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Atmospheric
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Discussions

Interactive comment on "Impact of primary formaldehyde on air pollution in the Mexico City Metropolitan Area" *by* W. Lei et al.

W. Lei et al.

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We thank the two anonymous referees and the Editor for their thoughtful comments, which help to improve the quality of this article. Here are our responses to their comments.

Referee #1:

The paper studies the impacts of HCHO on atmospheric chemistry in a large city (Mexico City). The study includes many important aspects; including the effects of primary HCHO emission on the HCHO budget in this region, the influences of HCHO on radical budgets, and the impacts of HCHO on ozone budget. The model simulations are compared with surface measurement, and show a generally good agreement. The paper is well structured and well written. I recommend

to publishing this paper with some minor revisions.

(1) On page 19615, the equation (3) is not very well defined. The authors should clearly state what are the radical initiation rates (HOnew...)

[RESPONSE]: We have added the following statements to clarify the definition of the radical initiation rates: *"i.e. the rates of radicals produced during the radical initiation process (also defined as new radical production rates). OHnew is primarily contributed directly from photolysis of O3 and peroxides, alkene ozonolysis, and HONO photolysis. The HONO photolysis term here is actually the net OH production from the HONO photolysis minus the HO+NO -> HONO reaction. HO2new is contributed from photolysis of carbonyls (such as aldehydes and ketones) and alkene-O3 reactions. RO2new is contributed from photolysis of carbonyls and alkene-O3/NO3 reactions; RO2 radical production from the PAN reservoir (when PAN thermal decomposition minus PAN formation is positive) is also included."*

(2) In Fig 5, they use 1.5 ppbv HCHO as the background condition. I think this should be better justified, including what is the physical meaning of the background condition, and why use 1.5 ppbv as the background condition.

[RESPONSE]: We have redefined the HCHO BC (mainly from regional transport) and run additional model simulations to estimate the background values. Following sentences are added to access this term and its difference to that in Garcia et al. (2006): *"The background HCHO in the model comes from transport outside the model domain, i.e., from the vertically-varying HCHO boundary condition which was set to 1.5 ppb at surface in this study. The very low VOC boundary conditions used in this study lead to a negligible contribution to the HCHO background through photochemical oxidation.". "The contribution of the boundary condition on the ambient HCHO concentrations was obtained by calculating the difference of the HCHO concentrations from the control run above with a run where the HCHO boundary conditions were set to 0. The effect of the HCHO boundary condition is highest at nighttime but almost vanishes during the* *late morning to afternoon hours, because of the short chemical lifetime of HCHO in this period.". "The definition of the background HCHO in Garcia et al is significantly different because it represents the source unaccounted for by the tracers of CO (for emissions) and glyoxal (for secondary). A significant, if not major, portion of the background HCHO in Garcia et al consists of the photochemical secondary source that is not correlated with glyoxal. Therefore there are no direct comparisons for the secondary and background contributions."*

(3) In Fig 4, they discuss the impacts of VOCs (olefin) on the zone formation in the Mexico City region. This issue has been detailed discussed by Tie et al. (2007), and they should add contexts about their results regarding this issue.

[RESPONSE]: We have included Tie et al. (2007) and Zhang et al. (2004)'s findings on alkene's role in O3 production in urban cities by adding the sentences *"Oxidations of anthropogenic alkene also play a major role in daytime O3 production in the MCMA (Tie et al., 2007) and in the U.S. urban areas (Zhang et al., 2004), particularly in early morning when they dominate O3 production.".*

Referee #2:

...Calculations are credible and except for a lack of results on the magnitudes of various radical sources, well presented.

[RESPONSE]: The question regarding various radical source magnitudes will be answered in the response to the general comment below.

General Comments

In order to put primary HCHO in perspective it is necessary to have a diurnal diagram or a Table of the major categories of radical sources. The closest information that I can find is Sum OH(new) in Table 3 but this includes indirect effects and does not say anything about other sources and absolute magnitudes.

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[RESPONSE]: We have added a new table (Table 2) to show the magnitude of major radical sources as a function of time of the day, and also added the following statements for illustration: *“Table 2 shows the contribution of various radical sources to the radical production (initiation) as a function of time during the day (averaged over the episode) in the MCMA urban region. On a 24-hour basis the HO2 production is a major radical pool, followed by RO2 and OH in that order; HCHO is an important HO2 source, accounting for 33%. It is noted that during 7-9 AM although primary HCHO dominates ambient HCHO (80%), its contribution to radicals (on the order of 80%*0.5 ppb = 0.4 ppb) is overwhelmed by contributions from HONO photolysis and O3-OLE reactions (the major HO2 production is from O3-OLE reactions). This is consistent with the finding of Volkamer et al. (2007) which suggests that primary HCHO does not significantly influence the early morning photochemistry.”*

2. This is somewhat of a digression: It would be of interest to distinguish the direct effects of primary HCHO on O3 production from the indirect effects. According to Page 19618, line 9, primary HCHO increases surface peak O3 concentrations by an average of 8%. What is the percent increase in Sum OH(new) due just to the direct effect of increased HCHO? What O3 production rate increase would be expected if it were proportional to radical production rate under high NOx conditions?

[RESPONSE]: Our current model configuration is not able to partition the direct and indirect effects on the HCHO concentration. To do that a tracer technique would have to be applied, which would demand substantial time to achieve. We also attempted to derive the indirect effects based on modeling results available, such as employing regression analysis on the primary HCHO concentrations using CO as the emission marker, but no reasonable/logical results were obtained, which may imply that CO and HCHO are not very well co-emitted (50% of HCHO comes from mobile emissions while over 99% of CO comes from the same source). Since both direct and indirect effects are the impact of primary HCHO, we don’t think the partitioning is essential. Therefore

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we decide not to make further efforts on the partitioning. However, Volkamer et al .(2007) estimated the indirect effects of primary HCHO in the MCMA, which are about 10% (upper limit) of the total primary HCHO contribution. Using this result, the indirect effects of primary on the peak O3 concentration would be 8% * 10% =1%. We have included a sentence in the text for the clarification: *"The model configuration we used did not allow us to quantify the indirect effect, but according to Volkamer et al. (2007), the indirect effect accounts for about 10% (upper limit) of the primary HCHO."*

Specific comments

(1) Page 19611. line 5. factor of 7 increase in HCHO emission relative to inventory This is a very important point as the factor of 7 increase causes primary HCHO to be a significant factor in the photochemistry. There are literature references but it would be worthwhile to summarize a few key findings that show the inventory to be low.

[RESPONSE]: First of all, a clarification: classical official EIs do not report speciated VOC emissions. Emissions of speciated VOCs including HCHO are generally derived after applying a certain emission model/procedure and speciation databases to the total VOC emissions reported in the official EI. We have added the following statements to summarize the relevant findings by Kolb et al and Zavala et al.: "*...both Kolb et al. and Zavala et al. show that on average HCHO/CO2 emission ratio in traffic exhaust plumes is a factor of 7 higher in the MCMA than in the greater Boston area (2x10-4 vs. 3x10-5), although the emission ratio varies with traffic.*"

(2) Background HCHO, Section 3.1 Why is there a separate category for background HCHO with a fixed concentration. Background HCHO occurs in Garcia et al (2006) as an unaccounted source in a regression analysis (i.e. not correlated with CO or O3). What sources in the present model study are not accounted for? There is transport from outside the region but that should follow from boundary conditions. Are there emission sources of HCHO or HCHO precursors miss-

ing from the model calculation? Otherwise all HCHO should be primary or secondary.

[RESPONSE]: We have redefined and reevaluated the HCHO BC term. See the response to referee #1's comment #2.

(3) Page 19614, line 21 and elsewhere. indirect effect of emitted HCHO is bracketed in the secondary term. Maybe this can be re-worded. I do not understand the use of bracketed.

[RESPONSE]: bracketed is reworded as included.

(4) Page 19615, line 15, Eq. (3) Could you please clarify equation. Are OH(new), HO2(new) and RO2(new) production of radicals by photolysis and ozoneolysis? How is HONO treated?

[RESPONSE] We have clarified these terms and specified the HONO treatment. See our response to referee #1's comment #1.

(5) Page 19615, lines 22-23 contribution of primary HCHO to OH concentration increases from 7% in the early morning to 16% in the late morning ... Also time trends for HO2 and sum OH(new) and on Page 19616, lines 8-11 a summary statement that primary HCHO is most important to HCHO in the morning and most important to radicals and production rates later in the day. I would have thought that primary HCHO would reach its peak importance to photochemistry in the early morning when there are low concentrations of secondary O3 and HCHO. Are the effects of primary HCHO in the early morning diluted by large contributions from HONO and ozone+alkenes? Or is there another explanation?

[RESPONSE] You are correct; the effects of primary HCHO in the early morning are diluted by large contributions from HONO and ozone+alkenes. We have shown the results in a new Table 2, and extended discussions by adding the following statements: "It is noted that during 7-9 AM although primary HCHO dominates ambient HCHO (80%), its contribution to radicals (on the order of 80%*0.5 ppb = 0.4 ppb) is overwhelmed by contributions from HONO photolysis and O3-OLE reactions (the major HO2 production is from O3-OLE reactions). This is consistent with the finding of Volkamer et al. (2007) which suggests that primary HCHO does not significantly influence the early morning photochemistry."

(6). Page 19619, lines 16-18. Why do daily and daytime OH have the same 8% enhancement but daily and daytime HO2 and Sum OH(new) differ by almost a factor of 2? I assume that daily means a 24 hour value. I would expect that the daily values would all be about a factor of 2 lower than the daytime because all 3 quantities are high in the daytime and near zero at night. Is the averaging done by calculating an enhancement for each hour and then averaging those numbers over either 24 hours or daylight hours? In that case the daily enhancements are hard to interpret.

[RESPONSE] Thanks for the observation. We have now clarified the averaging calculations in the text, in which the change in the concentration is done by calculating the enhancement for each hour then averaging over the hours of interest, while the change for integrated production rate (radical or O3) is calculated by integrating the production rate over the time duration of interest then computing the enhancement. The separate definitions for the concentration and integrated production rate should be more physically sound. In addition the enhancement in the radical production rate is also calculated using the former method in order to compare with Volkamer et al. (2007)'s results in which they use the former averaging method. We have also carefully examined the numbers in all the tables.

(7). Fig. 7. Should bottom right ellipse be H2O2, ROOH?

[RESPONSE]: Correct. We have included explanations in the figure caption.

Typographical errors, etc.

Page 19615, line 1 either HCHO can also affect or HCHO can affect.

Page 19619, line 2 should be A distinguishing feature.

[RESPONSE]: Have been corrected.

C. Kolb (Editor):

Both reviewers have ratified the basic worth of the manuscript and have made suggestions for minor edits and clarifications that will improve the paper. The authors should carefully consider the reviewers' suggestions and prepare a final version of the discussion manuscript for submission. I believe that ozone formation in Mexico City has historically had two interesting characteristics. The first is the high frequency of days with significant ozone levels and the manuscript clearly addresses the role of primary HCHO in enhancing peak O3 levels. The second is that daily MCMA ozone concentrations tend to peak earlier in the day than in many other urban areas. The authors do discuss the time dependence of primary HCHO ozone production in section 3.4 of their manuscript. I would like to see some additional discussion about whether or not the fact that since much of the primary HCHO is emitted during the morning rush hour has a significant impact on the timing of the daily ozone production peak and subsequent ozone concentration peak (which can't occur until much of the early morning rush hour NO is converted to other nitrogen oxide species).

[RESPONSE]: Thanks to Dr. Kolb for pointing out this topic. The effect of primary HCHO on the timing of peak O3 is indeed another important aspect of the O3 formation issue. We have added the results of the effect of primary HCHO on O3 production (represented as P(Ox), Ox=O3+NO2) in both Table 4 (old Table 3) and Figure 8, and the timing effects on both P(Ox) and O3 concentration are discussed as follows: *"The effect of primary HCHO on O3 production is similar to that of O3 concentration (the higher increase of P(Ox) at photochemically-dark times, when changes in both O3 and*

P(Ox) are nearly zeros, is mainly due to the difference in the enhancement calculation procedure). Nevertheless, the effect of primary HCHO on P(Ox) starts earlier than the effects on O3 concentration (note the difference at 7-9 AM). A rapid increase in P(Ox) between from 8 to 9 AM in Fig. 8 is attributed to the HONO radical source.”... “Primary HCHO affects not only the magnitude of O3 concentration and photochemical production, but also their timing. As shown in Fig. 8, although there are flat and broad peaks in both P(Ox) and O3 concentration (model output frequency is 1-hr), it appears that the primary HCHO causes P(Ox) to peak a half hour earlier (12.5 LT vs. 13 LT). It is expected that the timing shift would stand out with a higher output frequency. The peak P(Ox) time shift and greater enhancement of P(Ox) at earlier time stated above lead O3 concentration to peak about half hour earlier too (14.5 LT vs. 15 LT), even though the peak O3 concentration is also flat and broad. The timing shift in peak O3 concentration due to primary HCHO suggests the VOC-limited O3 production chemistry in the MCMA source area. Lei et al. (2007, 2008) found that a 50% reduction in NOx emissions or a 50% increase in VOC emissions leads to a one-hour advance in the peak O3 concentration. The timing change together with the influence on peak O3 concentration demonstrates the importance of primary HCHO in O3 formation in the MCMA.”

In addition, although not closely related to the comments, but relevant to the uncertainty in early morning radical sources that were raised in the conclusion section, we have added a brief discussion of the influence of the possible NO2*+H2O radical source on O3: *“It has been reported that the reaction of electronically-excited NO2 (NO2*) with water vapor could be a potentially important OH radical source at high solar zenith angles in the troposphere (Li et al., 2008), and inclusion of this source could improve the estimation of radical budget and O3 production in the MCMA (Spencer et al., 2009). However, the contribution of this source for Los Angeles O3 production is disputed (Wennberg and Dabdub, 2008). Our preliminary CTM simulation results using the rate constant reported by Li et al. (2008), which are in preparation for publication, show that the NO2* + H2O radical source is negligible to O3 production in the polluted* *atmosphere over the MCMA where photochemistry is characterized by complicated radical sources.”*

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