Response to reviewers – Apel acp-2009-657

Anonymous Referee #1

Thanks much for your helpful comments.

The paper deals with the emission and conversion of volatile organic compounds (VOC) in the Mexico City Metropolitan Area. The paper includes interpretations of measurements of both oxygenated (OVOC) and nonoxygenated compounds (NMHC) from airborne platforms and stationary measurement sites. Also, data from different measurement techniques are combined, e.g. online and offline gas chromatography data, mass spectrometry data, and data of colorimetric formaldehyde determination. The dataset is unique with respect to its comprehensiveness. Such amount of data is always hard to interpret, and sometimes even harder to condense to be published in a paper, so the authors have focussed on comparing the total OH reactivity of VOC and OVOC and the formation of selected OVOC. The authors show that the OH reactivity is determined by nonoxygenated VOC except in the afternoon hours, when OVOC dominate, and that this behaviour can largely be explained by the MOZART and the WRF-Chem models. Moreover, the evolution of VOC in a plume was monitored on a selected flight and their general trend and the formation of OVOC could largely be described with a detailed chemistry model. The paper underlines the importance of a rather comprehensive data set of both OVOCs and NMHC for interpreting field campaign data, especially of the OVOC which are still rarely measured, despite their great importance. The paper is well structured, and easy to read. The paper should be published.

Small remarks:

Table 1 The abbreviation DFGAS does not appear in the text.

In section 2.1 the following now appears:

The TOGA measurements for OVOCs were used in this analysis. Formaldehyde was continuously measured on the C-130 with a Difference Frequency Generation Absorption Spectrometer (DFGAS) [Weibring et al., 2007].

Fig 4. In figure 4 data with a different time set a compared. This should be mentioned in the text. Also, the sampling duration should be given.

Under the following section, additional discussion was added about the canister collection times and duration:

2.2.1 Ground-based measurements

Canister measurements conducted by the University of California, Irvine (UCI) were used to characterize the NMHCs at the T0 and T1 sites. Air samples were collected in previously evacuated canisters. At T0, individual canisters were filled to 350-700 hPa over 30-60 minutes with variable sampling times;

a total of 200 canisters were collected. At T1, canisters were filled to 1000 hPa with the sampling time centered at midnight, 3:00 AM, 6 AM, etc.; a total of 200 canisters were collected.

Units are now given

This error occurred during typeset and will be corrected

Reviewer 2
Summary. The paper presents analysis of VOC data collected at ground sites and aircraft from the MILAGRO/MIRAGE-Mex field experiment conducted in and around Mexico City in March 2006. The paper presents an analysis of VOC data collected from 2 ground sites and 2 aircraft. This is a very comprehensive, high quality data set complied by a large group of investigators. The analysis investigates the relative importance of nonmethane hydrocarbons compared to oxygenated hydrocarbons in driving ozone production. The principal observation is the importance of oxygenated VOCs (OVOCs), such as methanol, formaldehyde and acetaldehyde at all sampling locations, in terms of their abundance and contribution to OH radical loss frequency. In the city center, during morning hours, non-methane hydrocarbons dominate VOC abundance and OH reactivity as might be expected. In the afternoon OVOCs have a dominant role. The authors show from aircraft data that as the plume photochemically ages through downwind transport , OVOCs become more important as ozone precursors than non-methane hydrocarbons. These general observations are compared to results from 2 chemical transport models (MOZART and WRF-Chem) and a box model to see if models capture the evolving importance of OVOCs on air mass reactivity. The authors conclude from observations and model studies that NMHCs fuel production of OVOCs in the plume, and these OVOCs then become the principal precursors for ozone production as the plume is transported away from the city.
Overall this was a clear, well written paper, presenting a useful analysis of good data. I would recommend publication in ACP. I have a few editorial comments that I think the authors should address to help clarify a few points.

Thank you for your helpful comments.

Yes, this was corrected

More detail is now given in section 2.2.1 as shown above in response to a similar concern by Reviewer 1.

Further clarification is given in the following paragraph about the 24 hour samples (blue):

3.1.1 Characterization of VOCs at T1 and T0

Table 2 shows the mean methane, carbon monoxide, and NMHC mixing ratios obtained during March, 2006 at T0 and T1 using the UCI canister measurements. The first two columns represent the samples collected between 9:00 and 18:00 local time for T0 and T1, respectively. The second two columns show averaged mixing ratios for T0 and T1, respectively, over the full 24 hour period. The median [CO] at T1 is about a third of the T0 [CO] with corresponding lower values for the NMHCs at T1 as well. These data along with a more complete data set supplied by UCI were used to derive NMHC abundance and OH reactivity for the T0 and T1 sites. Data from the Texas A&M PTR-MS (T0) and the NOAA PIT-MS (T1) were used for the OVOC abundance and reactivity (see Table 1).

P 24100. Table 3 discussion has lots more data than actually shown in Table 3. Need to fix Table 3.

This was fixed. Thanks!

P 24101. Does the slope really equal the emission ratio for a compound like CO that has a non-zero background. If emissions from city sources went to zero CO would still persist due to ubiquitous presence in the troposphere. Don't you have to subtract off the "regional background" component for CO and perhaps other VOCs?

Yes, it does equal the emission ratio because the ER is most often defined as the slope - $\Delta y/\Delta x$ – the intercepts don't change the slope.

P 24105 line 6. Can you state what features in the experimental data the models reproduce. For example, neither model displays a morning rush hour peak that characterizes the T1 data and that to me seems to be a big feature you would hope a model could capture. What features do they capture that are important?

There is an extensive discussion of Figure 5 in the text. The morning "rush hour" peak we now believe is not due so much to the rush hour but more to boundary layer dynamics. We modified the paragraph preceding the discussion of Figure 5 as follows to reflect this:

These observations may be attributed to high mixing ratios at night when VOC emissions accumulate in a shallow boundary layer followed by further reduction of the boundary layer height in the morning along with some contribution from traffic and industry during the early morning before the boundary layer has expanded.

The failure of the models to accurately reproduce the early morning feature is mostly due to a failure to accurately reproduce the nighttime PBL and this is reflected in the discussion highlighted in blue below:

…..In spite of these differences, the relative contributions to the reactivity from OVOCs are better represented in MOZART than in the WRF-Chem model (lower panel). Large differences between measurements and models occur at night. For the WRF-Chem simulations, there is a problem with either the nighttime emissions or the PBL height; a simulated shallow PBL height would lead to higher surface concentrations during the night which could potentially explain the results. For MOZART, there are clear

We also changed a portion of the abstract as follows to be more accurate:

The WRF-Chem (Weather Research and Forecasting with Chemistry) model and MOZART (Model for Ozone and Related chemical Tracers) were able to approximate the observed MCMA daytime patterns and absolute values of the VOC OH reactivity. The MOZART model is also in agreement with observations showing that NMHCs dominate the distribution except in the afternoon hours.

Page 24017 section 3.2 It struck me that the inclusion of methanol in the OVOC group complicates conclusions such as one made on line 25 " rapid photochemistry occurs that quickly transforms : : : dominated by NMHC to dominated by OVOCs aloft : : :". If the OVOC distribution is dominated by methanol I don't think this is a fair conclusion regarding the role of photochemistry. In general the paper considers OVOCs to be a photoproduct category. Methanol is not being produced as a photoproduct, it just happens to be one of the more abundant VOCs in "background" air. Could you please quantify which OVOC species are driving OH reactivity downwind. Showing the detailed distribution of VOCs downwind would be a useful supplement to Figure 9 and may make an interesting comparison to Figure 3.

The reviewer makes some good points here, however although methanol is present in high mixing ratios and it is important its contribution is relatively small compared to the aldehydes, the species that are chiefly driving the reactivity downwind. The following bit was added for clarification – quantifying the distribution of VOCs downwind:

……It is apparent from the data that rapid photochemistry occurs that quickly transforms the OH (VOC) reactivity from being dominated by NMHCs to being dominated by OVOCs aloft (G1), as noted earlier (see Figure 8), and further downwind (C130 plumes). At the C130 sampling point, a large part of the VOC reactivity is provided by the OVOCs: aldehydes (65%); alcohols (15%); ketones (3%). The proportional contributions from NMHCs were alkanes (10%), alkenes (5%), and aromatics (2%). As shown in the figure, CO plays a relatively more important role in OH reactivity compared to VOCs as the plume ages.

24108. Figure 11. Why is there a larger range of C130 CO data in benzene vs. CO plot than O3 vs. CO plot? The O3 vs CO plot is missing high CO data which would be the most important part of the plume.

This was corrected. The figure and figure caption were modified to clearly distinguish between the outflow event and non-ouflow time periods. (The O3-CO plot shows only data from the outflow, e.g., 2100-2400 UTC but in the original figure the benzene CO plot contained data from the entire flight, thus having higher CO values showing when we were closer to the city. This has now been fixed by highlighting the data that was part of the outflow event)

Edits and Typos.

P 24088, line 18 " Fewer studies : : :and time." What do you mean by " and time"?

Changed sentence to read a bit better:

Fewer studies have looked at the outflow from the city in terms of spatial extent and temporal evolution.

P 24090 line 26. Should this be VOC + OH reaction.

As you wish -

P 24091 reaction 4. A is undefined.

Eliminated this equation because it isn't needed

P 24092 line 9 delete "with".

OK

P 24092 line 20. Is TOGA a method or the name of an instrument? Perhaps just state in-situ GC-MS or something that pertains to the method.

Now reads…analysis in the laboratory, proton transfer mass spectrometry (PTR-MS), and the Trace Organic Gas Analyzer (TOGA), an in-situ gas chromatograph/mass spectrometer (GC-MS).

P 24092 line 23. What do you mean by "single functional non-acid OVOCs"? Functional group?

 Changed to:

and monofunctional non-acid OVOCs.

P 24093 line 4. ".. age of 1-2 days was sampled." Sounds funny. Do you mean 1-2 day transport time from source?

Changed to: Air with one to two day transport time from the source was sampled [Voss et al., 2010].

P 24095 line 9. Welsh-Bon (2009) not in reference list.

Changed to: A full description of the T1 VOC measurements, including techniques, is given by de Gouw et al. [2009].

P 24098 line 23. Missing superscript "10-12"

This problem apparently occurred during the typeset

P 24109 line 15 and line 20 Missing superscript "10-12", "106"

This problem also apparently occurred during the typeset

P 24111 line 23. Should be OH + O2. Can O2 be placed over top the reaction arrow? This is a multistep reaction so it is misleading to write it as such. Same applies to (R1) also shown as a 3-body reaction. Your meaning is understandble if you know the reaction but otherwise not technically correct.

Changed sequence to:

$$CH_3OH + OH \cdot \rightarrow \cdot CH_2OH + H_2O \tag{R6}$$

$$\cdot CH_2OH + O_2 \rightarrow HCHO + HO_2 \tag{R7}$$

$$CH_3CH_2OH + OH \cdot \rightarrow \cdot CH_2CH_2OH + H_2O \tag{R8}$$

$$\cdot CH_2CH_2OH + O_2 \rightarrow CH_3CHO + HO_2 \tag{R9}$$
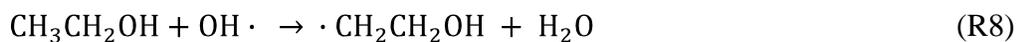
P 24112 line 12. Typo "methanols"

OK

P 24113 line 17 and 18. Consider replacing "is" with "are".

I disagree because these are considered as lumped quantities

Fig 6 and Fig 7 Legend font size for pie charts and figures labels is perhaps too small.

Will check with editor

Please make Fig 6 pie chart legend bigger at least, I can't read it.

OK – see revised Figure

P 24139 Fig 12. Need superscript on OH concentration.

This problem apparently occurred during the typeset – will check on all of these in final version.