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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Evidence for ambient dark aqueous SOA formation in the Po Valley, Italy" *by* A. P. Sullivan et al.

Anonymous Referee #3

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This manuscript provides evidence for the formation of secondary organic aerosol in aqueous aerosol particles based on their field observations in Po Valley, Italy. Particle-into-liquid sampler equipped with total organic carbon analyzer (PILS-TOC) was deployed to measure water-soluble organic carbon (WSOC). Positive matrix factorization (PMF) analysis of organic aerosol measured by aerosol mass spectrometer (AMS) data was performed to identify potential sources of aqSOA. While many previous laboratory studies have highlighted the atmospheric importance of aqSOA, direct evidence of aqSOA formation in the field is rather limited. This work can certainly improve our current understanding of SOA formation via aqueous chemistry but there are a few key issues to be addressed (see below). Overall, I recommended this manuscript to be published in Atmospheric Chemistry and Physics after address the following comments in the

revised version:

Specific comments:

1. Page 35488, line 16-21: Lee et al. (2012) experimentally demonstrated formation of aqueous SOA through photo-oxidation of real cloud water samples. It is recommended to include this reference here.

2. Page 35492, line 17-25: The justification of using Periods A and B to represent the first and second halves of the study, respectively, is unclear. Are the two selected periods defined based on meteorological conditions and/or aerosol chemical compositions? In particular, the mass loadings of nitrate and ALW content in Period B are very different to those observed in the rest of second half. Furthermore, the authors mention that Periods A and B had similar air mass origins in general (line 20-22), which is somewhat contradict to the following sentence highlighting that Period A occurred during the end of a stagnation event and Period B represents typical background conditions influenced by regional transport (line 23-25).

3. Page 35493, line 8-10 and Figure 2: Please add time series of ambient temperature and RH in Figure 2 for better illustration. Please also briefly explain how the RH variations can be used to diminish the influence of dilution and mixing. I wonder if the RH increasing period represents the period with a stable nocturnal layer.

4. Page 35494, second paragraph: It is recommended to discuss the potential formation mechanism of particle nitrate. In particular, NOx concentration in Period A was higher than that observed in Period B. It is well known that NOx can be lost at night to form N2O5, which can further react with water on aerosol surfaces to yield nitric acid. Increasing ambient RH may actually increase nitrate concentrations in particle-phase through N2O5 hydrolysis, that subsequently enhances ALW content for aqSOA production. In addition, it is possible that some nitrate can be formed in the residual layer at night and then convectively mixed after boundary layer break up, resulting in strong nitrate peaks (with relative low ALW probably because of the low RH after mixing) ob-

served at around 9-11am.

5. Page 35495, line 6-17: I agree with the authors that oxalate is not a unique marker for aqSOA. As highlighted in the manuscript, previous laboratory studies have shown that photo-oxidation of glyoxal generates oligomers as major products through radical-radical reactions in aerosol water when OH radical concentrations is on the order of 10e-12M. However, oxalate can be largely produced in aerosol water at a lower OH radical concentration (10e-13M) likely due to insufficient organic radicals concentration for oligomers formation (Lee et al., 2011). Considering the uncertainty of OH radical concentrations in aerosol water, it is inappropriate to rule out the possibility of oxalate production in aqueous aerosol particles.

6. Page 35497, line 9-14: Please explain the connection between Fig. 9a (i.e., correlation of WSOC with OOA-1 during the times of RH increasing for only Period A) and the argument in line 9-11 (i.e., OOA-1 reversibility and its concentrations declined steeply in the late morning hours when RH and ALW decreased). Similar to comment 3, It is difficult to follow the description here without a time series of ambient RH and temperature in Figure 8.

7. Page 35498, Section 3.4: It is recommended to add some discussion regarding OOA-1 and OOA-2 formation outside Periods A and B. In particular, significant amounts of OOA-1 and OOA-2 were produced during July 6-7, which are comparable to those observed in Period A. Therefore, the weak correlations between WSOC and nitrate (also OOA-1 and OOA-2) are probably due to the large contribution of background organic aerosol. In addition, the temporal variations of OOA-1 and OOA-2 looks very different. OOA-1 was formed and correlated well with nitrate throughout the whole sampling period. If OOA-1 and OOA-2 represent volatile/semi-volatile aqSOA and stable aqSOA respectively, can the authors comments on the atmospheric conditions that can produce OOA-1 but not OOA-2?

References:

Lee, A.K.Y., Zhao, R., Gao, S.S. and Abbatt, J.P.D. (2011), Aqueous-phase OH oxidation of glyoxal: a novel analytical approach employing aerosol mass spectrometry and off-line techniques, Journal of Physical Chemistry A, 115, 10517–10526, doi: 10.1021/jp204099g.

Lee, A.K.Y., Herckes, P., Liggio, J., Leaitch, W.R., Macdonald, A.M. and Abbatt, J.P.D. (2012), Characterization of aerosol and cloud water at a mountain site at WACS 2010: Secondary organic aerosol formation through oxidative cloud processing, Atmospheric Chemistry and Physics, 12, 6019-6047.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 35485, 2015.