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***Interactive comment on* “First measurements of reactive  $\alpha$ -dicarbonyl concentrations on PM<sub>2.5</sub> 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 his valuable comments and respond below:

**Specific Comments**

Referee 3: Because of the interest in reactions of dicarbonyl compounds with ammonium salts and amines, could the authors add a statement about the filter-based primary amine concentrations from the FTIR measurements? Are they detectable, and if so, is any correlation or trend relative to the dicarbonyls observed?

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Reply: Yes, amines were detected by FTIR. The PM1 concentrations ranged from 0.02 to 1.03  $\mu\text{g m}^{-3}$ . Data interpretation is difficult due to the dependence of glyoxal concentration from the distinct sources identified in the paper. If one looks at the “pristine” boreal aerosol periods, no anti-correlation between amine and glyoxal concentration is observed. This may also be due to the time resolution of the filter sampling. Additionally, in a recent paper Yu et al. (2011) showed that the fraction of glyoxal being processed to imidazoles in ammonium salt solutions depends on the initial glyoxal concentration, ammonium salt concentration and strongly on the pH value of the solution. All these parameters likely varied also during the campaign and thus a correlation to primary amine concentration might be hard to see.

Referee 3: A second issue is that glyoxal and methylglyoxal are believed to enter aerosol particles during periods of high humidity (or cloud processing) when particle-phase water content is high. I am quite sure that an analysis of cloud processing is beyond the scope of this paper, but is there any correlation between ambient humidity at the field site and measured dicarbonyl concentrations?

Reply: We agree with the referee, but the variability found in glyoxal concentrations was found to originate mainly from anthropogenic influences or biomass burning events rather than relative humidity. Again this could be addressed with a better time resolution.

Referee 3: It is relevant to the analysis that methylglyoxal can oligomerize by two competing mechanisms: acetal formation and aldol condensation. The latter mechanism is irreversible, and its products would not likely be analyzed as methylglyoxal by the analytical methods used in this study. This is an additional reason why methylglyoxal concentrations may be lower than glyoxal concentrations in this study. A statement to this effect should be added.

Reply: The referee is right. The different types of oligomerization reactions glyoxal and methylglyoxal can undergo influence their recovery rates during analysis. However,

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this effect has already been taken into account and the results have been corrected for the recovery rate of methylglyoxal, which was thoroughly tested during the method development process.

#### Technical Corrections

p. 8 line 1: The Henrys Law constant describes equilibrium, not flux.

Reply: Has been corrected.

#### Literature:

Yu, G., Bayer A. R., Galloway, M. M., Korshavn, K. J., Fry, C. G., and Keutsch, F. N.: Glyoxal in aqueous ammonium sulfate solutions: products, kinetics and hydration effects, *Environ. Sci. Technol.*, 45, 6336–6342, 2011.

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

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