

Interactive comment on “Rates and regimes of photochemical ozone production over Central East China in June 2006: a box model analysis using comprehensive measurements of ozone precursors” by Y. Kanaya et al.

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Reply to the Referee 1

We are grateful to valuable comments that the referee made on this manuscript. Detailed responses to the comments are given below.

Comment 1. It is implied from the discussion of Figure 1 in page 12973 that convection from the boundary layer to the top of the mountain during daytime is the major cause for the differences between high and low ozone days. I think more justification is needed

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apart from the diurnal cycle of ozone and NO_y. For example the authors could look at other tracers for convection as water vapour mixing ratio to justify if convection makes the difference between high and low ozone days. They could also probably look the transport for the high and low ozone days using back trajectories. My impression from figure 1 is that there differences in the regional ozone transport between the high and the low ozone days with the high ozone days being more affected by boundary layer air.

Reply 1. The sentences in the previous manuscript were unclear. We focus on the diurnal variations of primary precursors (CO and NMHCs) and NO_y, which is not a primary pollutant but could preserve information of NO_x (as another primary precursor) before oxidation. The concentrations of the precursors had diurnal variations with the daytime maximum especially for the low-O₃ days. This analysis suggests that the mountain top observations were affected by the development of the polluted layer in the daytime. In the revised manuscript, we revise the sentences as above to make this point clearer. We did not mean that the convection was stronger for the high-O₃ days, as the referee mentioned. We performed additional analysis of H₂O and the trajectory altitude upon the referee's suggestion and confirmed that the influence from the lower layer is rather stronger for the low-O₃ days. The next sentence about O₃ buildup in the daytime is preserved. O₃ should be influenced by photochemistry and its diurnal variation should be treated separately from those of the precursors. The primary cause for the different levels of precursor concentrations between high and low-O₃ days is the presence of open biomass burning for high-O₃ days.

Comment 2. The authors state in page 12974 that the production and loss rates of the radicals were almost in balance. What does it mean almost in balance? Does it mean that the box model did not reach a steady state for radicals? I guess constraining a box model with measurements you expect to reach a steady state after a few diurnal cycles.

Reply 2. We remove the word “almost”. We only tried to indicate in the previous

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manuscript that a very subtle imbalance was present, under the time-dependent modeling approach where the boundary conditions (e.g., concentrations of ancillary species) were changed every 10 minutes. Some imbalance between radicals and the reservoir species (HNO₄ and PANs) can occur, immediately after the introduction of the new boundary condition.

Comment 3. I would suggest that the authors add error bar values for the calculated daily values of ozone formation, loss and net production for the high and low ozone days in page 12975.

Reply 3. In the revised manuscript, we add the ranges of ozone formation, loss, and net production for the high and low ozone days, on the basis of standard deviations of the daily values.

Comment 4. The authors state at line 19 of page 12975 that their calculated value of 58 ppbv/day is slightly larger than 32 ppbv/day from another study. From my point of view this difference is not slight. The value of this study is almost double compared with the other study. The authors should specify what they mean with the word "slight". Similarly at line 24 of page 12975, the authors state that their value is roughly consistent with the production rate of 38 ppbv/day estimated from another study at the same location. The authors should specify what they mean with the wording "roughly consistent".

Reply 4. We remove "slightly" in the revised manuscript. For the second point, we revise the sentence and mention that our value is larger than the production rate (38 ppb h⁻¹) estimated from the slope of . . . We also made the explanation for this clearer; the difference would be attributed to dilution and deposition, effective only for the rate estimated using the residence time.

Comment 5. At lines 5-7 of page 12975 the authors explain that the modeled F(O₃) was higher at high ozone days than in low ozone days because the modeled peroxy radical concentration was higher. This is expected since the calculated values of F(O₃) from the box model are proportional to the modeled values of peroxy radicals. Unfortunately,

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there are no real measurements of peroxy radicals to justify in an independent way.

Reply 5. Here we only explained an expected relationship between F(O₃) and peroxy radical concentrations to make the logic clear. The peroxy radical measurements were not made and cannot be used to justify the ozone production rates.

Comment 6. At lines 14-15 of page 12976 the authors reach a conclusion that the observed ozone build up is not merely affected by local chemistry although earlier in the paragraph they state that in-situ (local) photochemistry is capable of explaining the ozone build up in high and low ozone days. This makes confusion to the reader. More clarification is needed. The paragraph should be rewritten in a more thorough and consistent way.

Reply 6. We modify the sentence in the earlier part and now mention that the in-situ photochemistry is active enough to explain the ozone buildup. We simply compare the magnitude here first.

Comment 7. At lines 17-21 of page 12977 the authors state "The analysis also implied that the ozone production should have been more efficient in the fresh air mass where . . .". This sounds sensible but how it is implied in this study from the analysis of the measurements and the model calculations? More clarification is needed.

Reply 7. The sentence is revised: The analysis also implied that the ozone production should have been more efficient when the air mass was fresh and the NO_x/NO_y ratio (and thus the NO_x concentration for a given NO_y concentration for that air mass) was higher than that observed on the mountain . . . We assume that NO_y is preserved for the air mass during its travel.

Comment 8. To my knowledge there is limited referencing and comparison to similar experiments at high altitude sites e.g. MLOPEX experiments at Mauna Loa Observatory, FREETEX experiments at Jungfrauoch and other.

Reply 8. In the last but one paragraph of section 4.2, we added the following sentences:

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The production rates for Mount Tai are significantly higher than the F-D(O₃) values at other mountain stations: from -0.05 to +0.4 ppb h⁻¹ at Jungfrauoch (3590 m a.s.l.) for midday in winter, spring, and summer (Parker et al., 2009; Zanis et al., 2003), 2–3 ppb d⁻¹ for Mt. Cimone (2165 m a.s.l.) in June (Fischer et al., 2003), and from -0.8 to -0.4 ppb d⁻¹ for Mauna Loa (3.4 km a.s.l.) for four seasons (Cantrell et al., 1996).

References

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, 9, 12965, 2009.