 10491) as follows:

’Using the same instrument and sampling set-up as field measurement, when the pure synthetic air was introduced to the sampling inlet instead of the ambient air, we could not find any peroxides in the samples. So the artefact production of peroxides within the sampling set-up was negligible.’

(Q5): Results and discussion It is interesting the sampling has been conducted under a range of conditions, but the results are presented in a sometimes confusing way, switching between conditions, leading to some repetition and some contradiction between sections. This should be considered carefully and sections written more clearly to make the article flow more easily. It is interesting that MHP is detected in the rainwater samples.

(A5): Because of the limitation of our knowledge, we agree that there were some problems in the description for these sections. We will try our best to write them more clearly.

(Q6): 10493 and throughout - It is encouraging to see that several hydroperoxides were observed in samples but I think a little more discussion of these could be included, rather than focusing on H_2O_2 and MHP.

(A6): This is an important suggestion. According to this suggestion, we add a new paragraph to discuss about other organic peroxides in the end of section 3.4 the (Line 5 Page 10505) as follows:

'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 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 H_2O_2 (H BHMP=6.0E5 M atm-1, 293K), thus, it could enter into the aqueous phase easily. BHMP could easily decompose and convert to H_2O_2, and then it might take part in the formation of sulfate and SOA in the form of H_2O_2. PAA is an important acid in its own right and could decompose into acetic acid and H_2O_2 under typical tropospheric conditions. As a result, PAA could play a role in acid deposition both as an oxidant and an acid.’

(Q7): 10496 – toluene / benzene ratio mentioned but not given.

(A7): According to this suggestion, we add toluene / benzene ratio to Figure 4. Moreover, we modify the (Line 15 Page 10496) as follows:

’This classification was supported also by the ratio of toluene/benzene almost lower than 0.5.’

(Q8): Many of the equations and descriptions of previous studies in certain sections can be significantly reduced / condensed if not deleted (i.e. sections 3.2.1, 3.4, 3.5 and 3.6)

(A8): We agree the reviewer’s point, so we condense section 3.2.1 and removed equations 2-8. We modify the (Line 22 Page 10496) to (Line 21 10498) as follows:

’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 ˜2.0E9 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.’

Moreover, we also delete the equations (13)-(16) and (21)-(23) in Sect. 3.5.1 and the description from the (Lines 2-7 Page 10504) in the Sect. 3.4.

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

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