

Interactive comment on “Air quality in North America’s most populous city – overview of MCMA-2003 Campaign” by L. T. Molina et al.

L. T. Molina et al.

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Response to Reviewers’ comments:

We would like to thank the two reviewers for their thoughtful comments and helpful suggestions of our manuscript. Our response follows:

Response to Reviewer #1:

3116/23,24: Is there really evidence that the mountains trap pollutants in Mexico City? Modeling studies (e.g. de Foy et al., ACP, 6, 2321,2006) indicate nearly complete ventilation of the basin each day. The trapping is a long-standing popular notion which may, or may not, be correct. Could it be worth commenting on it here?

We have changed the sentence "The surrounding mountains, together with frequent thermal inversions, temporarily trap pollutants within the MCMA basin." to: "The sur-

rounding mountains, together with frequent thermal inversions, trap pollutants within the MCMA basin during the early hours of the day but are followed by efficient afternoon venting due to terrain-induced winds."

3117/15: The statement that PM and O3 are "the two most important pollutants" is too absolute, since the relative ranking could depend on circumstances (e.g. CO or Pb could be as important in some localities). Perhaps "the two most important" could be replaced by "two very important".

We agree - the text has been changed.

3130/footnote 1: As stated, the footnote seems to indicate that ca. 90% of industry was NOT included in the emissions inventory. If so, this should be discussed in more detail.

Please note the 4900 industries in the EI include all of the 460 large and 4200 medium size industries ; the missing ones are essentially in the "small" category. We have revised Footnote 1 as follows.

"According to the 2004 Emissions Inventory (CAM, 2006): There are about 42,000 micro-industries, 4,200 small and medium size industries and 460 large industries. The point sources emissions estimates in the 2004 EI were constructed with information from about 4,900 industries, which include large and medium size industries; the missing ones are all in the "small" category."

3133/19-24: Fig. 3 shows total emissions (not emission indices) presumably integrated over the entire MCMA. Since the ARI van, DOAS, and other measurements are local, it would be useful to say a few words on how these data were up-scaled to the entire MCMA basin (even if this is described in greater detail in the specific papers).

We agree. Figure 3 shows total emissions, not indices, per year and this has been corrected in the text as follows:

"Figure 3 shows mobile emissions estimated from measured on-road emission indices

by the ARI mobile laboratory on a wide range of MCMA roadways for NO_x from light-duty gasoline vehicles (Zavala et al., 2006), and CO and VOC from the full on-road fleet (Jiang et al., 2005), although without distinction of the corresponding type of vehicle and are more likely to represent aggregated emission factors of everything on the road (diesel, gasoline, LPG, CNG) plus some non-road emissions. Figure 3 also shows estimated on-road fleet SO₂ emissions determined from SO₂/CO₂ concentration growth measurements obtained by long open-path absorption at CENICA (de Foy et al., 2007). These are compared to the relevant MCMA EI estimates for 2002 (CAM, 2004).”

3140/14: The relative contributions to OH reactivity from VOCs, NO_x, CO, and HCHO, given on this line, are likely to change during the day. To which time period do the given values apply?

The following sentence has been added to the text: “The fractions are averages for all hours, day and night, over the campaign.”

3140/16: The broad statement that measured VOCs are sufficient to produce observed SOA is in conflict with later statements in this paper and with the Volkamer et al. (2006) study. Models constrained by observed VOCs underpredict the observed SOA rather seriously.

The SOA measured is only a small fraction of the VOC emissions, so the statement is true on a mass balance basis. We have modified the statement as follows: “These gaseous emissions are precursors for the large observed abundances of ozone, SOA, and other secondary pollutants observed in the MCMA, although not all of the photochemical conversion processes are fully understood at present.”

3141/12: The nighttime HO₂ values (Fig. 5) seem to hover around 5-8 ppt, except after about 3:00am when they fall much lower. Are these non-zero values as real as the drop around sunrise? If so, what is their chemical origin?

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The model captures this behavior rather well, although the model is slightly lower than the measurement. Both fall rapidly at 4-5 am. (From all of our interference tests, we have no evidence that these signals are an interference in the instrument.) The source of the nighttime HO₂ is ozone and alkenes, which are actually a well-known source of OH. But, in the absence of significant amounts of NO at night, OH is cycled rapidly to HO₂, which builds up. The loss of HO₂ is reaction with RO₂ and HO₂. During the morning rush hours, NO and NO₂ concentrations grow as can be seen in the figure; NO cycles HO₂ to OH and OH reacts with NO₂ to form nitric acid at a rapid rate. As a result, both HO₂ and OH rapidly decrease, despite the rapid increase in their own sources.

3144/17-21: The discussion of the HO₂/OH ratio as a function of NO is a bit cryptic. Of course the reader could go to Shirley et al., but with some clarification of the text, this interesting point could be brought forward in this overview paper.

We have added the sentence: "In other urban areas, the observed HO₂/OH ratio is roughly five to twenty times the steady-state analysis ratio for NO exceeding 10 ppbv." after the following two sentences already in the text: "A surprising result is the good agreement between the HO₂/OH ratio as a function of NO that is measured and the ratio from a measurement-based steady-state model and a photochemical point model, although the measured ratio is two times greater than the steady-state analysis ratio when NO exceeds 20 ppbv (Shirley et al., 2006). This agreement is better than has been seen in any other environment where NO exceeded a few ppbv."

Technical comments: 3125/3: Presumably 03:00am local time, not UT. Please specify, since both times are being used.

Yes, the local time is correct. We have added "local time" after 3:00 am.

3131/29: Change "agrees" to "agree"

Rather than change "agrees" to "agree", we have changed "NO_x emissions" to "NO_x

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emissions estimate" and leave "agrees" as is.

3134/5: Grammar: run-on sentence. Break into 2 sentences or put appropriate conjunctions.

We have changed the comma to a period after "approaching 1 mg m⁻² s⁻¹." and we have capitalized "The daily mean" to start a new sentence.

3139/15: Sentence seems incomplete. Perhaps clarify that these % values refer to formaldehyde (not glyoxal).

The percentages do correspond to formaldehyde. We have clarified by inserting "formaldehyde" between "primary" and "emissions"

3142/13: Remove extra X from HO_x

We agree: the non-subscript "x" has been deleted.

3142/22 - 3143/3: These statements are repetitions of earlier statements, e.g. 3136/3 for HCHO, 3139/11 for glyoxal

We believe we should leave this as is. Given the structure of the paper, some repetition is required and it is not necessarily bad when the point is important - as it is here.

3144/27-3145/7: It should be noted that other recent studies have also suggested that Mexico City O₃ production is VOC-limited, e.g. Tie et al., Atmos. Env., 41, 1989-2008, 2007.

We have added Tie et al. article in the reference.

Fig. 8 caption, 2nd line: delete "image plot of" (obvious).

We agree: "image plot of" has been deleted in the caption.

Response to Reviewer #2:

We have improved the resolution of the figures, as suggested by the reviewer.

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