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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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The authors thank the referee for the thorough reading of the manuscript and will respond to all comments in detail:

General comments:

Referee: The lower glyoxal to OM ratios at first glance may be indicative of more processing to other acids etc., but how much confidence can one have in these ratios? A more aged air mass will very likely mean much lower OM mass measured, which

in turn likely increases the uncertainty in those OM measurements. The same can be said for the GLY in these aged air masses. In that case, are these ratios meaningful? The ratios are very small but will likely be more uncertain. The authors need to make a reasonable estimation of their confidence in these ratios before they can claim that the small differences in ratios are truly indicative of more or less aging, and glyoxal processing.

Reply: The referee points out a valid concern. However, source apportionment via analysis of backward trajectories and analysis of trace gases allowed the estimation of the aging state of the advected aerosols. What we compare here are very fresh aerosols (a few hours to < 1 day), background aerosols, and aerosols that have traveled for 4 to 5 days. Glyoxal concentrations were always well above the detection limit. Also the functional group masses were always above the detection limit for the time periods discussed here, except for carbonyl functional groups, which were below the detection limit during the nucleation event. So this ratio might be more uncertain than the others. The observed trend for the Gly/OM ratio would still hold true even if high errors in glyoxal and OM concentrations are assumed (e.g. 50%). The Gly/OM ratios for the aerosols with the smallest distance from source to sampling site and during the nucleation event are at least a factor of 3 (in case of the highest uncertainty event) to 5 higher than for aerosols that have been addressed as being more aged. Nevertheless, the data point during the nucleation event on 23 July might exhibit a higher uncertainty than the other values. A corresponding statement has been added to the discussion on page 12.

Referee: The authors need to be careful when claiming that glyoxal processing occurred as particles age. In this study it is not clear how one can differentiate between lower source strength and more aged or higher source strength and less aged. Although back trajectories help somewhat, you cannot be certain. The authors need to explain how they can differentiate between the two or at least include a caveat stating the possibility.

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Reply: The authors thank the referee for bringing up this concern. We agree that we cannot be 100% sure about the relative importance of aerosol aging state and source strength for the specific events. A corresponding statement has been added to the discussion on page 12.

Referee: If the authors assertion that Gly is processed as the particles age is true, then the FTIR data should be able to corroborate this assertion. Oxidation of Gly should produce org acids ultimately. If the OH functional group is related to GLY/MGLY, then the same should be true for the acid functional group to some degree. If the authors want to make the claim the OH functional group in aerosols is related to dicarbonyls, then the COOH group should be related in the opposite way (ie: as OH decreases, COOH increases), and be highest when GLY is lowest. Is this the case here? More analysis of the FTIR is required to strengthen their argument.

Reply: There seems to be a misunderstanding here. The authors do not claim that the -OH functional groups measured by FTIR are solely related to Gly and Mgly. As pointed out on page 11 -OH, -COOH functional groups, or OM in total are on scales of μg m^{-3}, while α-dicarbonyl concentrations measured are on a scale of ng m^{-3}. We agree with the referee's next comment, that -OH functional group mass will likely be related to other non-dicarbonyl related sources to a great extent. However, from a chemical point of view it makes sense to compare Gly concentrations and -OH functional group concentrations when looking for a correlation, since (reversibly processed) Gly is present as its mono- or dihydrate as well as in the form of cyclic acetal oligomers, which also contain -OH functional groups.

Referee: It is also possible, if not likely, that the OH functional group mass is almost entirely from other non-dicarbonyl related sources. In this case, the ratio of GLY to OH is meaningless, and that changes in other sources of this OH functional group will cause changes in the GLY/OH ratio which has nothing to do with aging, oxidation or glyoxal chemistry. The authors need to discuss this issue, and provide more convincing evidence that this is not the case. Perhaps looking deeper into the FTIR data will shed

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some light on this.

Reply: As mentioned above, the authors agree that the OH functional group mass is likely dominated by non-dicarbonyl related sources. Maybe this specific part of the discussion was over-interpreting the data and therefore we decided to remove it in the revised manuscript.

Specific comments:

Referee: Pg 4, line 21: what are these “additional experiments”?

Reply: The additional experiments relate to the time resolution of sampling and diurnal trends in α-dicarbonyl $PM_{2.5}$ concentrations. It was not clear before the campaign what sampling durations would be necessary for a reliable quantification of α-dicarbonyls, so the sampling devices were run using different sampling times. A statement about this was added in the revised manuscript.

Referee: Pg 4, lines 28-32: Although a reference is provided, some more information on the method would be helpful here. For example, how long are the samples extracted for? How do you know the oligomers are completely reversible and de-oligomerized? How long does this process take?

Reply: The extraction and concentration procedure took 3 h in total. The subsequent derivatization of the extracts adds another 0.5 h. The recovery was tested by spiking experiments: three different amounts of Gly and Mgly, covering the range of the calibration curve, were spiked on quarters of ambient aerosol filter samples and analyzed as described.

Referee: Pg 6, line 8: “more details about the. . .” This is does not sound grammatically correct.

Reply: Has been changed to “More details on the description of the instrument can be found in Williams et al. (2007).”

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Referee: Pg 7, line 8-9: “High concentrations...” The term high is too subjective. In fact the levels are not really high at all. High relative to what?

Reply: Has been changed to “The highest concentrations of Gly and Mgly during the campaign...” to point out the context more clearly.

Referee: Pg 7, line 18: remove “. . .and left aside”

Reply: Has been removed.

Referee: Pg 9, line 5, remove “the”

Reply: Has been removed.

Referee: Pg 9, line 22: “. . .barely show” should be removed and re-worded.

Reply: Has been changed to “These events don’t show elevated Mgly concentrations,..”

Referee: Pg 10: What is the transit time for biomass burning plumes on July 28-29? This is not mentioned but could be valuable information for subsequent interpretation.

Reply: The transit times for these events were on the order of 4-5 days. This is now included in the discussion.

Referee: Pg 11, line 4-5: “. . .useful information. . .” useful to who? Useful why? How?

Reply: Has been changed to “. . .was investigated due to the following reasons. Gly and Mgly. . .”

Referee: Pg 11, lines 12-18: It might also simply mean that there was very little glyoxal associated with this burning event. The authors cannot rule this out.

Reply: The referee is right. A statement concerning this comment was added in the revised manuscript.

Referee: Pg 12, section 3.4: this entire section does not add anything useful to the paper. By their own admission there was no obvious correlation. If so, why bother with

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these paragraphs at all. The paper would be better served by removing this section all together and the associated figure.

Reply: We respectfully disagree with the referee's point of view. We think showing the diurnal trends is necessary to complete the picture of glyoxal measurements over the boreal forest. No correlation with single types of other data does not necessarily mean that they are not related to the measured glyoxal concentrations, but in reality it demonstrates the complexity of factors influencing glyoxal formation as well as potential conditions of efficient glyoxal uptake and/or processing. A statement about this has been added to the revised manuscript. Additionally, this section was used to demonstrate that sampling time related artifacts play a minor role for the analytical method applied for the analysis of α-dicarbonyl concentrations in $PM_{2.5}$ aerosols. Therefore, we decided to keep this section as well as figure 4 in the revised manuscript.

Referee: All figures: The figures would be easier to read if the scales were properly adjusted (or split) to see the data more clearly in between the higher concentration periods. Also, the figures need legends, to improve readability.

Reply: Legends have been added to the figures and the figure captions have been adjusted correspondingly.

Referee: Figure 2. This figure is hardly different than figure 1 except for the change from trajectory direction to source type. They should be consolidated in some way.

Reply: We agree with the referee that it would be beneficial to have all the information easily accessible in one figure. However, we think that a consolidation of both wind sector and source type information into one figure would impair readability more than what would be gained by a consolidation of the information.

Referee: Figure 3: As noted above, COOH functional group should also be shown here.

Reply: Has been addressed in the reply on the third general comment.

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Referee: Figure 4: there is no useful information here as noted above. I would remove it all together.

Reply: Has been addressed in the reply on the comment about Pg 12, section 3.4.

The authors want to thank the referee again and acknowledge him in the paper for the improvements of the manuscript related to his comments.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 723, 2012.