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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Modeling of HCHO and CHOCHO at a semi-rural site in southern China during the PRIDE-PRD2006 campaign" *by* X. Li et al.

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General comment:

The paper deals with a modeling study on HCHO and CHOCHO at a semi-rural site in southern China during the PRIDE-PRD2006 campaign. It presents some valuable data and interpretations which should be published eventually. However, the paper as is contains a major deficiency which needs to be corrected before publication.

The major deficiency lies in the assumption of a box model with a well-mixed boundary layer height of about 1 km, and the model calculations being constrained to measure-

ments of OH, NO, NO2, HONO, O3, CO, CH4, C3 – C12 NMHCs. The assumption of a well-mixed boundary layer for long-lived species is appropriate, but not for shortlived (shorter than a few hours) species such as OH, NO, NO2, isoprene and some other NMHCs. In fact, some of the findings in the paper are obviously the result of this assumption, for instance the high concentrations of modeled HCHO, and the large contribution from isoprene (reaction with OH) to the production of HCHO. It is well known that isoprene concentration decreases rapidly with height because of its fast reaction with OH, observed surface concentrations of isoprene should not be used to represent the concentration of isoprene in the entire boundary layer. Same argument applies to other short-lived species such as OH. I would suggest that the authors use a simple 1-dimensional model with enough resolution for evaluation of the vertical distribution of isoprene.

Answer:

We thank Referee #2 for his/her comments on our paper, which are absolutely correct. But for the reasons described below we would prefer to keep our sensitivity analysis with a box model because the use of a simple 1-D model would barely cover our lack of knowledge about the parameters needed to drive it.

(1) The simulation of HCHO and CHOCHO in our box model is constrained by measured OH, NO_X, HONO, O_3, CO, CH_4, NMHCs, etc.. It is not possible to setup a set of observational constraints for different layers in a 1-D model, since we do not have measured data for these layers. Any assumption on the model constraints for the upper layers can result in non-quantifiable uncertainties for the modeled HCHO and CHOCHO concentration, which is difficult to estimate given the limited information of vertical distributions of OH, NO_X, and NMHCs around the measurement site. We preferred to use a box model and to perform sensitivity studies about processes which might have the potential to significantly change our results.

(2) If we would have used a 1-D model without observational constrains, a key factor determining the vertical distribution of trace gases would be vertical transport for example by turbulent diffusion. Turbulent diffusion can be presented by a coefficient Kz using K-Theory. However, due to lack of wind and temperature measurements at different altitudes, we are not able to calculate Kz. We are able to calculate Kz at ground level. But this value is certainly different from values in upper layers. Without a realistic estimation of Kz, a 1-D model simulation of HCHO and CHOCHO would suffer from a non-quantifiable uncertainty. Moreover, vertical transport is expected to be dominated most of the day by convection which can not be described in a simple 1-D model [see (3)].

(3) Our campaign has taken place in summer time in a sub-tropical region. Given the strong solar radiation during the campaign, convective vertical mixing of trace gases can be quite efficient. According to Stull (1988), around noon, the typical mixing time for a species to be well-mixed in the boundary layer is about 15 min. This is comparable with the lifetime of isoprene but much shorter than other measured NMHCs (given the measured noontime OH concentration of around 1.5×10^7 cm^{-3}). Our recent measurements of trace gases and radicals on-board a Zeppelin NT airship showed that, at a hot region in Italy, OH, NO_X, HONO, O_3, CO, VOCs besides isoprene were well-mixed inside the boundary layer when the boundary layer was fully developed (Kaiser et al., 2014; Li et al., 2014), at least within the height range up to 1 km which the Zeppelin could visit. Therefore, we think the assumption that OH and trace gases except isoprene are well-mixed in the boundary layer is also justifiable for the campaign in PRD.

(4) In our model calculation (model scenarios M1 – M4), we have considered the depletion of isoprene during its vertical transport. Assuming an exponential decay of isoprene along the altitude, we estimated an effective isoprene concentration which is 52% of the value measured at ground. (We also applied this simple estimation to our measurements on-board the Zeppelin and got the same results.) As already stated

above, we prefer to use a box model and to perform sensitivity studies about processes which might have the potential to significantly change our results. For example, a convective transport time scale of 15 min was used to estimate the effect on the average isoprene concentration inside the PBL in one of the scenarios.

(5) Let us assume we would have the necessary physical parameters to drive a realistic 1-D model. What about chemistry? We repeat here our arguments in the answers to the comments of referee #1. As described in Lu et al. (2012), our box model could not well reproduce the measured OH concentrations unless when we included an additional OH recycling mechanism. This effect was huge since OH concentrations calculated by the base model were a factor 3 – 5 off the observations during most of the day. In the expanded mechanism, a NO like species X was proposed to convert RO2 to HO2 and HO2 to OH. In the model used by Lu et al. (2012), HCHO and CHOCHO were also produced during reactions involving X, which might not be correct. The exact properties of X was further investigated in our SAPHIR chamber. For isoprene degradation, X could have been a mean to describe unimolecular reactions (Fuchs et al., 2013). However, Fuchs et al. (2013) also showed that those unimolecular reactions of isoprene were far not enough to explain the observed OH concentrations at the BG site. Therefore, without knowing the properties of X, we think it is not possible to use this kind of chemistry within a 1-D model. We would have to assume the vertical distribution of X.

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