

## ***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.***

**Y. Zhang et al.**

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### Referee General Comment:

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  $\alpha$ -/ $\beta$ -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 pinene

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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-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.

### Response:

We thank M. Claeys for the review and the positive evaluation of our manuscript. The constructive suggestions for improvement are very welcome and will be implemented upon revision. Detailed responses to the individual comments are given below.

### Referee Specific Comment 1:

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<sub>2.5</sub> 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>.

### Response:

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Extracted chromatograms of all investigated compounds will be provided in the online supplement. There is no product eluting later than phthalic acid, which should be the case for terephthalic acid. No significant isomer of 3-MBTCA was observed.

Referee Specific Comment 2:

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?

Response:

The high concentrations of these two acids in the atmosphere could always lead to contaminations by these acids during filter handling, extraction and measurement. During the measurement, filter blank and extraction solvent blank have been performed. High background values were found not only in filter blank but also in the extraction solvent. Thus, the high blank values could be due to contaminations during extraction or measurement, i.e., contaminations in extraction solvent, mobile phases and vials, left-over in the capillaries of the LC system and etc.. In the measurement, high-purity solvents have been used as the mobile phases to avoid contaminations in mobile phases and extraction solvents. In future study, we should pay attention to the vials for the samples because it's open to air before use.

Referee Specific Comment 3:

Page 13263 – line 15: Could the authors provide a reference for: “Long-chain dicarboxylic acids (C12-C16) are generally attributed to the oxidation of -hydroxy fatty acids from vascular plants or other biogenic sources”?

Response:

The reference (Stephanou and Stratigakis, 1993) was added in the text.

Referee Specific Comment 4:

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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  $\text{kJ mol}^{-1}$ ) TSP values obtained for pinonic and pinic acid are  $46.9 \pm 12.7$  and  $83.9 \pm 9.1$ , respectively, while that for pinene emission is  $75.6 \pm 3.3$ . 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).

Response:

Indeed, our pinic acid concentration data do exhibit a pronounced temperature dependence as specified and discussed in our manuscript (Page 13265, Line 14 ff). The  $E_a$  value obtained from the observed temperature dependence of pinic acid in TSP ( $83.9 \pm 9.1 \text{ kJ mol}^{-1}$ ) is not significantly different from the value calculated for pinene emission ( $75.6 \pm 3.3 \text{ kJ mol}^{-1}$ ). Therefore, and in view of the short chemical lifetime of pinene, it appears plausible to assume that pinene emission may be the rate-limiting step of pinic acid formation and thus explain the observed temperature dependence of pinic acid.

On the other hand, the pinic acid  $E_a$  value of ( $83.9 \pm 9.1 \text{ kJ mol}^{-1}$ ) is significantly smaller than the  $E_a$  value obtained for OH ( $110 \pm 8 \text{ kJ mol}^{-1}$ ). Thus, our measurement data and model results do not suggest that OH-initiated oxidation of pinonic acid was the rate limiting step of pinic acid formation. Nevertheless, we agree that our tentative explanation is not definitive, and that further studies will be required to fully unravel the pathways of pinene oxidation and product formation. We hope that the results of our study can provide useful information for future studies in this direction.

References:

Stephanou, E. G., and Stratigakis, N.: Oxocarboxylic and alpha,omega-dicarboxylic

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acids - photooxidation products of biogenic unsaturated fatty acids present in urban aerosols, *Environmental Science & Technology*, 27, 1403-1407, 1993.

Please also note the supplement to this comment:  
<http://www.atmos-chem-phys-discuss.net/10/C5457/2010/acpd-10-C5457-2010-supplement.pdf>

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, 10, 13253, 2010.

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