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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Overview of the Mount Tai Experiment (MTX2006) in Central East China in June 2006: studies of significant regional air pollution" *by* Y. Kanaya et al.

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We appreciate the comments given by reviewer #2 after careful reading of our manuscript.

Comment 1: There are portions of the present paper that appear to be based on new ways of analyzing the data. The trouble is that I don't know where the presentation of work by others stops and presentation of new work begins. I suppose I could go back to the papers cited and figure it our by looking for overlaps, but in most cases I didn't. Should I assume that all of Section 6, titled Overview of MTX2006 contains only work

previously published? Or is there a value added component of Sec. 6, where new insights come from combining the results of several previously published studies? Or are there places where you go off into new territory? This paper needs a statement of intent, probably placed in the blank spot between Heading 6 and Heading 6.1. Page 1532, line 5 does contain the statement that this paper presents an overview of obtained results and a synthesis of individual papers. However, it is often unclear as to what has been previously presented. An example is the first few paragraphs in Section 6.1 presenting temporal variations of gasses and aerosols. There are references to measurements at other location, but as far as I can tell none to MTX2006. Readers should know where the data is presented in more detail. Also, this lack of clarity makes the Reviewers job difficult. Am, I raising issues about studies that have already been vetted or about new material? I realize that there is significant overlap between the authors of the primary papers and the Overview. The attribution "we" is usually enough to distinguish the current paper from others. In this case I don't know who the "we" are. Primary work is cited but not always in places that address my question. I recommend that this paper be published after there is clarification about what is original and also after the following points are taken care of.

Answer: This overview manuscript consists of 1) summary of works previously published and 2) original analysis on several aspects, to complement the published results. In the revised manuscript, we will clarify where original analyses and results are mentioned. For example, at the end of section 1, the sentences will be revised as follows:

This paper presents an overview of the campaign and the obtained results, and a synthesis of the individual papers presented in this special issue on MTX2006, encompassing from field observations to modeling, remote sensing, and laboratory studies. Also, we newly explore comparisons of ΔCO/ΔNOy, ΔO3/ΔNOz, and NO/NO2 ratios between observations and model simulations (in subsections 6.1 and 6.4), correlations between VOCs and levoglucosan (in subsection 6.6), dependence of OC mass

concentrations on airmass age (in subsection 6.9), and fractions of OC which were molecularly identified (in subsection 6.9).

We clarify this point again at the beginning of section 6, as suggested by the reviewer, by including the following sentences:

In this section, our findings with MTX2006 are sorted by topics and overviewed. First, in subsection 6.1, after showing overall time series of major species, we compare their concentration levels, their ratios (e.g., ΔCO/ΔNOy), and air mass ages with those reported for past regional and urban studies, to highlight chemical conditions and their features during the MTX2006 field campaign. Then, key findings from companion papers are given in an integrated manner in subsections 6.2–6.9. Moreover, in subsections 6.4, 6.6, and 6.9, we added original analyses with respect to ΔCO/ΔNOy, ΔO3/ΔNOz, and NO/NO2 ratios, correlations between VOCs and levoglucosan, dependence of OC mass concentrations on airmass age, and fractions of OC which were molecularly identified.

In subsections 6.1–6.9, we will include references more often to suggest references where more detailed information can be obtained.

Comment 2: There are many comparisons for gas phase and aerosol species between Mt Tai and other locations in and out of China. Some of these are easy for those of us who are not familiar with Chinese geography to appreciate, for example Beijing. Other locations have little context. For example Miyun is described as a rural site 80 km NE of Beijing. I don't know what to expect. Are there several "small" cities near Miyun with population 1 – 2 million people?

Answer: Miyun is one of the outermost counties of Beijing city, having a population of 120,000. Changping is the rural district of Beijing city, with a population of 610,000. For these sites, the influence from Beijing is the strongest. To make this point clearer, we will add "In the north outskirt region of Beijing, for example," before mentioning concentration levels at Miyun and Changping.

Comment 3. I have a general impression that the daytime NO/NO2 ratio is too low, but no calculations to back that up.

Answer: The observed daytime NO/NO2 ratios are typically in the range of 0.2–0.4, relatively lower than what we generally see in other field studies. As first approximation, this is virtually explained by very high O3 concentrations during MTX2006, converting NO to NO2 efficiently. Peroxy radicals would additionally reduce the ratio to some degree. We will add a new figure (Fig. 10) to demonstrate this by comparing the average diurnal variation of the observed NO/NO2 ratios with theoretical ratios derived from photostationary state analysis, considering NO-to-NO2 conversion by O3, with and without additional conversion by peroxy radicals, and with and without considering heterogeneous loss of HO2.

Comment 4. Page 1530, line 18. Site is 1534m above sea level. What is approximate altitude above surrounding terrain. This is important later on when free tropospheric air is mentioned.

Answer: Fig. 1b will be added to show terrain of CEC. The altitude of the surrounding region is generally low (<200 m). In section 3, we will mention that Shandong Province is mostly flat in terrain; only its central part is relatively hilly, and Mt. Tai is the highest and isolated peak located in a UNESCO (United Nations Educational, Scientific, and Cultural Organization) World Heritage site. The data of the mixed layer height (to be included in Fig. 2) suggest that we observed air in the residual layer in the nighttime, rather than in the free troposphere.

Comment 5. Page 1533, line 17. Please supply a date that separates the first and second halves of the campaign.

Answer: We will just mention here that during early June, we easily recognized that the atmospheric composition at the field site was strongly influenced by large-scale post-harvest open crop residue burning (OCRB, winter wheat).

Comment 6. Page 1537 line 7. 1950 ppb is higher than 1500 ppb. Species concentration live on a log scale. I do not believe the description, “much higher” is warranted.

Answer: We agree with the comment. We will mention in the revised manuscript that the maximum level of 1769 ppbv (the value here is corrected) at Mt Tai is also in a similar range to that in the outskirts of Beijing ($\sim$1500 ppbv).

Comment 7. Page 1537, line 13. Work by Parrish in about 2010 showed that the CO to NOy emission ratio in the US had decreased to around 6, because of emission controls.

Answer: We will add Parrish (Atmos. Environ., 2006) showing a decreased vehicular CO/NOy emission ratio $\sim$6.

Comment 8. Page 1538, line 3. Is PM 2.1 a misprint?

Answer Here PM2.1 is correct. The data are from an Andersen sampler.

Comment 9. Page 1538, line 20 Air quality, in the sense of concentration of harmful pollutants is according to your data similar to Beijing. However, the chemical composition is very different because of photochemical ageing.

Answer: We will revise the sentence as follows: In conclusion, O3 and aerosol concentration levels at the top of Mt. Tai are comparable to those in the outflow region or even the central urban area of Beijing, although photochemical age must be different.

Comment 10. Page 1539, Diurnal profiles in Fig. 6. Are there differences in diurnal profile between BB and non BB periods. Is there evidence that fire emissions are being transported within FT. If so, does this account for differences in OC and BC as compared with NOy and CO. If not where does the early morning BC come from? My recommendation is to just show non-fire data on diurnal cycle graphs.

Answer: We will add diurnal profiles of O3, CO, NOy, and BC for the period after 16 June. In text, we will add the following sentences: The peak of BC in the early morning

(04:00–06:00 LT) was influenced by very high concentrations occurred in these hours on 7 and 13 June, which are ascribed to OCRB. After 16 June, O3, CO, NOy, and BC commonly showed diurnal patterns with single afternoon peaks. For O3 and BC, the amplitudes of the daytime increase for this period are similar to those for the whole period, while the concentration levels are lower. For CO and NOy, the daytime peak concentrations and the amplitudes of the diurnal variations are larger after 16 June. The data of the mixed layer height (to be included in Fig. 2) suggest that the nighttime transport of fire emissions occurred within the residual layer.

Comment 11. P1542 line 16. Regarding regional photochemical production of ozone within CEC: It would be very helpful to have a map showing the CEC other than Fig. 1 of Li et al (2008a). Or at least a sense of the dimensions of the region. Percentage contributions to ozone from CEC (regional photochemical production, I assume) are given. Are these percentages for the daytime or for all 24 hours. Is free tropospheric air, which is observed at night, affected by regional sources? On line 9, local photochemical production is discussed. Again a description of local is needed besides a reference. This is an important part of the story and at least the geography should be self-contained.

Answer: We will add Fig. 1b showing the major source regions used in the NAQPMS model simulations (including "local"). In section 6.3, we will also mention that "Local" represents a region including Tai’an and Laiwu cities and Mt. Tai, with a 1 $\times$ 105 km2 area. The shown percentages are for all 24 hours. It should be noted that the site was usually within the residual layer during nighttime, and it was rare that measurements were made in the free troposphere.

Comment 12. Page 1543 line 15. Am I to assume that low ozone days had hourly values under 100 ppb or is there a stricter criteria, leaving a gap between low and high ozone days?

Answer: We used <100 ppbv as a criterion for the low-ozone days and this will be

mentioned in the revised manuscript.

Comment 13. Page 1543, line 22. The unspoken assumption in comparing a change in ozone with a time integral of an ozone production rate is that the air does not move. Nor does the mixed layer increase resulting in dilution. This may be why it was felt that heterogeneous chemistry was needed to get agreement.

Answer: We discuss "potential" ozone production in a Lagrangian air mass and just mention simply that the magnitude is larger than the observed increases in the O3 concentration in the daytime.

Comment 14. Page 1544, line 5. Changing "this heterogeneous loss" to "this heterogeneous loss of HO2" would add clarity.

Answer: We will revise the sentence accordingly.

Comment 15. Page 1544, line 1 – 9. I was surprised to find that the ozone loss was calculated in Taketani et al. (2012). It is not mentioned in this paper that this high ozone loss depends on a net reaction HO2 + aerosol which yields no gas phase products (Eq. 14). This should be added along with a one sentence description of Mao et al (2013) in which coupled catalytic reaction were invoked to explain why hydrogen peroxide is not generated. Mao et al (2013) admit in their conclusion that there are large uncertainties about the mechanism. In this paper the appearance is that having determined the uptake coefficient for HO2, a large loss of ozone follows.

Answer: For clarification, we will mention that we assumed no production of H2O2 by citing Mao et al. (2013).

Comment 16. Page 1548, line 23. MAAP results based on absorption gave overestimates. Please correct me if I'm wrong. The MAAP measures light absorption. It yields BC only because there is a conversion factor built into software. It is hard enough to measure absorption and one can argue whether the MAAP does or does not do a good job compared to less intrusive measurements such as a PASS. As the MAAP does not

measure BC mass, a comparison with real mass measurements is solely an assessment of how well the mass absorption coefficient in the MAAP software compares to the real atmosphere.

Answer: The MAAP observation (or "working" absorption coefficient built in the software) is directly calibrated in terms of BC concentrations measured at two places in Germany (Petzold et al., 2002) using the VDI2465 Part 1 protocol. Thus MAAP should produce correct readings of BC mass concentrations as long as the particle properties are similar, and the protocol is valid. (Correct determination of absorbance is not always a premise to obtain right values of concentrations.) The systematic difference in MAAP_BC from other instruments during this field campaign could arise from the different optical properties from those in Germany and/or the bias in the standard method (i.e., VDI2465 Part 1). Thus the comparison with real mass measurements here provides an assessment of how well the mass absorption coefficient in the MAAP software, determined for the German sites, can be applied to the particles present at Mt. Tai, as stated by the reviewer. But it should be noted that the possible systematic bias in the standard mass measurement methodology could also influence.

Comment 17. Page 1550 line 1. Regarding Fig. 10: The data is extremely noise and the change OC/(CO-background) from youngest to oldest samples is only about 15%. It may not be statistically significant. Its hard to draw conclusions from this data. The dots representing binned data do not persuade me of statistical significance.

Answer: After considering this important comment, we will mention in the revised manuscript that the Δ[OC]/Δ[CO] ratio is almost unchanged with photochemical aging, and shows a trend clearly different from a decay with a lifetime of $\sim$6 days assumed for primary organic matters in chemistry-climate models (IPCC, 2007), or a decay with an even shorter time constant of $\sim$1.8 days, suggested from the analysis for the air masses influenced by biomass burning during the first-half period of MTX2006 (Pan et al., 2013). This analysis clearly suggests that carbon mass flux from gas-to-particle conversion is present for the studied time scale. The corresponding figure will include

two theoretical curves representing the two different lifetimes.

Comment 18. Fig. 3 There is a brown trace on the second pane (CO, CO2, benzene) that is not identified. It is almost impossible to see light color traces. In particular the yellow used for NO in the third panel and for NOy in the fourth panel.

Answer: The brown trace was for CO2. The colors will be changed for better visibility.

Comment 19. Fig. 4 Color coding with a range of colors rather than a brown monotone would allow the reader to more easily distinguish between high emission regions and extremely high emission regions. To better make that clarification, I would consider changing the display to a Log scale. Emission rates are per unit area. The figure caption or legend should specify what that area is.

Answer: The revised figure will employ a range of colors as suggested. Now the figure is clear enough even with a linear scale. The emission rates are per 0.1×0.1 degree. This is now mentioned at the legend.

Comment 20. Fig. 6 Yellow traces are nearly invisible. NO in one plot and NOy in another. Greenish blue and turquoise traces in bottom two panels are hard to distinguish.

Answer: The colors will be changed for better visibility.

Comment 21. Fig. 7 The view has shifted between the top and middle panel. What looks to be a tower in the top panel has not disappeared (no claim made to that effect). It certainly is hazier in the bottom two panels but the nearby mountain is still clearly visible. There are some hills in the distance in the top panel, which become covered with haze. Unfortunately these hills are do not protrude much above the nearby mountain. It would be helpful to know distances to objects.

Answer: We will add labels "A" and "B–D" for the objects in the figure. The distances from the observational site to the objects will be mentioned in text.

We thank the reviewer for their comments helping us to improve our manuscript.

References

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