Atmos. Chem. Phys. Discuss., 8, S10972–S10978, 2009
www.atmos-chem-phys-discuss.net/8/S10972/2009/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Ozone production, nitrogen oxides, and radical budgets in Mexico City: observations from Pico de Tres Padres" *by* E. C. Wood et al.

E. C. Wood et al.

Received and published: 5 February 2009

We thank referee 1 for the review. The original review has been quoted in italics:

The paper by Wood et al discusses data from a field campaign held in the Mexico City basin in 2006. Such data are potentially interesting, owing to the high concentrations of atmospheric pollutants commonly observed in this area. The authors aim to study ozone production under such conditions. The paper is generally well written. General problems are understanding what the results are representative of, given they focus mainly on one hour of one day. Also, there are a large number of assumptions made, which I'm not always sure are well justified.

Specific Comments 1. The main issue I have with this paper is what conclusions can

be drawn from 1-2 days of data? Even then, much of the focus is within 1 hour. The title of the paper is somewhat misleading. The reader might expect a more complete assessment of ozone production in the Mexico City basin. I would suggest it is altered to reflect the fact that it is really a case study for a very short period of time with particular conditions.

We thank reviewer 1 for the comments. The observations described in the manuscript are not meant to be representative of more than just the time periods discussed. We agree that the original title was not appropriate and we have reentitled it "A case study of ozone production, nitrogen oxides, and the radical budget in Mexico City" The first 2 sentences of the abstract now read as follows:

"Observations at a mountain-top site within the Mexico City basin are used to characterize ozone production and destruction, the nitrogen oxide budget, and the radical budget, with an emphasis on a stagnant air mass observed on one afternoon. The observations compare well with the results of recent photochemical models."

The final paragraph of the introduction now reads as follows:

"In this paper, we present measurements from Pico de Tres Padres, a unique mountain-top stationary site that is situated within the Mexico City basin but is minimally impacted by nearby emissions. The air masses observed on 12 March 2006 were stagnant in the afternoon and provided an excellent opportunity to study ozone chemistry, since the impact of chemistry was mostly isolated from the impacts of transport. Secondary organic aerosol formation at this site is analyzed and described in two related manuscripts (Wood et al., 2008), (Herndon et al., 2008). The observations and inferences regarding tropospheric chemistry are compared to the predictions of several photochemical models (Lei et al., 2007;Madronich, 2006;Tie et al., 2007). Such observational-based characterizations of photochemistry, even if focused on a short period of time, are crucial for testing our understanding of the underlying photochemical processes that control secondary air pollution."

ACPD

8, S10972–S10978, 2009

Interactive Comment

And the 1st sentence of the final paragraph of the conclusion now reads as follows:

"Although this analysis focused on only a short time period, the chemistry characterized is in agreement with previous modeling work and lends confidence to the state of knowledge regarding ozone chemistry, nitrogen oxides, and the underlying fast radical chemistry."

A primary goal of the paper was to test photochemical models (such as Lei et al 2007, Madronich et al 2006, and Tie et al 2007) against actual measurements. We believe such quantitative comparisons between models and measurements, even if only focused on a short period of time, are a crucial test of our understanding of ozone photochemistry. In the manuscript, the following predictions from photochemical models have been quantitatively compared to observations, and found to agree reasonably well:

1) The relationship between P(O3) and P(ROx) described by Lei et al (2007) 2) O3 production is VOC-limited (Lei et al 2007, Tie et al 2007) 3) The values for the OPE modeled by Lei et al (2007) 4) The temporal evolution of NOy speciation described in Madronich (2006) (compared to 11 days of data at PTP)

Additionally, the following observations described are useful:

1) The comparison of P(ROx) and P(NOz) has, to our knowledge, never been done before using measurements. This is a new way of testing our understanding of the ROx budget and determining the sensitivity of ozone production to VOCs and NOx.

2) The inferred value of [OH] is well within the range of measurements described in Shirley et al (2006) and Dusanter et al (2008). The accuracy of such OH measurements still (rightfully) receive scrutiny, even as they become more commonplace. Our estimation of [OH] is only for one hour, but still a useful exercise.

3) Some studies have questioned the high ozone production rates calculated using measurements of HO2 and NO (e.g., see editor comments to Dusanter et al 2008,

ACPD

8, S10972–S10978, 2009

Interactive Comment

Atmos. Chem. Phys. Discuss., 8, 13689-13739, 2008 and references therein). The comparison of our single point inference of the ozone production rate to P(O3) values calculated by other means is thus a useful exercise.

4) There are few studies that quantify how much of the NOy budget is taken up by coarse-mode aerosol. Although this study does not definitively conclude that this is important in Mexico City, the presentation of the relevant data (section 3.3.2) provides clues as to the importance of coarse-mode aerosol, and is complementary to other studies (e.g., Zheng et al, 2008).

Lei, W., et al, "Characterizing ozone production in the Mexico City Metropolitan Area: a case study using a chemical transport model", Atmospheric Chemistry and Physics, 7, 1347-1366, 2007.

Madronich, S.: "Chemical Evolution of gaseous air pollutants down-wind of tropical megacities: Mexico City case study"; Atmospheric Environment, 40, 6012-6018, 2006.

Tie, X., "Characterizations of chemical oxidants in Mexico City: A regional chemical dynamical model (WRF-Chem) study", Atmospheric Environment, 41, 1989-2008, 2007.

Zheng et al., "Measurements of HNO3 and N2O5 using Ion drift - Chemical Ionization Mass Spectrometry during the MCMA - 2006 Campaign", Atmospheric Chemistry and Physics, 8, 6823-6838, 2008.

2. On a related note, how applicable are the results? The authors note that O3 production reached 50 ppb/h at one point, which is indeed a high value. However, nowhere do they discuss how frequently such high values occur, and whether they think they are applicable across the whole of the Mexico City basin.

We believe the revisions to the title, abstract, introduction, and conclusion described above should remove this confusion; i.e., the observations do not apply to any other times besides the time period of interest, though are still useful for comparisons to models. On a related note, the companion manuscript "Investigation of the correlation

ACPD

8, S10972–S10978, 2009

between oxygenated organic aerosol and odd-oxygen in Mexico City and Houston" (Wood et al, in preparation), will contain more information regarding the range of P(O3) values observed at both T0 and PTP.

3. On page 15741, line 25, the authors mention that ozone values are frequently "unsafe" in the MCB. This sentence would be more informative if they told us what the unsafe values were and how unsafe is defined in this context.

This sentence has been rewritten as "it remains highly polluted, with ozone concentrations frequently exceeding 100 ppbv";

4. The other main issue with the paper is the large number of assumptions made. The authors have done their best to justify the assumptions, but the reader is still left wondering about the conclusions drawn, given the small amount of data and the number of assumptions made. For instance, where does the value of 40 ppt of HO2 come from given the authors calculate the HO2+RO2 sum to be 95 ppt?

This value for HO2/(HO2+RO2) of just under 50% is based on measurements aboard the C-130 aircraft; a reference has been added (Cantrell et al., "HOx Behavor as Observed Aboard the C-130 during MILAGRO", MILAGRO Science Meeting, Mexico City, 2007). The final paragraph of section 3.2 now contains the following text:

"Observations aboard the C-130 aircraft at comparable NOx concentrations (>10 ppbv) have shown that HO2 comprised slightly less than 50% of the sum of HO2 and RO2 (Cantrell et al., 2007). This value is useful for estimating the rate of the HO2 self-reaction and the rate of HO2 + O3. The large uncertainties do not affect the conclusions of this paper."

5. The value for O3 deposition of 0.4 cm/s needs to be justifed by at least a reference (page 15754, line 2).

The following reference has been added:

Wesely, M. L. and B. B. Hicks (2000). "A review of the current status of knowledge on

ACPD

8, S10972–S10978, 2009

dry deposition." Atmospheric Environment 34: 2261-2282.

6. In section 3.3.3, the authors state that significant partitioning of the organic nitrates to aerosol would decrease their OH estimate - would this be a linear relationship and how would the overall results be affected?

Yes, this would be a linear relationship. The end of section 3.3.3 has been edited to read as follows:

"...i.e., if the increase in the sum of HNO3(g) and total particulate nitrate were 30% higher than our measurement of HNO3(g) and accumulation mode particulate nitrate, then OH would be underestimated by 30%. Conversely, this is an overestimate of [OH] if HNO3 was not the sole source of particulate nitrate (i.e., if there was significant partitioning of organic nitrates to the condensed phase). Besides the comparison to previous measurements of OH in Mexico City, this estimate of [OH] is only used to quantify the rates of R11 and R19. The uncertainty in this estimate does not affect the conclusions presented. For example, this estimate would have to be more than a factor of 6 too low in order for R11 to account for an appreciable fraction (>10%) of the total Ox loss."

7. At the bottom of page 15762, top of page 15763, it transpires that alkene measurements are not available for this period. Past studies have shown that alkene-ozone reactions play a crucial role in OH production in urban areas (including some of the papers quoted by the authors as well as the BERLIOZ study). Do the uncertainty limits quoted here really reflect the real situation?

We agree that alkene ozonolysis can play a crucial role in OH (and RO2) production, which is why we calculated the ROx production rate using our available alkene measurements. We had mistakenly omitted the uncertainties in our values for the photolytic contribution to P(ROx) ($\pm$0.4 pptv/s) and the contribution from alkene ozonolysis ($\pm$0.2 pptv/s), which we have corrected in the revision. The estimate used (0.4 $\pm$ 0.2 ppt/s) is based on measurements from other afternoons, as described in the text. Thus the

ACPD

8, S10972–S10978, 2009

combined uncertainty in the sum (calculated in quadrature) is 0.5 pptv/s. If the uncertainty in the contribution from alkene ozonolysis is increased to 0.3 pptv/s, the total uncertainty in P(ROx) is still 0.5 pptv/s when rounded to the nearest 0.1 pptv/s.

8. Much of the results section is quite hard to digest. The reader has to read through and remember many assumptions to follow the calculations through. There is a lot of information here and the paper seems to move rapidly from calculating one indicator to the next. I wonder if it may be better to present fewer of the calculated parameters here, but to stick to those that are based on firmer assumptions?

In the revision we have removed the paragraph in 3.3.2 that described the relative rates of P(HNO3) and P(RONO2), since it was not definitive. As for calculating "indicators", the comparison of P(NOz) to P(ROx) to deduce information on the radical budget is a new approach that we strongly believe is worthwhile enough to remain in the manuscript. The concept of the OPE has been studied for decades and has strong historical precedent in the literature, and we believe our contributions are warranted as well.

issues 1. Page 15744,line 2. New paragraph after (R2 and R3).

This has been added in the revision.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 15739, 2008.