

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

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This article is very interesting and will certainly stimulate much needed discussion and further work in the field. Although I'm not a reviewer, I had a couple of short comments for the authors to only consider:

1.) Effect of increasing NO₂/NO ratio on isoprene SOA yields

The authors likely have not seen the work of Chan et al. (2010, ACP), which is completely understandable since it was only just published in ACP. This study from the research groups at Caltech is very relevant to the discussion contained within the present manuscript. Specifically, the authors have shown at atmospherically relevant NO₂/NO ratios (3-8), the SOA yields from isoprene high-NO_x photooxidation are 3

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times higher than that previously measured at lower-NO₂/NO ratios (Kroll et al., 2006, ES&T). Higher NO₂/NO ratios are shown to favor the formation of MPAN through the acyl RO₂ + NO channel, and as a result, the further oxidation of MPAN leads to aerosol from isoprene under this high NO₂/NO condition (Surratt et al., 2010, PNAS). Thus, at sufficiently high NO₂ levels, in VOC systems that produce alpha,beta-unsaturated aldehydes as oxidation products, such as isoprene producing methacrolein, SOA formation from subsequent oxidation of products from acyl RO₂+NO₂ can exceed that from RO₂+HO₂ reactions. This effect was also demonstrated for acrolein and crotonaldehyde. What is intriguing about this chemistry is that oligoester formation occurs; specifically, diesters formed from the further oxidation of MPAN have been observed both in the Caltech chamber experiments and in fine aerosol collected from the southeastern U.S.A. (Jaoui et al., 2008, JGR). These diesters are only seen under the high NO₂/NO condition studied. Clearly, this NO₂/NO effect from isoprene is interesting and could certainly have impacts on aerosol formation in urban areas impacted by isoprene emissions, especially since the yields observed under atmospherically relevant NO₂/NO ratios by Chan et al. (2010, ACP) are larger than those under previously studied low-NO_x conditions (Kroll et al., 2006). This latter finding suggests that isoprene SOA formation is actually more efficient in urban plumes than in remote locations (Chan et al., 2010, ACP). The authors may want to briefly include this effect in their manuscript. I should note that SOA yields from isoprene were found to be 0.031-0.074 at organic aerosol loadings of 3-47 ug m⁻³. Further study is warranted on examining the potential effect of RO₂ + NO₂ chemistry on monoterpenes and sesquiterpenes. Currently, this is not well understood. It may not matter since many of these monoterpenes may not produce the necessary alpha,beta-unsaturated aldehyde products.

2.) Effect of acidity on isoprene SOA yields

The effect of acidity on isoprene SOA formation has been demonstrated by a number of studies (e.g., Edney et al., 2005, Atmos. Environ; Kleindienst et al., 2006, ES&T; Surratt et al., 2007, ES&T). Recently, Paulot et al. (2009, Science) discovered the for-

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mation of epoxydiols of isoprene (called IEPOX for short) under low-NO_x conditions. Surratt et al. (2010, PNAS) showed that these epoxydiols of isoprene will be reactively taken up by acidic aerosols; specifically, SOA yields from isoprene increased from 1 % to 28 % when going from neutral sulfate seed aerosol conditions to acidified sulfate seed aerosol conditions. Much of this enhancement in the SOA yields was shown to come primarily from the reactive uptake of these epoxydiols. More importantly and relevant to the present manuscript, the SOA constituents characterized from this study using GC/MS and UPLC/ESI-HR-TOFMS techniques have also been observed in ambient aerosol samples. Thus, the 2-methyltetrols, C₅-alkene triols, dimers, and the organosulfates derived from the acid-catalyzed ring-opening reactions of the epoxydiols all have been observed in ambient aerosol samples (e.g., Claeys et al., 2004; Wang et al., 2005; Edney et al., 2005; Surratt et al., 2006). Interestingly, Chan et al. (2010, ES&T) showed that the unreacted forms of the isoprene epoxydiols, albeit they were in smaller concentrations than the known isoprene SOA tracers, could be detected in fine aerosols collected during the AMIGAS campaign. All of the isoprene SOA constituents formed from reactive uptake of epoxydiols of isoprene are only enhanced in the presence of aerosol acidity. Naturally, the difficulty in all of this is in accurately estimating ambient aerosol acidity. The results of these studies are relevant to the discussion by the present authors since it is clear that anthropogenic SO₂ emissions will enhance SOA from isoprene, especially if the epoxydiols are transported into urban areas impacted by biogenic (i.e., terrestrial vegetation) emissions.

3.) Tracer compounds for the anthropogenic enhancement of biogenic SOA

Couldn't the organic nitrates, organosulfates, and nitrated organosulfates derived from BVOCs (e.g., Surratt et al., 2008, JPCA; Liggio et al., 2005; Iinuma et al., 2007b, ES&T; Noziere et al., 2010, GRL; Alteri et al., 2009, ES&T) found in continental locations serve as potential markers for this effect? This of course is assuming that sulfate is not coming from marine sources and or volcanic eruptions. This wasn't made clear in this paper. I think these compounds at least allow for a first attempt to try and quantify this

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effect discussed in the manuscript. Although I admit that not all of these compounds have been synthesized or are available at this time.

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