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Interactive comment on "In-situ submicron organic aerosol characterization at a boreal forest research station during HUMPPA-COPEC 2010 using soft and hard ionization mass spectrometry" *by* A. L. Vogel et al.

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Answer on Referee #2:

The authors thank the referee for thorough reading and improving the manuscript by helpful comments. The manuscript will be revised based on the referee's comments as follows:

Comment 1: Page 17915, lines 15-25: What about aging due to gas-phase organic

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oxidation reactions?

Reply: The referee is correct that the oxidative aging not only occurs in the particle phase but also gas phase compounds are oxidized and if the products vapor pressure is sufficiently decreased, the products partition into the particle phase. We forgot about this oxidation mechanism in this particular passage. Especially for biomass burning events it is known that the emissions of VOCs are dramatically higher (Andreae & Merlet, 2001), thus their oxidative processing in the plume can be a major contribution pathway to the total organic acid fraction which was measured. The passage will be rewritten as follows: "The back trajectories suggest that the emitted aerosol from central Russia spent more than three days at low altitudes before arriving at Hyytiälä without encountering wet deposition. During this time, biomass burning markers, like levoglucosan and other lignin derived organic compounds, can undergo strong heterogeneous oxidation and either become volatilized, oligomerized or functionalized (Kroll et al., 2011). Functionalized (e.g. carboxylic acid functionalities) compounds can then be detected in the negative ionization mode of the APCI-IT-MS. Gas phase oxidation of additionally released VOCs through biomass burning (Andreae & Merlet, 2001) and subsequent gas-to-particle conversion increases the aerosol mass as the plume is transported to the SMEAR station. Kessler et al. (2010) illustrated the significant volatilization during the heterogeneous oxidation of levoglucosan. In contrast to levoglucosan, organic acids show little mass volatilization during heterogeneous OH oxidation, since the loss of carbon is roughly equivalent to the increase of oxygen (Kessler et al., 2012). Therefore it can be concluded, that the proportion of organic acids in biomass burning aerosol increases during aging not only due to gas phase- and heterogeneous oxidation but also due to the oxidative volatilization of non-acidic compounds in the aerosol phase."

Comment 2: Page 17916: The ambient measurements are compared only with products formed from reactions of monoterpenes with O3, but for typical remote air conditions monoterpenes react nearly as fast or faster with OH radicals. Although very

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limited laboratory studies indicate that there are some similarities in the reaction products for these two oxidants, on the basis of the reaction mechanisms it is to be expected that there will be many different products. It is worth mentioning this and considering how it might affect the data interpretation.

Reply: The referee is correct and we will add on page 17916, l. 14 the following statement: Although there is a certain amount of OH radicals which are formed during the terpene ozonolysis, a recent study by Hall et al. (2013) shows that the additional oxidation of α-pinene ozonolysis products by OH radicals leads to the fragmentation of the dimeric products and an overall increase of the oxidation state. Therefore we like to mention that the different oxidative environment between laboratory and ambient air might result in different products which cannot be distinguished by the used method.

Comment 3: Page 17917: It would be worth comparing measured gas phase product concentrations to the saturation concentrations calculated solely from the vapor pressures of the pure compounds in the absence of OA. These saturation concentrations should provide an estimate of the upper limit on gas phase concentrations since if these values are exceeded the compounds should condense regardless of the nature of the organic particle phase.

Reply: This is a very interesting point in regard to the very low volatile tricarboxylic acid MBTCA. In Table 1 we calculated the saturation concentration based on the SIMPOL.1 vapor pressure prediction, the campaign average values of fom, MWom, T and on $\gamma=1$ using Eq. (4). If we calculate the saturation mass concentration (C* (inverse of Kp)) for the pure compounds (MWi instead of MWom) and fom=1, we get values in the same order of magnitude:

Pinonic Acid: 265 μg/m3 at 294 K

Pinic Acid: 4.3 μg/m3 at 294 K

We quantified the gas phase mixing ratios of these acids in an earlier paper (Nölscher

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et al., 2012) – the maximum gas phase concentration during the campaign was 0.5 μg/m3 ($\pm$ 0.25 μg/m3) and 1.0 μg/m3 ($\pm$ 0.5 μg/m3) for pinic acid and pinonic acid, respectively, and thus significantly below their saturation vapor pressures. For the case of MBTCA, dealing with a saturation mass concentration of 3.5 ng/m3 at 294 K (0.6 ng/m3 at 284 K to 22 ng/m3 at 305 K- (min and max T during HUMPPA)), the ambient gas phase concentration falls within this order of magnitude (assuming the same ionization efficiency of MBTCA and pinic acid). However, as it is described by Shiraiwa & Seinfeld (2012), the gas phase concentration of compounds with a C* of 1e-3 can exceed the saturation concentration by up to three orders of magnitude due to continuous production of the low volatile compound in the gas phase and due to kinetic limitation of gas phase diffusion. Only for the near surface gas phase it is true that the concentration does not exceed the saturation mass concentration. Furthermore, for the case of semi-solid particles, the equilibration timescales can even be higher, which would result in a higher discrepancy between gas phase concentration and saturation mass concentration.

Technical comment: Page 17916, line 9: It sounds from the wording of this sentence that the most abundant biogenic compounds had concentrations from a few pptv to over a ppbv, and thus the concentrations of all other biogenics must be less than a few pptv. I don't think this is what is meant, so I suggest rewording the sentence to convey the correct meaning.

Reply: Indeed, this sentence is not clear enough. In order to avoid misunderstanding, the sentence was rephrased to: "Those measurements showed that the mixing ratios of the most abundant biogenic compounds (α pinene, Δ3 carene and ß pinene) in ambient air ranged between a few pptV and 1.5 ppbV (Yassaa et al., 2012)."

Andreae, M. O. and Merlet, P.: Emission of trace gases and aerosols from biomass burning, Global Biochem. Cy., 15, 955-966, doi:10.1029/2000GB001382, 2001.

Hall, W. A., Pennington, M. R., and Johnston, M. V.: Molecular Transformations Ac-

companying the Aging of Laboratory Secondary Organic Aerosol, Environ. Sci. Tech., 47, 2230-2237, doi:10.1021/es303891q, 2013.

Shiraiwa, M., Seinfeld, J. H.: Equilibration timescale of atmospheric secondary organic aerosol partitioning, Geophysical Research Letters, 39, L24801, doi:10.1029/2012GL054008, 2012.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 17901, 2013.

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