

## ***Interactive comment on “Direct measurement of ozone production rates in Houston in 2009 and comparison with two estimation methods” by M. Cazorla et al.***

**M. Cazorla et al.**

cazorla.chem@gmail.com

Received and published: 3 January 2012

We thank the reviewer for comments and suggestions that have greatly improved our manuscript. Below are the comments from the REVIEWER followed by our RESPONSE:

REVIEWER:

This paper capitalizes upon the rich array of observations during the SHARP campaign to present the first evaluation of the Measurement of Ozone Production Sensor (MOPS) against modeled and calculated ozone production rates ( $P(O_3)$ ). Given the novelty of the MOPS approach and the value of intercomparing the three methods

C13831

during ozone pollution events, this paper certainly merits publication. However, since all three methods of estimating  $P(O_3)$  are prone to significant uncertainties, greater caution is needed in diagnosing the cause of the discrepancies as discussed below. Several specific comments and minor edits should also be addressed prior to publication.

Major comments:

The conclusion that discrepancies among the approaches indicates underprediction of  $P(O_3)$  by the model has not been proven. The authors appropriately note that all three approaches have significant uncertainties, and acknowledge that the uncertainties of the MOPS are poorly understood given the newness of the technique. However, at several points the paper suggests without clear justification that “missing radical sources” in the model are the likely cause of the discrepancies. The focus on error in the model seems to be driven by the claim that the calculated results have “better quantitative agreement” with measured  $P(O_3)$  than the model does. However, that depends on the statistic used. The model was closer to measured for  $R^2$ , RMSE, and the shape of the  $P(O_3)$  vs NO response, whereas the calculated was closer to measured for IA, MBE, and the magnitude of  $P(O_3)$ . For the model to be showing  $P(O_3)$  peaking at the right NO level, it is surprising that there would be a major missing radical source. A limitation of all of these comparisons is that  $P(O_3)$  is a highly uncertain quantity. The authors should first directly compare the measurements of HO<sub>2</sub> and OH to those predicted by the model.

RESPONSE:

We agree with the referee on the need to restate and clarify some points regarding model radicals on our paper. It is true that the material presented in this study is not conclusive regarding missing radical sources. A comparison between measured and modeled radicals, however, has been done and is being thoroughly explained in an upcoming paper by Ren et al. In general, modeled HO<sub>2</sub> is lower than measured HO<sub>2</sub>.

C13832

We have included results from this study in the current manuscript. The manuscript has been edited in the following way:

Abstract: Lines 10-16 on pg 27522 were replaced with the following:

While statistical analyses are not conclusive regarding the comparisons between MOPS measurements and the two estimations methods, the calculated P(O<sub>3</sub>) with measured HO<sub>2</sub> produce peak values similar to the measured P(O<sub>3</sub>) when ozone is high. In contrast, the model estimations of P(O<sub>3</sub>) are in general too low since they were obtained with lower modeled-than-measured HO<sub>2</sub>. Although the MOPS is new and more testing is required to verify its observations, the measurements in the SHARP field campaign show this new technique's potential for contributing to the understanding of ozone-producing chemistry and to the monitoring of ozone's response to future air quality regulatory actions.

End of section 3.2: the following results were included:

A comparison of the median diurnal variation between measured and model HO<sub>x</sub> radicals for the SHARP campaign shows that the ratio of measured to modeled HO<sub>2</sub> between 05:00 and 06:00 was about 2; between 06:00 and 07:00 this ratio was 8-10, just when NO reached its peak at a median value of 4.5 ppbv; and then the ratio decreased from about 4 to 2 between 07:00 am and noon, while NO decreased from 4 to 0.5 ppbv. Details will be presented in a thorough radical study prepared by Ren et al. (2012), although these results are similar to those of Chen et al. (2010) and Mao et al. (2010) for the same site in September 2006. Higher measured-than-modeled HO<sub>2</sub> when NO is high explains why the calculated P(O<sub>3</sub>) is high and peaks in the early morning before 7:00. Therefore, the difference in the calculated and modeled P(O<sub>3</sub>) are linked to the difference between the measured and modeled HO<sub>2</sub>. From a comparison of the median diurnal variation, P(O<sub>3</sub>) from the MOPS measurements agrees with the calculated P(O<sub>3</sub>) to within the estimated uncertainties but is twice the modeled P(O<sub>3</sub>) in the morning.

C13833

Reference: X. Ren, Van Duin, D., Cazorla, M., Chen, S., Brune, W. H., Flynn, J. H., Grossberg, N., Lefer, B. L., Rappenglück, B., Wong, K. W., Tsai, C., Stutz, J., Dibb, J. E., Jobson, B. T., Luke, W., Kelley, P.: Atmospheric oxidation chemistry and ozone production: Results from SHARP 2009 in Houston, Texas, in preparation, 2012.

Erased from line 11 on page 27533: indicating underestimated modeled results

Added to line 28 on page 27534, at the end of the paragraph: In total, these statistical analyses provide no clear answer to whether the measured P(O<sub>3</sub>) agrees better with the calculated P(O<sub>3</sub>) or the modeled P(O<sub>3</sub>). Additional field campaign studies are necessary to draw more conclusive explanations on differences between measurements and calculations.

On line 16, page 27535: Removed from the text: suggesting a potential lack of a source of radicals in the model

The conclusions were revised as well. Please look at revised conclusions under the answer to the next comment.

REVIEWER:

Also, it may be possible to infer an approximate "true" P(O<sub>3</sub>) from the time series of ozone mixing ratios. The MOPS and calculated predictions of average P(O<sub>3</sub>) \_ 20 ppbv/h in the morning seem quite high given the relatively moderate daily rise in O<sub>3</sub> mixing ratios on most days in Figure 1. That makes it possible that the relatively low predictions of P(O<sub>3</sub>) in the model are closer to reality.

RESPONSE:

Regarding the ozone budget equation, it is important to keep in mind that the MOPS measures the net chemical production and does not sense other processes such as dry deposition or advection. We have included the ozone budget equation in the introduction of the revised manuscript to explain that the MOPS measures the chemical component of this equation alone, which we refer to as P(O<sub>3</sub>). From this perspective

C13834

it is possible to have high production of ozone with low ambient ozone if advection of ozone to some other areas takes place. We did perform a quick calculation of the total ozone rate of change in the ambient air which does not compare directly with the MOPS  $P(O_3)$ . This quick calculation is discussed in the conclusions section. In general, we have clarified differences between ambient ozone rate of change and the potential of MOPS to help determine the advection component of this rate of change in the introduction and conclusions of the revised manuscript. Both revised sections are reproduced below as they also contain answers to other comments regarding corrected statements about missing radicals and the potential of the MOPS to contribute to improving air quality regulations.

#### Introduction

It has long been known that ozone pollution damages human health (Ho et al., 2007) as well as crops and forests (Madden and Hogswett, 2001), but a growing body of evidence indicates that these harmful effects occur at even lower ozone levels than previously thought. In response, governmental regulatory agencies are considering reductions in the primary and secondary Ambient Air Quality Standards for ozone. For example, a reduction in the primary standard from 75 ppbv to a new level between 60–70 ppbv has been recently proposed (US EPA, 2010), although consideration of this new ozone standard has been delayed until 2013. At present, the number of counties nationwide in non-attainment with a standard of 70 ppbv would increase by 50% whereas if the standard were set to 60 ppbv, this increase would be 90% (McCarthy, 2010). Attaining these ozone standards is a challenge for air quality managers.

Areas designated as being in non-attainment with the current ozone standard such as Houston-Galveston-Brazoria would face a more difficult challenge under new rules. As an example, during the month of May 2009, the Texas Commission on Environmental Quality (2011) reported four cases of exceedances of the current primary ozone standard in Houston. Thus, developing economically viable reduction policies will require more exigent controls on mobile and point sources of the ozone precursors, nitrogen

C13835

oxides ( $NO_x=NO+NO_2$ ) and volatile organic compounds (VOCs). Determining the effectiveness of these new policies could benefit from new monitoring strategies that include measurements of not only ambient ozone but also the actual ozone production rate. Ambient ozone is the result of local photochemical production, surface deposition, and transport processes, as given in the ozone budget equation (Eq. 1):

Please look at supplement Eq. (1)

where the time-rate-of-change of measured ambient  $O_3$  is on the left-hand side of the equation,  $P(O_3)$  is the instantaneous net chemical ozone production rate,  $\nu_d$  is the ozone deposition velocity,  $H$  is the mixed layer height, and  $v$  is the wind velocity. The amount of ground-level ozone and its time rate of change can be obtained from a direct measurement using a commercial ozone analyzer. These ambient ozone measurements, however, do not indicate whether ozone is produced locally or advected from other areas. Thus the relationship between ozone and its precursors cannot be obtained from simple ambient ozone measurements alone. Typically, ozone is linked to its precursors with an air quality model that includes  $NO_x$  and VOC emissions, the photochemistry that produces ozone, and the meteorology that drives the ozone transport. The emissions inventories and transport are both uncertain (Fox, 1984; NRC, 1991; Gilliland et al., 2008), thus complicating the ability for the models to test the effectiveness of emissions reductions on ozone production.

The chemistry of tropospheric ozone production has been presented in a thorough manner by several authors (Haagen-Smit et al., 1953; Finlayson-Pitts and Pitts, 1977; Logan et al., 1981; Gery et al., 1989; Kleinman, 2005; Seinfeld and Pandis, 2006). The current understanding of the ozone-forming chemistry in the troposphere indicates that the photolysis of nitrogen dioxide ( $NO_2$ ) is the only known source of ozone in the daytime. In the absence of hydroperoxyl radical ( $HO_2$ ) and organic peroxy radicals ( $RO_2$ ), nitric oxide ( $NO$ ), nitrogen dioxide ( $NO_2$ ) and ozone ( $O_3$ ) achieve photosteady state (PSS) and no new ozone is formed. New ozone is formed via reactions of peroxy radicals ( $HO_2+RO_2$ ) and  $NO$  to make  $NO_2$ , which solar ultraviolet light dissociates into  $NO$

C13836

and O, with O rapidly reacting with O<sub>2</sub> to make ozone. Peroxy radicals come from reaction sequences that continuously cycle OH, HO<sub>2</sub>, and RO<sub>2</sub> radicals; these sequences are fast enough that the steady state of the HO<sub>x</sub> (OH+HO<sub>2</sub>) species can be assumed. The estimation of the rate of net ozone production, P(O<sub>3</sub>), from measurements requires the knowledge of the abundance of peroxy radicals and NO present in the ambient air. The instantaneous production of ozone in the troposphere can be represented by the kinetic rate equations:

Please look at supplement Eqs. (2) – (4)

Equation 2 summarizes the production of NO<sub>2</sub>. The k terms are the reaction rate coefficients and the terms in brackets are the concentration of chemical species. The two terms on the right-hand side of Equation 2 indicate production of NO<sub>2</sub>, and therefore of ozone, from peroxy radicals reacting with NO. The terms of Eq. 3 corresponds to the reaction of OH and NO<sub>2</sub> to form nitric acid, the reaction of HO<sub>2</sub> with O<sub>3</sub>, and finally the formation of organic radicals RONO<sub>2</sub>. Eq. 3 represents the reactions that reduce the ozone production rate, either by direct ozone loss or by shifting the NO<sub>2</sub> that is in steady-state balance with ozone into reservoir species. The instantaneous net production of ozone is the difference between chemical ozone production and chemical removal, as shown by Equation 4.

The calculation of the ozone production rate has been traditionally done by chemical modeling. In this study, we use the Regional Atmospheric Chemistry Mechanism Version 2, or RACM2, (Goliff and Stockwell, 2008; Goliff and Stockwell, 2010). Past studies have found that ozone production rates calculated from measured radicals were greater than those calculated from modeled radicals (Martinez et al., 2003; Ren et al., 2003; Ren et al., 2004; Shirley et al., 2006; Kanaya et al., 2007). These differences have been attributed to the underprediction of HO<sub>2</sub> by the models. Recent studies by Hofzumahaus et al. (2009) suggest a mechanism for the production of OH that maintains the ratio HO<sub>2</sub>/OH and does not involve the reaction of HO<sub>2</sub> with NO and, therefore, does not result in the production of ozone at low NO levels. Although the

C13837

conditions for the present study are different from those in Hofzumahaus et al. (2009), the hypothesis by Hofzumahaus et al. is an example of a mechanism that is not included in the traditional models and calculations. Monitoring the ozone production rate in real time could help identify additional mechanisms or confirm the chemistry included in the models.

The Measurement of Ozone Production Sensor (MOPS) (Cazorla and Brune, 2010) measures P(O<sub>3</sub>). This term in the ozone budget equation (Eq. 1) is the only term that is directly affected by NO<sub>x</sub> and VOC emissions and their photochemistry. All other terms are proportional to ozone or its gradient, so that as measured P(O<sub>3</sub>) decreases, so should measured ozone if ozone is being produced locally and not advected from production regions elsewhere. Thus, P(O<sub>3</sub>) measurements can be used to quantify local production versus transport by comparing the measured ozone change against P(O<sub>3</sub>), especially if a network of these instruments is located along the path of meteorological features that are associated with ozone advection. P(O<sub>3</sub>) measurements also provide a test of the ozone production rates that are calculated from Eq. 4 using either modeled or measured chemical species, where the measurements come from intensive field campaigns. Further, adding NO<sub>x</sub> or VOCs to ambient air sampled by the MOPS, directly tests the sensitivity of ozone production to NO<sub>x</sub> or VOCs. Thus MOPS has the potential to contribute significantly to improving the monitoring of ozone and its response to changes in NO<sub>x</sub> and VOC emissions.

The direct measurement of ambient ozone production rate was first proposed about forty years ago (Jeffries, 1973), but we independently developed a technique using an improved understanding of the photochemistry and better materials and methods that were not available then. These improvements have made a quantitative direct ambient measurement feasible. This paper presents the first P(O<sub>3</sub>) measurements using the MOPS, a new, relatively untested, yet promising technique. These measurements were made during an intensive field campaign in Houston in 2009 in which environmental parameters and many atmospheric constituents including radicals were measured. As

C13838

a result, the measured  $P(O_3)$  can be compared to the ozone production rates that are calculated using Eq. 4 and either measured  $HO_2$ ,  $NO$ , and  $OH$  or modeled radicals. A goal is to determine whether the comparison of the MOPS-measured  $P(O_3)$  can be used to distinguish between the ozone production rate calculated from measured  $HO_2$ , which is typically greater than the ozone production rate calculated from modeled  $HO_2$ .

#### Conclusions

The Measurement of Ozone Production Sensor (MOPS) successfully measured the net ozone production rate  $P(O_3)$  during its first field campaign, SHARP in Houston during April/May 2009. Measured  $P(O_3)$  generally peaked in the mid-to-late morning at values ranging from 20 ppbv h<sup>-1</sup> to more than 50 ppbv h<sup>-1</sup>, with the higher  $P(O_3)$  generally occurring on days with higher ambient  $O_3$ . When these ozone production rates were integrated over a day, the cumulative ozone was generally greater than the observed ozone, indicating that ozone was being produced locally and then advected elsewhere. Examining this issue in more detail will require another study that compares the MOPS  $P(O_3)$  measurement to an air quality model. MOPS measurements of  $P(O_3)$  provide a good check on the differences between calculated  $P(O_3)$ , which is based on measured  $HO_2$  and  $OH$ , and modeled  $P(O_3)$ , which is based on modeled radicals. The peak measured values generally agree with the peak calculated values and are about twice the modeled values. Further, the measured  $P(O_3)$  peaks in midmorning, later than the calculated  $P(O_3)$  but earlier than the modeled  $P(O_3)$ . On the other hand, for  $NO$  greater than about 10 ppbv, the measured  $P(O_3)$  is only half of the calculated  $P(O_3)$  but is roughly four times the modeled  $P(O_3)$ . The statistical analyses provide mixed evidence that is consistent with these more qualitative comparisons. Some analyses indicate a better agreement between measured and modeled  $P(O_3)$  while other indicate a better agreement between measured and calculated  $P(O_3)$ . Hence, it is premature to draw general conclusions from these comparisons, however, some evidence from measured  $P(O_3)$  and  $HO_2$  during the SHARP campaign suggest that the modeled  $HO_2$  is too low. Providing more conclusive evidence will require greater pre-

C13839

cision and reduced uncertainties in the MOPS measurements and more observations with the MOPS during intensive field campaigns. Increasing the precision will come from decreasing the statistical noise in the differential ozone sensor. Reducing the uncertainties will require more testing of both ozone and radical losses and of ozone production by degassing of  $NO_x$  and VOC products from the chamber walls. Improving the statistics will require more observing with the MOPS. These are all under way.

The deployment of the MOPS during the SHARP field campaign has enabled the first measurements of the direct ambient ozone production rate that have been compared to both modeled and calculated  $P(O_3)$ . As more measurements are made in different environments by more groups, and as more laboratory studies of the MOPS are undertaken, it is likely that more will be learned about the strengths and weaknesses of the technique. Issues of calibration and artifacts are likely to emerge, as they have for all previous new measurements. The SHARP data demonstrate the potential of the MOPS. Our ability to verify the calibration and reduce any possible artifacts will determine the value that the MOPS will provide for understanding ozone photochemistry, clarifying the discrepancies between measurements and model  $HO_2$ , and improving air quality regulations.

REVIEWER:

Specific comments:

p. 27525, lines 19-28: The rationale behind the difference in PSS in the MOPS chambers providing a measure of  $P(O_3)$  should be justified, and key uncertainties noted.

RESPONSE:

The difference in the PSS in the MOPS chambers is not what provides a measure of  $P(O_3)$ . As a matter of fact, the photosteady state ozone is cancelled out between the MOPS chambers. The difference in radical chemistry is what yields real time  $P(O_3)$ . To make this point clear we have edited the second paragraph of section 2.1 in the

C13840

following manner:

The Penn State MOPS (Cazorla and Brune, 2010) was deployed during the SHARP campaign between 15 April and 31 May 2009. The MOPS measures P(O<sub>3</sub>) by finding the differential ozone between a transparent chamber (sample) and a chamber covered with a UV-blocking film (reference) that continuously sample ambient air and are exposed to the sun. Since sunlight below 400 nm is blocked in the reference chamber, the production of OH and HO<sub>2</sub> radicals is restricted while the NO-NO<sub>2</sub>-O<sub>3</sub> PSS shifts towards NO<sub>2</sub>. In contrast, the clear sample chamber contains the PSS plus radical production, and consequently non-PSS NO<sub>2</sub> that leads to the production of “new ozone”. By finding the difference in the total NO<sub>2</sub>+O<sub>3</sub> between the two chambers, the PSS is cancelled out and the new ozone related to the chamber exposure time yields the real time P(O<sub>3</sub>). An NO<sub>2</sub>-to-O<sub>3</sub> converter between the chambers and the ozone monitor accounts for the differences in PSS between the sample and reference chambers by converting NO<sub>2</sub> to O<sub>3</sub> so that the sum of NO<sub>2</sub> and O<sub>3</sub> is measured as O<sub>3</sub>. The estimated uncertainty of the MOPS is 30% at the 2 $\sigma$  confidence level and 10-min integration time, although longer operation of this new technique will be needed to truly understand the uncertainties and possible interferences. A complete description of the instrument can be found in Cazorla and Brune (2010). MOPS data is available for 20 days out of the 42-day intensive SHARP study.

REVIEWER:

p. 27527, lines 15-16: Clarify how the model was constrained. For example, were NO and NO<sub>2</sub> both specified?

RESPONSE:

A sentence was to line 16 on page 27527 as follows:

In the present study, atmospheric constituents and environmental parameters were used to constrain the model. Field measurements of NO, NO<sub>2</sub>, SO<sub>2</sub>, CO, O<sub>3</sub>, VOCs

C13841

C2-C10, oxygenated hydrocarbons, photolysis rates, and meteorological data were specified explicitly in the model.

REVIEWER:

p. 27530, lines 18-21: The logic of this statement is unclear. Photolysis of NO<sub>2</sub> to NO just maintains the null cycle if followed by NO+O<sub>3</sub> reaction.

RESPONSE:

The fragment on the noted page and lines was reworded as follows: The model, however, never shows net P (O<sub>3</sub>) to be negative because if there is sufficient photolysis to produce OH, then there is also sufficient photolysis to form O<sub>3</sub> from NO<sub>2</sub> that comes from the reaction of radicals and NO emissions, thus keeping net P (O<sub>3</sub>) positive.

REVIEWER:

Minor edits:

p. 27522, line 18: change the phrase “holding a debate”

RESPONSE:

The first paragraph of the introduction was modified as shown above under the revised introduction section.

REVIEWER:

p. 27522, line 24: correct “designed” to “designated” various lines: Define NO<sub>x</sub>, VOCs, RO<sub>2</sub>, and HO<sub>x</sub> on first use

RESPONSE:

These changes were applied to the revised manuscript on the noted page and lines.

REVIEWER:

p. 27523, lines 20-21: unjustified to claim that MOPS provides basis for designing reg-

C13842

ulations and controls, or contributes to the "efficacy of air pollution management" (p. 27537, line 3). Strategy development requires understanding of ambient responsiveness to control measures, which is not provided by MOPS.

RESPONSE:

There are a number of reasons why we believe that the MOPS could improve the making of air quality regulations. We are aware, however, that more testing and further campaigns are necessary before our instrument is at this stage. Therefore, we have edited the manuscript referring to this capability of the MOPS as a potential being tested. So we have modified statements in the abstract, as shown earlier and also we do present all the justifications for these potential claims under the revised introduction and conclusions.

REVIEWER:

p. 27253, lines 25 and 29: clarify that you're referring to tropospheric ozone production

RESPONSE:

This clarification was applied on the noted lines and page.

REVIEWER:

p. 27525, line 24: define "sample" and reference" chambers

RESPONSE:

This paragraph was modified and the definitions were included as stated earlier.

REVIEWER:

p. 27529, line 15: change "considerably" to "considerable" Fig 1: Is the y-axis scale also for O<sub>3</sub> (ppb)?

RESPONSE:

C13843

The y-axis scale is also valid for O<sub>3</sub>. This plot was relabeled on the y-axis with "P(O<sub>3</sub>) (ppbv h<sup>-1</sup>) or O<sub>3</sub> (ppbv)". The x-axis was relabeled with the date instead of the day of the year. Please take a look at the new relabeled plot.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/11/C13831/2012/acpd-11-C13831-2012-supplement.pdf>

---

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 27521, 2011.

C13844

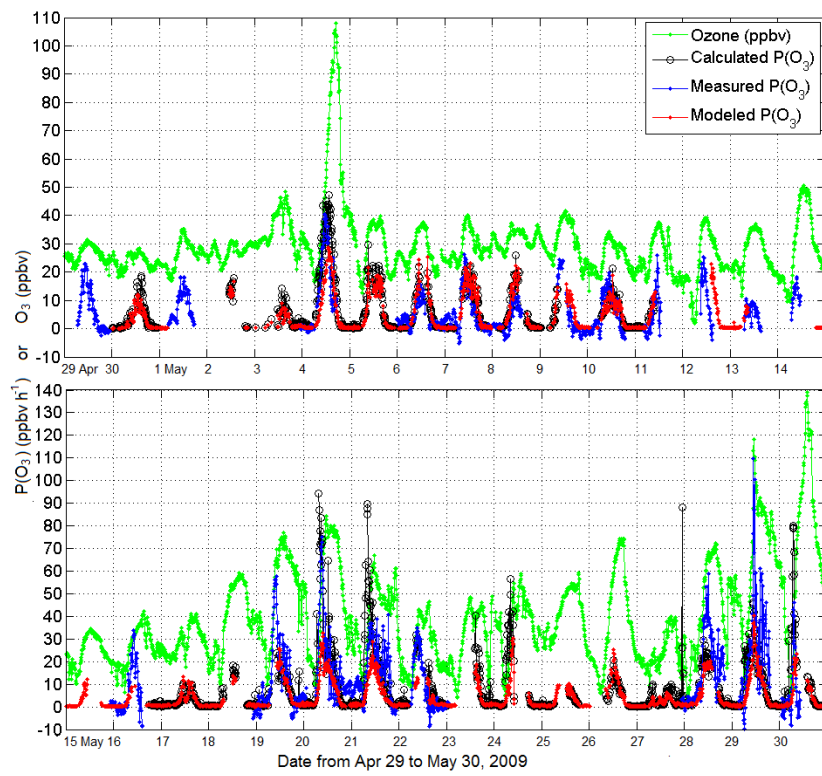


Fig. 1.

C13845