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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.

Anonymous Referee #2

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This manuscript describes the results from a recent study in Finland where aerosol samples collected in a boreal forest are analyzed specifically for glyoxal and methylglyoxal. These two species have received significant attention recently as important components of cloud droplets, and as precursors to other organic acids during cloud processes. While much research has focused on the importance of these species to cloud processes, few studies have measured these species in non-cloud related particles and particularly in a forested environment. The manuscript uses a recently developed method to measure the monomer forms of these compounds in aerosols

and attempts to explain variations in the concentrations of these species in terms of the age of the associated air mass. Specifically, lower glyoxal to OM ratios are said to be a result of further aerosol processing during the aging process, which is apparently consistent with recent literature on the topic. The paper is well written and the analytical method is sound. It will make a valuable contribution to the field of atmospheric chemistry; however, there are several issues with the paper and the interpretation of the associated data that needs to be addressed before full publication. These issues are described below.

General comments:

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.

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.

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

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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.

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 some light on this.

Specific comments:

Pg 4, line 21: what are these "additional experiments"?

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?

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

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?

Pg 7, line 18: remove ". . .and left aside"

Pg 9, line 5, remove "the"

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

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

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

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.

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

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.

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.

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

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

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