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

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We would like to thank Jason Surratt for taking the time to make such a detailed comment which lead to the improvement of this manuscript. Our changes are detailed below:

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 formation of epoxydiols of isoprene (called IEPOX for short) under low-NOx 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

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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.

Dr Surratt raises an important issue about the role of acidity which has only been mentioned briefly in the manuscript. Indeed this is a point that strengthens the argument for anthropogenic effects on biogenic SOA yields. It also highlights the difficulty to apply equilibrium partitioning models under conditions when heterogeneous aerosol chemistry irreversibly ties up volatile compounds. We now include more detailed discussion on acid heterogeneous chemistry as suggested by the reviewers. The revised paragraph is as follows:

“Finally, reversible and irreversible condensed-phase accretion reactions (Barsanti and Pankow, 2004), may significantly increase condensed-phase products due to esterfication, oligomerization, hemiacetal formation, aldol addition, or Criegee intermediate adduct reactions (Kroll and Seinfeld, 2008), though at least in chamber experiments condensation of biogenic SOA remains reversible upon dilution after many hours (Grieshop et al., 2007). Heterogeneous reactions that proceed at low pH (a subset of aforementioned reactions) may be particularly important since anthropogenic activities can provide acidic aerosol seed material in the form of sulfuric and nitric acid production from SO2 and NOx emissions (Jang et al., 2002).

Zhang et al. (2007) examined Aerosol mass spectrometer (AMS) data collected in Pittsburgh, and found a 25% increase in SOA mass during periods when the aerosol was more acidic. They did not, however, find evidence for any chemical difference in the SOA which would explain this increase, such as oligomer formation. Takahama et al. (2006) also observed a mild (0.61) correlation between aerosol acidity and OA burden in Pittsburugh, and were also unable to find any evidence for acid catalyzed heterogeneous chemistry which would lead to enhanced SOA. In both cases, the observed increase in OA with aerosol acidity could also be explained by processes which affect both acidity and SOA, such as air mass origin and history. On the other hand, several laboratory studies show dramatically increased aerosol yields under acidic conditions (e.g. Edney et al., 2005; Kleindienst et al., 2006; Surratt et al., 2007). Additionally, for SOA formed from isoprene oxidation products, Surratt et al. (2007) demonstrate the existence of particle phase acid catalysed reactions, leading to the formation of 2-methytetrols, sulphate esters and high molecular weight SOA products. Isoprene derived SOA was also investigated by Edney et al. (2005), who found that concentrations of 2-methyltetrols and 2-methylglyceric acid increased significantly under acidic conditions. In regions where isoprene is present, sulfuric acid seeds may lead to the formation of epoxydiols (Paulot et al. 2009) and reactive uptake of these on acidic aerosols may lead to a 30-fold increase in OA mass yields from isoprene (Surratt et al., 2010). Similarly, sulfuric acid may pull in glyoxal into the particle phase due to esterification (Liggio et al., 2005).

The unreacted forms of the isoprene epoxydiols were detected at relatively low concentrations in ambient aerosol by Chan et al. (2010). Interestingly, many of the products of the acid catalysed particle phase reactions of these compounds, such as organosulphates, 2-methyltetrols, 2-methylglyceric acid, 2,3-dihydroxymethacrylic acid and C5 alkene triols have also been observed in ambient aerosol (Claeys et al., 2004; Edney et al., 2005; Surratt et al., 2006), suggesting that these reactions do indeed lead to enhanced aerosol mass in the atmosphere under acidic conditions.

This body of work suggests that (1) equilibrium the equilibrium partitioning framework may not be sufficient to fully model OA aerosol formation unless heterogeneous chemistry is included, and (2) that anthropogenic activities may indeed influence biogenic SOA formation, perhaps explaining the correlation of modern carbon found in the condensed phase with concentrations of anthropogenic OA precursors. “

p 19524: Some discussion of the recent Chan et al and Surratt et al papers which looked at SOA formation from isoprene under high NO2/NO conditions should be included....

The paragraph on p 19524 regarding isoprene/NOx has been edited to include the work of Chan et al. and Surratt et al.

“Yields for low VOC:NO_x ratios reported by Chan et al. (2010) are higher than those reported by Kroll et al. (2006). The experiments of Chan et al. (2010) were carried out at atmospherically relevant NO_2/NO ratios (3-8), which favors the formation of a second generation product methacryloylperoxynitrate (MPAN), which in turn leads to aerosol formation upon further oxidation (Surratt et al., 2010). NO_2 was also found to increase the SOA formation from acrolein and crotonaldehyde (Chan et al. 2010), and therefore similar effects may be seen for other VOC which have α,β-unsaturated aldehydes as oxidation products. The low VOC:NO_x SOA yields measured by Chan et al. (2010) were also larger than those seen by Kroll et al. (2006) for high VOC:NO_x ratios. Since the NO_2/NO ratio tends to be higher in urban regions than rural regions, this suggests that SOA from isoprene and particular other VOC could actually be enhanced in urban areas. This is certainly an effect which warrants further investigation, particularly though field studies."

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

We have added the following text:

"Compounds such as organosulfates and nitrooxy-organosulfates from oxidation of isoprene and monoterpenes may serve as potential tracers of anthropogenic enhancement of BSOA since these molecules are formed in reactions involving BVOC and sulphate (e.g. Iinuma et al., 2007, Surratt et al., 2008; Nozière et al., 2010). Sulphate sources in the specific study region should obviously be evaluated, to account for the relative contribution of anthropogenic and natural sources (DMS and volcanoes). Unfortunately, quantitative studies would presently be hampered by the lack of commercially available authentic standards for organosulfates."

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