

Interactive comment on “MAX-DOAS measurements of NO₂, HCHO and CHOCHO at a rural site in Southern China” by X. Li et al.

Anonymous Referee #1

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This manuscript describes remote observations of HCHO, CHOCHO, and NO₂ by MAX-DOAS technique at Back Garden site, near Guangzhou, China, during summer 2006. To convert slant column densities to vertical densities or profiles, the authors employ two approaches: using geometric air mass factors (AMFs) for the highest off-axis measurements and using AMFs derived from a radiative transfer model, for box shape profiles with variable mixing layer height. For the nine clear-sky days, the vertical column density of NO₂ derived from the two methods agreed fairly well. Diurnal evolution of the mixing layer height was found to be variable for the three species, likely related to the fact that NO₂ is a primary species, while HCHO and CHOCHO are secondary or later generation products. The observed tropospheric NO₂ vertical column densities on clear days agreed well with the OMI satellite retrievals using DOMINO ver. 2.0 algorithm, while they were lower than those simulated by a chemical transport model.

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The observed CHOCHO/HCHO ratio, ~ 0.135 , is higher than those reported by past studies under similar rural conditions, implying the influence from high photochemical activity at Back Garden site. The ratio is significantly higher than that determined from satellite observations in the same region, needing more studies.

The observational site in Southern China is regarded as regionally polluted with very high photochemical activity. Thus the results are of particular interest from the viewpoints of comparison to satellite data and the applicability of the MAX-DOAS analysis methodology.

In my opinion the authors have made analysis and interpretation carefully and thus the paper merits publication. Simultaneously, however, I suppose that additional analyses addressing the following four questions would improve the manuscript.

1. Can the assumption of box shape profiles affect the degree of agreement in the vertical column densities derived from the geometric and RTM approaches? If assuming different shapes, the agreement is perturbed significantly?
2. Do the differences in the NO₂ VCD derived from the two approaches depend systematically on the aerosol abundance? This information, defining the conditions where the simple geometric approach is valid, would be useful when the MAX-DOAS analysis methodology is chosen.
3. Can the nighttime chemistry of HCHO and CHOCHO result in unique behaviors of the CHOCHO/HCHO ratio at this location? Even with this nighttime source, can the CHOCHO/HCHO ratios during this field campaign be compared systematically with those in the past studies?
4. In my opinion the HCHO diurnal variation pattern with daytime decrease is unique. Can the authors find past studies suggesting similar diurnal patterns and increase discussion more on this point?

In addition, the following technical corrections and specific questions should be con-

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sidered.

Technical and specific points:

1. Abstract, lines 5-6. The NO₂ mixing ratios measured by MAX-DOAS showed ...
2. Page 3985, line 13. Given the routine MAX-DOAS measurements ...
3. Page 3987, line 14. suite
4. Page 3989, line 10. Remove "been" or rewrite.
5. Page 3989, line 9. "Box" air mass factor is a more correct term than simple air mass factor?
6. Page 3989, line 20. Remove transfer (duplicated)
7. Page 3989, line 28. The assumption of the constant number density results in mixing ratios at a high altitude (e.g., 3 km) higher than those at the ground level.
8. Page 3991, line 11. The authors fix $F = 1$: is this applied only for the gases (i.e., NO₂, HCHO, and CHOCHO)? Is the previous detailed description of the profiles (i.e., page 3990, equations (2)-(4)) still necessary for describing aerosol profiles used in this study?
9. Page 3991, line 20 and Figure 2. How is the NO₂ information used in the further HCHO and CHOCHO analysis?
10. Page 3992, lines 7-8. The increase of AOD results in a decrease of modeled DSCDs – in Table 3, however, the values of the sensitivities are always positive.
11. Page 3995, line 16. Fig. 10 appears earlier than Figs. 8 and 9. Figure numbers should be sorted.
12. Page 3997, line 18. R^2 value is 0.23 according to the figure?
13. Page 3997, line 22. $B_0 = 1.01 \pm 0.26$ according to the figure?

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14. Page 3997, line 22. ... when we compare ...
15. Pages 3998-3999, comparison to CMAQ. More discussion should be made about the degrees of agreement between the observed and modeled NO_x and O₃ concentrations etc. at the same/different locations during the same period, to confirm the author's conclusion that the NO_x emission rates need to be reduced in the model.
16. Page 4000, lines 8-10. Is the primary emission of HCHO from local sources important, as well as nighttime production, to explain the high concentrations in the morning?
17. Page 4000, line 16. It is not fair to define the NO₂ lifetime against its photolysis, because the photolysis gives NO that easily reproduces NO₂ via its reactions with O₃ and peroxy radicals.
18. Page 4000, line 25. The authors should give references suggesting that HCHO is produced before CHOCHO. Do the authors mainly think about isoprene oxidation? How high were the isoprene concentrations?
19. From last line of page 4001 to line 7 of page 4002. Are Giesta, Sao Paulo, and Mexico City raised as exceptions for the generally accepted tendency that the CHOCHO/HCHO ratio is high in the rural environment and low under urban conditions? The logic is not very clear here.
20. Page 4002, line 19. ...due to the fact that R_{GF} is ...
21. Page 4002, line 24. It should be mentioned that the satellite-derived value is for the morning, around 9:30 LT as observed from GOME2.
22. Page 4003, at the end of section 4.2. Can the authors discuss potential impact of the nighttime production of CHOCHO and HCHO?
23. Page 4003, line 18. How high were the AOD values during the nine days under investigation?

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24. Page 4004, lines 4-5. I do not think that "R_GF values are lower than 0.1 in rural areas" is derived from the authors' ground-based measurements for this field campaign.
25. Table 3. How does the O₃ concentration affect the HCHO and CHOCHO retrievals?
26. Table 4. Are all of the listed mixing ratios observed in the midday periods?
27. Figure 9. If the regression lines are not forced to pass the origin, significant y-intercepts could occur?
28. In Figures S2-S4, grey circles cannot be found, although mentioned in the captions.

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