

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.

Anonymous Referee #2

Received and published: 17 April 2010

This paper deals with observations of oxygenated organic aerosol (used as a surrogate for secondary organic aerosol) and odd-oxygen (the sum of ozone and NO_x) in Mexico City and Houston, both areas with strong ozone production, but with different VOC mixtures and therefore different SOA formation rates. The observations are largely previously published, however the current work reinterprets them and performs a more detailed analysis of the relationships between the measurements, in an attempt to better understand whether Ox production rates might be used to empirically predict SOA. As in many previous studies, the authors are forced to conclude that traditional descriptions of SOA formation are inadequate, however the current study does provide valuable insights, including: 1) the ratio of SOA production to Ox production will de-

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pend on the composition of the local fuel mixture; 2) the relationship between the two production rates varies during the day. This change is attributed to differences between the reactivity and emission profile of the sets of precursors for SOA and for Ox. The paper is generally very clearly written. It is long, but perhaps this is unavoidable. It would benefit from some clarifications, listed 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 k_i and y_i increase with increasing carbon number, Equation 10, but this is not discussed until pg 3580!

Why is a value for M_o of 5 $\mu\text{g}\cdot\text{cm}^{-3}$ 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 M_o .

Pg 3556: The authors reappportion 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?

Pg 3558, last 2 lines: Please give R values or refer to a figure to support the 'good' correlations between OOA and Ox & NO_z. 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

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(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.

Pg 3563: Equation 10 relies on lab-determined SOA formation yields Y_i . 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.

This reviewer suggests moving the first half of Section 4.5 (dealing with Δ -OOA/ Δ -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.

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.

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

Minor Points:

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

pg 3551, ln13: Is there true disagreement about the relative importance of the SOA precursors, or might it be more accurate to say that the relative importances vary according to location and season?

Very Minor Points:

Pg 3566, ln 6: do you mean Eq (11)? (No Eq 16 has been presented)

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Pg 3571, ln 23: is this Ng 2007 a or b?

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

The use of /g or g-1 should be made consistent.

References in text but not in list: de Gouw (2008), Nemitz (2008)

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 3547, 2010.

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