

***Interactive comment on “Measurements of volatile organic compounds in the middle of Central East China during Mount Tai Experiment 2006 (MTX2006): observation of regional background and impact of biomass burning” by J. Suthawaree et al.***

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GENERAL COMMENTS The manuscript “Measurements of volatile organic compounds in the middle of Central East China during Mount Tai Experiment 2006 (MTX2006): observation of regional background and impact of biomass burning” by Suthawaree et al., presents a data set potentially very interesting. The literature on the distribution and characterization of VOC in China is greatly increasing (especially

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within the past 10 years), but new measurements can improve the present knowledge of Chinese emissions and can document the change in emission pattern from China. The “Introduction” is very well organized and comprehensive. However, in the reviewer opinion the manuscript (as it was submitted) is not ready to be published in a high profile journal such as ACP for the reasons listed in the comment

Response The authors appreciate the valuable and comprehensive comments and suggestions given by the reviewer for improving the quality of the manuscript. Every comment is taken into account for improvement, revision, and correction. Detailed responses for comments are given below.

SPECIFIC COMMENTS 1- The experimental part lacks important information about the quantification of the reported VOCs. For instance, there is no discussion on the use of the standards used to quantify the VOC, the limit of detection, accuracy, and precision of the measurements.

Response 1. Comment is taken. The use of standard, limit of detection, accuracy and precision of the measurements are added to experimental section.

2- The discussion about the halocarbon fraction is worrisome. The minimum levels reported for CFC-11 and CFC-12 (215 and 483 pptv) can be justified only if representative of stratospheric intrusion (which most likely can be excluded for this set of samples). An average value of 511 pptv for CFC-12 and 232 pptv for CFC-11 in 2006 is hard to believe. The NOAA global monitoring program is reporting for the month of June 2006 an average of  $532 \pm 1$  pptv for CFC-12 and  $249 \pm 0.4$  pptv for CFC-11. The average values reported in this manuscript for CFCs have not yet been reached despite the declining in CFCs recently observed as result of the implementation of the Montreal Protocol. Also, in the text it is stated that the average concentration of CFCs reported in Table 1 were comparable to the background levels reported by Barletta et al (2006) for China's background. In the Barletta et al. paper, the reported background was calculated from TRACE-P, a project carried out in 2001. It is not meaningful to com-

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pare regulated halocarbons, such as CFCs, among data sets that are 5 years apart (TRACE-P 2001 vs Mount Tai, 2006). Moreover, in Barletta et al (2005) the CFC-12 and CFC-11 background levels were reported as 535 and 259 pptv respectively. These values are not at all comparable to the 511 and 232 pptv reported in this manuscript for CFC-12 and CFC-11.

Response 2. Comments are taken. The comparison statement is revised. Comparison between measurement at Mount Tai and more recent reports for CFC levels in China are added to discussion part. The authors agreed with the reviewer comment that the averaged level from observation is relatively large compare to the background values reported by Barletta et al., (2006) and reported value from NOAA global monitoring program. This lower level and the minimum mixing ratios of CFC-11 and CFC-12 are most likely owing to the 10% accuracy with our instrument and analysis method used in this study. This detail and uncertainty is added to manuscript. For comparison, additional more recent reports of CFCs levels are added for airborne and rural area observations to provide more direct comparison of the closer measurement period (Barletta et al., 2009; Qin, D., 2007; C. Y. Chan et al., 2006).

3- The authors keep discussing about “concentrations” (see also axis labels in Figures 1 and 2) while “mixing ratios” are reported. This oversight is not acceptable for a publication in ACP.

Response 3. The comment is taken. “Concentration” is corrected to “mixing ratio” through out the manuscript.

4- Section 3.1.1 line 23 (p. 16722), the weak enhancement of n-hexane could be the result of lack of n-hexane sources in the region. The age of air masses is quite a complex issue and the overall levels of n-hexane are not generally used as indicator of air mass aging.

Response 4. The comment is taken. The sentence was revised in the manuscript. The sentence was revised into “Judging from weak enhancements of n-hexane throughout

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the period and its relatively short lifetime of several hours, air masses sampled here were insignificantly impacted from industrial emission.”

5- Table 1 does not indicate the units (which are clearly pptv, but still it needs to be indicated). The average level of CH<sub>3</sub>Cl is incredibly high for a remote location (990 pptv) with a maximum of 2 ppbv. These levels are often hard to be reached in a urban center. The last sentence of page 16722 (“This also supports the belief that the air masses were aged and well mixed before reaching to the site”) is definitely not supported by the average CH<sub>3</sub>Cl measured at this site and it is not consistent with the last sentence of section 3.1.1 where the region is found to be affected by emissions from biomass/biofuel burning. Is Mt Tai representative of the regional background? Or is it directly impacted by emission sources such as biomass burning? Also, bearing in mind the change in the global background of many VOCs (halocarbons in particular), the authors should indicate when a background level was measured. For instance, the reader should know when the background of 520-560 pptv and 8-9 pptv reported for CH<sub>3</sub>Cl and CH<sub>3</sub>Br was observed. Finally, CH<sub>3</sub>Br is emitted by biomass/biofuel burning but it has other important anthropogenic sources such as fumigation and vehicle emission (for cars using leaded gasoline).

Response 5. For the first comment, indication of unit is added to Table 1. For second issue on CH<sub>3</sub>Cl levels, although the level of CH<sub>3</sub>Cl is significantly high, but we found no evidence indicated direct impact from local or near the proximity contamination. The sampling site is located on the top of mountain and believed to be only slightly impacted from activities of local residences. Moreover, GC-FID and GC-MS were used to confirm the levels, thus, we are very positive that the level of CH<sub>3</sub>Cl is acceptable. The last sentence of page 16722 is revised and modified. Location of the Mount Tai is located in the area where biomass burning is active during the harvest season. Nonetheless, due to altitude and temporal variation of burning period, indicated by the fire spot data from satellite, regional background concentration can also be observed. In this manuscript, nighttime mixing ratios were proposed to be regional background. We aware that this

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is not necessary true, however, with this analysis, it provides interesting feature of the site which can be intensively study in the future. As suggested, information on potential source of CH<sub>3</sub>Br is also added into the section, fumigation (Blake et al., 1996) and leaded gasoline vehicular emission (Thomas et al., 1997).

6- Section 3.4. It would be useful to have an error associated with the slopes calculated for the different correlation plots (Figure 4,5,6,8).

Response 6. The comment is taken. Error with 99 percent confidence associated with each slope was added to annotation shown in Fig 4, 5, 6, and 8.

7- Figure 7. The distribution profile of the alkenes looks quite similar too, with 1,3-butadiene being the only alkenes with noticeably different.

Response 7. The sentence is revised for explanation of Fig. 7.

8- It is not clear to the reviewer why the profile illustrated in figure 7 indicates impact of biomass burning at Mt Tai. The profile indicated higher normalized levels in Beijing with respect to Mt Tai. This is consistent with Mt Tai being a remote sampling site and Beijing being an urban center characterized by the presence of many VOC sources.

Response 8. The comment is taken. As reviewer has commented, comparison between ratios profiles obtained for Mount Tai and Beijing reveals similar trend despite different in normalized levels. Nonetheless, normalized values of combustion related species, acetylene, ethene, and benzene, are relatively high for observation from Mount Tai compared to other species. Without enhancement of toluene and i-pentane (Barletta et al., 2005) which can be used for indication of impact from vehicular emission, the fact suggests the influence from biomass burning at Mount Tai.

TECHNICAL COMMENTS 1. Page 16722 line 8, the sentence starting with "In brief, . . ." needs to be rephrased, it is not clear what the subject is.

Response 1. Comment is taken. The sentence is revised. "In brief" is removed.

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2. P. 16722, line 20 the verbs are not consistent. "Chan et al. (2006) found. . .was the most abundant VOC. . ." (rather than ". . .is the most abundant VOC. . .").

Response 2. The sentence is corrected.

3. Section 3.4. Please indicate how many samples were collected in Beijing and the sampling time (daytime or nighttime samples).

Response 3. The comment is taken. The number of sample and sampling time is added.

4. Figure 1. It would be useful to indicate which are the nighttime samples and try to find an explanation about the considerably lower levels measured between June 22 and June 25.

Response 4. Fig. 1 is revised. Arrows are added to Fig. 1 for indication of nighttime samples. For the second point, possible explanations of lower levels of VOCs during the night of June 23 and 24 were included in section 3.1.1.: impact from shifting in planetary boundary layer height and arrival of relatively clean air mass from above boundary layer.

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