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Atmospheric Chemistry and Physics Discussions

Interactive comment on "First measurements of reactive α-dicarbonyl concentrations on PM$_{2.5}$ aerosol over the boreal forest in Finland during HUMPPA-COPEC 2010 – source apportionment and links to aerosol aging" *by* C. J. Kampf et al.

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Due to some unknown reasons the comments of referee 1 are not visible online. Nevertheless, the authors thank referee 1 for his comments and will respond to all of them in detail:

Referee 1: Review report for ACPD

Kampf et al., First measurements of reactive α-dicarbonyl concentrations on PM2.5 aerosol over the boreal forest in Finland during HUMPPA-COPEC2010 – Source apportionment and links to aerosol aging

This manuscript reports the concentrations of glyoxal and methylglyoxal in PM2.5 aerosols in the boreal forest in Finland, together with FTIR measurements of OH functional groups in PM1. Authors discuss their source apportionment based on backward air mass trajectory analyses and abundance of α-dicarbonyls relative to OH functional group-containing organics. I found this paper provides an interesting result, which can be considered for publication in ACP. The manuscript is relatively well written. However, the paper contains several unclear sentences and several mistakes, which should be clarified/corrected before further consideration for possible publication. I could recommend publication after the revision, but this manuscript should not be accepted as its present form.

Specific comments are:

Referee 1: 1. Page 726/lines 28-29. This sentence is not clear; natural background concentrations of what?

Reply: The sentence has been changed to "… natural background concentrations of two prominent α-dicarbonyl compounds;…".

Referee 1: 2. Page 727/line 14, …oxalic and pyruvic acid → oxalic and pyruvic acids

Reply: Has been corrected.

Referee 1: 3. Page 729/line 10. What solvent did you use for extraction? Did you use water? Authors should describe the type of solvent used.

Reply: The extraction was carried out using a mixture of methanol and water (1:1). This was missing and has been included in the revised manuscript.

Referee 1: 4. Page 731/line 6. …1.0 μmm pore size → 1.0 μm pore size

Reply: The referee is right. This error can be addressed during proof reading, because it was a problem during the conversion of the draft manuscript word file for online publication. We will take special care of all units when potentially proof reading for final publication.

Referee 1: 5. Section 2.4. How did you calibrate the method to measure the amounts of OH-functional groups? Please briefly mention about the calibration and standards you used for the calculation of the concentration of OH-groups. How about the accuracy of the method?

Reply: The method and quantification algorithm have been described in previous publications: Russell et al. 2009; Gilardoni et al., 2007; Maria and Russell, 2005; Maria et al., 2003; and Maria et al., 2002. The text has been modified as follows, "Spectra were interpreted to quantify organic functional groups by using calibration standards and a revised automated algorithm based on the linear response of absorption peak area to the number of moles of organic bond present on the Teflon filters (Russell et al. 2009; Gilardoni et al., 2007, Maria et al., 2003)." The error associated with the uncertainty of reference compounds, peak integration, and absorption artifacts is between 5-20% (Russell, 2003). OH calibration standards include 1-docosanol, glucose, and other various saccharides (Russell et al., 2010).

Referee 1: 6. Page 731/line 24 and others. LOD without giving the values means nothing. Authors should give the detection limit as a value in the text. Otherwise, the readers cannot understand the level of detection limits. Please add the detection limit (e.g., 0.1 ng/m3) for LOD and LOQ in the text. Discussion on LOD without values is meaningless.

Reply: The instrumental limit of detection for OH functional groups using the FTIR analysis described in the manuscript is 0.02 μmol of bonds. Since filter samples for FTIR analysis were collected for 6, 9, 12, and 24 hours we think it is not meaningful to give distinct numbers for LODs or LOQs. The same is true for α-dicarbonyl analytical limits using HPLC-ESI-MS/MS analysis. The instrumental limit of detection for glyoxal and methylglyoxal using the HPLC-ESI-MS/MS method described in the manuscript

are 0.51 and 0.62 ng/mL, respectively.

Referee 1: 7. P.732, lines 21-27. This sentence is bit unclear to understand. Please reword to clarify.

Reply: We thank the referee for his thorough reading and reword the sentence as follows: However, the observed Mgly concentrations are surprisingly low considering that major precursors for Gly and Mgly production in this area are monoterpenes and isoprene. Both are abundant and possess a relatively high molar Mgly formation yield upon their atmospheric oxidation. Molar yields of 25% (isoprene) and 4.2% (monoterpenes) for Mgly and 6.2% (isoprene) and 2.8% (monoterpenes) for Gly are reported by Fu et al. (2008). However, in the same study the modeled summertime mixing ratios of Gly and Mgly for southern Finland in 2006 are reported to be similar, i.e. 10–20 ppt for Gly and 5–20 ppt for Mgly (Fu et al., 2008).

Referee 1: 8. Page 734/line 8. Saw mill should be Sawmill.

Reply: Has been corrected.

Referee 1: 9. Page 734/lines 14-22. These sentences are not clear. They should be re-phrased for better reading.

Reply: Has been reworded as follows: On 12 July an event with high submicron particle number counts was observed, which was deduced to be related to a pollution plume from the city of Tampere in the southwest of the sampling site (Williams et al., 2011). Gly and Mgly concentrations show a local maximum during this event. Ensemble 4 day back trajectories of other events attributed to have an urban/anthropogenic origin, i.e. on 14 July (St. Petersburg, Russia), 16 July (Poland and Germany), 26 July to 30 July (partly anthropogenic influence from St. Petersburg, Russia, coincident with Russian wildfire emissions) and 6 August (unclear origin, but identified as anthropogenic via peak in n-pentane mixing ratio), are available in the supporting material (Figs. S1 to S5 in the Supplement).

Referee 1: 10. Section 3.2. Authors discuss the contributions from pollution events and wildfires. Authors could compare the concentrations and relative abundance of Gly and Mgly reported in the biomass burning aerosols from Amazonia, Brazil (Kundu et al., ACP, 2010), in which Mgly > Gly. Such comparison between authors' results with biomass burning results would be of interest and strengthen the authors' interpretation. Kundu et al. (JGR, 2010) also reported α-dicarbonyls in the Asian aerosols collected from Gosan site, Jeju Island, outflow region of Chinese pollutants. It can also be referenced.

Reply: We agree and thank the referee for these references. They have been included in the revised manuscript. Kundu et al. (JGR, 2010) has been placed in section 3.1 along with the other references for α-dicarbonyl field data. Kundu et al. (ACP, 2010) has been placed in the discussion about biomass burning aerosols in section 3.2 as suggested by the referee.

Referee 1: 11. Page 735/line 1 and page 736/line 27. What is the meaning of sawmill event and what do you want to discuss here? Does sawmill factory use fossil fuels and emit their combustion exhausts to the air? Or does it emit only biogenic VOCs, which can be oxidized in the air during transport to result in Gly and Mgly? Both anthropogenic and biogenic precursors can produce Gly and Mgly. It was not clear to me what the authors want to discuss for sawmill events. This point should be clarified.

Reply: When air was advected from an operating sawmill near the sampling site, we refer to this as a sawmill event. Those events were accompanied by peaks of BVOC mixing ratios as well as minima in the (-)/(+)-α-pinene ratio as pointed out in section 3.2. Therefore, we attribute increased glyoxal concentrations during these events to the increased BVOC mixing ratios.

Referee 1: 12. Page 736/line23. Concentration of 3.05 μg m^{-3} is really high. Does the value also include the amount of water in aerosols? Or it is just OH groups associated with carbon?

Reply: We agree that the alcohol concentration was very high on July 29th. However, since this period of biomass burning produced OM concentrations > 15 μg m^{-3}, the fraction of OM that was alcohol groups is consistent with the rest of the project. The alcohol group concentration reported here does not include water associated with aerosols for a variety of reasons: 1) The aerosol was dried before filter sampling 2) Filter samples undergo a 24-hour equilibration period at <40% RH prior to analysis by FTIR, and 3) Spectra did not contain peaks consistent with water at 3260 cm^{-1} and 1640 cm^{-1}. Dust hydrates can persist at RH <40%; however, calculations from XRF dust concentrations estimate that no more than 10% of the alcohol concentration could be water. This is well below the FTIR uncertainty of 20%.

Referee 1: 13. Page 737/lines 1-4. FTIR OH-group concentrations are three orders magnitudes higher than Gly concentrations. I am very skeptical on the reliability of FTIR results. What kind of functionality does the technique measure?

Reply: The OH functional group concentrations do not solely relate to Gly and Mgly. Other sources of OH functional groups for this project include biogenic SOA and even primary sources from vegetative detritus. The reliability of total OM measured from FTIR in this project appears even better than reported previously, for example – the correlation between summed FTIR groups and AMS OM was found to be r=0.95, FTIR$_{OM}$ = 0.9AMS$_{OM}$ + 0.15. The OH functional group is measured by quantifying the absorption in the O-H stretch (3200-3600 cm^{-1}), including primary, secondary, and tertiary alcohol groups (Russell et al., 2009). For this reason, it includes alcohol groups other than those associated with Gly and Mgly, so the fact that it is higher and uncorrelated to these moieties is not surprising.

Referee 1: 14. Table 1 and page 736/line 12. OM is not defined in the table and text. How did you calculate OM? This point should be clarified in the text.

Reply: The sum of all measured FTIR organic functional groups (alcohol, alkane, amine, carbonyl, and carboxylic acid) is used to determine organic mass (OM) concentrations from each filter. This has been clarified in the text and specific references for this technique were added (Russell, 2003; Russell et al., 2009).

Referee 1: 15. Figures 1 and 2. These two figures are almost same, except for the colors; Fig. 1 is associated with wind vectors of air mass origin whereas Fig. 2 is related with source apportionments. These two figures could be combined and shown as Fig. 1a (upper panel) and 1b (lower panel). Readers could better understand the distributions of α-dicarbonyls as a function of air mass origin and sources.

Reply: The authors thank the referee for this suggestion. Combining Fig. 1 and Fig. 2 into Fig. 1a and Fig. 1b improves the overview of α-dicarbonyl concentrations with regard to wind sectors and types of events influencing the sampling site. This and has been included in the revised manuscript. Figure references in the text have been changed accordingly.

Referee 1: 16. Figure 3. There are no blue squares. I just found blue circles.

Reply: The figure has been adjusted for better readability and consistency with the discussion. It now shows Gly PM2.5 concentrations, as well as -OH and OM PM1 concentrations.

Referee 1: 17. Figure 4 is a bit difficult for the readers to understand. Figure itself or legend or both should be improved.

Reply: A legend has been added to the figure to improve its understandability.

Literature:

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Kundu, S., Kawamura, K., Andreae, T. W., Hoffer, A., and Andreae, M. O.: Molecular distributions of dicarboxylic acids, ketocarboxylic acids and a-dicarbonyls in biomass burning aerosols: implications for photochemical production and degradation in smoke layers, Atmos. Chem. Phys., 10, 2209-2225, 2010.

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