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Comment

## ***Interactive comment on “Anthropogenic influence on biogenic secondary organic aerosol” by C. R. Hoyle et al.***

**Anonymous Referee #2**

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This manuscript reviews evidence for anthropogenic enhancement of SOA formed from biogenic VOC emissions from field studies, discusses potential mechanism proposed by smog chamber work, and proposes a methodology to quantify its contribution to ambient SOA. This is an important area of study, since the ability to control particulate matter requires knowledge of the quantitative dependence of BSOA formation on anthropogenic activities. However, it is not clear from the current form of the manuscript what the objective of the paper is. Since the manuscript presents no new data or results, it is essentially a review paper. The results from other studies summarized here do not completely reflect the current understanding of BVOC oxidation systems (see detailed comment below). The authors assert that "[a] major objective of this paper is to propose a methodology for separating OA into the fractions identified above" (pg. 19531; the fractions include natural and anthropogenically-enhanced BSOC). Unfortu-

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nately, the remainder of the manuscript proceeds to describe radiocarbon and OC/EC ratio analysis, two techniques which have been used often in the past and are therefore review not new. The modeling approach was proposed but not implemented, and this is a major weakness in this manuscript. I recommend reworking this as a review paper, removing the claims that anything new is being presented, and improving the figures (see detailed comments below).

Detailed comments:

Section 2.2.1 While the authors stress the importance of nighttime chemistry of BVOCs as the focus of future studies, I would like to add that nighttime chemistry of monoterpenes are especially important. It is worthy to note that monoterpene emissions are only weakly dependent on available sunlight (while temperature dependence is strong). This means that the reaction of monoterpenes with  $\text{NO}_3$  could represent a larger source of oxidized hydrocarbons than other BVOCs.

Section 2.2.2 The  $\text{NO}_x$  dependence of SOA yields is nicely summarized here. However, as Dr. Surratt pointed out in his short comment, there has been new understanding of the  $\text{NO}_x$  effect on SOA formation from isoprene, and possibly other conjugated dienes (such as myrcene, ocimene). The importance of PAN-type compounds as an SOA intermediate could imply that at high  $\text{NO}_2/\text{NO}$  ratios, SOA formation could be even more efficient than under pristine (low  $\text{NO}_x$ ) conditions. This effect observed in chamber studies should be verified by field measurements, because this could represent an important enhancement on BSOA by anthropogenic  $\text{NO}_2$ . Future models should calculate the contribution of isoprene to SOA formation directly from MPAN, instead of parameterization using indirect proxies like  $\text{NO}_2/\text{NO}$  ratio.

Pg. 19524 Section 2.2.2 lines 7-14 Using initial VOC/ $\text{NO}_x$  ratio is only a proxy for the branching ratio between  $\text{RO}_2+\text{NO}$  and  $\text{RO}_2+\text{HO}_2$  reactions, and can be misleading. In experiments by Dommen et al. (2006), no OH precursor was used and  $\text{HO}_2$  is generated from alkoxy radical +  $\text{O}_2$ . In experiments by Kroll et al. (2006),  $\text{OH}+\text{H}_2\text{O}_2$

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provides a much stronger source of HO<sub>2</sub>. As a result, even at the same initial VOC/NO<sub>x</sub> ratio, the HO<sub>2</sub>/NO ratio, which truly governs the branching ratio between RO<sub>2</sub>+NO (high NO<sub>x</sub> low yield) and RO<sub>2</sub>+HO<sub>2</sub> (low NO<sub>x</sub> high yield), is much higher in Kroll et al. (2006). Therefore, SOA yields between the two studies should not be compared using VOC/NO<sub>x</sub> as a parameter.

Pg. 19525 line 20-21 The reverse of the NO<sub>x</sub> effect seen in sesquiterpenes is attributed to higher yield of sesquiterpene nitrates (as higher carbon number allow for more efficient isomerization) and lower yield of decomposition products, not just lower volatility of sesquiterpene nitrates.

Section 2.4 Can the authors discuss the role of amines in new particle formation? Amines are produced by agricultural activities, and have been shown to form aminium salts efficiently. This could also represent a significant anthropogenic perturbation to new particle formation.

Pg. 19537 line 25-27 I would consider, e.g., Weber et al. (2007) to be "quantitative evidence." Also, the authors could mention Goldstein et al, PNAS 2009 in the field study review section, as it provides evidence of BSOA in populated regions from satellite observations.

Figures The figures are probably the weakest part of this manuscript. There are only 3: Fig. 1 (SOA yields vs. VOC/NO<sub>x</sub>) might be out of date (see comment above and by short comment by Dr Jason Surratt), and Figs 2 and 3 could be expanded (e.g. Fig 2 can include a more comprehensive review of radiocarbon measurements). Also, additional figures will be helpful. One can summarize the correlation between BSOA proxies and anthropogenic emissions, since this is the best field evidence supporting the concept of anthropogenically enhanced BSOA. Also, a workflow diagram of the proposed approach to isolate the anthropogenic component of BSOA might be helpful.

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