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Interactive comment on “Investigation of the correlation between odd oxygen and secondary organic aerosol in Mexico City and Houston” by E. C. Wood et al.

E. C. Wood et al.

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We thank reviewer #1 for the comments and suggestions. We are very appreciative of the time that was obviously put in to recreate some of the calculations.

*** This paper presents an analysis of data from Mexico City in 2006 and Houston in 2000. In particular, an examination of the correlation between Ox and SOA is shown, and expectations of the correlation based on Ox and SOA production is given. The authors conclude that $P(\text{SOA})/P(\text{Ox})$ can serve as a test of improved formulations for production of SOA.

Overall, I believe the paper presents a point of view that is consistent with current un-
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derstanding of ozone and SOA chemistry. I would like to see the authors take the analysis further and speculate on the aspects of the problem that would bring the observations and numerical studies into agreement.

I also would like to see some realistic propagation of error estimates for calculated quantities. ***

It is difficult to quantify the uncertainty in the SOA yields given the various and sometimes conflicting laboratory results. Furthermore, the impact of the choice of Mo value is discussed at length on pg 3572 of the ACPD version. We have added the following liberal estimate of the uncertainty to the beginning of section 4.3 ("The discrepancy between models and measurements"):

"We estimate that the uncertainty in $P(\text{SOA})/P(\text{Ox})$ calculated using eq. 11 is at most a factor of three, and dominated by the uncertainty in the SOA yields."

By a "liberal estimate" we mean on the high side. Since the calculations are a factor of 5 to 15 lower than the observations, this level of uncertainty is acceptable.

***** Finally, I believe that some of the derivations should be included in the supplemental material rather than just taken on faith by the reader. ***

A detailed response to this is presented later

***** Page 3551. Near end of last paragraph. It is stated that OOA accounts for 64% to 95% with higher percentages at more rural sites. This implies that OOA might be half of the OA in Mexico City. Was this taken into account? Also, how was OA quantified in these estimate? It appears that OOA was used later in the paper, assuming OOA is approximately equal to OA, but the discussion in the paragraph at the top 3552 calls this assumption into question. ***

We have measurements of both OA (total organic aerosol) and OOA (the oxygenated OA subcomponent) in Mexico City and Houston, and both quantities are discussed in the manuscript. We have reviewed and confirmed that both quantities were used

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appropriately (ie., OA was never mistakenly used for OOA). The discussion on page 3552 presents the current and past OOA measurements in the context of total organic aerosol (OA). The only location where OOA is assumed to be approximately equal to OA is in the reference to Dunlea et al on pg 3577.

***** Page 3552. Second paragraph. The analysis is done for VOCs up to carbon number of 12. But, it is likely that the amount of SOA from larger hydrocarbons is significant. Estimates of the abundance of C13-C20 species should be made and their impact assessed. This includes estimating the abundance of products from these species that might be further oxidized (e.g. C13-C20 aldehydes and ketones). Together these could be very important since although their concentrations are decreasing with carbon number, the SOA yields are increasing. The last part of the paragraph is very good – if this could be done it would be a big boon for understanding this chemistry. ***

We agree this is important, but believe that such an analysis would go beyond the scope of the paper. We have done the calculations for measured VOCs (up to carbon number 12) and also for VOCs emitted by gasoline and diesel vehicles. To account for all secondary chemistry of all species would turn this into more of a modeling paper.

***** Page 3556. The FPEAK parameter has not been defined in this paper. It should be at least briefly described. ***

This has been clarified in the text:

"PMF solutions are not necessarily unique particularly with respect to rotations (i.e. linear transformations of the factor time series and mass spectra). The rotational ambiguity of solutions in PMF can be explored with the FPEAK parameter (Ulbrich et al. 2009). The central solution obtained with PMF corresponds to an FPEAK value of 0. Qualitatively, when compared with the FPEAK=0 solution, negative FPEAK values result in factor mass spectra that differ more and factor time series that are more similar. The opposite is observed when comparing solutions from positive FPEAK values with FPEAK=0 solutions (Ulbrich et al. 2009). For the La Porte AMS dataset the PMF

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solution obtained with..."

***** Page 3557. The statement that "correlation of OOA with the secondary species Ox and NOz suggest its use as a proxy for SOA is appropriate" is not really justified. If the authors wish to demonstrate that the abundance of OOA is proportional to SOA, perhaps they could do this. It has not been done in this version, as I read it. ***

We agree that that it is a poorly justified statement and it has been removed in the revision.

***** Page 3558. Near the bottom. So linear regressions were performed on the OOA vs Ox scatter plots to obtain slopes. How were the regressions done – standard least squares (likely not appropriate) or some distance minimization technique? What are the uncertainties in the derived slopes? What are the uncertainties in the individual OOA and Ox values? And at what confidence level (1 sigma, 95%, etc.). ***

A linear regression technique that accounts for errors in both variables was used; this and the uncertainties are clarified in the text.

***** Page 3559. Near the top. It is stated that NO2 accounted for a significant fraction of Ox, but this isn't apparent in Figures 1 and 2. Perhaps state the range and average values of the fraction. Do the slopes derived depend on NO2/Ox? ***

The last 2 sentences of section 3.1 now read as follows:

"OOA and O3 (rather than Ox) are not as well correlated since NO2 can account for a variable and sometimes large portion of Ox. At PTP, NO2 accounted for 20% to 50% of Ox during the morning and usually less than 10% during the rest of the day. "

The dependence of the slopes on the partitioning of Ox (O3 vs NO2) is a bit complicated. The OOA/Ox slopes are variable, and are frequently higher in the morning (when NO2/Ox is highest) than in the afternoon (low NO2/Ox) as discussed in the text. But correlation, of course, does not imply causation. This question would best be investigated with the T0 data (where NO2/Ox is often 80-100% in the morning).

*** ** Page 3560. It is stated that the air in the residual layer appears to highly aged. I suppose this is a relative statement, since it probably not as aged as air transport over the Gulf of Mexico. In any case, aged air likely contains a higher abundance of VOC oxidation products than fresh, making the analyses performed in this paper even more uncertain. ***

We agree that “aged” is a relative term, but don’t agree that this adds considerable uncertainty to the analysis. It is not always true that the aged air has higher concentrations of VOC oxidation products, since aged air has also undergone much dilution (mixing with other air masses). In fact, acetone and acetaldehyde were always lowest at night at PTP (when the air observed was above the mixing layer). No change to text required.

Page 3561. Paragraph below 4.1 label. Here the assumptions of this analysis are stated: long lifetimes of Ox and SOA, both are formed from VOC oxidation (yes, but. . .). Thus “it is reasonable to expect” that their concentrations should be correlated. When I first read this statement, it seemed sensible. After some thought and calculations, I am now not so sure. Some “VOCs” as defined (which includes CO, CH₂O, as well as alkanes, alkenes and aromatics) produce O₃ but not SOA, whereas other VOCs produce both O₃ and SOA. This means that correlation Ox and SOA is simply showing correlation between the VOCs that make O₃ and the VOCs that make SOA. I took individual PSOA and POx values, such as shown in Tables SI-2 and SI-3, and found that they are almost uncorrelated ($R^2 = 0.062$ for one case). This explains at least in part, I think, why there are widely varying values for PSOA/POx. *** We agree, and have rewritten that sentence as follows:

“Since Ox is also formed as a by-product of VOC oxidation and both SOA and Ox have long lifetimes (>12 hrs), it is tempting to expect that SOA and Ox concentrations should be correlated to some extent.”

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Later in the manuscript it is explained that O₃ and SOA have different precursors as discussed in the comment above (e.g. pg 3578 of ACPD version - “A high degree of correlation does not necessarily indicate that the formation mechanisms of OOA and Ox are actually correlated.”)

Page 3562. Equations (8) and (9). The “alternative formulation” for P(O_x) is shown without reference or derivation. I suggest adding one or more references here, and performing a derivation in the supplemental material. ***

This equation has been well-described in the literature. We have added references to Kleinman et al. 2005 and Rosen et al 2004.

The equality of these two formulations involves some assumptions that are not readily apparent, and have not been explicitly stated in this paper. Some simplifying assumptions are discussed at end of this page and the top of 3563. One is the assumption that HO₂ only reacts with NO. It would be good to give some range of NO values observed, and give a percentage of HO₂ reacting with NO versus other processes (HO₂+HO₂, HO₂+RO₂, possible HO₂ loss on aerosols).

Information has been added to the Supporting Information that quantifies these reaction pathways using available HO₂ and NO measurements.

***** Page 3563. There is a discussion of how F is determined. I infer, but it is not explicitly stated, that the value of F for each species is the average of the F for each of the peroxy radicals formed. This should be added to the text. ***

The following text has been added to section 4.2 in order to clarify::

“F is equivalent to the term $(1-\alpha)$ used by Rosen et al. (2004) where α is the yield for alkyl nitrate formation” *****

From the F values in Table SI-1, I infer that HO₂+NO is greater than 99% of the HO₂

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loss, and that peroxy nitrate formation is unimportant (CH₃CHO value for F is 1). The latter is in contrast with the observation of significant fraction of NO_y as PAN measured on the C-130. ***

The following text has been added to section 4.2:

“Lowering the F values for acetaldehyde and acetone (to account for net formation of peroxyacetyl nitrates) to 0.8 leads to calculated values of P(OOA)/P(Ox) that are at most 10% higher than the base case calculations” *****

At the end of the page, the problems with the Yi values are mentioned. How much does the uncertainty in these issues affect the calculated P(SOA)? ***

See earlier response regarding the overall uncertainty analysis (estimate that the uncertainty of the calculations is a factor of 3) *****

Page 3564. The ratio in equation (11) can be calculated with the measured VOCs, but it is known that all of the VOCs are not observed. Attempts should be made to estimate the abundance of species not measured and to assess their impact on the calculated ratios. ***

See above (“pg 3552 comment”) for response. *****

It is also stated (correctly) that P(SOA)/P(Ox) is not the same as [OOA]/[Ox]. It is stated that if the production rates do not change with time and if the losses are not significant, then the two ratios should “mirror” each other. Further caveats are listed (absolute Ox and SOA are not predicted). It is stated then that P(SOA)/P(Ox) comparison with $\Delta[\text{OOA}]/\Delta[\text{Ox}]$ “serves as a useful test of our general understanding”. I do not disagree with this statement, but later in the paper quantitative conclusions are drawn from the comparison rather than tests of general understanding. I suggest making the assumptions here a bit more quantitative. For a generic species, X, the time rate of change is related to production and loss rates (neglecting transport): $d[X]/dt = P(X) - L(X)[X]$ if $L(X)[X]$ is small compared to $P(X)$, then $d[X] = P(X) dt$ then if $P(X)$ is time

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invariant over the period of observation, $[X_t] - [X_0] = P(X) t$ So, $[X_t] = P(X)t + [X_0]$ Or if $P(X)$ does change, the equation describes the average $P(X)$ over the time period. This means that $\delta[X_t]$ depends on $\delta(P(X)t+[X_0])$ which depends on $\delta(P(X))$, $\delta(t)$, and/or $\delta([X_0])$. The ratio of two species (such as performed in this paper) is: $\delta[X_t]/\delta[Y_t] = \delta\{P(X)t+[X_0]\}/\delta\{P(Y)t+[Y_0]\}$ For $\delta[X_t]/\delta[Y_t]$ to be proportional to $\delta\{P(X)\}/\delta\{P(Y)\}$, $\delta[X_0]$ and $\delta[Y_0]$ must be small. We know that the concentration within the basin changes during the day as a result of boundary layer growth and decay, so it appears that this assumption is not met. Equality between the ratio in the change in concentrations and the ratio in the change in production rates appears to be only valid if $[X_0]$ and $[Y_0]$ are either very small or known. This doesn't appear to be the case in this analysis. Alternatively, the ratios are comparable and the caveats given by the authors are unfounded. Either way, clarification is needed. ***

We agree these are good points, and have added similar equations and revised the text (addressing the background values of OOA and Ox, equal to X_0 and Y_0 in the comments above) in section 4.1. We have also noted that the dilution caused by the rising boundary layer can alter the OOA/Ox ratios, this is discussed in section 4.5 of the revision.

Page 3564 and 3465. Giving the reader quantitative information about the relative rates of various processes (in this case Ox production and loss) is very valuable. I suggest doing more of this. The impact of aerosol evaporation and wet and dry deposition, as well as heterogeneous oxidation on measured [SOA] are considered. Perhaps other sources of uncertainty in the observed and calculated should be considered. ***

We believe we have covered the most important sources of uncertainty, though would be willing to address any additional specific concerns.

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Page 3566. Paragraph below 4.2. Impacts of changing a, kOH and F values on calculated P(SOA)/POx are considered. It is concluded that the uncertainties have small effects on the ratio. The small impact due to kOH makes sense, since the values are in the numerator and denominator. Actually it seems that it should make no difference, since: $\frac{2ki[VOCi]yi}{2_ki[VOCi]yi} = \frac{2_ki[VOCi]yi}{2_ki[VOCi]yi} = 1$

The sentence is “doubling or halving the estimates for a and kOH changes the calculated ratios by less than 10%.” If all k values are doubled then agreed, this has no effect. But if the ka values for some (but not all) compounds are doubled, this will change the ratio. The following text has been added to the revision to clarify:

We note that the VOCs that account for over 80% of calculated P(Ox) have a, kOH, and F values available in the literature. *****

The other quantities (a and F) should have a larger impact than stated. Doubling all “a” values should reduce the ratio a factor of 2. *** See above response.

***** Similarly, changing all F values between 0.7 and 1 should change the ratio by 43% (1-1/0.7). ***

Same response as above. Also, uncertainty in F does not matter unless the kOH and concentration values actually make those VOCs important. *****

The rest of this page and part of the next discuss the Yi values, but it is not stated that the P(SOA)/P(Ox) ratios are directly proportional to these values. In other words, if all Yi values are doubled, it results in a doubling of the ratio. I suggest taking a closer look at the dependence of the ratio on the uncertainties in the input parameters. Also, many of the yields in Table SI-1 are listed as 0% or very small values. How large could these small and zero values be and still be consistent with the laboratory measurements?

*** These (at times) small values were obtained from laboratory measurements! This

is stated at length in the second paragraph of section 4.2. *****

What would happen if all the zero yields were set to 0.1% or some similar small value? What are the uncertainties in the VOC concentrations?

*** With the exception of the value of zero used for the SOA yield for CO oxidation (which is exactly 0.0), all yields that appear as 0 in table SI-1 actually have finite values but have been rounded to the nearest 0.1% for the table. This has been clarified in the caption. The uncertainties in the VOC measurements have been added to the text.

Page 3567. Below equation (12). Alkanes with 22 carbons are described, but are chains this long used in the calculations? Indeed, Table SI-1 (and the others supplemental tables) indicate that not all species are listed. Somewhere please indicate which species are considered in the calculation. This can be done by class rather than listing each individual species. At the end of this page and the top of the next, quantitative comparison ("almost an order of magnitude lower") is made between $P(\text{SOA})/P(\text{Ox})$ and $[\text{OOA}]/[\text{Ox}]$ in spite of the earlier caveats. This needs to be justified in detail. This is the weakest part of this paper – jumping from caution to comparison without discussion and careful justification. ***

The revised SI more clearly indicates which VOCs were used for all calculations. We would not describe the text as a "jump" from caution to comparison. The fact that $P(\text{SOA})/P(\text{O}_3)$ does not equal SOA/O_3 does not mean that we cannot compare the 2 quantities – as long as the proper discussion of caveats is included. With the expanded discussion of the growth of the boundary layer and the OOA and Ox values that mix into the BL, we believe that this comparison is sound.

***** I would like to see an estimate of including SOA formation due to oxidation of VOCs by O_3 and NO_3 . It may be small, according to current understanding, but a statement justifying leaving it out of the calculations is needed. ***

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As suspected it is usually a small calculated effect, in agreement with the reviewer's assessment presented below. The following text has been added:

section 4.2: "SOA formation from the oxidation of VOCs by O₃ and NO₃ is disregarded in these calculations but can be included by substituting the relevant analogous quantities (e.g., VOC + O₃ rate constants, O₃ concentrations, and SOA yields from ozonolysis reactions) in eq. 10. The product of these three terms is only competitive with OH reactions for biogenic VOCs."

end of section 4.2:

"[O₃] was near zero due to the high NO concentration, and we can deduce that [NO₃] was near zero as well. Thus SOA formation from reactions of organic compounds with O₃ and NO₃ was negligible."

and

"Ozonolysis was not included in the calculations depicted in fig. 7. We calculate that the contribution to SOA formation from ozonolysis of isoprene, α -pinene, and limonene is comparable to that from OH reactions."

The discussion of differences between the calculated and observed ratios seems irrelevant given the incorrect assumption that they should be quantitatively comparable (unless I am missing something). At a minimum, some uncertainties for the observed ratios should be given.

*** As discussed earlier, discussion of the comparison between P(SOA)/P(O_x) and [OOA]/[O_x] has been improved. Even given the caveats of the comparison, to ignore the information contained in [OOA]/[O_x] (ie, integrated P(SOA)/integrated P(O_x)) because they are not exactly equivalent does not make use of all available information.

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Page 3572. I do not understand the statement (made here for the second time) that using the observed Mo results in an upper limit for SOA, and I also do not understand the relevance to a 3-D model. As I understand it, nothing in this analysis had anything to do with a 3-D model. The statement seems strange to me and perhaps needs some clarification. ***

The following sentence has been inserted to clarify (existing sentence included below as well):

“We note that the calculations of P(SOA)/P(Ox) described here use measurements of OOA itself, an “advantage” that a 3-D predictive model would not have. If a model tends to underpredict SOA, using the measured Mo rather than a model calculation of this quantity results in an upper limit of the calculated SOA (Dzepina et al., 2009).”

The 2nd mention of this (pg 3572 of the ACPD paper) has been deleted since it was redundant and possibly confusing. *****

Page 3573. It is stated that oxidation of POA is another source of OOA that is not included. Can you estimate what the magnitude of its impact?

The following text (w/ reference) has been added to that sentence:

“ though likely a minor one (Zhang et al., 2007)” *****

Page 3573 (bottom) and 3574. This discussion of missing VOCs is good. Of course, it is not the degree of discrepancy, but the product of the concentration of the missing species times their OH rate coefficient times their SOA yield that would help increase P(SOA). The OH reactivity could have relatively small differences, but P(SOA) from those missing species could be large. ***

see response below. *****

Page 3582. Last sentence of manuscript (before Acknowledgement). The authors recognize that the reactivities of SOA and O₃ forming precursors are different. This

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recognition should be incorporated into the paper. For this reviewer to better understand the calculations presented in this paper, I performed some calculations using an augmented version of Tables SI-1 and SI-2, as well as a simplified calculation with 4 species. I present these calculations to help the authors understand my quandary with this paper. I was able to reproduce the values for P(SOA)/P(O_x) presented in the paper. I also added reactions of alkenes with ozone and reactions of NO₃ radicals. It appears to me that these probably don't make a huge difference unless the SOA yields are much higher than the corresponding yields from the OH reactions. Addition of small yields from alkene oxidation increases the ratio. Addition of large alkanes at 10 ppbv total concentration and 20% average yield increases the ratio significantly (up to about 120). Are these estimates within the uncertainty of field observation and laboratory studies? That is what the authors need to include in this paper. A simple model with 4 species (CH₄, CO, VOC1 and VOC2) is instructive to understand the dynamics of the problem. The first three species generate Ox but not SOA according to their concentrations, k_{OH}, and F values. The fourth species generates Ox and SOA. I assumed an [OH] of 1E6 so that absolute rates can be calculated. For "background-like" conditions (CH₄=2000, CO=200, VOC1=1, VOC2=1 ppbv), the P(SOA)/P(O_x) ratios is 38. Increasing the CO to 2500 (like MC) reduces the ratio to 5. Obviously, increasing VOC2 increase P(SOA) and the ratio. After exploring a range of conditions, I noticed that the ratio correlated strongly with the fraction of OH that reacts with VOC2. There are slight differences in the ratio changing the relative amounts of CO and VOC1, but overall large ratios such as observed in this study (160 ug/m³/ppmv) are only possible if VOCs with reasonably high (10 percent) SOA yields are the primary reactants for OH (>90%).

If the yields are smaller, then the fraction of the OH reactivity needs to be even higher to get large ratios. There are maximum values the ratio can be. For standard CH₄ and CO (1800 and 100 respectively), if Y(VOC2) is 1%, then P(SOA)/P(O_x) cannot be larger than about 18. The maximum scales with the yield assumed. The value of P(SOA)/P(O_x) scales with the fraction of OH that reacts with VOC2, but not linearly. I



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found a quadratic that is concave down fit the data pretty well (Figure R1). Calculations such as these might be useful to the reader to better understand this system. It also appears to me that the P(SOA)/P(O_x) ratio doesn't say so much about the mechanism of SOA formation as the relative reactivity of the SOA precursors and their SOA yields. It does seem to indicate that there are atmospheric species with relatively large SOA yields that are not being accounted for. It might be useful to include the fraction of OH reactivity due to SOA forming species in the calculations in this paper. Regarding the derivation of the formulas in equations 8-11, I found that it must be assumed that HO₂+HO₂, HO₂+RO₂ are insignificant peroxy radical sinks, and that photolysis of VOCs are insignificant peroxy radical sources (this was discussed in the paper) for the derivation of P(O_x). I must admit less familiarity with SOA formation, including the use of equation (12), but the calculations shown appear to be correct. In summary, I think this is a good paper, but needs some clarification in a few areas. I hope the authors can do this to make it better understood by the readers.

***** This is a very interesting way of looking at the analysis and we are grateful for the insight. We have considered this and added a text to the end of section 4.4 addressing some of these issues, with a more quantitative discussion in the SI. In short, the fact that the measured OH reactivity and that calculated using VOC measurements agree (to within ~20%) constrains the product of the missing SOA precursors' molecular weight and SOA yield. We note that the molecular weight of VOC1 and VOC2 used in the reviewer's example above is not specified; this is a key parameter since a very high MW VOC need not have a high SOA yield to produce a large amount of SOA. We find that the product MW(missing) x Y(missing) ~ 16, as discussed in the revision.

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