Atmos. Chem. Phys. Discuss., 5, S2790–S2792, 2005
www.atmos-chem-phys.org/acpd/5/S2790/
European Geosciences Union

Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

Received and published: 23 September 2005

The paper entitled "Atmospheric oxidation in the Mexico City Metropolitan Area (MCMA) during April 2003" by Shirley et al. presents the measurements of OH and HO2 as well as of the OH reactivity in Mexico City during a measurement intensive when many other trace gases were measured. In the paper the measurements of OH and HO2 are compared to the predictions of a photochemical steady state box model. The results obtained in Mexico City are further contrasted to measurements and model results from an earlier study in New York City, a mega city in the USA with in general lower ozone pollution levels. In particular this contrast between the two cities is important in the development of pollution control measures for Mexico City that benefit from the lessons learned in the U.S. cities. It will important that the comparison started in

this paper will be followed by a detailed comparison of detailed VOC profiles and VOC to NOx ratios in Mexico City to cities in the U.S. or Europe.

Specific Comments:

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

In the absence of VOC measurements during the HOx measurements, were there at least concurrent CO and NOx measurements 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. On the days when VOCs were measured, do the VOCs correlate with CO during the early morning hours?

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

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.

How did the CO to NOx ratios compare for Mexico City and New York?

Pg. 6052: Considering the large variability of the OH reactivity measurements at any

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Interactive Comment

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.

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.

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

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

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 6041, 2005.