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 #2 for the comments, and have addressed comments below:

This reviewer would like some clarification about the inclusion or otherwise of larger (C>12) hydrocarbons. It would be good to state more clearly which VOCs are included in the analysis (say at the start of Section 4.2, or included as a Table), given that there is some inconsistency about the range of carbon numbers measured and considered from the Texas data and that Table SI-1 does not list all VOCs used. On Page 3567 (very top) it is stated that PAHs are assumed to be 'high-yield', and long-chain oxygenated organics are also mentioned. But these species are not measured. Are they

included in the analysis of the Texas and PTP data? And if not, it would be good to have some discussion earlier in the paper about the implications of their omission, given that P(SOA) increases rapidly with increasing carbon number. Both ki and yi increase with increasing carbon number, Equation 10, but this is not discussed until pg 3580!. ***

As requested by reviewer #1 as well, the SI has clarified which VOC measurements are used. The PAHs and long-chain oxygenated organics are only important for the gasoline and diesel emission calculations. *****

Why is a value for Mo of 5ug.m-3 for the absorbing particle phase used instead of the actual measured OOA mass concentration? This could be explained more clearly (pgs 3566-7, 3572). This reviewer is left wondering whether the intent is to be able to duplicate 3-D model calculations (pg 3572, line 12) which underestimate Mo. ***

Actually 2 values for Mo were used: 1) the actual time-varying OOA value, and 2) a fixed value, somewhat arbitrarily set to 5. This has been clarified in section 4.2 (pg 3566 of the ACPD version):

"...the yields for each half-hour average P(SOA)/P(Ox) calculation are based on the ambient temperature and mass concentration of the absorbing particle phase (Mo, set equal to [OOA]) at the time of the VOC measurements. ... a second set of calculations was performed with Mo set constant to a value of 5 μg/m3 for comparison."

***** Pg 3556: The authors reapportion the BBOA, and use smaller values for HOA than in Herndon '08. What are the implications of this for OOA? Please explain. Is this why the red points in Fig 3 show greater OOA values than reported in Herndon '08? ***

The following text has been added to the revision:

"In the absence of biomass burning plumes, the OOA values used in this analysis are typically about 0.4 μg/m3 lower than those used by Herndon et al. (2008), but the OOA/Ox slopes in this analysis differ from those reported by Herndon et al. (2008) by

less than 20%. Note also that the aerosol mass loadings (μg/m3) shown in Herndon et al. (2008) were expressed at ambient conditions while in this work the mass loadings for all datasets are converted to standard temperature and pressure (273 K, 1 atm) in order to facilitate comparison."

The last sentence was moved from its original location at the end of section 2.

***** Pg 3558, last 2 lines: Please give R values or refer to a figure to support the 'good' correlations between OOA and Ox & NOz. Please explain the reasoning leading to the conclusion that the correlation supports the use of OOA as a proxy for SOA. Surely the subset of reactants leading to the formation of OOA and SOA is different from (and smaller than) that leading to gaseous species (Herndon '08), and the correlations can also arise from meteorology (current work, pg 3578)? Also, this reviewer had been under the (perhaps naive) impression that OOA was already widely viewed as a reasonable surrogate for SOA. It would be good to explain the assumptions involved in this approximation, since apparently it still needs supporting. ***

That sentence (on the correlation between OOA, Ox, and NOz) has been removed. The use of OOA as a proxy for SOA was already discussed in the penultimate paragraph of section 1. *****

Pg 3563: Equation 10 relies on lab-determined SOA formation yields Yi. Some possible shortcomings of this approach were mentioned in the Introduction (e.g. failure to account for synergistic gas- or particle-phase interactions between species). It would be worth briefly discussing in section 4.1.2. the influence of these shortcomings on the P(SOA) calculations. This may be the crux of the observed disagreement. ***

Missing syngerstic interactions in lab studies would likely lead to underestimates of SOA yields. The following sentence has been edited in section 4.3:

"Although these yields are a function of several parameters such as [NOx] and existing gas-phase and aerosol concentrations, and though synergistic interactions between

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various compounds not captured by laboratory studies could lead to underestimates, increases by a factor of 10 are unlikely."

***** This reviewer suggests moving the first half of Section 4.5 (dealing with delta-OOA/Delta-Ox) to the end of Section 3, and the second half (dealing with P-SOA/P-Ox) to the end of section 4.2, as that sequence might make more sense to the reader and allow for some shortening of the text.

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Section 4.2 focuses on the P(SOA)/P(Ox) calculations using VOC measurements, while section 4.5 addresses the observed changes in the ratio of concentrations ([OOA]/[Ox] and [SV-OOA]/[Ox]) and not production-rate ratios. We suspect most readers would become confused if these different quantities were not kept separate as they currently are (though we acknowledge that the 1st paragraph of section 4.5 does describe past measurements). We have not changed the text.

***** Fig 3: It would be helpful to include the research flight number either in the caption or the key, since the flights are referred to by number in the text. ***

The research flight numbers have been added to the caption.

***** Figs 7 and 8: if the pie charts are not shown to scale, what is the significance of their different sizes? Please explain.

*** The following text was added to the caption to explain: "...(i.e., since absolute P(Ox) and P(SOA) rates depend on [OH], the sizes of the La Porte and Mexico City pie charts should not be compared quantitatively)"

***** Minor Points: pg 3551,ln18: please briefly define the 'EC-tracer method'

*** The following words were added to that sentence: "which is based on the ratio of organic aerosol to elemental carbon"

***** pg 3551, ln13: Is there true disagreement about the relative importance of the

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SOA precursors, or might it be more accurate to say that the relative importances vary according to location and season? ***

While the relative importances of course do vary with location and season, there is also genuine disagreement over the relative sources even after controlling for those 2 parameters. We have not changed the text. *****

Very Minor Points: Pg 3566, ln 6: do you mean Eq (11)? (No Eq 16 has been presented) *** yes; corrected. ***** Pg 3571, ln 23: is this Ng 2007 a or b? *** b; corrected.

***** Pg 3578, ln 24: maybe you mean Fig 3?***

Yes; corrected.

*** The use of /g or g-1 should be made consistent. For the revision, negative exponents are only used for the units of OOA/Ox (ug m-3/ppmv) – this is to emphasize that it is a mass loading (numerator) divided by a mixing ratio (denominator). *****

References in text but not in list: de Gouw (2008), Nemitz (2008) *** This has been corrected.

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