



Interactive comment on “Characterization of aerosol photooxidation flow reactors: heterogeneous oxidation, secondary organic aerosol formation and cloud condensation nuclei activity measurements” by A. T. Lambe et al.

Anonymous Referee #1

Received and published: 4 January 2011

General Comments:

This paper presents an extensive side-by-side comparison of two aerosol oxidation flow tubes: the Toronto Photo-Oxidation Tube (TPOT) and Potential Aerosol Mass (PAM) reactor. The authors systemically explore how OH reactions in each flow tube influence various aerosol properties: SOA yield, CCN activity, elemental composition, etc. The authors do an excellent job showing the differences in performance of these two systems and show some very nice comparisons with the Caltech Smog chamber. The

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paper is well written, the measurements appear to be carefully made and the content is well within the scope of Atmos. Meas. Tech. I would ask the authors however, to give some careful thought to the technical issues outlined below.

In my mind the unfortunate complexity, which is clearly described in this study, is the broad somewhat complex residence time distribution (RTD) for these reactors. As the authors clearly show, both flow tubes do not have RTD's that resemble plug or laminar flow reactors. In fact the overall form of the RTD's more closely resemble a continuous flow stirred tank reactor (CFSTR) or a PFR with significant dead zones (long tail), bypass or channeling flows (Folger 2010). Are the authors sure that these reactors are not inadvertently behaving as CFSTR's and as a result subsequent analysis should utilize flow equations for this reactor type?

In any case, it seems as the RTD's introduce many uncertainties since particles or gas phase species exiting the flow tube will have sampled a broad distribution of oxidizing environments. This could impact for example, how the OH exposure axis is determined. The authors need to provide more details about how OH exposure was computed using SO₂. Was this a relative rate measurement or a one time calibration? What is the major sink for OH in the flow tubes for each experiment? Walls? Particles? VOC's etc.? At what residence time was the decay of SO₂ measured? What kinetic modeling is necessary to extract an OH exposure, do the authors need to know wall losses since SO₂ is the most sticky of gases used in these experiments? Given the anomalous behavior of SO₂ (relative to CO₂) in the flow tubes, this gas seems like a poor choice for determining OH. Nevertheless, the authors need to show that extracting an OH exposure from reactors that do not behave as idealized plug flow, batch or continuous flow stirred tank (CFSTR) reactors is reliable. For example, Che et al. (2009) worked out the mathematical framework for quantifying OH in a CFSTR. In this case, rate coefficients measured in a CFSTR using a relative rate technique but analyzed assuming a reaction in a PFR, which neglects flow dynamics of a CFSTR, would yield incorrect results.

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The authors need to discuss as much as possible how having a distribution of aging times might impact their results. For example, in an ideal PFR reactor every BES or SOA particle has the same age. Would the CCN properties or O/C of an aged BES particle from a PFR be the same as the average of the distribution of aged particles from the PAM or TPOT? One could image that somehow particles at the tail end of the RTD (highly oxidized) might disproportionately contribute to O/C or CCN activity?

In general, I agree with the authors when they say, in the conclusion section, developing reactors that have well behaved and mathematically tractable flow dynamics could be a better option for investigating both heterogeneous and gas to particle oxidation reactions.

Specific Comments

1. For SOA yield, how was the precursor gas concentration reacted determined (pinene, xylene)?
2. Why is the measured O/C for BES so inaccurate (measured = 0.04 vs. expected = 0.15). Is this a simple linear offset? Can the trend of O/C with OH exposure be corrected by this simple offset?
3. The term “Convection currents” used throughout the manuscript suggest thermal gradients in the flow tubes? Have these been measured? Would convection currents vs. dead volume impact the RTD is distinctly different ways? What is the average temperature of the gas exiting the TPOT and PAM?
4. Fig 2 and Fig 3 captions are incorrect (they are reversed)
5. The authors should show H/C ratios as well as O/C ratios for each system. This gives a more complete picture of the elemental composition of the particles?
6. Page 5214 line 10. References to flow tube studies of organic particles needs to be expanded to accurately represent the larger number of groups conducting these kinds of studies. For example,

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1. D. L. Che, J. D. Smith, S. R. Leone, M. Ahmed and K. R. Wilson, Physical Chemistry Chemical Physics, 2009, 11, 7885-7895. 2. H.S. Fogler, Elements of Chemical Reaction Engineering., 4th edition Prentice Hall.

Interactive comment on Atmos. Meas. Tech. Discuss., 3, 5211, 2010.

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3, C2392–C2395, 2011

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