Atmos. Chem. Phys. Discuss., 11, C13349–C13352, 2011
www.atmos-chem-phys-discuss.net/11/C13349/2011/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Seasonal variations of stable carbon isotopic ratios and biogenic tracer compounds of water-soluble organic aerosols in a deciduous forest" *by* Y. Miyazaki et al.

Anonymous Referee #1

Received and published: 18 December 2011

General comments:

This study investigates seasonal changes in biogenic water-soluble organic carbon aerosols that were collected over an 18-month period in a boreal forest located in Northern Japan, and contains a unique long-term data set. Measurements include water-soluble organic carbon (WSOC), stable carbon isotope ratios of WSOC (δ 13CWSOC), tracers for biogenic secondary organic aerosol (SOA) that are related to isoprene, α-/β-pinene, and dimethylsulfide, and tracers for primary organic aerosol (POA) that originate from plant fragments and fungi. Positive matrix factorization was applied to the data set and clearly results in five interpretable factors, i.e.,

isoprene-SOA-rich, α-/β-pinene-SOA-rich, sucrose-POA-rich, trehalose-POA-rich, and sea salt/anthropogenic WSOC. The overall results demonstrate that both primary and secondary WSOC are significant during the growing season. Very interesting outcomes are that the forest floor is a source for methanesulfonic acid and for primary and secondary organic aerosols. It is likely that the study will inspire colleagues in the field to conduct similar long-term studies and examine the forest floor in more detail and at the molecular tracer level as a source for both primary and secondary WSOC.

Specific comments:

Page 30778 – line 12: a reference to a previous study of the authors, in which the analysis by ion chromatography is reported in sufficient detail, is lacking here.

Page 30779 – line 8: Not all readers interested in this article will be acquainted with the term "C3 plant origin". I suggest to briefly explain this term.

Page 30780 – lines 12-14: It would be appropriate to provide some references for the biogenic SOA markers; some of them are already rather well known but others like MBTCA are less well established:

- 2-methylerythritol and 2-methylthreitol (Claeys et al., 2004)

- pinic acid (e.g., Yu et al., 1999)

- MBTCA (Szmigielski et al., 2007). The latter article is referred to later in the text but it is relevant to already mention it at this early stage

- 3-HGA (Claeys et al., 2007)

Page 30781 – line 12: 3-HGA showed the highest concentrations throughout the study period. It would be relevant to compare this result with other field studies where 3-HGA was measured. For example, 3-HGA also showed the highest concentrations (in μg/m3; median, 6.8; average,19.7; range: 5.4–113) among the α-/β-pinene SOA tracers for PM2.5 aerosols that were collected during a 2003 spring-summer campaign

in K-puszta, Hungary (Kourtchev et al., 2009).

Page 30781 – lines 19-25: Trehalose is together with the sugar alcohols, arabitol and mannitol, a known constituent of fungal spores and fragments (Bieleski, 1982; Lewis and Smith, 1967). I therefore suggest that a more clear link is made here to fungal spores and fragments as a possible primary source. The authors mention resuspended soil and associated biota, which is rather vague. If the authors have arabitol and mannitol concentrations, it would also be very relevant to compare them with those of trehalose and to see whether there is a correlation. In this way, they could provide additional support that the primary source of trehalose is indeed fungal spores and fragments.

Page 30783 – section 3.4: The negative vertical gradients found for the α-/β-pinene SOA tracers are puzzling in my opinion. The authors try to come up with a reasonable explanation. However, did they consider the possibility that there could be trapping of biogenic SOA beneath the canopy? I find it quite unlikely that a large fraction of the α-/β-pinene SOA would be produced beneath the canopy from forest floor emissions. In this respect, there is evidence for a Californian pine forest that biogenic SOA is formed just above the canopy (Holzinger et al., 2005). To support the hypothesis that a large fraction of biogenic SOA is due to forest floor emissions, measurements of α-/β-pinene just above the forest floor would be warranted. Since such measurements are not available, the authors may want to consider trapping of biogenic SOA beneath the canopy as an alternative explanation for their findings.

Technical corrections:

Page 30777 – line 1: delete "the": . . .. . . show that 68% of the local . . .. . .

Page 30778 – line 8: I would write: . . .. using a gas chromatograph (HP GC6890N, Hewlett-Packard, Palo Alto, CA, USA) equipped with a capillary column (mention here which one and the supplier) and coupled to . . ...

References:

Bieleski, R. L.: Sugar alcohols, in: Encyclopedia of Plant Physiology, volume 13A, Plant Carbohydrates, volume I, Intracellular Carbohydrates, edited by: Loewis, A. and Tanner, W., Springer-Verlag, Berlin, 158–170, 1982.

Claeys, M., Graham, B., Vas, G.,Wang,W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., Andreae, M. O., Artaxo, P., and Maenhaut, W.: Formation of secondary organic aerosols through photooxidation of isoprene, Science, 303, 1173–1176, 2004.

Claeys, M., Szmigielski, R., Kourtchev, I., Van der Veken, P., Vermeylen, R., Maenhaut, W., Jaoui, M., Kleindienst, T. E., Lewandowski, M., Offenberg, J. H., and Edney, E. O.: Hydroxydicarboxylic acids: novel markers for secondary organic aerosol from the photooxidation of α-pinene, Environ. Sci. Technol., 41, 1628–1634, 2007.

Holzinger, R., Lee, A., Paw U., K. T., and Goldstein, A. H.: Observations of oxidation products above a forest imply biogenic emissions of very reactive compounds, Atmos. Chem. Phys., 5, 67–75, 2005.

Kourtchev, I., Copolovici, L., Claeys, M., and Maenhaut, W.: Characterization of aerosols at a forested site in central Europe, Environ. Sci. Technol., 43, 4665–4671, 2009.

Lewis, D. H. and Smith, D. C.: Sugar alcohols (polyols) in fungi and green plants: 1. Distribution, physiology and metabolism, New Phytol., 66, 143–184, 1967.

Yu, J., Cocker III, D. R., Griffin, R. J., Flagan, R. C., and Seinfeld, J. H.: Gas-phase ozone oxidation of monoterpenes: Gaseous and particulate products, J. Atmos. Chem., 34, 207–258, 1999.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 30773, 2011.