

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

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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:

The paper describes field measurements of a recently developed instrument (MOPS: Penn State Measurement of Ozone Production Sensor) used in a recent study in Houston, USA to derive ozone production rates in ambient air. The results of the ozone production rates of the measurements are compared with “calculated” production rates  
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derived from simultaneous measurements of concentrations of NO and hydroxyl- and hydroperoxyradicals and “modeled” values derived from numerical simulations of the model RACM2. The concept and the results are very interesting. It is not completely clear to me whether the results are unexpected, but I have the feeling that more experiences with the method are required to get a better handling of the uncertainty determination. In my view the paper merits publication if the following comments are carefully considered.

1. Abstract: I am not sure whether I agree with the last sentence: “This difference indicates possible missing radical sources : : .”; I find the combination “indicates and possible” not convincing and I have reservations with the interpretation (see next comment) and therefore I suggest to delete this sentence

RESPONSE:

We agree with the reviewer regarding the need of more evidence to support the hypothesis of missing radical sources in the model. We have discussed more regarding this topic under comments #2, #9 and #11. However, we have performed comparisons between modeled and measured radicals and we have found that for this study the modeled HO<sub>2</sub> is lower than the measured HO<sub>2</sub>. These points have been acknowledged in the abstract by substituting lines 10-16 on pg 27522 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.

REVIEWER:

2. I think LIF measurements allow to quantify simultaneously OH and HO<sub>2</sub> and I suggest to produce plots equivalent to Fig. 3a (and 3b) of Hofzumahaus et al. (2008): I find it only adequate to stress the results of the Pearl River Delta study in the context of this study if the measured OH concentrations very strongly deviate from the modeled OH ones

RESPONSE:

The suggested comparison between measured and modeled radicals is being thoroughly explained in an upcoming paper by Ren et al. We have included results regarding this comparison in the current manuscript in the following paragraph, which has been added to the paper at the end of section 3.2:

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.

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,

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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.

REVIEWER:

3. Introduction, first paragraphs: Lowering Ambient Air Quality Standards: I my view the effects of elevated ozone on human health and ecosystems should be in the center of such a debate rather than how often the standards are violated

4. Page 27524, line 20, Equation (2): First term on the right side, related to HNO<sub>3</sub> production: I don't believe that the term "ozone loss" is appropriate because no ozone is destructed when NO<sub>2</sub> reacts with OH to form HNO<sub>3</sub>: I think you mean that further (net) ozone production by NO<sub>x</sub> is prevented by production of HNO<sub>3</sub>. I think P(RONO<sub>2</sub>) includes PAN formation which is again no "ozone loss".

5. Page 27524, Equation (2) and (3): Is ozone loss by dry deposition (not) considered in your study?

6. Page 27525, line 2: I think the study of Hofzumahaus et al., (2008) refers to a very peculiar receptor site in China and the difference between modeling and measurements is very large at this site (compare comment 2) and therefore I suggest to be careful to stress this case (too much) in the context of this study

RESPONSE:

We agree with these four comments. Emphasizing the impact of ozone in humans and the environment should be at the core of the discussion. We also agree about the production of nitric acid being a true ozone loss only if wet deposition takes place. It is also true that PAN species are reservoir species for RO<sub>2</sub> radicals and NO<sub>2</sub>. In addition, we have clarified in the revised manuscript that the MOPS does not measure the rate of change of ambient ozone, which includes dry deposition or advection. Finally, it is true that the conditions for Hofzumahaus' study are different from the SHARP campaign. In order to address all these points plus some comments from our second referee, we

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have revised the introduction of the manuscript as it is presented below:

## REVISED INTRODUCTION

### 1 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 oxides ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) 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)

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where the time-rate-of-change of measured ambient  $\text{O}_3$  is on the left-hand side of the equation,  $P(\text{O}_3)$  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  $\text{NO}_x$  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 ( $\text{NO}_2$ ) is the only known source of ozone in the daytime. In the absence of hydroperoxyl radical ( $\text{HO}_2$ ) and organic peroxy radicals ( $\text{RO}_2$ ), nitric oxide ( $\text{NO}$ ), nitrogen dioxide ( $\text{NO}_2$ ) and ozone ( $\text{O}_3$ ) achieve photosteady state (PSS) and no new ozone is formed. New ozone is formed via reactions of peroxy radicals ( $\text{HO}_2 + \text{RO}_2$ ) and  $\text{NO}$  to make  $\text{NO}_2$ , which solar ultraviolet light dissociates into  $\text{NO}$  and  $\text{O}$ , with  $\text{O}$  rapidly reacting with  $\text{O}_2$  to make ozone. Peroxy radicals come from reaction sequences that continuously cycle  $\text{OH}$ ,  $\text{HO}_2$ , and  $\text{RO}_2$  radicals; these sequences are fast enough that the steady state of the  $\text{HO}_x$  ( $\text{OH} + \text{HO}_2$ ) species can be assumed. The estimation of the rate of net ozone production,  $P(\text{O}_3)$ , from measurements requires the knowledge of the abundance of peroxy radicals and  $\text{NO}$  present in the ambient air. The instantaneous production of ozone in the troposphere can be represented by the kinetic rate equations:

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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 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

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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 a result, the measured P(O<sub>3</sub>) can be compared to the ozone production rates that are calculated using Eq. 4 and either measured HO<sub>2</sub>, NO, and OH or modeled radicals. A goal is to determine whether the comparison of the MOPS-measured P(O<sub>3</sub>) can be used to distinguish between the ozone production rate calculated from measured HO<sub>2</sub>, which is typically greater than the ozone production rate calculated from modeled HO<sub>2</sub>.

REVIEWER:

7. Page 27527, line 25: I find the term "chemical loss" problematic in the context of this

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study (comp. comment 4)

RESPONSE:

This term has been removed from line 25 leaving only: The production of nitric acid. . .

REVIEWER:

8. Page 27529, line 6, Fig 1: I recommend to use calendar months and days instead if "day of the year" for labeling of time

RESPONSE:

We agree on this suggestion. The change was applied to the revised manuscript. Please look at new Fig. 1.

REVIEWER:

9. I am little worried that the correlation coefficients ( $R^2$ ) between "measured" and "calculated"  $P(O_3)$  (see Fig. 3, b) values are that low without any visible tendency ( $R^2$ : 0.34). Do both measurements measure the same quantity? Are there obvious problems with the measurements used for the determination  $P(O_3)$ ? Obviously the correlation between "modeled" vs. "measured" values are substantially better (though the plot shows a systematic deviation).

RESPONSE:

As stated on page 27534, lines 22-28 of the original manuscript, there are uncertainties in the estimation methods for  $P(O_3)$  and the MOPS measurements that affect the comparison. According with the statistics, the model agreed better with the measurements if the regression  $R^2$  and the RMSE are considered as well as the behavior of the  $P(O_3)$  response with NO. It is also true, however, that the measurements agreed better with the calculated  $P(O_3)$  if the index of agreement and the MBE are considered as well as the magnitude of the  $P(O_3)$ . As stated under comment #2, differences between model and calculated  $P(O_3)$  come from differences between model and measured  $HO_2$ . At

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the same time, two independent measurement-based techniques agree, in particular when ozone production is high. It is possible that there are true differences in the three methods that only more extensive testing and comparison could reveal. Such testing will reveal if biases affect the measurements or if differences with the model point towards missing radical sources or sinks. The revised text introduces all these explanations, as stated under answers to previous comments. In addition, the following parts were modified in the revised manuscript:

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  $P(O_3)$  agrees better with the calculated  $P(O_3)$  or the modeled  $P(O_3)$ . Additional field campaign studies are necessary to draw more conclusive explanations on differences between measurements and calculations.

On line 16, page 27535 suggesting a potential lack of a source of radicals in the model was removed from the text.

The conclusions were revised. Please look at answer to comment # 11.

REVIEWER:

10. Fig. 5: is the plot looking (much) different when using  $NO_x$  instead of NO? Possibly Fig. 5 shows the basic relation of  $P(O_3)$  vs  $NO_x$  as expected from a radical chain reaction system implying that this kinetic system seems to be applicable to the measurements

RESPONSE:

The plots look similar when  $NO+NO_2$  is used on the x-axis, except the values on the x axes correspond to the sum and therefore are larger. The fact that the shape is the same is attributable to the photosteady state. This point was clarified on the revised paper by adding the following sentence to line 3 on page 27535:

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Since NO and NO<sub>2</sub> are in photosteady state, the shape of the curves in Fig. 5 turns out to look the same if P(O<sub>3</sub>) is plotted against NO<sub>x</sub> with the x-axis shifted toward larger values of the sum NO+NO<sub>2</sub>.

REVIEWER:

11. Page, 27537: I think the last sentence is premature (“MOPS measurements of SHARP challenge the understanding of photochemistry”) – unless the authors present more material concerning strong disagreement between OH measurements and photochemical model

RESPONSE:

Following up to what is stated under comments #2 and #11, the conclusions section has been revisited as follows:

Conclusions

The Measurement of Ozone Production Sensor (MOPS) successfully measured the net ozone production rate P(O<sub>3</sub>) during its first field campaign, SHARP in Houston during April/May 2009. Measured P(O<sub>3</sub>) 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<sub>3</sub>) generally occurring on days with higher ambient O<sub>3</sub>. 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<sub>3</sub>) measurement to an air quality model. MOPS measurements of P(O<sub>3</sub>) provide a good check on the differences between calculated P(O<sub>3</sub>), which is based on measured HO<sub>2</sub> and OH, and modeled P(O<sub>3</sub>), 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<sub>3</sub>) peaks in midmorning, later than the calculated P(O<sub>3</sub>) but earlier than the modeled P(O<sub>3</sub>). On the other hand, for NO greater

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than about 10 ppbv, the measured P(O<sub>3</sub>) is only half of the calculated P(O<sub>3</sub>) but is roughly four times the modeled P(O<sub>3</sub>). 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<sub>3</sub>) while other indicate a better agreement between measured and calculated P(O<sub>3</sub>). Hence, it is premature to draw general conclusions from these comparisons, however, some evidence from measured P(O<sub>3</sub>) and HO<sub>2</sub> during the SHARP campaign suggest that the modeled HO<sub>2</sub> is too low.

Providing more conclusive evidence will require greater precision 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<sub>x</sub> 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<sub>3</sub>). 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<sub>2</sub>, and improving air quality regulations.

Please also note the supplement to this comment:

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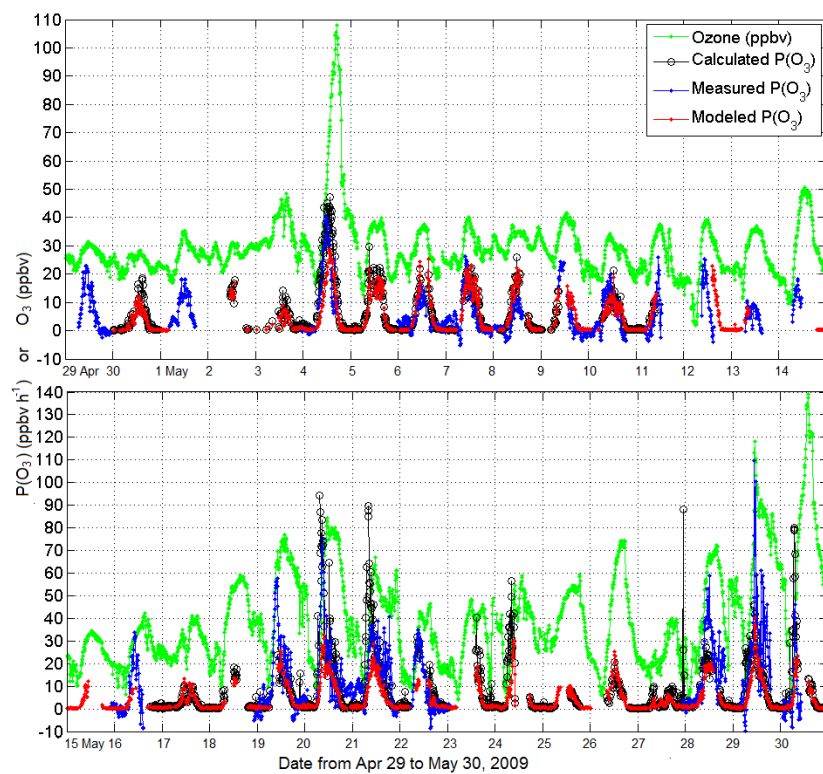


Fig. 1.

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