

Interactive comment on “Atmospheric oxidation in the Mexico City Metropolitan Area (MCMA) during April 2003” by T. R. Shirley et al.

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Response to reviewer's comments for manuscript MS-NR: acpd-2005-0215 Version: 1; Received: 1 July 2005, 9:19 CET; Title: Atmospheric oxidation in the Mexico City Metropolitan Area (MCMA) during April 2003; Author(s): T. Shirley, W. Brune, X. Ren, J. Mao, L. Leshner, B. Cadenas, R. Volkamer, L. Molina, M. Molina, B. Lamb, and The MCMA fast photochemistry team

We thank the reviewers for their thoughtful comments. We believe that we have responded to all their concerns. Two revised figures, added paragraphs with expanded explanations and new information, and a few corrections have made the paper better.

Reviewer #1. 1. As requested, we have plotted the modeled results day-to-day on

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figures 7 and 8.

Figure 7. Time series in CST of all 1-minute averaged measured OH (line) and 10-minute averaged modeled OH (small circles).

Figure 8. Time series in CST of all 1-minute averaged measured HO₂ (line) and 10-minute averaged modeled HO₂ (small circles).

We have also added the following paragraph in section 3.2 OH and HO₂: Measured and modeled values: “OH and HO₂, plotted as small circles on Figure 7 and Figure 8, were calculated by the model for 11 April and 14-22 April. The measured-to-modeled comparison for OH and HO₂ is similar from day to day, with the modeled OH tending to be higher than the measured OH during midday. The modeled HO₂ in particular is somewhat scattered around the measured HO₂. This scatter is not surprising, considering that the mean fraction of VOC types were used for each half-hour and that the actual fraction of VOC types varied by 35%. None-the-less, the day-to-day consistency in the OH and HO₂ comparison indicates that our modeling approach provides a useful simulation of MCMA’s air chemistry.”

2. In section 3.3, we state “The first three OH production terms were calculated from measurements; the fourth term, OH production from O₃ and alkenes, was taken from model results and was less than 5% of the total.” Thus we make have made it clear that the O₃ + alkene source was calculated. However, we have improved our discussion of the possibility of missing VOC reactants by using more information to compare measured and calculated OH reactivity. The result is that we cannot rule out missing OH reactivity to about the 30% level.

3. We have added the word “measured” to the existing sentence and have added a sentence: “Typically, the measured OH wall loss rate, k_{wall} , was $1.5 \pm 0.4 \text{ s}^{-1}$. This value was the same in measurements before, during, and after the study.”

4. The RO₂+NO channel is in the model. We use the standard RACM model which

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includes these reactions.

5. The technical correction has been made; the correct units are ppbv.

Reviewer #2. (Reviewer's comments in braces { })

{Model description The absence of concurrent measurements of OH, HO₂ and the OH reactivity and VOC measurements in Mexico City is a very unfortunate shortcoming of this measurement intensive which handicaps the comparison of the measurements and the model predictions seriously. It is imperative that the authors attempt to be as specific as possible how they tried to accommodate for this shortcoming. In the present model description it is not clear how the box model was constrained in the absence of concurrent VOC measurements. It appears that the model is primarily constrained by the measured OH reactivity and that the relative VOC contribution to the OH reactivity was scaled to the detailed VOC measurements during other time periods of the intensive.}

We agree that the absence of simultaneous VOC measurements was indeed unfortunate. However, from our publication on work at other sites and from the tests that we have performed on the data set, we do not believe that this lack of concurrent VOC measurements seriously handicaps the comparison of the measurements and the model predictions. We have greatly expanded the discussion of this method in section 2.5, Model Description, and in section 3.1, OH reactivity measurements. We discuss three pieces of information that help demonstrate our case. These are the following: two VOC measurements that overlap with the OH reactivity measurements and are within 30%; fast olefin measurements that overlap both the VOC measurements and the OH reactivity measurements at CENICA have a similar ratio to the measured OH reactivity and to OH reactivity calculated from measured VOCs, especially during mid-day; and the fractions of VOC types measured at other urban sites made while OH was being measured at CENICA are similar to the fractions measured at CENICA before and after the OH measurements were made.

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{It is not clear to me what is meant by “categorized VOCs”}.

The categorized VOCs are the lumped groups that are used in the RACM model. We have removed this term.

{In the absence of VOC measurements during the HOx measurements, were there at least concurrent CO and NOx measurements available?}

As we discuss in the text, concurrent CO and NOx measurements were available.

{During the early morning hours, when very high OH reactivities are typically observed in Mexico City, do the measured OH reactivities correlate with CO.}

The measured OH reactivities correlate qualitatively with CO; both are greatest during morning rush hour. For daytime, $R^2 \sim 0.5$.

{On the days when VOCs were measured, do the VOCs correlate with CO during the early morning hours?}

CO correlates with VOCs, but not perfectly. There are a few points that are well off a line. However, the general trend is there.

{How were secondary VOCs, such as CH₂O, CH₃CHO, glyoxal and others, treated in the constrained box model?}

The model was constrained to the secondary VOCs. We have added this to the list of constraining variables. We have stated this more explicitly in section 2.5:

“Speciated VOCs were measured at CENICA for four days before and three days after the HOx measurements (Lamb et al., 2004) with only two data points that overlapped with the OH reactivity measurements. They were measured at other locations while HOx and OH reactivity were being measured at CENICA. These speciated VOCs were lumped into the different VOC types (i.e., alkanes, internal alkenes, aromatics) that are the required inputs to the model.

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While VOCs were not being measured at CENICA when HOx and OH reactivity were, except for two points, VOCs were being measured at other urban sites in MCMA. As described in section 3.1, the mean fraction of the VOC types at these other sites were similar to those at CENICA. For each hour of the day at CENICA, the standard deviation of the fraction of each VOC type was generally less than 35%. In addition, the mean fraction of each VOC type was the same to within 30% at CENICA and three other urban sites. This and other information given in section 3.1 provides strong evidence that the mean fraction of each VOC type can be confidently estimated for the time period when HOx and OH reactivity were being measured at CENICA. What is not known is the total amount of VOCs at CENICA during the HOx measurements; what is known is the measured OH reactivity.

To get the VOC inputs to the model, the information from the measured OH reactivity is used with the mean fractions of VOCs types combined from CENICA and the other three sites. This combined data set provides full daytime and limited night-time coverage. The speciated VOCs were averaged for each half-hour that they were measured and summed into VOC types (e.g., internal alkenes) that the model uses. For the model calculations, the abundance for each VOC type was determined by assigning the same fraction of the measured OH reactivity from VOCs to that VOC type and then calculating the VOC type's abundance from that fraction of the OH reactivity divided by the reaction rate coefficient. This method should work in an average sense. This method has been shown to give good results between measured and modeled HOx in other studies (Ren et al., 2005a; Ren et al., 2005b)”

{Results and discussions: Pg. 6051: “The speciated VOCs measured in MCMA 2003 have been compared to the typical US urban values (Lamb et al., 2004). This reference is just to a conference talk and it is important that the authors make this information available in the open literature.}

The information in the conference presentation has unfortunately not been submitted for publication yet.

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{How did the CO to NO_x ratios compare for Mexico City and New York?}

The CO/NO_x ratio is less than 20% greater in MCMA than in NYC from mid-afternoon to morning, but is 2.5 times larger from 5 am to noon. We have added this sentence in section 3.

{Pg. 6052: Considering the large variability of the OH reactivity measurements at any given time interval in Fig. 6 and the poor coverage of the VOC samples, the qualitative comparison of measured OH reactivities and calculated OH reactivities is highly questionable at best.}

Figure 6 is meant to show that the calculated and the measured OH reactivity are similar, certainly not different by more than a factor of two. The scatter is indeed large. We have other evidence that they are not greatly different. The following has been added to describe this other information:

“The comparison of the measured OH reactivity to the calculated OH reactivity is complicated by the timing of the two measurements during the study, with only two VOC measurements that overlap with the OH reactivity measurements. A direct comparison is thus difficult. However, when the measured and calculated OH reactivity are plotted as a function of time of day, they are similar in absolute value and diurnal behavior (Figure 6), despite significant scatter in the data.

Additional data suggest that the measured OH reactivity and the OH reactivity calculated from the speciated VOC measurements are similar, although the measured OH reactivity may be larger during morning rush hour. First, two VOC measurements were made one morning when the OH reactivity instrument was operating. The measured OH reactivity was 1.3 times the calculated OH reactivity, within the combined 28% uncertainties, especially for a sample of two. Second, fast measurements of olefins were made during the periods when VOCs were measured and when OH reactivity was measured (Valesco et al., 2005). The mean ratios of olefins-to-OH reactivity are the same for both to within 30% for 9 - 13 CST, although the olefin-to-calculated OH

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reactivity is larger than the olefin-to-measured OH reactivity by ~1.5 between 6 and 9 CST. These results suggest that while as much as 1/3 of the measured OH reactivity may be missing during morning rush hour, the calculated and measured OH reactivity are within 30% during midday.”

By adding the model results to Figures 7 and 8, which show individual OH and HO₂ measurements for all days, we demonstrate that there is no wild variation in the comparison between the model and the measurements, except for a few individual points. To us, this indicates that using the mean VOC fractions scaled to the measured OH reactivity does a pretty good job of describing the air chemistry in MCMA.

{Fig. 6: As there are multiple plusses for a given half hour time interval, the plusses do not seem to represent “the composite median profile of OH reactivity calculated from measured inorganic and VOC species” as indicated in the figure caption. If the plusses indeed represent the individual available VOC measurements, it demonstrates a rather poor coverage.}

This is not a composite profile; we have removed this language. We agree that the coverage was poor. However, we addressed the issue of why this is not a serious problem in sections 2.5 and 3.1, as included in our response above. The coverage is better when the results from other sites are included, but we have not done this for the figure. The main purpose of this figure was to show the OH reactivity in MCMA, show its variability, and compare it to New York City.

{Pg. 6054: In equation (7) the right hand numerator should read simply koh instead of koh[OH].”}

This error is fixed.

{Pg 6048 Typo: “75 pptb of NO” should read 75 pptv of NO.}

This typo is now fixed.

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