

Interactive comment on “Seasonal cycle and temperature dependence of pinene oxidation products, dicarboxylic acids and nitrophenols in fine and coarse air particulate matter” by Y. Zhang et al.

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In this study a number of aerosol tracers have been measured by LC/MS using negative ion electrospray ionization in fine, coarse and total suspended particulate matter collected from Mainz, Germany, during an annual cycle, including the α/β -pinene SOA tracers pinonic, pinic and 3-methyl-1,2,3-butanetricarboxylic acid, a number of dicarboxylic acids and nitrophenols. Very interesting results are obtained for the α/β -pinene SOA tracer 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), which is found to show a strong Arrhenius-type correlation with inverse temperature, indicating that OH-

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initiated oxidation of pinonic acid is a rate-limiting step in its formation and that MBTCA is a suitable tracer for the aging of biogenic SOA by OH radicals. On the whole, the tracer data have been thoroughly interpreted in the light of available literature data. An interesting finding that warrants to be explored in future studies relates to the nitrophenols 2-nitrophenol and 4-nitrocatechol, which appear to maximize during summer, and for which the origin is still unclear.

Specific comments:

Page 13257 – Experimental part: Could the authors provide representative LC/MS data (perhaps in the supplement) to show how the various analytes behave under their experimental conditions? I wonder whether no isomer of phthalic acid could be detected such as terephthalic acid? I also wonder whether no minor isomer of MBTCA could be detected, more specifically, 3-carboxyheptanedioic acid, which originates from the oxidation of d-limonene. The latter MW 204 isomer has been reported in recent studies (Jaoui et al., 2006; Kourtchev et al., 2009).

Refs:

Jaoui, M., Corse, E., Kleindienst, T. E., Offenberg, J. H., Lewandowski, M., and Edney, E. O.: Analysis of secondary organic aerosol from the photooxidation of d-limonene and their detection in ambient PM_{2.5} aerosol, *Environ. Sci. Technol.*, 40, 3819–3828, 2006.

Kourtchev, I., Copolovici, L., Claeys, M., and Maenhaut, W.: Characterization of atmospheric aerosols at a forested site in Central Europe, *Environ. Sci. Technol.*, 43, 4665–4671, 2009; supporting information available at <http://www.acs.com>.

Page 13259 – line 14: rather high blank values were observed for adipic and azelaic acid. Do the authors have any clue how these high blank values can be explained? Were there any experiments done to reduce them?

Page 13263 – line 15: Could the authors provide a reference for: “Long-chain dicar-

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boxylic acids (C12-C16) are generally attributed to the oxidation of ω -hydroxy fatty acids from vascular plants or other biogenic sources”?

Page 13266 – lines 3-8: Based on the data presented in Table 4, it appears hard to treat pinonic and pinic acid in the same way and to conclude that their temperature dependence can be approximated by that of pinene emission. The E_a (in kJ mol⁻¹) TSP values obtained for pinonic and pinic acid are 46.9 ± 12.7 and 83.9 ± 9.1 , respectively, while that for pinene emission is 75.6 ± 3.3 . It appears to me that pinic acid also shows a temperature dependence, although lower than that observed for MBTCA. This would also be logical, considering that pinic acid can be regarded as an oxidation product of pinonic acid, involving OH-initiated reactions (see formation scheme presented in Szmigielski et al., 2007).

Technical corrections:

Page 13256 – lines 8 and 12 (and places elsewhere): I suggest to use a slash to denote a hyphenated technique “GC/MS” (instead of “GC-MS”); MS is a spectrometric technique and more than just a detection technique.

Page 13256 – line 15 and 16: HPLC/MS

Page 13258 – line 4: The employed HPLC/MS system

Page 13258 – line 22: it would be more correct to write: “deprotonated molecule signals”; the term “deprotonated molecule ion” is rather confusing since a molecule ion is already deprotonated.

Page 13264 – line 13: . . . various reactions including the OH-initiated . . .

Page 13264 – line 17: . . . nitrophenol (R2 = . . .) [delete “(”]

Page 13266 – line 18: . . . the online supplement . . .

Page 13267 – line 9: and it appears . . . (delete “the”)

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Page 13267 – line 12: . . . , which may result

Page 13267 – line 27: . . . the OH-initiated oxidation is the rate-limiting step . . .

Page 13279 – line 5 from bottom: SEARCH network

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