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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Chemical evolution of volatile organic compounds in the outflow of the Mexico City Metropolitan area" *by* E. C. Apel et al.

Anonymous Referee #2

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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

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Interactive Discussion

Discussion Paper

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.

Comments.

P 24097 Table 1. Table 1. ethylene and ethene. Why is this molecule listed twice? I suspect ethylene = acetylene?

P 24100 line 13, P 24104 line 12, and section 2.2 It would be good to add to section 2.2 some more discussion of how the canisters were filled (fill times, sample schedule, apparatus). You state that 24 h samples were collected on page 24100 which was new experimental detail and somewhat confusing. How many 24 hr samples were collected? How many can samples were collected overall from TO and T1?

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

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?

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

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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?

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.

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.

Edits and Typos.

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

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

P 24091 reaction 4. A is undefined.

P 24092 line 9 delete "with".

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.

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

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

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transport time from source?

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

P 24098 line 23. Missing superscript “10-12”

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

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.

P 24112 line 12. Typo “methanols”

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

Fig 6 and Fig 7 Legend font size for pie charts and figures labels is perhaps too small. Please make Fig 6 pie chart legend bigger at least, I can’t read it.

P 24139 Fig 12. Need superscript on OH concentration.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 24085, 2009.

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