

Interactive comment on “Reversible and irreversible processing of biogenic olefins on acidic aerosols” by J. Liggió and S.-M. Li

Anonymous Referee #1

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This work represents an extension of several previous laboratory studies by the authors, in which it has been shown that glyoxal, pinonaldehyde, α -pinene, and isoprene may be taken up into the aerosol phase via heterogeneous reactions (usually in the presence of acidic sulfate particles). Here it is shown that a wide range of terpenes (monoterpenes, sesquiterpenes, and oxygenates) can undergo similar uptake reactions as well. It is inferred that such reactions may have reversible and irreversible components; uptake coefficients, mass accommodation coefficients, and partitioning coefficients are estimated. These results are interesting, and the experiments appear to have been carried out carefully. The paper concludes by estimating additional organic aerosol loading from this mechanism to be as high as $2.7 \mu\text{g}/\text{m}^3$. This increase in loading (which is cited in the abstract) seems unrealistically large. Before this work

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can be published in ACP, this estimate needs to be revisited, with special consideration of the acidities of atmospheric particles, as well as of previous ambient measurements; this will probably lower the upper range of the estimated loadings considerably.

- First, the sulfate particles used in this study are exceedingly acidic (with ammonium:sulfate ratios of 1:14). Environments with high concentrations of the biogenic hydrocarbons studied in this work are unlikely to have aerosol particles that are so high in acidity. The authors cite a few studies which find highly acidic ambient aerosol particles: one [Ferek, et al, 1983] involved measurements taken in 1979-80, when SO₂ concentrations in the U.S. were substantially higher than they are today; another [Kato-shevski, et al, 1999] is a modeling study of the remote marine boundary layer; and a third [Li, et al, 1997] taken in Southern California, with the highest acidities found in urban regions. The relevance of these studies to areas strongly impacted by biogenic emissions (10 ppb monoterpenes, 100 ppt sesquiterpenes/oxygenates) is not clear.

The authors suggest (p. 11992) that freshly nucleated particles may be sufficiently acidic to promote such reactions. This is a good point, and is probably worth more attention (the role of chemical reactions in promoting new particle formation has been discussed by Zhang and Wexler [2002]). However, as the particles grow the acidity is neutralized (or at least diluted) so that the promotion of particle growth cannot be directly translated into such large increases in particulate loading.

- Additionally, it would seem that if such a large aerosol source exists (leading to the formation of up to several $\mu\text{g}/\text{m}^3$ of organic aerosol), there should be substantial evidence for it in existing ambient measurements. Does any such evidence exist? There is now a substantial database of AMS measurements of the loading and composition of ambient organic aerosol. This is summarized by the work of Zhang et al [2007a]; it is shown that practically all ambient organic aerosol can be broken down into two primary components, “oxygenated organic aerosol” (OOA) and “hydrocarbon-like organic aerosol” (HOA). The mass spectra from the present uptake experiments (Fig 4 and S2) share few features in common with either component. Additionally, under rural/remote

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conditions (where biogenic hydrocarbons are expected to have the largest influence), total loadings are low (averaging $2.8 \mu\text{g}/\text{m}^3$). That aerosol is dominated by the OOA component, which has a strong signal at m/z 44, a negligible ion in the present experiments. Thus it would appear that there as yet exists little AMS evidence for such a large source of relatively unoxidized organic aerosol, suggesting the calculated aerosol formation of $2.7 \mu\text{g}/\text{m}^3$ may be a substantial overestimate.

- It is not clear how the authors arrive at their estimate of up to $2.7 \mu\text{g}/\text{m}^3$ of aerosol formed from the uptake of sesquiterpenes and oxygenated monoterpenes. Initial gas-phase concentrations are assumed to be 100 ppt; for sesquiterpenes this corresponds to a mass concentration of $0.85 \mu\text{g}/\text{m}^3$ (lower for oxygenates). Thus, as mentioned in the text, uptake would have to be a major sink of such compounds. Given this, it would seem a simple kinetic calculation starting with an assumed concentration is not appropriate. Instead, aerosol uptake should be calculated with a full accounting of terpene sources and sinks. For example, how does this sink compare with that of ozone + sesquiterpenes (which can have a lifetime of under 5 minutes)?

Other comments:

p. 11977, line 10 (or Table 1): the concentrations of the seed solutions should be given as well.

p. 11981, line 7; p. 11984, line 22; and elsewhere: changes to loading (or organic or sulfate signal) are described, but with no discussion of collection efficiency (CE, particle bounce off the AMS vaporizer). CE might change substantially when the physical properties of the particles are altered, as would be the case upon the uptake of water or organics. A decrease in sulfate signal upon addition of organics has been observed previously, and attributed to CE changes [Bahreini et al 2005]. Were changes in loading observed with an SMPS?

p. 11981, Eq. 1: might product p2 arise from the irreversible reaction of product p instead?

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p. 11981, line 16: Because an increase in RH does not reduce organic loading to levels corresponding to the lower acidity, it is inferred that irreversible reactions have occurred. However, this assumes the particles are well-mixed. If instead the organics simply coated the sulfate droplet, changes in RH would not rapidly affect the acidity of the particle, and the smaller change in organic mass might be expected.

p. 11986, line 13: C_{TSP} only refers to aerosol mass that can participate in absorptive partitioning. Typically it is assumed that organics can partition only into organic mass. Is that what's assumed here? If not, is it safe to assume that sesquiterpenes are miscible in acidic solutions?

p. 11992, line 9 (and Table 1): how meaningful is pH for describing such concentrated solutions? Do other models (such as ISORROPIA) yield similar pH values? Some other metric such as excess acidity may be better for comparisons of highly acidic particles.

p. 11992, line 15: when the RH was increased, by how much was the acidity reduced? If it was only a modest decrease, it may not be safe to extrapolate results to more common atmospheric particles.

p. 11992, line 21: this is an interesting point about the PILS measurements affecting organic equilibria, but studies using other techniques (including the AMS) have also found little correlation between particle acidity and organic loading [Takahama, et al. 2006; Zhang, et al. 2007b]

p. 11992, line 27: perhaps a larger concern than the high gas-phase concentration is the particle-phase concentration. As described by Kalberer, et al. [2004], dilution in the particle phase (from primary organic aerosol, etc) could slow rates of oligomerization.

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