Reviewer #1

Section 3.1: In the discussion of cloud cover, as indicated by satellites, the authors should provide the exact details of the cloud data (parameter value, time of data, and spatial area of data obtained relative to the sample site) and discuss the satellite retrieval(s) used.

The presence of clouds was determined by examining satellite pictures provided by Sat24. We used the view over Europe at 11:00 LT. The text has been updated to indicate this and Lines 219-222 now read as "Cloud cover, as indicated from satellite measurements, showed that the days preceding Period A were generally cloud free whereas clouds developed west of the ground sites preceding Periods B, C, and D (not shown). The presence of clouds was determined by examining satellite pictures set to the view of Europe at 11:00 LT provided by Sat24 (http://en.sat24.com/en/eu)."

Section 3.1: In addition to the previous comment, were there reports of precipitation in Period B to the west or anywhere near the measurement site? In other words, was wet scavenging important in explaining any aspect of the data?

Wet scavenging was not likely important as very little precipitation was observed during the study period. There was little evidence of precipitation west of the site and measurable precipitation was recorded at SPC only on the afternoons of 23 June and 6 July. The text has been updated to reflect this and Lines 223-225 now read as "Also, wet scavenging was not likely important as there was very little precipitation at SPC or west of the site during the entire study period. Only two cases of light rain lasting ~30 min, which occurred on the afternoons of 23 June and 6 July, were recorded at SPC."

Section 3.1, Lines 11-25 on pg 35493: the discussion about correlation coefficients is useful, but I am not sure what rationale went into these three categories (>0.7, 0.4-0.7, <0.3). How do these relate to statistical significance on a standard students t-test table for the respective degrees of freedom used to generate the best fit lines? More discussion is required about the choice of these three categories.

We feel $R^2$ values are more informative for looking at the data since a $R^2$ value tells the fraction of variance in the y variable explained by the x variable. The three bins of $R^2$ values, therefore, are intended to quantify broad ranges of explained variance. p-values can also be useful for examining the statistical significance of a relationship, but even relationships where little variance is explained can be significant and thus not terribly interesting to discuss. For example, performing a t-test on both WSOC vs. OOA-4 for Period A (now Figure 10g) and Period C (now Figure 10h) would suggest their relationships were significant (Period A WSOC - OOA-4 = 3.07 > t-test = 0.89 and Period C WSOC - OOA-4 = 0.75 > t-test = 0.35). However, the $R^2$ value for Period A is 0.04 and Period C is 0.64, respectively. Therefore, while the t-test shows both relationships are statistically significant, the $R^2$ values are telling us more about the importance of the relationship between WSOC and OOA-4. Lines 238-248 now read as "We first will compare all four periods to examine for evidence of aqSOA. Then we will provide a further examination of aqueous aerosol tracers and WSOC for the two periods with similar air flow

(Periods A and C). Our analysis will largely be based on least square regression correlation analysis to examine the relationship between various species and provide a general approach to examine for evidence of aqSOA. We have chosen to examine $R^2$ values as opposed to p-values since $R^2$ values can provide a useful tool for explaining the amount of observed variance in a dependent variable that is explained by variation in an independent variable. p-values merely indicate whether a relationship is statistically significant without information about the amount of variance explained. To help categorize the fraction of variance explained, we consider a high correlation as $R^2$ values greater than 0.7, a moderate correlation as $R^2$ values between 0.3 to 0.7, and a low correlation as $R^2$ values less than 0.3."

Figure 2: for Period B there seems to be a gap in the ALW data. Why is that? Also, why aren't data used (in the context of Figures 3-5) for the next couple of days when large changes in ALW are observed?

The gap in the ALW data is due to missing PILS-IC data. The caption of Figure 2 (now Figure 3) has been updated to indicate this and it now reads as "**Figure 3.** Times series of hourly averaged measured (a) WSOC, (b) calculated ALW, (c) RH, and (d) Temperature at SPC. Any gaps in ALW are due to missing PILS-IC data. The dashed vertical lines indicate midnight local time (UTC+2). Periods A, B, C, and D are also indicated."

As suggested by the reviewer, we have also expanded the analysis to cover the periods before and after the original Period B. The original Period B is now called Period C. The new Period B covers 30 June, 1-2 July and Period D covers 6-7 July. The new Period B has moderate ALW and Period D has the highest ALW observed during the study. This allows comparison of different scenarios to help strengthen our results. Figures 3-5 (now Figures 4-6 and Figures S8-S9) have been updated to include all four Periods. The discussion about these figures in Section 3.2 has been updated and Lines 251-281 now read as "WSOC is shown as a function of RH for the times of RH increasing (Fig. 4a and 4b) and decreasing (Fig. 4c and 4d) during Periods A, B, C, and D. For Periods B, C, and D, WSOC had no relationship with RH. Only during the times of increasing RH did Period A have a relationship of increasing WSOC with RH, consistent with local aqSOA formation. This can further be illustrated by examining the correlation of WSOC vs. organic aerosol (OA), aerosol liquid water (ALW), and RH for Periods A, B, C, and D during the times of RH increasing (Fig. 5 and S8). In general, WSOC had a strong relationship with OA, but only Period A additionally had a moderate correlation of the WSOC with both ALW (Period A $R^2$ = 0.65 vs. Period B $R^2$ = 0.15, Period C $R^2$ = 0.29, and Period D $R^2$ = 0.01) and RH (Period A $R^2$ = 0.39 vs. Period B $R^2$ = 0.01, Period C $R^2$ = 0.12, and Period D $R^2$ = 0.07). The good correlation between WSOC and ALW is in agreement with a previous smog chamber study that found that ALW is a key determinant of SOA yield [*Zhou et al.*, 2011]. This also supports a recent study that observed ambient aqSOA formation during the nighttime as evident by the increased partitioning of gas-phase WSOC to the particle-phase with increasing RH [*El-Sayed et al.*, 2015]. The study by *El-Sayed et al.* [2015] found the increase in the fraction of total WSOC in the particle phase ($F_p$) at the two highest RH levels (70-80%, >80%) to be statistically significant compared to the $F_p$ values at RH < 60%. The main focus of their work was to investigate if the uptake of gas-phase WSOC to aerosol water occurs through reversible or

irreversible pathways. The data suggested the aqSOA was formed irreversibly. We investigate this with our data in section 3.3.2.

Figures 6 and S9 show the correlation of WSOC vs. nitrate, oxalate, and sulfate for the times of RH increasing. Nitrate and WSOC are strongly correlated only during the times of RH increasing for Period A. Early morning nitrate peaks were observed at SPC during the first part of the study, but were absent at the upwind Bologna site (Fig. 7). The occurrence of these peaks overlaps with Period A. (Note, the nitrate event observed on 6 and 7 July during Period D will be discussed in Sect. 3.4.) This additionally suggested that the nitrate formation or the ammonium-nitrate-ammonia-nitric acid equilibrium at SPC was locally controlled since the back trajectory analysis indicated both the SPC and Bologna sites were sampling similar upwind air masses to each other in each period (Fig. 2). Therefore, the correlation with locally formed particulate nitrate suggests local formation of WSOC. (Note, increased nitrate also results in higher ALW at the same RH.) This argues that aqSOA formation was predominately local during Period A."

It should also be noted that we updated the overview section to explain the expanded analysis and Lines 206-218 now read as "Therefore, our analysis will focus on comparing these two different halves of the study. Given our interest in examining for evidence of aqSOA we picked four periods with varying levels of WSOC and ALW. We also picked cases with both sites sampling similar air masses on a given day. Period A represents the first half of the study and covers 19-21 June. Period A has elevated WSOC and moderate ALW. As indicated by the difference in the length of the back trajectories [*Draxler and Rolph*, 2013; *Rolph*, 2013] shown in Fig. 2, Period A occurred during the end of a stagnation. Period B (30 June, 1-2 July), Period C (3-5 July), and Period D (6-7 July) represent three different cases in the second half of the study. Period B has moderate ALW, Period C has low ALW, and Period D has the highest ALW observed during the study. As indicated by Fig. 2, all three of these periods represent typical background conditions influenced by regional transport, but with slightly different flow patterns. The flows of Periods A and C are most similar. Due to changes in the WSOC concentrations and a non-consistent flow pattern on a daily basis, no periods between 23-29 June were examined."

Figure 2: Avoid having numbers overlap on the y-axis for the two panels.

The y-axis has been fixed. The updated figure is shown below.

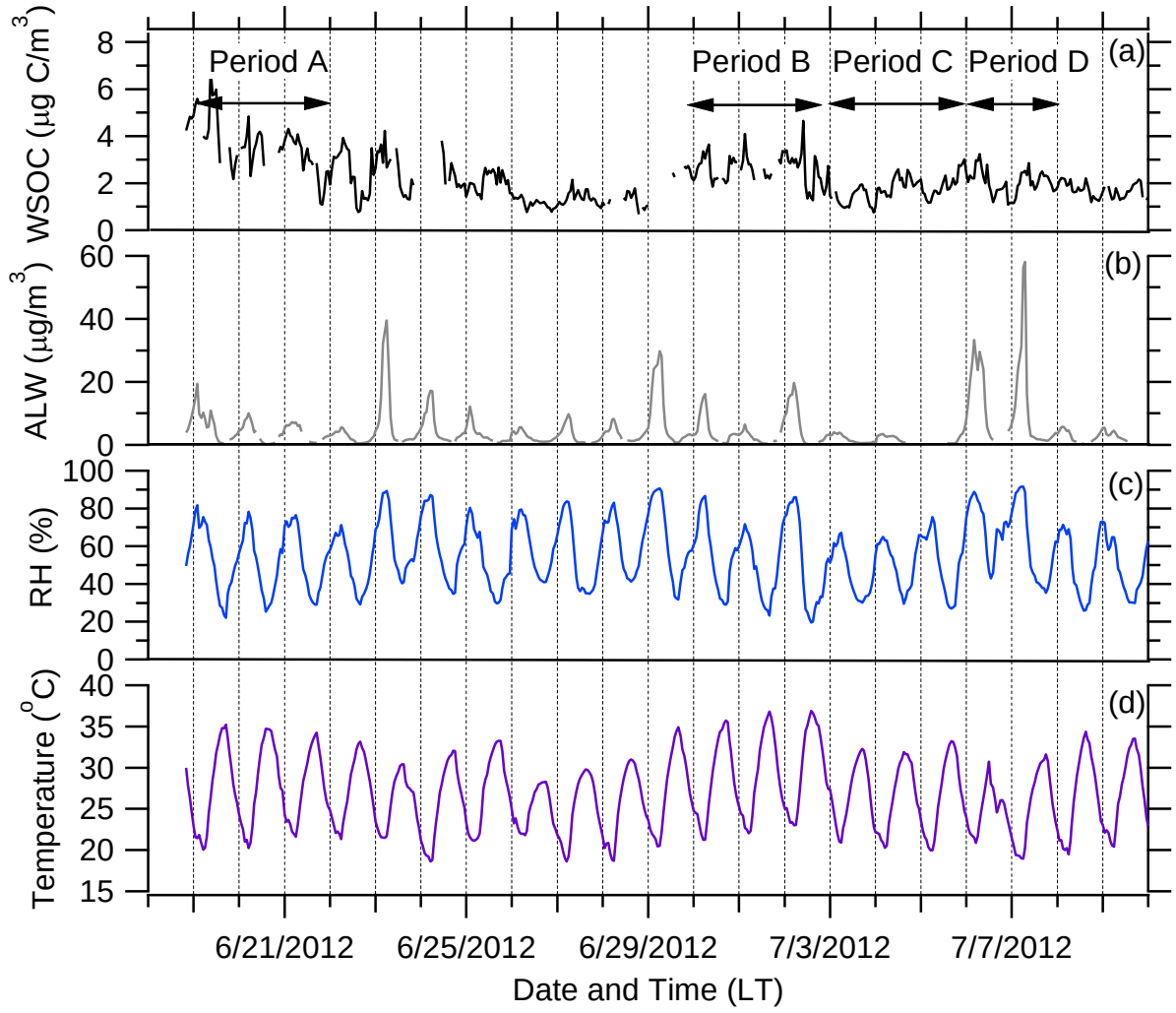



Figure 3: add error bars in the RH axis too for each marker. Also, it would be useful to report the number of points used for each marker in the two panels. For example, is the 80% RH point in panel A based on very few points compared to the other markers? And why isn't there a point at 80% RH for the bottom panel for Period A. The decrease in RH should start at 80% if the increase in RH ended near 80%. It seems as though if the RH increased to 80% that one can be picky as to which panel that marker is placed in and obviously it looks much better in the top panel to make the case for the reported conclusions. This is an issue that needs to be discussed in a revision.

Errors bars on the RH axis have been added to the figure as suggested. The number of points used in each RH bin has also been included in the figure. The updated Figure 3 (now Figure 4) is shown below. The 80% point in Period A was due to only one point, which is why it was included in only the RH increasing figure. However, this point does not drive the observations. Therefore, to show how robust the results are we have redone the analysis going from 40% to 70% RH and then from 70% to 40% RH. All relevant figures and text in the paper have been updated accordingly for this reanalysis.

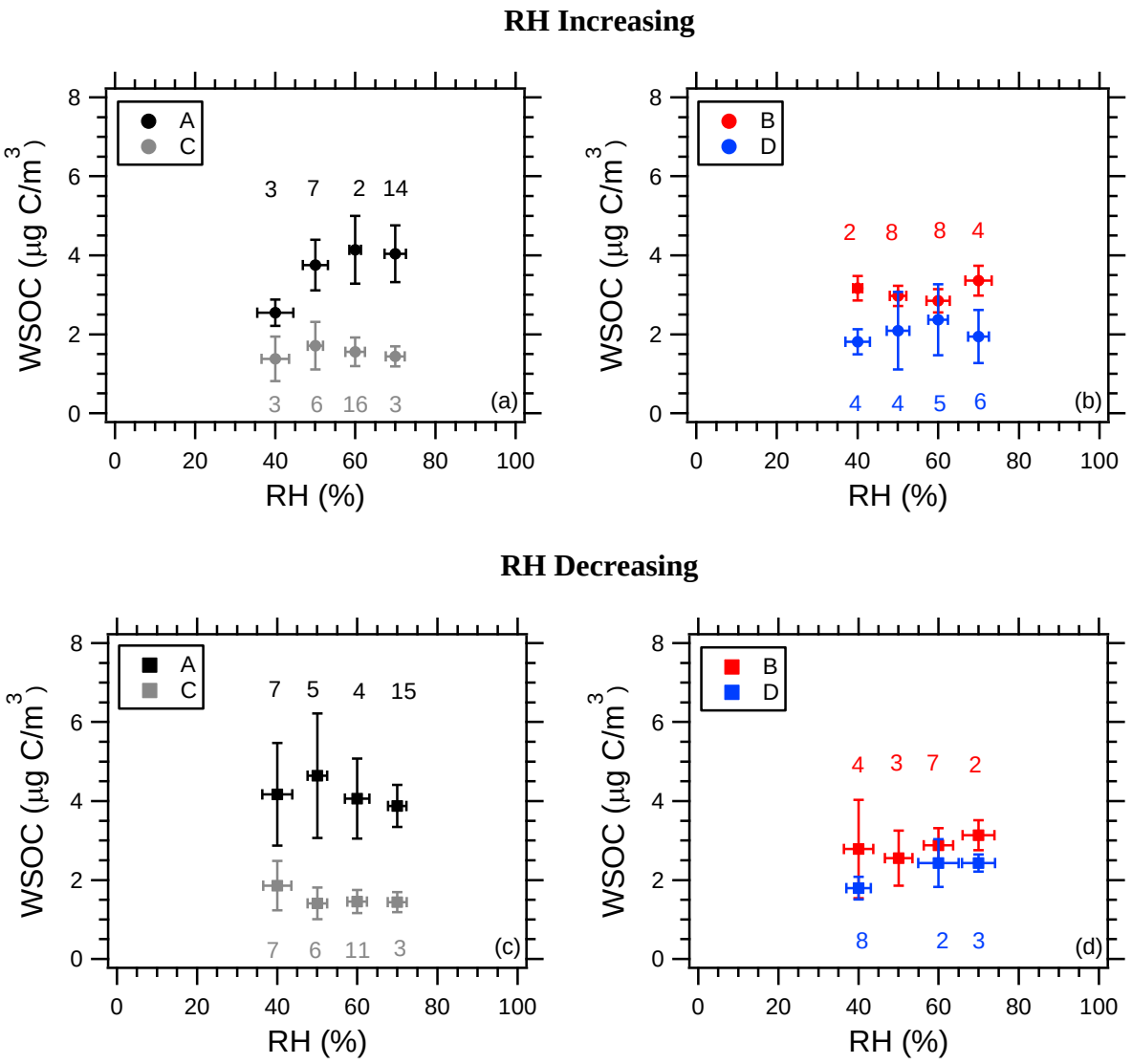



Figure 8C: what would the correlation be if the outlier point farthest to the left is omitted and are there any special characteristics associated with that datapoint? In the absence of that point it could be argues that a somewhat similar relationship exists as compared to panel D.

We believe this is in reference to Figure 5c (now Figure 6c) as Figure 8 is a time series. The outlier point does not dramatically change the correlation. If the outlier point is not included in the fit the $R^2$ value remains low, changing from 0.16 to 0.32. The point itself does not appear to have any special characteristics. It looks like the oxalate concentration could possibly be a bit lower than would be expected at its WSOC concentration, but we double checked even the chromatogram and it appears to be correct. Therefore, the point is still included.

Figure 8A-B: it seems that the same general positive trend exists in both panels. The issue in panel B could be that there is a bit more noise and it has (what appears to be) fewer data points.

We believe this is also in reference to Figures 5a and 5b (now Figures 6a and 6b). We agree that due to the differences in the axes the same general trend does appear in both plots. There is a bit less data in Figure 5b due to the missing anion data during the original Period B. Therefore, we have supplemented AMS nitrate and sulfate data into the new Figures 6b and 6f. However, this does not change the lack of relationship between WSOC and nitrate, the $R^2$ value changes from 0.18 to 0.01 when including the AMS data.

Figure 9: Panel B shows the presence of 2 outlier points to the middle-right that reduce its correlation. Having more datapoints would help in this case as it is unclear as to what explained those outlier points. The same applies to Panel B; note also that the right value on the x-axis of panel d is cut off.

The two outliers appear to be an artifact from the PMF analysis. However, they do not significantly change the correlation. If those two points are removed then the $R^2$ value for WSOC vs. OOA-1 (Figure 9b, now 10b) changes from 0.02 to 0.09 and the $R^2$ value for WSOC vs. OOA-2 (Figure 9d, now 10d) changes from 0.03 to 0.14. Also, the x-axis on Figure 9d (now 10d) has been fixed.

Table 2/3: These tables seem somewhat distracting in my view and I am not sure how important they are to the discussion in the paper. The authors should strongly consider incorporating discussion of those tables to a larger extent if they think they should be kept.

We have removed Table 2. However, since Table 3 includes the results from the two different fits used to perform the multilinear regression to determine the contribution of each AMS ME-2 factor to the WSOC, we have moved Table 3 to the supporting information (now Table S2).

-It would be useful to know exactly the times corresponding to when RH was increasing and decreasing for the plots shown in Figures 3/4/5. Some discussion about what other factors varying during those two periods of time would be helpful to show that the authors have considered all possibilities affecting their organic aerosol data and why their stated conclusions are the most obvious reason as to why different results exist.

We have added a table to the supporting information (Table S1) that now lists the exact dates and times used to create the times of RH increasing and decreasing in each Period. A copy is shown below. We also have expanded Table 1, which provides the concentrations of the various aerosol and gas-phase species measured in each period. The updated table is shown below. We also added some text in the overview section to point out that the only differences across all of Period A and the other periods are elevated OA, WSOC, and NOx concentrations. Lines 225-228 now read as "Table 1 provides a comparison of the various concentrations and parameters observed during all four periods. With the exception of WSOC mentioned above, only the OA and $NO_x$ (nitric oxides) concentrations across all of Period A are noticeably elevated compared to Periods B, C, and D."

**Table S1.** Dates and times for the times of RH increasing and decreasing during Periods A, B, C, and D.

| Period | RH Increasing | RH Decreasing |
|---|---|---|
| A | 18 June at 20:00 – 19 June at 01:00,<br>19 June at 20:00 – 20 June at 06:00,<br>20 June at 21:00 – 21 June at 07:00 | 19 June at 02:00 – 19 June at 12:00,<br>20 June at 03:00 – 20 June at 11:00,<br>21 June at 00:00 – 21 June at 12:00 |
| B | 29 June at 19:00 – 30 June at 06:00,<br>30 June at 19:00 – 1 July at 06:00,<br>1 July at 21:00 – 2 July at 07:00 | 30 June at 04:00 – 1 July at 12:00,<br>1 July at 01:00 – 1 July at 08:00,<br>2 July at 02:00 – 2 July at 10:00 |
| C | 2 July at 21:00 – 3 July at 07:00,<br>3 July at 23:00 – 4 July at 06:00,<br>4 July at 20:00 – 5 July at 07:00 | 3 July at 03:00 – 3 July at 11:00,<br>4 July at 01:00 – 4 July at 12:00,<br>5 July at 05:00 – 5 July at 11:00 |
| D | 5 July at 19:00 – 6 July at 07:00,<br>6 July at 16:00 – 7 July at 03:00 | 6 July at 01:00 – 6 July at 15:00,<br>7 July at 07:00 – 7 July at 14:00 |

**Table 1.** Average concentrations of aerosol and gas-phase species along with various meteorological parameters observed during the times of RH increasing and decreasing during Periods A, B, C, and D. NA = not available

| | OA ($\mu g/m^3$) | WSOC ($\mu g C/m^3$) | Glycolate ($\mu g/m^3$) | Acetate ($\mu g/m^3$) | Formate ($\mu g/m^3$) | Chloride ($\mu g/m^3$) | Sulfate ($\mu g/m^3$) | Oxalate ($\mu g/m^3$) | Nitrate ($\mu g/m^3$) | Sodium ($\mu g/m^3$) | Ammonium ($\mu g/m^3$) | Potassium ($\mu g/m^3$) | Magnesium ($\mu g/m^3$) | Calcium ($\mu g/m^3$) | ALW ($\mu g/m^3$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Period A RH Increasing | 8.93 | 4.73 | 0.28 | 0.40 | 0.43 | 0.13 | 3.49 | 0.24 | 2.91 | NA | NA | NA | NA | NA | 6.81 |
| Period A RH Decreasing | 9.63 | 5.09 | 0.30 | 0.33 | 0.47 | 0.17 | 3.23 | 0.23 | 5.61 | NA | NA | NA | NA | NA | 7.29 |
| Period B RH Increasing | 4.06 | 2.87 | 0.22 | 0.24 | 0.24 | 0.09 | 3.22 | 0.12 | 1.67 | 0.01 | 1.04 | 0.43 | 0.10 | 0.37 | 4.21 |
| Period B RH Decreasing | 3.78 | 2.89 | 0.22 | 0.24 | 0.23 | 0.09 | 2.69 | 0.11 | 1.56 | 0.01 | 1.04 | 0.48 | 0.09 | 0.13 | 4.34 |
| Period C RH Increasing | 2.05 | 1.55 | 0.24 | 0.28 | 0.23 | 0.11 | 2.80 | 0.13 | 1.18 | 0.04 | 0.92 | 0.51 | 0.11 | 0.26 | 2.89 |
| Period C RH Decreasing | 2.01 | 1.54 | 0.22 | 0.32 | 0.23 | 0.10 | 2.75 | 0.12 | 1.28 | 0.04 | 0.94 | 0.54 | 0.09 | 0.06 | 2.64 |
| Period D RH Increasing | 2.89 | 1.92 | 0.17 | 0.18 | 0.21 | 0.11 | 3.38 | 0.12 | 1.31 | 0.02 | 1.07 | 0.48 | 0.10 | 0.32 | 4.10 |
| Period D RH Decreasing | 3.02 | 1.99 | 0.19 | 0.19 | 0.24 | 0.14 | 4.89 | 0.13 | 3.56 | 0.03 | 2.00 | 0.55 | 0.10 | 0.20 | 7.90 |

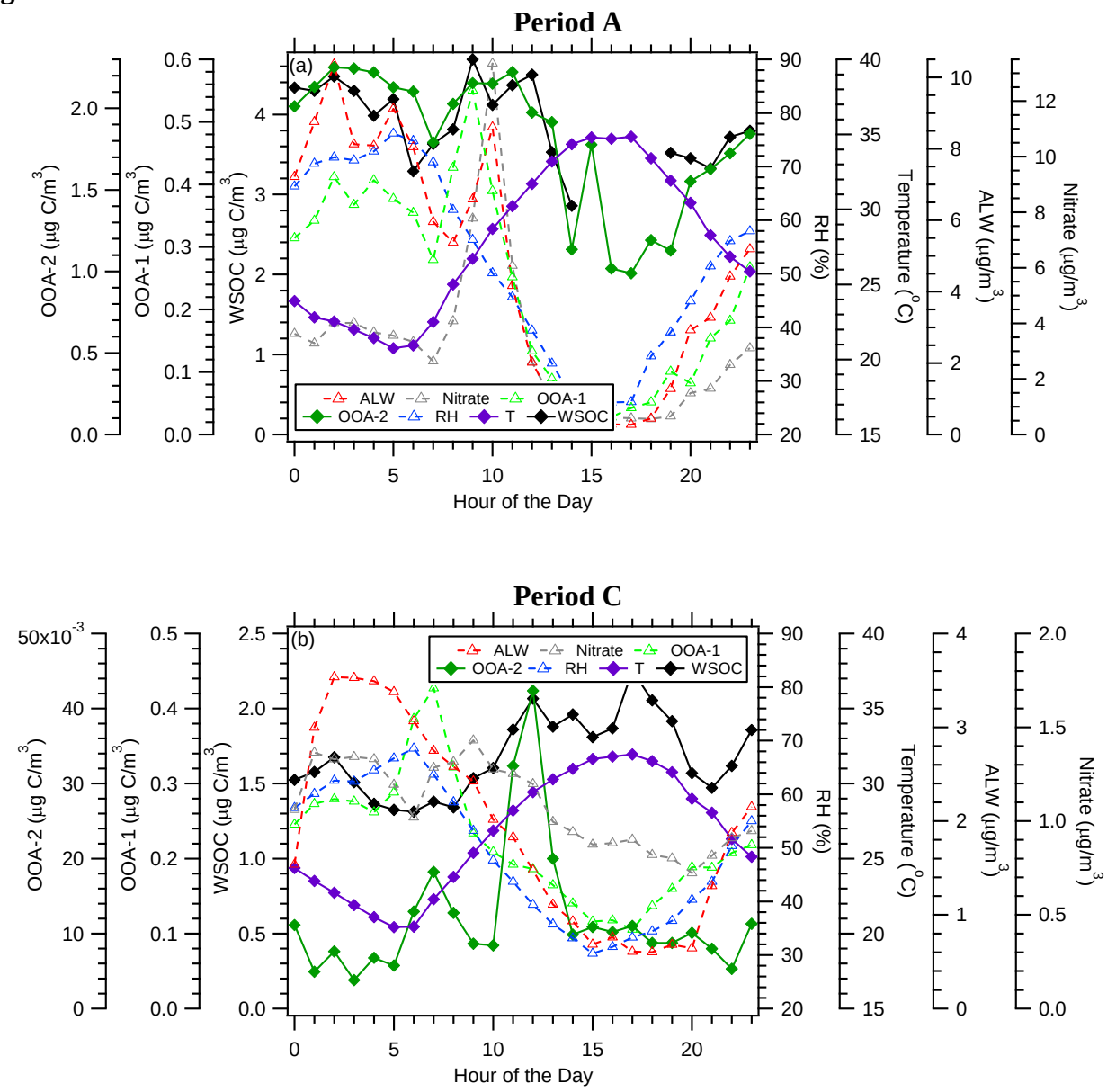
| | Ozone ($\mu g/m^3$) | $NO_x$ ($\mu g/m^3$) | $SO_2$ (ppb) | Benzene ($\mu g/m^3$) | Toluene ($\mu g/m^3$) | Xylene ($\mu g/m^3$) | Glyoxal (ppb) | T ($^oC$) | RH (%) |
|---|---|---|---|---|---|---|---|---|---|
| Period A RH Increasing | 47.42 | 28.90 | 0.65 | 0.21 | 1.21 | 0.26 | 0.05 | 24.47 | 64.49 |
| Period A RH Decreasing | 63.70 | 17.75 | 1.14 | 0.27 | 1.78 | 0.34 | 0.09 | 26.09 | 57.66 |
| Period B RH Increasing | 76.6 | 10.94 | 0.68 | 0.19 | 0.83 | 0.53 | 0.06 | 26.74 | 60.87 |
| Period B RH Decreasing | 51.6 | 9.30 | 0.69 | 0.29 | 1.43 | 0.66 | 0.07 | 26.2 | 61.20 |
| Period C RH Increasing | 61.29 | 9.72 | 0.40 | 0.17 | 1.18 | 0.40 | 0.05 | 23.31 | 60.60 |
| Period C RH Decreasing | 75.40 | 8.08 | 0.51 | 0.17 | 1.11 | 0.44 | 0.07 | 25.02 | 53.88 |
| Period D RH Increasing | 87.21 | 8.93 | 0.30 | 0.12 | 0.52 | 0.23 | 0.05 | 25.63 | 63.45 |
| Period D RH Decreasing | 93.73 | 5.12 | 0.38 | 0.15 | 0.85 | 0.28 | 0.07 | 27.32 | 54.92 |

Reviewer #2

p. 35497 lines 3-19: This argument distinguishing between OOA-1 and OOA-2 needs to be clarified, and requires more data to be shown in support of the distinction. The authors state in line 12 that OOA-1 correlates with WSOC during increasing RH in period A, but not period B, as shown in Figure 9. This also appears to be the case for OOA-2. Furthermore, the authors state in line 5 that both OOA-1 and OOA-2 increase with RH and WSOC throughout period A, but do not show this data. They state in line 10 that OOA-1 drops in late morning when the RH declines (perhaps visible in Figure 8a?), and use this to argue for reversible aqueous formation of OOA-1. Then, the authors "illustrate" this, reversibility by appealing to increasing RH data. They state that OOA-1, but not OOA-2, correlates with RH during times of increasing RH during period A, but fail to show this data, either. These observations are then used to make inferences about the different natures of OOA-1 and OOA-2, but too little data distinguishing the two (beyond the O/C ratio) has been shown to make the argument convincing.

In order to better explain and illustrate the differences between OOA-1 and OOA-2 we have added diurnal profiles of WSOC, OOA-1, OOA-2, RH, temperature, ALW, and nitrate for Periods A and B (now Period C). This figure, shown below, helps to better show the relationship and timing of when OOA-1, OOA-2, RH, and ALW decrease. The discussion has also been updated and Lines 344-356 now read as "The multilinear regression analysis performed on the Period A measurements suggests that the largest water-soluble fractions are exhibited by OOA-1 and OOA-2, whose concentrations were observed to increase along with RH and WSOC for all the days in this period of the campaign. Due to the very different absolute average concentrations, the second factor (OOA-2) provided the largest contribution to WSOC, accounting for more than one third of the total water-soluble organic carbon concentration. Interestingly, the diurnal trend of OOA-1 indicated that its partitioning to the aerosol phase was largely reversible, and its concentrations declined steeply in the late morning hours when RH and ALW decreased (Fig. 12a). In the same hours of the day, the OOA-2 concentrations were largely unaffected by RH indicating (a) that OOA-2 mainly accounted for oxidized compounds stable in the aerosol phase and (b) that boundary layer growth is not the reason for the decrease in OOA-1 as this should have affected all factors. OOA-1 and OOA-2 can therefore be hypothesized as two aging stages of aqSOA formation during Period A."

**Figure 12**


Period A
(a)
ALW
Nitrate
OOA-1
OOA-2
RH
T
WSOC
OOA-2 (µg C/m3)
OOA-1 (µg C/m3)
WSOC (µg C/m3)
RH (%)
Temperature (oC)
ALW (µg/m3)
Nitrate (µg/m3)
Hour of the Day
Period C
(b)
50x10-3
ALW
Nitrate
OOA-1
OOA-2
RH
T
WSOC
OOA-2 (µg C/m3)
OOA-1 (µg C/m3)
WSOC (µg C/m3)
RH (%)
Temperature (oC)
ALW (µg/m3)
Nitrate (µg/m3)
Hour of the Day

It would be appropriate to reference the paper by Jian Yu et al. (2005), who identified the correlation between aerosol oxalate and sulfate, either in the last paragraph of the introduction or with the Sorooshian reference at the bottom of p. 35494.

The *Yu et al.* [2005] paper has been added. Lines 127-130 now read as "We also look at the relationship of oxalate with sulfate and gas-phase glyoxal; oxalate and sulfate are both produced by cloud processing and glyoxal is a known precursor to aqSOA formation [*Yu et al.*, 2005; *Tan et al.*, 2009; *Ervens and Volkamer*, 2010; *Lim et al.*, 2010; *Sorooshian et al.*, 2010]." and Lines 286-288 as "Oxalate and sulfate are known tracers for aerosol formation through cloud processing [*Yu et al.*, 2005; *Sorooshian et al.*, 2010], although sulfate does also have a substantial, albeit slower, gas-phase formation pathway [*Seinfeld and Pandis*, 2006]."

This reviewer would like to see more connection or comparison made between the results of this study and the closely related work of El-Sayed (2015), briefly references in line 12 of p 35494.

A discussion about the *El-Sayed et al.* [2015] paper has been added. Lines 262-269 now read as "This also supports a recent study that observed ambient aqSOA formation during the nighttime as evident by the increased partitioning of gas-phase WSOC to the particle-phase with increasing RH [*El-Sayed et al.*, 2015]. The study by *El-Sayed et al.* [2015] found the increase in the fraction of total WSOC in the particle phase ($F_p$) at the two highest RH levels (70-80%, >80%) to be statistically significant compared to the $F_p$ values at RH < 60%. The main focus of their work was to investigate if the uptake of gas-phase WSOC to aerosol water occurs through reversible or irreversible pathways. The data suggested the aqSOA was formed irreversibly. We investigate this with our data in section 3.3.2."

Reviewer #3

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.

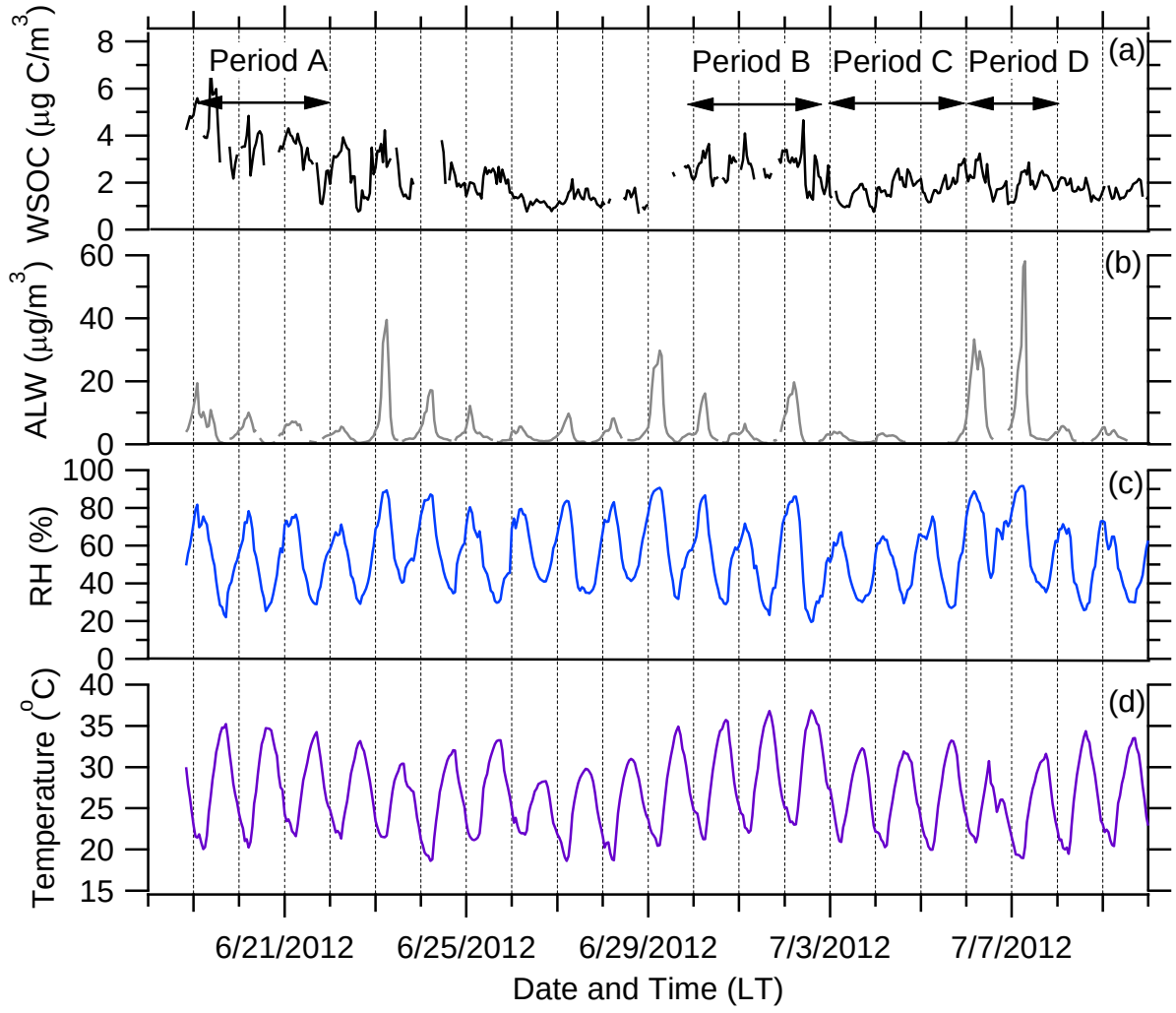
The *Lee et al.* [2012] reference has been added. Lines 99-103 now read as "These products can remain in the particle phase after water evaporation, forming what is termed aqueous secondary organic aerosol (aqSOA) (e.g. [*Blando et al.*, 2000; *Altieri et al.*, 2006; *Carlton et al.*, 2007; *de Haan et al.*, 2009; *Galloway et al.*, 2009; *Ervens and Volkamer*, 2010; *Sun et al.*, 2010; *Lee et al.*, 2012; *Monges et al.*, 2012; *Nguyen et al.*, 2012; *Tan et al.*, 2012; *Gaston et al.*, 2014])."

2.Page 35492, line 17-25: The justification of using Period 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 loading 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).

The two periods were originally picked because they have similar transport patterns. In response to reviewer comments, we have now updated our analysis to include two more periods. The original Period B is now called Period C. The new Period B covers 30 June, 1-2 July and Period D covers 6-7 July. The new Period B has moderate ALW and Period D has the highest ALW observed during the study. We have also tried to clarify our meaning of similar air mass origins by instead talking about the flow direction. Lines 206-218 now read as "Therefore, our analysis will focus on comparing these two different halves of the study. Given our interest in examining for evidence of aqSOA we picked four periods with varying levels of WSOC and ALW. We also picked cases with both sites sampling similar air masses on a given day. Period A represents the first half of the study and covers 19-21 June. Period A has elevated WSOC and moderate ALW. As indicated by the difference in the length of the back trajectories [*Draxler and Rolph*, 2013; *Rolph*, 2013] shown in Fig. 2, Period A occurred during the end of a stagnation. Period B (30 June, 1-2 July), Period C (3-5 July), and Period D (6-7 July) represent three different cases in the second half of the study. Period B has moderate ALW, Period C has low ALW, and Period D has the highest ALW observed during the study. As indicated by Fig. 2, all three of these periods represent typical background conditions influenced by regional transport, but with slightly different flow patterns. The flows of Periods A and C are most similar. Due to changes in the WSOC concentrations and a non-consistent flow pattern on a daily basis, no periods between 23-29 June were examined."

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.

Figure 2 (now Figure 3) has been updated to include temperature and RH. The new version of the figure is shown below. Also, our idea behind looking at the RH increasing vs. decreasing period is exactly as suggested, that the RH increasing period would represent a time with a stable nocturnal boundary layer. Lines 229-236 have been updated and read as "Each period will be examined in terms of the times when RH increased from 40 to 70% (times of RH increasing) and then when the RH decreased from 70 back to 40% (times of RH decreasing). This was done to try to diminish the influence of dilution and mixing on SOA concentrations and measurements of other key variables, since measurements of a conserved tracer were not available. The idea being that the times of RH increasing would represent a time with a stable nocturnal boundary layer. The switch in regimes on average occurs at 05:00 LT, but varied from 03:00 to 08:00 LT. Therefore, the times of RH increasing primarily occurred in the dark. "




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) observed at around 9-11am.

The question of how the nitrate forms overnight is very interesting. We had a similar hypothesis that the elevated NOx in Period A is contributing to the nitrate peak observed around midnight. Likely the second peak in nitrate observed in morning around 07:00 LT is due to mixing from aloft as the boundary layer breaks up. However, we prefer not to add any discussion to the text about this as we don't have any additional data to convincingly support these hypotheses.

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 one 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.

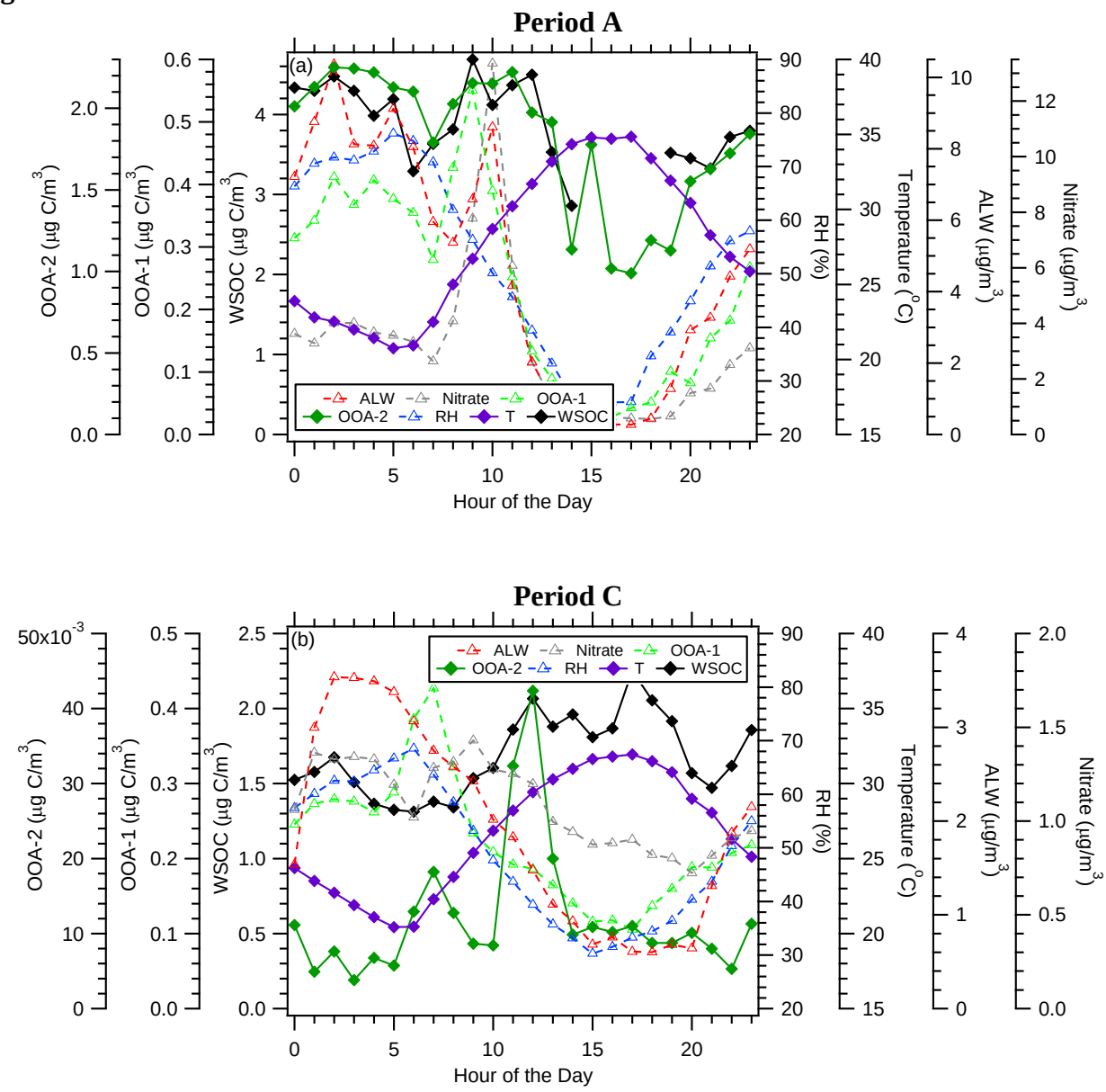
We have updated the discussion about oxalate to include the *Lee at al.* [2011] reference. We also now just mention that oxalate is not a universal marker for aqSOA, but do not go further to discuss it being a tracer for chemistry in clouds vs. wet aerosols. Lines 288-305 now read as "As shown in Fig. 8a and 8b for Periods A and C, during both the times of RH increasing and decreasing, there is a positive linear relationship between oxalate and sulfate ($R^2$ ranged from 0.39 to 0.68). The association between oxalate and sulfate but not oxalate and WSOC in Period A suggests that the local aqSOA formed in wet aerosols during Period A has little effect on oxalate. This result supports the supposition that oxalate is not a universal marker for aqSOA. This is further illustrated in our data by examining the correlation of oxalate vs. gas-phase glyoxal, a known precursor for aqSOA [*Tan et al.*, 2009; *Ervens and Volkamer*, 2010; *Lim et al.*, 2010], and ALW (Fig. 8c-f). Laboratory experiments suggest a relationship between oxalate and gas-phase glyoxal when there is in-cloud processing as oligomers have been proposed to be the dominant products from processing in aerosol water when hydroxyl radical concentrations are on the order of $10^{-12}$ M [*Lim et al.*, 2010; *Tan et al.*, 2010]. Oxalate could be produced in aerosol water at lower hydroxyl radical concentrations, such as $10^{-13}$ M, due to insufficient organic radical concentrations for oligomer formation [*Lee et al.*, 2011]. Although the hydroxyl radical concentrations are unknown, there is only a relationship between oxalate and gas-phase glyoxal for Period C during times of RH decreasing ($R^2 = 0.44$), which is when clouds were observed west of the site. In addition, there is no important relationship observed between oxalate and ALW for either period (all $R^2 < 0.17$)."

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 timer series of ambient RH and temperature in Figure 8.

In order to better explain and illustrate this we have added diurnal profiles of WSOC, OOA-1, OOA-2, RH, temperature, ALW, and nitrate for Periods A and C (Figures 12), which are shown below. These help to better show the relationship than our previous explanation, which has been removed. Lines 344-356 now read as "The multilinear regression analysis performed on the Period A measurements suggests that the largest water-soluble fractions are exhibited by OOA-1 and OOA-2, whose concentrations were observed to increase along with RH and WSOC for all the days in this period of the campaign. Due to the very different absolute average concentrations, the second factor (OOA-2) provided the largest contribution to WSOC, accounting for more than one third of the total water-soluble organic carbon concentration. Interestingly, the diurnal trend of OOA-1 indicated that its partitioning to the aerosol phase was largely reversible, and its concentrations declined steeply in the late morning hours when RH and ALW decreased (Fig. 12a). In the same hours of the day, the OOA-2 concentrations were largely unaffected by RH indicating (a) that OOA-2 mainly accounted for oxidized compounds stable in the aerosol phase and (b) that boundary layer growth is not the reason for the decrease in OOA-1 as this should have affected all factors. OOA-1 and OOA-2 can therefore be hypothesized as two aging stages of aqSOA formation during Period A."

**Figure 12**

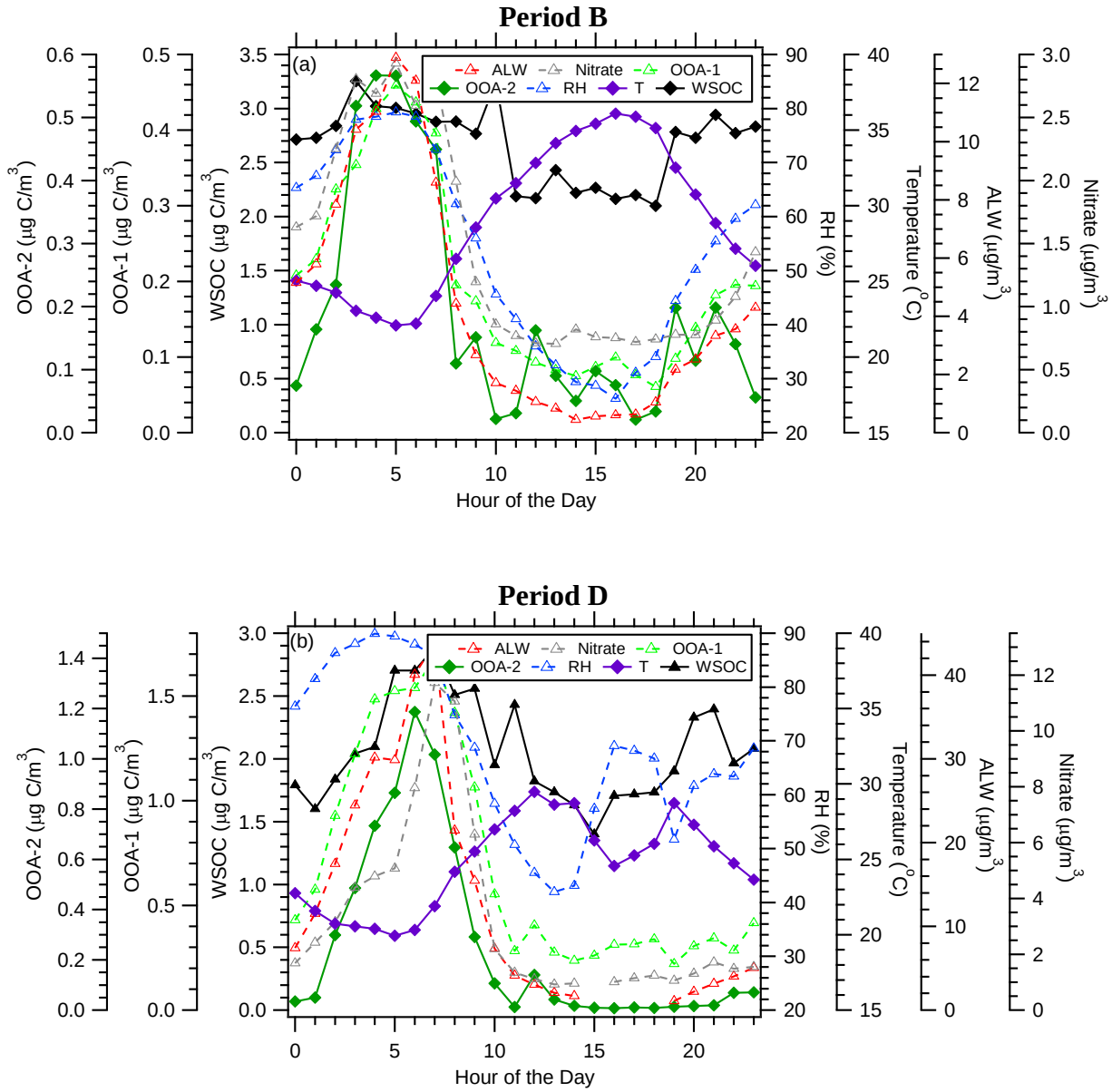

Period A
(a)
ALW
Nitrate
OOA-1
OOA-2
RH
T
WSOC
OOA-2 (µg C/m3)
OOA-1 (µg C/m3)
WSOC (µg C/m3)
RH (%)
Temperature (oC)
ALW (µg/m3)
Nitrate (µg/m3)
Hour of the Day
Period C
(b)
50x10-3
ALW
Nitrate
OOA-1
OOA-2
RH
T
WSOC
OOA-2 (µg C/m3)
OOA-1 (µg C/m3)
WSOC (µg C/m3)
RH (%)
Temperature (oC)
ALW (µg/m3)
Nitrate (µg/m3)
Hour of the Day

7.Page 35498, Section 3.4: It is recommended to add some discussion regarding OOA-1 and OOA-2 formation outside of Period 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?

We have added discussion about the formation of OOA-1 and OOA-2 outside of Period B. This is done in conjunction with the addition of the analysis of two more Periods. The original Period B is now called Period C. The new Period B covers 30 June, 1-2 July and Period D covers 6-7 July. Diurnal profiles of WSOC, OOA-1, OOA-2, RH, temperature, ALW, and nitrate for these two new periods are included in the supporting information (Figure S10, shown below). Lines 357-363 now read as "Interestingly, some OOA-2 is also produced in Periods B and D. Although the concentrations levels of OOA-2 observed are similar between Periods A and D, OOA-2 concentrations are much more sustained across the day in Period A. In addition, as illustrated in the diurnal profiles for these periods (Fig. S10) the OOA-2 follows along more closely with OOA-1, RH, and ALW in Periods B and D, likely due to the differences in meteorology and/or chemistry of these periods compared to Period A. Regardless of these differences the observations all still point to the strong relationship between OOA-1, OOA-2, and ALW."

We also added text to point out that the original Period B is an example of a case where OOA-1 is produced, but not OOA-2. Lines 370-373 now read as "Similar to Period A, here again the times when RH and ALW were high showed relatively high concentrations of OOA-1 (Fig. 12b), which represented an additional (though small compared to OOA-4) contribution to WSOC. Period C provides a case where significant OOA-1 is formed, but not OOA-2."

**Figure S10**


Period B
(a)
ALW
Nitrate
OOA-1
OOA-2
RH
T
WSOC
OOA-2 (μg C/m3)
OOA-1 (μg C/m3)
WSOC (μg C/m3)
RH (%)
Temperature (°C)
ALW (μg/m3)
Nitrate (μg/m3)
Hour of the Day
Period D
(b)
ALW
Nitrate
OOA-1
OOA-2
RH
T
WSOC
OOA-2 (μg C/m3)
OOA-1 (μg C/m3)
WSOC (μg C/m3)
RH (%)
Temperature (°C)
ALW (μg/m3)
Nitrate (μg/m3)
Hour of the Day

# Evidence for Ambient Dark Aqueous SOA Formation in the Po Valley, Italy

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**Abstract**

Laboratory experiments suggest that water-soluble products from the gas-phase oxidation of volatile organic compounds can partition into atmospheric waters where they are further oxidized to form low volatility products, providing an alternative route for oxidation in addition to further oxidation in the gas-phase. These products can remain in the particle phase after water evaporation forming what is termed as aqueous secondary organic aerosol (aqSOA). However, few studies have attempted to observe ambient aqSOA. Therefore, a suite of measurements, including near real-time WSOC (water-soluble organic carbon), inorganic anions/cations, organic acids, and gas-phase glyoxal, were made during the PEGASOS (Pan-European Gas-AeroSols-climate interaction Study) 2012 campaign in the Po Valley, Italy to search for evidence of aqSOA. Our analysis focused on ~~two~~ four ~~specific~~ periods: Period A on 19-21 June~~, and~~ Period B on 30 June, 1-2 July, Period C~~B~~ on 3-5 July~~,~~ and Period D on 6-7 July to represent the first (Period A) and second halves (Periods B, C, and D) of the study~~, respectively~~. These periods were picked to cover varying levels of WSOC and aerosol liquid water. ~~The large-scale circulation was predominately from the west in both periods.~~ Plus back trajectory analysis suggested all sites sampled similar air masses on a given day~~during both periods allowing for comparison of Periods A and B~~. The data collected during both periods were divided into times of increasing relative humidity (RH) and decreasing RH with the aim of diminishing the influence of dilution and mixing on SOA concentrations and other measured variables. Evidence for local aqSOA formation was only observed during Period A. When this occurred, there was a correlation of WSOC with organic aerosol ($R^2$ = 0.8~~4~~6), aerosol liquid water ($R^2$ = 0.6~~5~~9), RH ($R^2$ = 0.39~~45~~), and aerosol nitrate ($R^2$ = 0.66~~71~~). Additionally, this was only observed during times of increasing RH, which coincided with dark conditions. Comparisons of WSOC with oxygenated organic aerosol (OOA) factors determined from application of positive matrix factorization analysis on the aerosol mass spectrometer observations of the submicron non-refractory organic particle composition suggested that the WSOC ~~in Periods A and B~~ differed in the two halves of the study (Period A WSOC vs. OOA-2 $R^2$ = 0.8~~3~~5 and OOA-4 $R^2$= 0.0~~4~~3 whereas Period ~~B~~C WSOC vs. OOA-2 $R^2$= 0.03 and OOA-4 $R^2$ = 0.64). OOA-2 had a high O/C (oxygen/carbon) ratio of 0.77, providing evidence that aqueous processing was occurring during Period A. Key factors for local aqSOA production during Period A appear to include: air mass stagnation, which allows aqSOA precursors to accumulate in the region; the formation of substantial local particulate nitrate during the overnight hours, which enhances water uptake by the aerosol; and the presence of significant amounts of ammonia, which may contribute to ammonium nitrate formation and subsequent water uptake and/or play a more direct role in the aqSOA chemistry.

## 1. Introduction

The formation of secondary organic aerosol (SOA) remains a major source of uncertainty in predicting organic aerosol concentrations and properties that affect visibility, health, and climate [*Kanakidou et al.*, 2005]. SOA can form through gas-to-particle partitioning of semi-volatile organic compounds formed from gas-phase oxidation of VOCs (volatile organic compounds) [*Seinfeld and Pankow*, 2003]. However, laboratory experiments and predictions suggest that water-soluble products from the gas-phase oxidation of VOCs can also partition into atmospheric waters (i.e., clouds, fogs, and aerosol water) and react to form low volatility products. These products can remain in the particle phase after water evaporation, forming what is termed aqueous secondary organic aerosol (aqSOA) (e.g. [*Blando et al.*, 2000; *Altieri et al.*, 2006; *Carlton et al.*, 2007; *de Haan et al.*, 2009; *Galloway et al.*, 2009; *Ervens and Volkamer*, 2010; *Sun et al.*, 2010; *Lee et al.*, 2012; *Monges et al.*, 2012; *Nguyen et al.*, 2012; *Tan et al.*, 2012; *Gaston et al.*, 2014]).

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Evidence that aqSOA may be a contributor to ambient SOA includes a gap between observed SOA and SOA predicted by models that only include SOA formed via gas-phase oxidation and gas-particle partitioning [*de Gouw et al.*, 2005; *Heald et al.*, 2005]. In addition, there is a tendency for smog chamber experiments (generally conducted under dry conditions) to form SOA that is less oxygenated and hygroscopic than ambient SOA, suggesting a missing source of SOA [*Aiken et al.*, 2008]. In some locations, SOA surrogates have been shown to be more strongly correlated with liquid water than organic aerosol [*Hennigan et al.*, 2008; *Zhang et al.*, 2012], contrary to partitioning theory. Lastly, the abundance of ambient oxalate, an important product of aqSOA mechanisms [*Carlton et al.*, 2007; *Ervens et al.*, 2011], cannot be explained solely by gas-phase chemistry.

While it is important to study aqSOA, there have been few studies designed to observe aqSOA formation in the ambient atmosphere. Therefore, a suite of near real-time measurements was assembled with the goal of identifying evidence of aqSOA formation in the Po Valley of Italy during the summer of 2012. A key measurement for this analysis was water-soluble organic carbon (WSOC), which previous research has suggested is a good proxy for SOA (e.g., [*Sullivan et al.*, 2004; *Miyazaki et al.*, 2006; *Kondo et al.*, 2007]). Fog measurements in the Po Valley have been well documented (e.g., [*Facchini et al.*, 1999; *Fuzzi et al.*, 2002]). Fog is unlikely to occur in the summer. But even in summer, the region does have high relative humidity (60% to 80%) and is polluted, providing favorable conditions for aqSOA formation in wet aerosols.

Herein, we present an approach for the investigation of aqSOA formation in the ambient atmosphere and provide results from such analyses. We examine WSOC as a function of known parameters likely to be associated with aqSOA, such as relative humidity (RH), aerosol liquid water (ALW), and organic aerosol (OA) concentration. We also look at the relationship of oxalate with sulfate and gas-phase glyoxal; oxalate and sulfate are both produced by cloud processing and glyoxal is a known precursor to aqSOA formation [*Yu et al.*, 2005; *Tan et al.*, 2009; *Ervens and Volkamer*, 2010; *Lim et al.*, 2010; *Sorooshian et al.*, 2010]. This study aims to identify conditions conducive to aqSOA formation in this region.

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## 2. Methods

Measurements were conducted within the Italian field campaign of the European Project PEGASOS (Pan-European Gas-AeroSOls-climate interaction Study) in June and July 2012, focusing on the Po Valley. PEGASOS was a European wide study to address regional to global feedbacks between atmospheric chemistry and climate in different locations as well as in the laboratory. The observations included airborne measurements using a Zeppelin and multiple ground sites to study surface-atmosphere exchange, assess the vertical structure of the atmosphere, and study boundary layer photochemistry. An auxiliary site was located in Bologna. Our measurements were made at the main ground site in San Pietro Capofiume (SPC, Fig. 1 and 2). The SPC field station is located approximately 40 km northeast of Bologna and 30 km south of the Po River in flat terrain of agricultural fields (Fig. 1~~c and d~~).

Our measurements included running a Particle-into-Liquid Sampler – Ion Chromatography (PILS-IC) [*Orsini et al.*, 2003] system for inorganic cations, inorganic anions, and light organic acids and a Particle-into-Liquid Sampler – Total Organic Carbon (PILS-TOC) system [*Sullivan et al.*, 2004] for particle-phase WSOC. A PILS collects the ambient particles into purified water, providing the liquid sample for analysis. Both systems operated at 15 LPM with a 2.5 μm size-cut cyclone. Two annular denuders coated with sodium carbonate and phosphorous acid to remove inorganic gases were placed upstream of the PILS-IC and for the PILS-TOC an upstream activated carbon parallel plate denuder [*Eatough et al.*, 1993] was used to remove organic gases. In addition, for the PILS-TOC, a normally open actuated valve controlled by an external timer was periodically closed every 2 hours for 30 min forcing the airflow through a Teflon filter before entering the PILS. This was to allow for a real background measurement to be determined. Ambient $PM_{2.5}$ WSOC concentrations were calculated as the difference between the filtered and non-filtered measurements. The background was assumed to be constant between consecutive background measurements. Based on comparison with integrated quartz filter WSOC measurements, it appears the difference between filtered and non-filtered measurements was being overestimated by ~20% before the carbon denuder was switched out on June 25. Therefore, the WSOC concentrations before this date have been corrected for this.

For the PILS-IC, the liquid sample from the PILS was split between two Dionex ICS-1500 ion chromatographs. These systems include an isocratic pump, self-regenerating anion or cation SRS-ULTRA suppressor, and conductivity detector. The cations were separated using a Dionex IonPac CS12A analytical (4 x250 mm) column with eluent of 18 mM methanesulfonic acid at a flowrate of 1.0 ml/min. A Dionex IonPac AS15 analytical (4 x 250 mm) column employing an eluent of 38 mM sodium hydroxide at a flowrate of 1.5 ml/min was used for the anion analysis. A new chromatogram was obtained every 30 min with a sample loop fill time of 8 min. The limit of detection (LOD) for the various anions and cations was approximately 0.02 $\mu g/m^3$. These inorganic PILS data were also used to determine ALW from the Extended Aerosol Inorganics Model (E-AIM, [*Wexler and Clegg*, 2002]) run in a metastable state. More information on the ALW calculations can be found in *Hodas et al.* [2014].

In the PILS-TOC, the liquid sample obtained from the PILS was pushed through a 0.2 μm PTFE liquid filter by a set of syringe pumps to ensure any insoluble particles were removed. The flow was then directed into a Sievers Model 800 Turbo TOC (Total Organic Carbon) Analyzer. This analyzer works by converting the organic carbon in the liquid sample to carbon dioxide through chemical oxidation involving ammonium persulfate and ultraviolet light. The

conductivity of the dissolved carbon dioxide formed is determined. The amount of organic carbon in the liquid sample is proportional to the measured increase in conductivity. The analyzer was run in on-line mode providing a 6 min integrated measurement of WSOC with a LOD of 0.1 μg C/m$^3$.

Other measurements presented here include 2.5 min integrated organic aerosol (OA) concentrations determined by a High Resolution - Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) [*Drewnick et al.*, 2005; *DeCarlo et al.*, 2006; *Canagaratna et al.*, 2007]. Positive matrix factorization (PMF) analysis of the AMS OA data was performed using the Multilinear Engine algorithm (ME-2) [*Paatero*, 1999] implemented within the toolkit Solution Finder (SoFi) developed by *Canonaco et al.* [2013]. More details on the AMS ME-2 analysis can be found in the supplement text and Fig. S1-S7. Gas-phase glyoxal was determined by the Madison Laser-Induced Phosphorescence (Mad-LIP) instrument [*Huisman et al.*, 2008] at a time resolution of 51 s, hourly integrated ammonia was determined by a Monitor for AeRosols and Gases (MARGA) [*ten Brink et al.*, 2007] in SPC and 30 min ammonia was determined by AiRRmonia [*Erisman et al.*, 2001] in Bologna, and relative humidity was collected at an 1 min time resolution from a Vaisala weather transmitter WXT510. All data presented throughout is hourly averaged starting at the top of the hour.

## 3. Results and Discussion

### 3.1. Overview

As previously mentioned, WSOC is key to our analysis, since in the absence of biomass burning (see supplement for more details on the source apportionment of the AMS OA), the main contributor to WSOC has been found to be SOA [*Sullivan et al.*, 2006]. Figure ~~2a~~ 3 shows the time series for WSOC during the entire study at SPC. Overall, the WSOC concentration was higher in the first half of the study (before 25 June) compared with the second half. The WSOC concentration peaked on 19 June then steadily decreased through 22 June. During this time the concentration ranged from about 1 to 7 μg C/m$^3$. During July, the WSOC was relatively constant at around 2 μg C/m$^3$.

~~Therefore, our analysis will focus on two time periods (Periods A and B) to represent the two different halves of the study. Period A covers 19-21 June and Period B covers 3-5 July (Fig. 2). The large scale circulation indicated flow predominately from the west, typical for this region. Back trajectory analysis [*Draxler and Rolph*, 2013; *Rolph*, 2013] suggested both periods had generally similar air mass origins, but more importantly that both sites sampled similar air masses on a given day (Fig. 1). As indicated by the difference in the length of the back trajectories, Period A occurred during the end of a stagnation event and Period B represents typical background conditions influenced by regional transport. In addition, cloud cover, as indicated from satellite measurements, showed that the days preceding Period A were generally cloud free whereas clouds developed west of the ground sites preceding Period B (not shown). Table 1 provides a comparison of the various concentrations and parameters observed during both periods.~~

Therefore, our analysis will focus on comparing these two different halves of the study. Given our interest in examining for evidence of aqSOA we picked four periods with varying levels of WSOC and ALW. We also picked cases with both sites sampling similar air masses on a given day. Period A represents the first half of the study and covers 19-21 June. Period A has elevated WSOC and moderate ALW. As indicated by the difference in the length of the back

trajectories [*Draxler and Rolph*, 2013; *Rolph*, 2013] shown in Fig. 2, Period A occurred during the end of a stagnation. Period B (30 June, 1-2 July), Period C (3-5 July), and Period D (6-7 July) represent three different cases in the second half of the study. Period B has moderate ALW, Period C has low ALW, and Period D has the highest ALW observed during the study. As indicated by Fig. 2, all three of these periods represent typical background conditions influenced by regional transport, but with slightly different flow patterns. The flows of Periods A and C are most similar. Due to changes in the WSOC concentrations and a non-consistent flow pattern on a daily basis, no periods between 23-29 June were examined.

Cloud cover, as indicated from satellite measurements, showed that the days preceding Period A were generally cloud free whereas clouds developed west of the ground sites preceding Periods B, C, and D (not shown). The presence of clouds was determined by examining satellite pictures set to the view of Europe at 11:00 LT provided by Sat24 (http://en.sat24.com/en/eu). Also, wet scavenging was not likely important as there was very little precipitation at SPC or west of the site during the entire study period. Only two cases of light rain lasting ~30 min, which occurred on the afternoons of 23 June and 6 July, were recorded at SPC. Table 1 provides a comparison of the various concentrations and parameters observed during all four periods. With the exception of WSOC mentioned above, only the OA and $NO_x$ (nitric oxides)

Each period will be examined in terms of the times when RH increased from 40 to ~~80~~70% (times of RH increasing) and then when the RH decreased from ~~80~~ 70 back to 40% (times of RH decreasing). This was done to try to diminish the influence of dilution and mixing on SOA concentrations and measurements of other key variables, since measurements of a conserved tracer were not available. The idea being that the times of RH increasing would represent a time with a stable nocturnal boundary layer. The switch in regimes on average occurs at 05:00 LT, but ~~could vary~~varied from 03:00 to 08:00 LT. Therefore, the times of RH increasing primarily occurred in the dark. Table S1 provides a list of the exact times used for the times of RH increasing and decreasing in each period.

~~Our analysis will largely be based on least square regression correlation analysis to examine the relationship between various species and provide a general approach to examine for evidence of aqSOA. We have chosen to examine $R^2$ values as opposed to p-values since $R^2$ values can provide a more useful tool for understanding the influence of the x variable on the y variable. A $R^2$ value tells you the fraction of variance in the y variable explained by the x variable, whereas a p-value tells you if a relationship is significant. However, a relationship can be statistically significant regardless of the relationship between the x and y variables. In other words, the x variable could explain only a very small fraction of the variability in the y variable even when a small p-value was obtained. Therefore, the use of $R^2$ values would be more meaningful for our analysis. We consider a high correlation as a $R^2$ value greater than 0.7, a moderate correlation as a $R^2$ value between 0.4 to 0.7, and a low or poor correlation as a $R^2$ value less than 0.3. For clarity only the $R^2$ values are shown in the figures, but the equations for the least square regressions can be found in Table 2 for each individual correlation plot~~.

We first will compare all four periods to examine for evidence of aqSOA. Then we will provide a further examination of aqueous aerosol tracers and WSOC for the two periods with similar air flow (Periods A and C). Our analysis will largely be based on least square regression correlation analysis to examine the relationship between various species and provide a general approach to examine for evidence of aqSOA. We have chosen to examine $R^2$ values as opposed to p-values since $R^2$ values can provide a useful tool for explaining the amount of observed

variance in a dependent variable that is explained by variation in an independent variable. p-values merely indicate whether a relationship is statistically significant without information about the amount of variance explained. To help categorize the fraction of variance explained, we consider a high correlation as $R^2$ values greater than 0.7, a moderate correlation as $R^2$ values between 0.3 to 0.7, and a low correlation as $R^2$ values less than 0.3.

### 3.2. Evidence for aqSOA

WSOC is shown as a function of RH for the times of RH increasing (Fig. ~~3a~~4a and 4b) and decreasing (Fig. ~~3b~~4c and 4d) during both Periods A~~, and~~ B, C, and D. For Periods B, C, and D, WSOC had no relationship with RH. Only during the times of increasing RH did Period A have a relationship of increasing WSOC with RH, consistent with local aqSOA formation. This can further be illustrated by examining the correlation of WSOC vs. organic aerosol (OA), aerosol liquid water (ALW), and RH for Periods A~~, and~~ B, C, and D during the times of RH increasing (Fig. ~~4~~5 and S8). ~~In both periods during the time of RH increasing~~In general, WSOC had a strong relationship with OA ~~(Period A $R^2$ = 0.86 and Period B $R^2$ = 0.66)~~, but only Period A additionally had a moderate correlation of the WSOC with both ALW (Period A $R^2$ = 0.65 vs. Period B $R^2$ = 0.15, Period C $R^2$ = 0.29, and Period D $R^2$ = 0.01) and RH (Period A $R^2$ = 0.39 vs. Period B $R^2$ = 0.01, Period C $R^2$ = 0.12, and Period D $R^2$ = 0.07). The good correlation between WSOC and ALW is in agreement with a previous smog chamber study that found that ALW is a key determinant of SOA yield [*Zhou et al.*, 2011]. This also supports a recent study that observed ambient aqSOA formation during the nighttime as evident by the increased partitioning of gas-phase WSOC to the particle-phase with increasing RH [*El-Sayed et al.*, 2015]. The study by *El-Sayed et al.* [2015] found the increase in the fraction of total WSOC in the particle phase ($F_p$) at the two highest RH levels (70-80%, >80%) to be statistically significant compared to the $F_p$ values at RH < 60%. The main focus of their work was to investigate if the uptake of gas-phase WSOC to aerosol water occurs through reversible or irreversible pathways. The data suggested the aqSOA was formed irreversibly. We investigate this with our data in section 3.3.2.

Figures ~~5~~6 and S9 show~~s~~ the correlation of WSOC vs. nitrate, oxalate, and sulfate for the times of RH increasing. Nitrate and WSOC are strongly correlated only during the times of RH increasing for Period A ~~(Period A $R^2$ = 0.71 vs. Period B $R^2$ = 0.18). This likely reflects the difference in ALW in the two periods as well since nitrate drives ALW concentrations [*Hodas et al.*, 2014].~~ Early morning nitrate peaks were observed at SPC during the first part of the study, but were absent at the upwind Bologna site (Fig. ~~6~~7). The occurrence of these peaks overlaps with Period A. (Note, the nitrate event observed on 6 and 7 July during Period D will be discussed in Sect. 3.4.) This additionally suggested that the nitrate formation or the ammonium-nitrate-ammonia-nitric acid equilibrium at SPC was locally controlled since the back trajectory analysis indicated both the SPC and Bologna sites were sampling similar upwind air masses to each other in each period (Fig. ~~1~~2). Therefore, the correlation with locally formed particulate nitrate suggests local formation of WSOC. (Note, increased nitrate also results in higher ALW at the same RH.) This argues that aqSOA formation was predominately local during Period A.

### 3.3. Further Examination of Oxalate, Sulfate, and WSOC During Periods A and C

#### 3.3.1. Oxalate and Sulfate

To help better understand the potential for aqSOA formation, correlations with oxalate and sulfate can be examined. Oxalate and sulfate are known tracers for aerosol formation

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through cloud processing [*Yu et al.*, 2005; *Sorooshian et al.*, 2010], although sulfate does also have a substantial, albeit slower, gas-phase formation pathway [*Seinfeld and Pandis*, 2006]. As shown in Fig. ~~7a~~ 8a and ~~7b~~ 8b for Periods A and ~~B~~C, during both the times of RH increasing and decreasing, there is a positive linear relationship between oxalate and sulfate ($R^2$ ranged from 0.39 to 0.68). The association between oxalate and sulfate but not oxalate and WSOC in Period A suggests that the local aqSOA formed in wet aerosols during Period A has little effect on oxalate. This result supports the supposition that oxalate is not a universal marker for aqSOA~~; it is a tracer for chemistry in clouds rather than in wet aerosols [*Lim et al.*, 2010]~~. This is further illustrated in our data by examining the correlation of oxalate vs. gas-phase glyoxal, a known precursor for aqSOA [*Tan et al.*, 2009; *Ervens and Volkamer*, 2010; *Lim et al.*, 2010], and ALW (Fig. ~~7c~~8c-f). Laboratory experiments suggest a relationship between oxalate and gas-phase glyoxal only when there is in-cloud processing as oligomers have been proposed to be the dominant products from processing in aerosol water when hydroxyl radical concentrations are on the order of $10^{-12}$ M [*Lim et al.*, 2010; *Tan et al.*, 2010]. Oxalate could be produced in aerosol water at lower hydroxyl radical concentrations, such as $10^{-13}$ M, due to insufficient organic radical concentrations for oligomer formation [*Lee et al.*, 2011]. Although the hydroxyl radical concentrations are unknown, ~~T~~there is only a relationship between oxalate and gas-phase glyoxal for Period ~~B~~ C during times of RH decreasing ($R^2$ = 0.44), which is when clouds were observed west of the site. In addition, ~~T~~there is no important relationship observed between oxalate and ALW for either period (all $R^2$ < 0.17)~~, consistent with the expectation that the oxalate forms in clouds, not in aerosol water.~~

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~~3.3. Further Examination of WSOC During Periods A and B~~3.3.2. WSOC

The above analysis suggests that the majority of the WSOC observed during the first half of the study, as illustrated by Period A, is formed locally via chemistry in aerosol liquid water. Clearly, WSOC in the second half of the measurements appears to be different and to derive from different sources. As illustrated by Period ~~B~~C, the WSOC during this time is likely more regional with contributions from gas-to-particle partitioning and possibly in-cloud aqSOA.

To further explore this idea of different types of WSOC, the WSOC observations were compared to positive matrix factorization (PMF) analysis of the AMS OA data collected at SPC. Five factors, one HOA (hydrocarbon-like OA) and four OOA (oxygenated OA), were found. The four OOA factors include one semi-volatile type (OOA-1) and three low volatility types (OOA-2, OOA-3, and OOA-4). More details on the AMS ME-2 analysis can be found in the supporting information.

As shown in Fig. ~~8~~9, the measured WSOC from the first half of the study is dominated by OOA-2 and the second half by OOA-4. This can be further illustrated by looking at the correlation of WSOC vs. OOA-2 and OOA-4 during the times of RH increasing for Periods A and ~~B~~ C (Fig. ~~9~~10). The WSOC in Period A is most strongly correlated with OOA-2 ($R^2$ = 0.~~85~~83) and in Period ~~B~~ C with OOA-4 ($R^2$ = 0.64).

To estimate how each AMS ME-2 factor contributed to WSOC and what fraction of each factor was water-soluble, a multilinear regression analysis was tentatively performed using the method proposed by *Timonen et al.* [2013]. The results are shown in Table ~~3~~ S2 and Fig. ~~10~~11. This approach seeks to reproduce the total WSOC as a linear combination of the different factors, whilst minimizing the residuals and, unlike in *Timonen et al.* [2013], capping the individual factor contributions at 1 to allow conservation of the carbon mass. The regression

analysis was carried out with a zero intercept like in *Timonen et al.* [2013], as well as with a non-zero intercept to account for possible instrumental biases between the AMS and PILS methods. Only the four OOA factors were considered, while HOA was assumed to be completely insoluble. All concentrations are in carbon mass units, which for the AMS factors were derived from organic mass concentrations through factor-specific OM/OC ratios. The results of the regression are reported for the whole PILS measurement period and also for Periods A and ~~B~~ C separately.

The results for the whole measurement period indicate that the largest contributions to the WSOC must be attributed to the OOA types which were simply the most abundant (OOA-3 and OOA-4), but the water-soluble fractions as reflected in the regression coefficients were greatest for OOA-2 and OOA-4 in agreement with their high correlation coefficients with WSOC. Interestingly, OOA-2 and OOA-4 are also the factors possessing the highest O/C ratios (0.77 and 0.76, respectively), with respect to the other two (O/C = 0.48 for OOA-1 and 0.36 for OOA-3). Therefore, in this study the factor-specific WSOC fractions seem related to the oxygen contents measured by the AMS.

The multilinear regression analysis performed on the Period A measurements suggests that the largest water-soluble fractions are exhibited by OOA-1 and OOA-2, whose concentrations were observed to increase along with RH and WSOC for all the days in this period of the campaign. Due to the very different absolute average concentrations, the second factor (OOA-2) provided the largest contribution to WSOC, accounting for more than one third of the total water-soluble organic carbon concentration. Interestingly, the diurnal trend of OOA-1 indicated that its partitioning to the aerosol phase was largely reversible, and its concentrations declined steeply in the late morning hours when RH and ALW decreased (Fig. 12a). ~~This can be illustrated by the additional correlation of WSOC with OOA-1 during the times of RH increasing for only Period A (Fig. 9a, $R^2$ = 0.50). This is not surprising given the high correlation between OOA-1 and nitrate, which drives ALW in this region, during the whole measurement period ($R^2$ = 0.64).~~ In the same hours of the day, the OOA-2 concentrations were largely unaffected by RH indicating (a) that OOA-2 mainly accounted for oxidized compounds stable in the aerosol phase and (b) that boundary layer growth is not the reason for the decrease in OOA-1 as this should have affected all factors. OOA-1 and OOA-2 can therefore be ~~interpreted~~ hypothesized as two aging stages of aqSOA formation during Period A.

Interestingly, some OOA-2 is also produced in Periods B and D. Although the concentrations levels of OOA-2 observed are similar between Periods A and D, OOA-2 concentrations are much more sustained across the day in Period A. In addition, as illustrated in the diurnal profiles for these periods (Fig. S10) the OOA-2 follows along more closely with OOA-1, RH, and ALW in Periods B and D, likely due to the differences in meteorology and/or chemistry of these periods compared to Period A. Regardless of these differences the observations all still point to the strong relationship between OOA-1, OOA-2, and ALW.

The results obtained for Period ~~B~~ C show again that the greatest coefficients (hence the largest water-soluble fractions) were found for OOA-2 and OOA-4. However, due to its very small concentrations in this period, OOA-2 provided a negligible contribution to WSOC (1%), while OOA-4 was estimated to account for more than half of the WSOC carbon content. The examination of time trends indicates that OOA-4 is mainly a background component of the aerosol, showing no appreciable increase at the time when RH increased for a few hours on the mornings of 5 and 6 July. Similar to Period A, here again the times when RH and ALW were

high showed relatively high concentrations of OOA-1 (Fig. 12b), which represented an additional (though small compared to OOA-4) contribution to WSOC. Period C provides a case where significant OOA-1 is formed, but not OOA-2.

Overall, whilst not without uncertainty, the above findings support the idea that two different types of WSOC occurred during these two different periods. They also support the idea that aqueous processing is dominating during the times of RH increasing during Period A and OOA-2 represented the most important component. The high O/C ratio of OOA-2 is expected for SOA formed through aqueous-phase reactions, because precursors are water-soluble and thus have low carbon numbers and high O/C ratios. Average O/C ratios of ~0.7 to 1.1 have been observed in the oligomeric products formed from laboratory experiments involving hydroxyl radical oxidation and/or aqueous photolysis of methylglyoxal, glycolaldehyde, and phenolic compounds [*Altieri et al.*, 2008; *Tan et al.*, 2009; *Perri et al.*, 2010; *Sun et al.*, 2010]. The high O/C ratios observed for the other main WSOC component, OOA-4, which dominates Period B, could be explained by extensive aging of non-aqueous SOA [*Lambe et al.*, 2011]. However, in-cloud aqueous-phase reactions could have occurred upwind of the Po Valley, as indicated by the occurrence of oxalate and clouds previously discussed. Our measurements are fully consistent, in indicating that OOA-4 was mainly transported to the site and was not a product of the local aqueous-phase heterogeneous chemistry in the Po Valley atmospheric surface layer.

### 3.4. Conditions for local aqSOA

What leads to strong local aqSOA formation during Period A at SPC? High ALW was present throughout the study (Fig. ~~2b~~3b). It was observed that the days with the highest ALW also had the highest aerosol loading in the lowest layers of the atmosphere. However, no other day outside of Period A, except for 23 June, had a relationship of WSOC with RH during the times of RH increasing. This suggests that high ALW or aerosol loading alone are not sufficient for local aqSOA formation.

As previously mentioned, during Period A early morning nitrate peaks were observed only at the SPC ground site and not at the urban site. However, just the presence of high nitrate (above 2 $\mu g/m^3$) does not seem to lead to aqSOA as no relationship of WSOC as a function of RH was observed on 6 and 7 July (Period D) when nitrate in concentrations similar to those of Period A were observed at SPC. Interestingly, the nitrate observed on these days was also observed in Bologna (Fig. ~~6~~7). The timing of the peak nitrate concentration also differed from Period A; it occurred later in the morning, around 07:00 LT, whereas during Period A nitrate peaked around midnight or 01:00 LT and then again around 07:00 LT. This suggests that the presence and timing of elevated nitrate, which is a strong determinant of ALW, may be important for local aqSOA production and resulting WSOC aerosol concentrations in this region.

As previously mentioned, ~~A~~an examination of possible gas-phase precursors (e.g., aromatic VOCs and glyoxal, Table 1) shows no noticeable decline in concentration from the first to second half of the measurement period. Therefore, a possible explanation for the difference between Period A and ~~Period B~~ the other period is meteorology. Period A featured an anticyclonic condition that led to air stagnation; ~~Period B~~ the other periods featured stronger transport and ventilation. Therefore, during Periods B, C, and D intermediate products needed to form appreciable concentrations of aqSOA are less likely to quickly accumulate in the local boundary layer.

It is possible that another key ingredient in the chemistry is ammonia. Recent studies have suggested possible aqSOA formation processes mediated by ammonia and other atmospheric bases [*Galloway et al.*, 2009; *Nozière et al.*, 2009; *Ortiz-Montalvo et al.*, 2014; *Yu et al.*, 2011]. Ammonia is prevalent in the Po Valley due to agricultural activities. During Period A, high ammonia concentrations (greater than ~30 μg/m$^3$) were observed only at SPC (Fig. ~~11a~~13a).

Overall, the data suggest that local aqSOA production during the stagnation of Period A is not due to cloud processing. Our results also suggest that this aqueous chemistry occurs in the dark, which likely provides the favorable low temperatures and high RH for nitrate aerosol and ALW [*Hodas et al.*, 2014]. Based on other measurements at SPC, the stagnation conditions and elevated nitrate around midnight occurred each day from 14 June through 23 June, suggesting that the local aqSOA formation actually commenced five days earlier. When all these conditions were met, each day ~1 μg C/m$^3$ of new WSOC (determined as the change in WSOC concentration during the times of RH increasing) can be attributed to this process.

## 4. Summary

Measurements were conducted during the PEGASOS Study in the Po Valley of Italy during June and July 2012 in San Pietro Capofiume (SPC). The goal was to look for evidence of aqSOA in the ambient atmosphere. Measurements included near real-time WSOC (a good proxy for SOA), inorganic anions/cations, and organic acids. The data were analyzed in terms of the times when RH increased from 40 to ~~80~~70% (times of RH increasing) and then when the RH decreased from ~~80~~ 70 back to 40% (times of RH decreasing) in order to diminish influences from dilution and mixing on ambient measurements. The analysis focused on ~~two~~ four periods: Period A on 19-21 June~~, and~~ Period B on 30 June, 1-2 July, Period C on 3-5 July, and Period D on 6-7 July.

Evidence for local aqSOA formation in wet aerosols was observed during Period A. When this occurred there was a correlation of WSOC with OA, ALW, RH, and nitrate. Additionally, this was only observed during times of RH increasing, suggesting the aqSOA was formed in the dark. The aqSOA formation is thought to be local because elevated nitrate, the driver for aerosol water, was only observed at the main ground site in SPC even though the auxiliary site in Bologna was sampling similar upwind air masses at the time.

A comparison of Periods A and C suggested Period C~~B~~ differed from Period A. The WSOC during Period ~~B~~ C was likely formed regionally. Interestingly, during Period ~~B~~ C as well as Period A a correlation was found between oxalate and sulfate. This suggests that oxalate concentrations were not strongly affected by local aqSOA formation. More importantly, it indicates that oxalate is not a good universal marker for aqSOA. ~~It is probably better for observing aqSOA produced in clouds, which were present west of SPC only in Period B.~~

A comparison of WSOC with the AMS PMF OOA factors showed that Period A featured high O/C ratios, consistent with aqSOA formation. However, they also reinforce the conclusion that the composition of the WSOC differed between ~~Periods A and B~~the two halves of the study. Periods A and ~~B~~ C were dominated by two different OOA factors, OOA-2 (locally produced) and OOA-4 (long-range transported), respectively.

Overall, by examining the conditions observed in Period A, the data suggest that the local aqSOA formation observed is not due to cloud processing and occurs in the dark. The timing of elevated nitrate concentrations is critical (around midnight local time) to provide the liquid water

reservoir needed for aqueous chemistry. Approximately 1 μg C/$m^3$ of new WSOC was formed through this process each day these conditions were met, indicating the importance of aqSOA as a source of ambient OA in this region.

**Acknowledgements**

We acknowledge funding from the National Science Foundation under Projects AGS-1050052, AGS-1052611, and AGS-1051338. Measurements at SPC were also funded by the European Union FP7 project PEGASOS (FP7-ENV-2010/265148) and by the Regione Emilia Romagna (project SUPERSITO DRG n. 428/10). The authors thank the European Union FP7 ÉCLAIRE (FP7-ENV-2011/282910) project for funding the ammonia measurements in Bologna, the Energy Research Centre of the Netherlands (ECN) for providing the MARGA instrument at SPC, and C. DiMarco, M. Blom, S. Leeson, T. Hutchings, C. Braban, and L. Giulianelli for supporting the ammonia measurements. The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (http://www.arl.noaa.gov/ready.html) used in this publication.

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**Figure Captions**

**Figure 1.** ~~Left panel: characteristic 72 h air mass back trajectories for (a) Period A and (b) Period B at the PEGASOS ground sites of Bologna and SPC. All back trajectories are based on the NOAA ARL HYSPLIT trajectory model. Right panel: maps~~ Maps created using Google Earth (version 7.1.5.1557) to show the areas surrounding the (a~~c~~) Bologna and (b~~d~~) SPC sampling sites.

**Figure 2.** Characteristic 72 h air mass back trajectories for (a) Period A, (b) Period B, (c) Period C, and (d) Period D at the PEGASOS ground sites of Bologna and SPC. All back trajectories are based on the NOAA ARL HYSPLIT trajectory model.

**Figure ~~2~~3.** Times series of hourly averaged measured (a) WSOC, ~~and~~ (b) calculated ALW, (c) RH, and (d) Temperature at SPC. Any gaps in ALW are due to missing PILS-IC data. The dashed vertical lines indicate midnight local time (UTC+2). Periods A, ~~and~~ B, C, and D are also indicated.

**Figure ~~3~~4.** Hourly averaged WSOC as a function of RH for (a) Periods A and C~~B~~ and (b) Periods B and D during the times of RH ~~(a)~~ increasing and (c~~b~~) Periods A and C and (d) Periods B and D during the times of RH decreasing at SPC. The WSOC was binned into 10% RH bands starting at 40% RH. The error bars represent the standard deviation at each bin. Numbers above or below points represent the number of data points in each bin.

**Figure ~~4~~5.** Correlation of hourly averaged WSOC vs. OA for (a) Period A and (b) Period ~~B~~C, ALW for (c) Period A and (d) Period ~~B~~C, and RH for (e) Period A and (f) Period ~~B~~ C at SPC. All plots are for during the times of RH increasing.

**Figure ~~5~~6.** Correlation of hourly averaged WSOC vs. nitrate for (a) Period A and (b) Period ~~B~~C, oxalate for (c) Period A and (d) Period ~~B~~C, and sulfate for (e) Period A and (f) Period ~~B~~ C at SPC. All plots are for during the times of RH increasing.

**Figure ~~6~~7.** Times series of hourly averaged AMS nitrate observed at (a) SPC and (b) Bologna. The dashed vertical lines indicate midnight local time (UTC+2). Periods A, ~~and~~ B, C, and D are also indicated.

**Figure ~~7~~8.** Correlation of hourly averaged oxalate vs. sulfate for Periods A and ~~B~~ C during the times of RH (a) increasing and (b) decreasing, gas-phase glyoxal for Periods A and ~~B~~ C during the times of RH (c) increasing and (d) decreasing, and ALW for Periods A and ~~B~~ C during the times of RH (e) increasing and (f) decreasing at SPC.

**Figure ~~8~~9.** Times series of hourly averaged WSOC with AMS ME-2 factors (a) OOA-1, (b) OOA-2, (c) OOA-3, and (d) OOA-4 at SPC. The units for each factor have been converted from μg/m$^3$ to μg C/m$^3$ using their calculated OM/OC ratio (OOA-1 = 1.81, OOA-2 = 2.15, OOA-3 = 2.13, and OOA-4 = 1.62). The dashed vertical lines indicate midnight local time (UTC+2). Periods A, ~~and~~ B, C, and D are also indicated.

**Figure ~~9~~10.** Correlation of hourly averaged WSOC vs. AMS ME-2 factors OOA-1 for (a) Period A and (b) Period ~~B~~C, OOA-2 for (c) Period A and (d) Period ~~B~~C, OOA-3 for (e) Period A and (f) Period ~~B~~C, and OOA-4 for (g) Period A and (h) Period ~~B~~ C at SPC. All plots are for during the times of RH increasing.

**Figure ~~10~~11.** Time series of hourly averaged AMS ME-2 OOA factors, WSOC measured, and WSOC reconstructed for the whole measurement period (top), Period A (bottom left), and Period ~~B~~ C (bottom right) at SPC. The units for each OOA factor have been converted from μg/m$^3$ to μg C/m$^3$ using their calculated OM/OC ratio.

**Figure 12.** Diurnal profile of WSOC, OOA-1, OOA-2, RH, temperature, ALW, and nitrate for (a) Period A and (b) Period C at SPC.

**Figure ~~11~~13.** Times series of hourly averaged ammonia observed at (a) SPC and (b) Bologna. The dashed lines indicate midnight local time (UTC+2). Periods A, ~~and~~ B, C, and D are also indicated.

**Table 1.** Average concentrations of aerosol and gas-phase species along with various meteorological parameters observed during the times of RH increasing and decreasing during Periods A, and Period B, C, and D at SPC.

| | OA ($\mu g/m^3$) | WSOC ($\mu g C/m^3$) | Glycolate ($\mu g/m^3$) | Acetate ($\mu g/m^3$) | Formate ($\mu g/m^3$) | Chloride ($\mu g/m^3$) | Sulfate ($\mu g/m^3$) | Oxalate ($\mu g/m^3$) | Nitrate ($\mu g/m^3$) | Ozone ($\mu g/m^3$) | $NO_x$ ($\mu g/m^3$) | $SO_2$ (ppb) | Benzene ($\mu g/m^3$) | Toluene ($\mu g/m^3$) | Xylene ($\mu g/m^3$) | Glyoxal (ppb) | T (°C) | RH (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Period A RH Increasing | 8.93 | 4.73 | 0.28 | 0.40 | 0.43 | 0.13 | 3.49 | 0.24 | 2.91 | 47.42 | 28.90 | 0.65 | 0.21 | 1.21 | 0.26 | 0.05 | 24.47 | 64.49 |
| Period A RH Decreasing | 9.63 | 5.09 | 0.30 | 0.33 | 0.47 | 0.17 | 3.23 | 0.23 | 5.61 | 63.70 | 17.75 | 1.14 | 0.27 | 1.78 | 0.34 | 0.09 | 26.09 | 57.66 |
| Period B RH Increasing | 2.05 | 1.55 | 0.24 | 0.28 | 0.23 | 0.11 | 2.80 | 0.13 | 1.18 | 61.29 | 9.72 | 0.40 | 0.17 | 1.18 | 0.40 | 0.05 | 23.31 | 60.60 |
| Period B RH Decreasing | 2.01 | 1.54 | 0.22 | 0.32 | 0.23 | 0.10 | 2.75 | 0.12 | 1.28 | 75.40 | 8.08 | 0.51 | 0.17 | 1.11 | 0.44 | 0.07 | 25.02 | 53.88 |

| | OA ($\mu g/m^3$) | WSOC ($\mu g C/m^3$) | Glycolate ($\mu g/m^3$) | Acetate ($\mu g/m^3$) | Formate ($\mu g/m^3$) | Chloride ($\mu g/m^3$) | Sulfate ($\mu g/m^3$) | Oxalate ($\mu g/m^3$) | Nitrate ($\mu g/m^3$) | Sodium ($\mu g/m^3$) | Ammonium ($\mu g/m^3$) | Potassium ($\mu g/m^3$) | Magnesium ($\mu g/m^3$) | Calcium ($\mu g/m^3$) | ALW ($\mu g/m^3$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Period A RH Increasing | 8.93 | 4.73 | 0.28 | 0.40 | 0.43 | 0.13 | 3.49 | 0.24 | 2.91 | NA | NA | NA | NA | NA | 6.81 |
| Period A RH Decreasing | 9.63 | 5.09 | 0.30 | 0.33 | 0.47 | 0.17 | 3.23 | 0.23 | 5.61 | NA | NA | NA | NA | NA | 7.29 |
| Period B RH Increasing | 4.06 | 2.87 | 0.22 | 0.24 | 0.24 | 0.09 | 3.22 | 0.12 | 1.67 | 0.01 | 1.04 | 0.43 | 0.10 | 0.37 | 4.21 |
| Period B RH Decreasing | 3.78 | 2.89 | 0.22 | 0.24 | 0.23 | 0.09 | 2.69 | 0.11 | 1.56 | 0.01 | 1.04 | 0.48 | 0.09 | 0.13 | 4.34 |
| Period C RH Increasing | 2.05 | 1.55 | 0.24 | 0.28 | 0.23 | 0.11 | 2.80 | 0.13 | 1.18 | 0.04 | 0.92 | 0.51 | 0.11 | 0.26 | 2.89 |
| Period C RH Decreasing | 2.01 | 1.54 | 0.22 | 0.32 | 0.23 | 0.10 | 2.75 | 0.12 | 1.28 | 0.04 | 0.94 | 0.54 | 0.09 | 0.06 | 2.64 |
| Period D RH Increasing | 2.89 | 1.92 | 0.17 | 0.18 | 0.21 | 0.11 | 3.38 | 0.12 | 1.31 | 0.02 | 1.07 | 0.48 | 0.10 | 0.32 | 4.10 |
| Period D RH Decreasing | 3.02 | 1.99 | 0.19 | 0.19 | 0.24 | 0.14 | 4.89 | 0.13 | 3.56 | 0.03 | 2.00 | 0.55 | 0.10 | 0.20 | 7.90 |

| | Ozone ($\mu g/m^3$) | $NO_x$ ($\mu g/m^3$) | $SO_2$ (ppb) | Benzene ($\mu g/m^3$) | Toluene ($\mu g/m^3$) | Xylene ($\mu g/m^3$) | Glyoxal (ppb) | T (°C) | RH (%) |
|---|---|---|---|---|---|---|---|---|---|

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Period A RH Increasing | 47.42 | 28.90 | 0.65 | 0.21 | 1.21 | 0.26 | 0.05 | 24.47 | 64.49 |
| Period A RH Decreasing | 63.70 | 17.75 | 1.14 | 0.27 | 1.78 | 0.34 | 0.09 | 26.09 | 57.66 |
| Period B RH Increasing | 76.6 | 10.94 | 0.68 | 0.19 | 0.83 | 0.53 | 0.06 | 26.74 | 60.87 |
| Period B RH Decreasing | 51.6 | 9.30 | 0.69 | 0.29 | 1.43 | 0.66 | 0.07 | 26.2 | 61.20 |
| Period C RH Increasing | 61.29 | 9.72 | 0.40 | 0.17 | 1.18 | 0.40 | 0.05 | 23.31 | 60.60 |
| Period C RH Decreasing | 75.40 | 8.08 | 0.51 | 0.17 | 1.11 | 0.44 | 0.07 | 25.02 | 53.88 |
| Period D RH Increasing | 87.21 | 8.93 | 0.30 | 0.12 | 0.52 | 0.23 | 0.05 | 25.63 | 63.45 |
| Period D RH Decreasing | 93.73 | 5.12 | 0.38 | 0.15 | 0.85 | 0.28 | 0.07 | 27.32 | 54.92 |

**Table 2.** Equations for each of the linear regression plots shown in Figs. 4, 5, 7, and 9. Uncertainties with the least square regressions are one standard deviation.

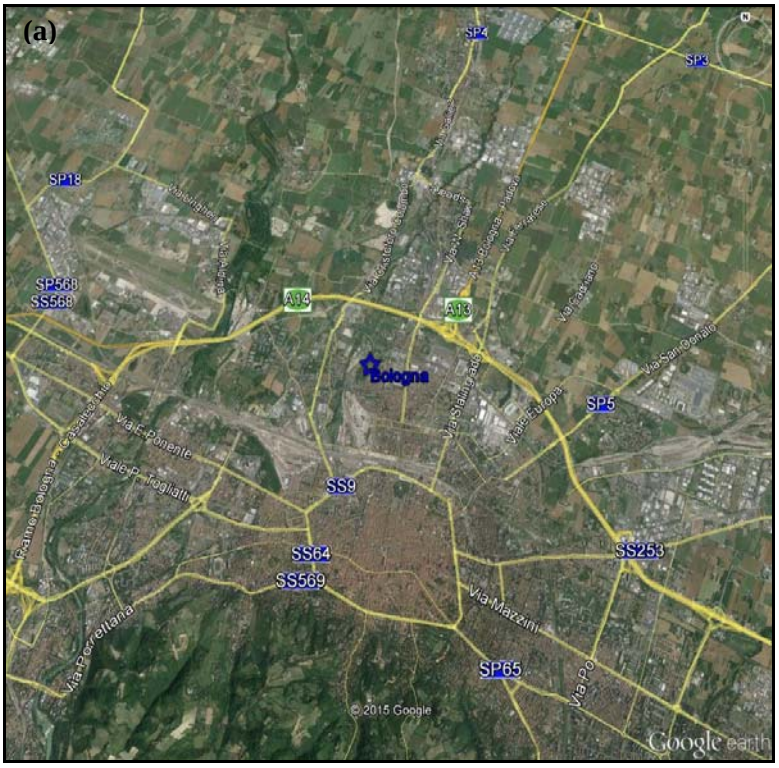
| Figure | Linear Regression Equation |
|---|---|
| 4a | y = 0.476x ± 0.039 − 0.345 ± 0.357 |
| 4b | y = 0.614x ± 0.084 + 0.300 ± 0.177 |
| 4c | y = 0.167x ± 0.023 + 2.825 ± 0.174 |
| 4d | y = 0.183x ± 0.108 + 0.962 ± 0.321 |
| 4e | y = 0.047x ± 0.010 + 0.898 ± 0.687 |
| 4f | y = −0.003x ± 0.010 + 1.711 ± 0.595 |
| 5a | y = 0.469x ± 0.060 + 2.574 ± 0.192 |
| 5b | y = 0.824x ± 0.441 + 0.512 ± 0.527 |
| 5c | y = 9.024x ± 3.560 + 1.753 ± 0.872 |
| 5d | y = 22.095x ± 2.990 − 1.354 ± 0.387 |
| 5e | y = 0.297x ± 0.187 + 2.902 ± 0.667 |
| 5f | y = 0.276x ± 0.124 + 0.718 ± 0.354 |
| 7a | Period A y = 0.040x ± 0.007 + 0.097 ± 0.025<br>Period B y = 0.014x ± 0.004 + 0.090 ± 0.012 |
| 7b | Period A y = 0.078x ± 0.020 − 0.021 ± 0.068<br>Period B y = 0.043x ± 0.007 + 0.006 ± 0.020 |
| 7c | Period A y = 0.904x ± 0.538 + 0.186 ± 0.030<br>Period B y = 0.388x ± 0.410 + 0.106 ± 0.024 |
| 7d | Period A y = −0.053x ± 0.365 + 0.241 ± 0.029<br>Period B y = 0.918x ± 0.252 + 0.062 ± 0.018 |
| 7e | Period A y = 0.001x ± 0.003 + 0.229 ± 0.019<br>Period B y = 0.005x ± 0.004 + 0.114 ± 0.013 |
| 7f | Period A y = 0.006x ± 0.003 + 0.193 ± 0.029<br>Period B y = −0.004x ± 0.005 + 0.136 ± 0.013 |
| 9a | y = 4.351x ± 0.874 + 2.648 ± 0.281 |
| 9b | y = 0.418x ± 0.535 + 1.432 ± 0.173 |
| 9c | y = 1.245x ± 0.103 + 1.526 ± 0.209 |
| 9d | y = 9.168x ± 10.900 + 1.499 ± 0.138 |
| 9e | y = 0.248x ± 0.236 + 3.572 ± 0.378 |
| 9f | y = 0.399x ± 0.328 + 1.373 ± 0.166 |

| | |
|---|---|
| 9g | y = 0.256x ± 0.312 + 4.138 ± 0292 |
| 9h | y = 1.165x ± 0.166 + 0.625 ± 0.140 |

**Table 3.** Parameters of the multilinear regression analysis of WSOC. Slope coefficients are reported for the individual AMS ME-2 factors, while y-intercepts are presented in the right column. Numbers in parenthesis refer to the percent contributions of each AMS factors (and of intercepts) to the measured WSOC. See the main text for further explanation.

| | | OOA-1 | OOA-2 | OOA-3 | OOA-4 | Intercept |
|---|---|---|---|---|---|---|
| Whole campaign | intercept forced to 0 | 0.56 (7%) | 0.87 (12%) | 0.83 (32%) | 1.00 (49%) | - |
| | unforced | 0.40 (5%) | 0.94 (12%) | 0.63 (24%) | 0.92 (44%) | 0.31 μgC/m$^3$ (15%) |
| Period A | intercept forced to 0 | 1.00 (7%) | 0.88 (37%) | 0.77 (32%) | 1.00 (24%) | - |
| | unforced | 0.88 (6%) | 0.92 (38%) | 0.48 (19%) | 0.59 (14%) | 0.72 μgC/m$^3$ (22%) |
| Period B | intercept forced to 0 | 0.83 (11%) | 1.00 (1%) | 0.93 (32%) | 1.00 (56%) | - |
| | unforced | 0.27 (4%) | 1.00 (1%) | 0.46 (15%) | 1.00 (53%) | 0.47 μgC/m$^3$ (28%) |

Figure 1


(a)
SP4
SP3
SP18
SP568
SS568
A14
A13
Bologna
SP5
SS9
SS64
SS569
SS253
SP65
Via Mazzini
Via Perettana
Viale Europa
Via E. Ponente
Viale P. Togliatti
Via San Donato
© 2015 Google
Google earth


(b)
Via Saveria Vecchia
SP25
San Pietro Capofiume
Strada della Boaria
Via Casoni
Via Idice Abbandonato
Via Canale
© 2015 Google
SP6
Google earth

Figure 2

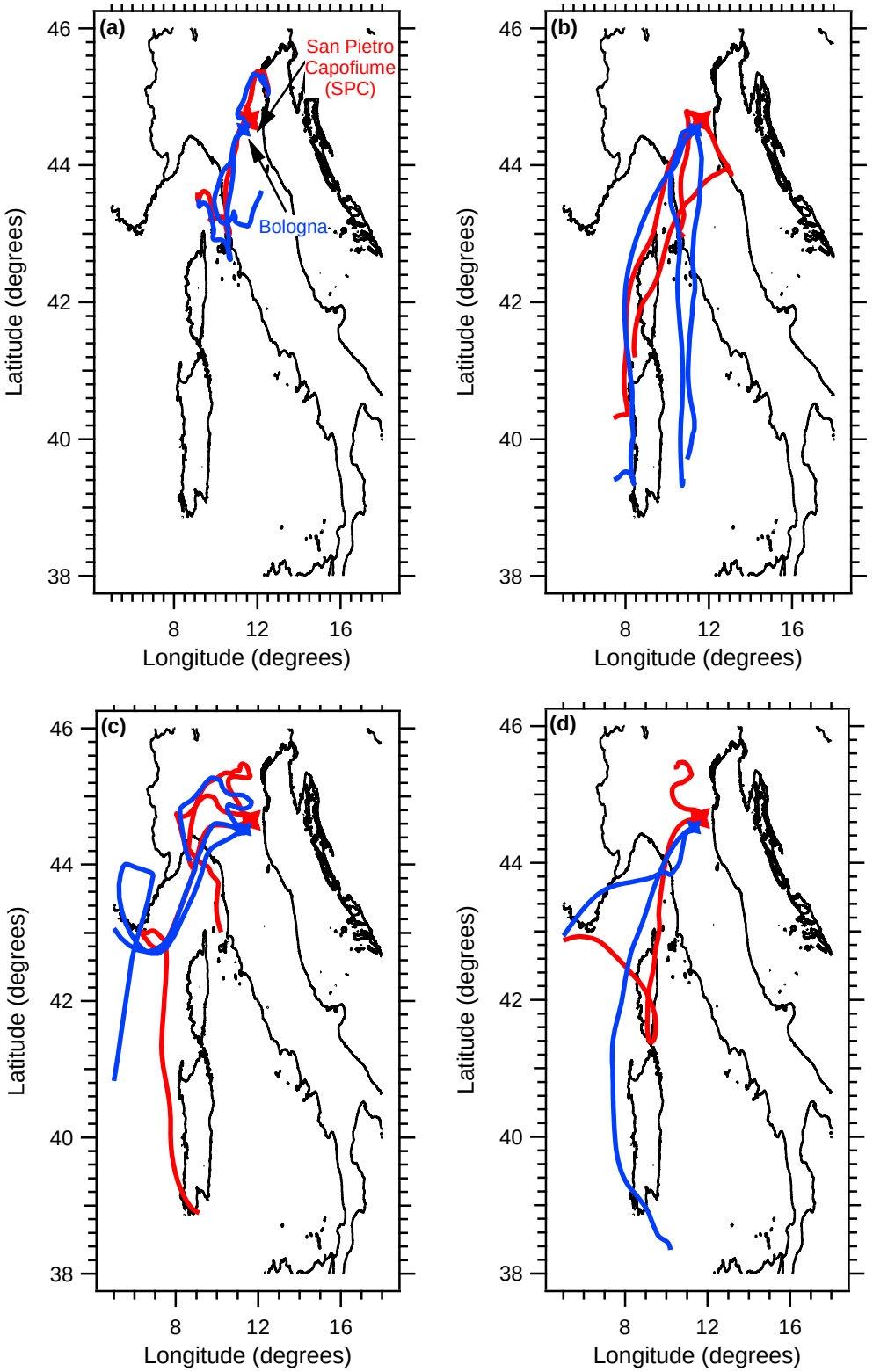

(a)
San Pietro
Capofiume
(SPC)
Bologna
(b)
(c)
(d)
Latitude (degrees)
Longitude (degrees)
46
44
42
40
38
8
12
16

Figure 3

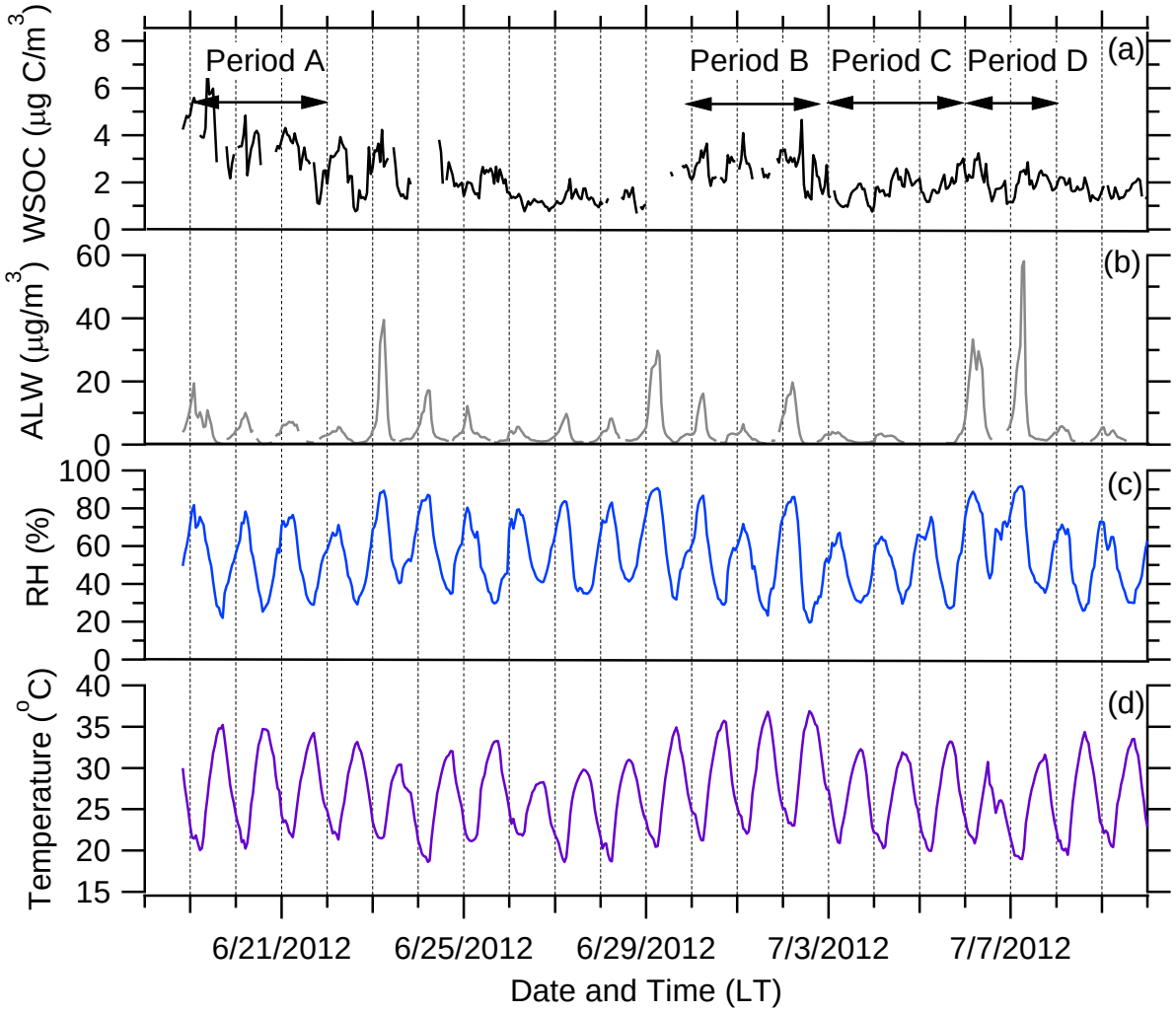

Period A
Period B
Period C
Period D
(a)
WSOC (μg C/m3)
(b)
ALW (μg/m3)
(c)
RH (%)
(d)
Temperature (oC)
6/21/2012
6/25/2012
6/29/2012
7/3/2012
7/7/2012
Date and Time (LT)

Figure 4

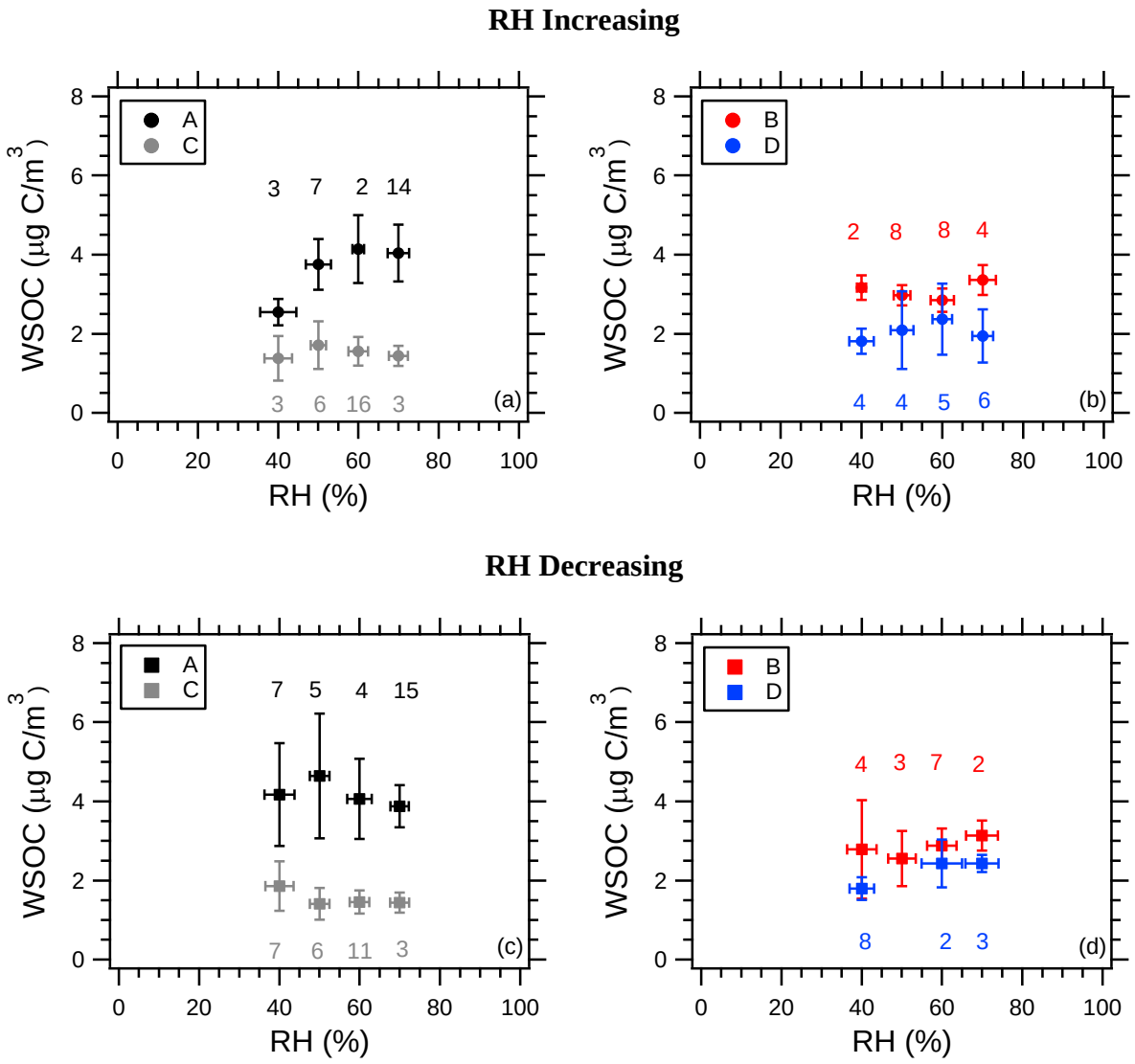

RH Increasing
RH Decreasing
WSOC (µg C/m3)
RH (%)
A
C
B
D
(a)
(b)
(c)
(d)
3 7 2 14
3 6 16 3
2 8 8 4
4 4 5 6
7 5 4 15
7 6 11 3
4 3 7 2
8 2 3

Figure 5

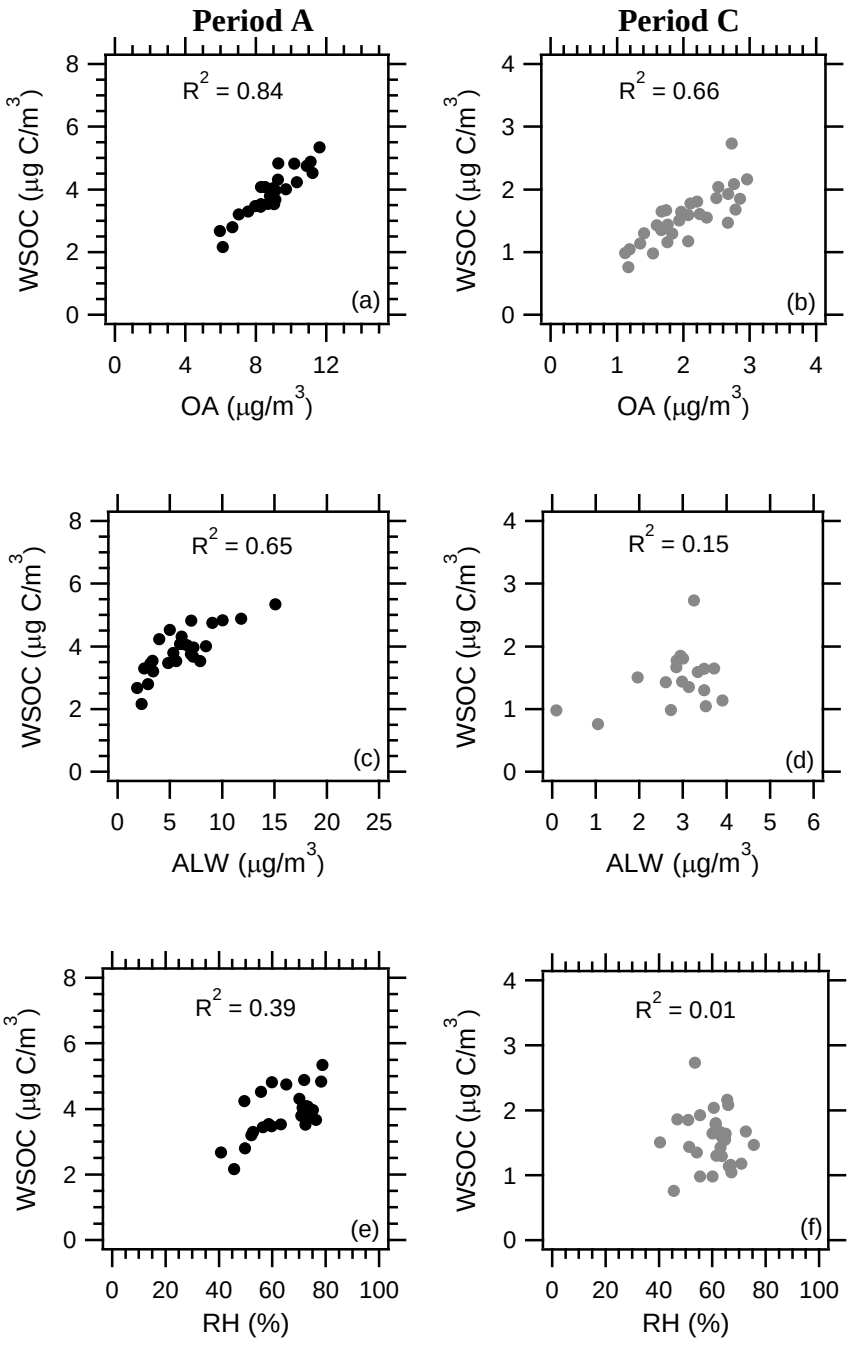

Period A
Period C
R2 = 0.84
R2 = 0.66
R2 = 0.65
R2 = 0.15
R2 = 0.39
R2 = 0.01
WSOC (μg C/m3)
OA (μg/m3)
ALW (μg/m3)
RH (%)
(a)
(b)
(c)
(d)
(e)
(f)

Figure 6

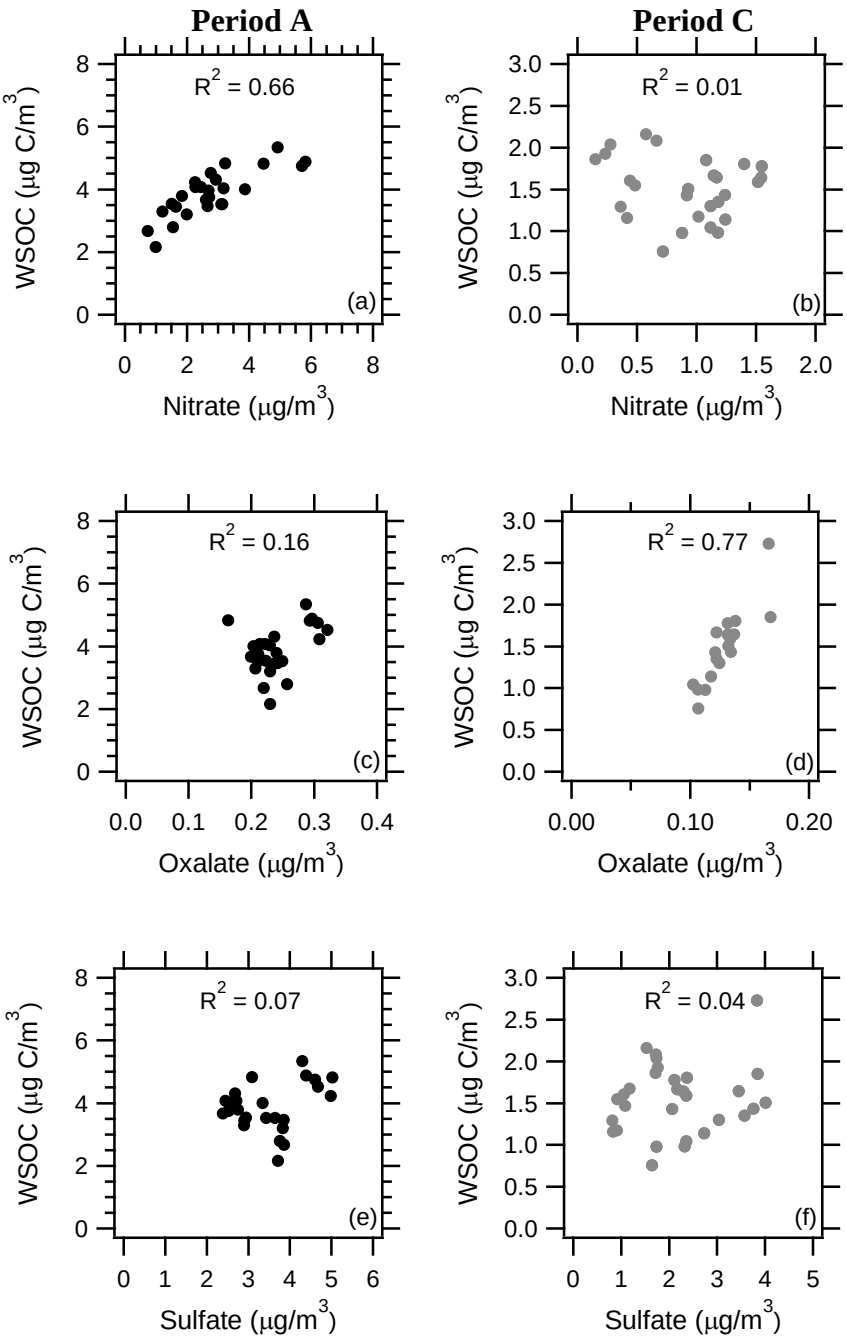

Period A
Period C
R2 = 0.66
R2 = 0.01
R2 = 0.16
R2 = 0.77
R2 = 0.07
R2 = 0.04
WSOC (μg C/m3)
Nitrate (μg/m3)
Oxalate (μg/m3)
Sulfate (μg/m3)
(a)
(b)
(c)
(d)
(e)
(f)

Figure 7

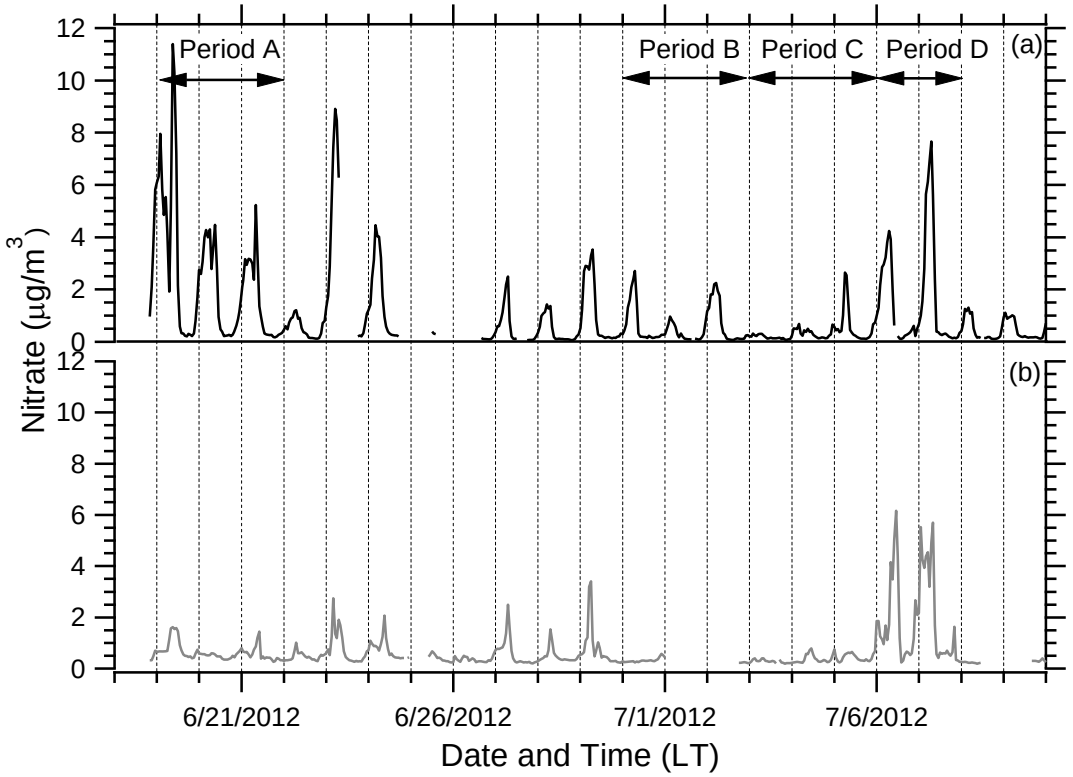

Period A
Period B
Period C
Period D
(a)
(b)
Nitrate (μg/m3)
0
2
4
6
8
10
12
6/21/2012
6/26/2012
7/1/2012
7/6/2012
Date and Time (LT)

Figure 8

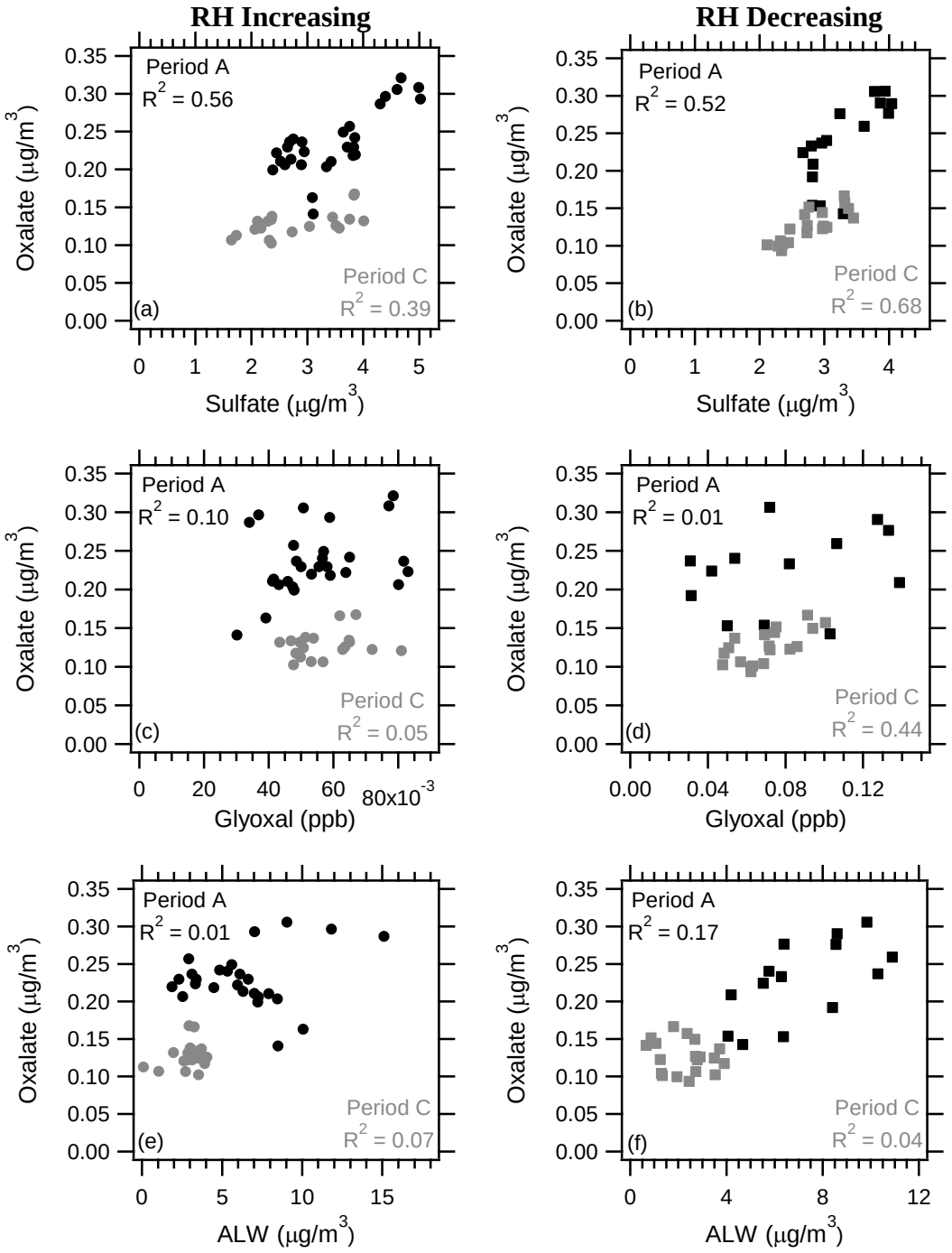

RH Increasing
RH Decreasing
Period A
Period C
(a)
(b)
(c)
(d)
(e)
(f)
Oxalate (μg/m3)
Sulfate (μg/m3)
Glyoxal (ppb)
ALW (μg/m3)
80x10-3

Figure 9

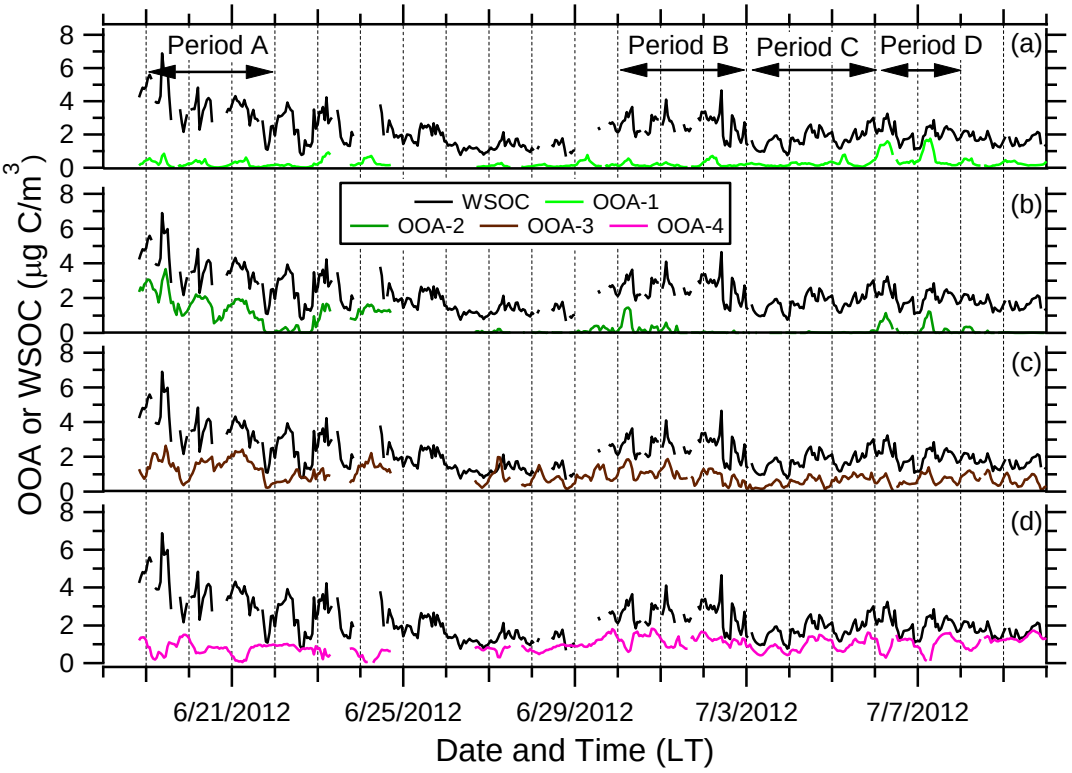

Period A
Period B
Period C
Period D
(a)
(b)
(c)
(d)
WSOC
OOA-1
OOA-2
OOA-3
OOA-4
OOA or WSOC (μg C/m3)
6/21/2012
6/25/2012
6/29/2012
7/3/2012
7/7/2012
Date and Time (LT)

Figure 10

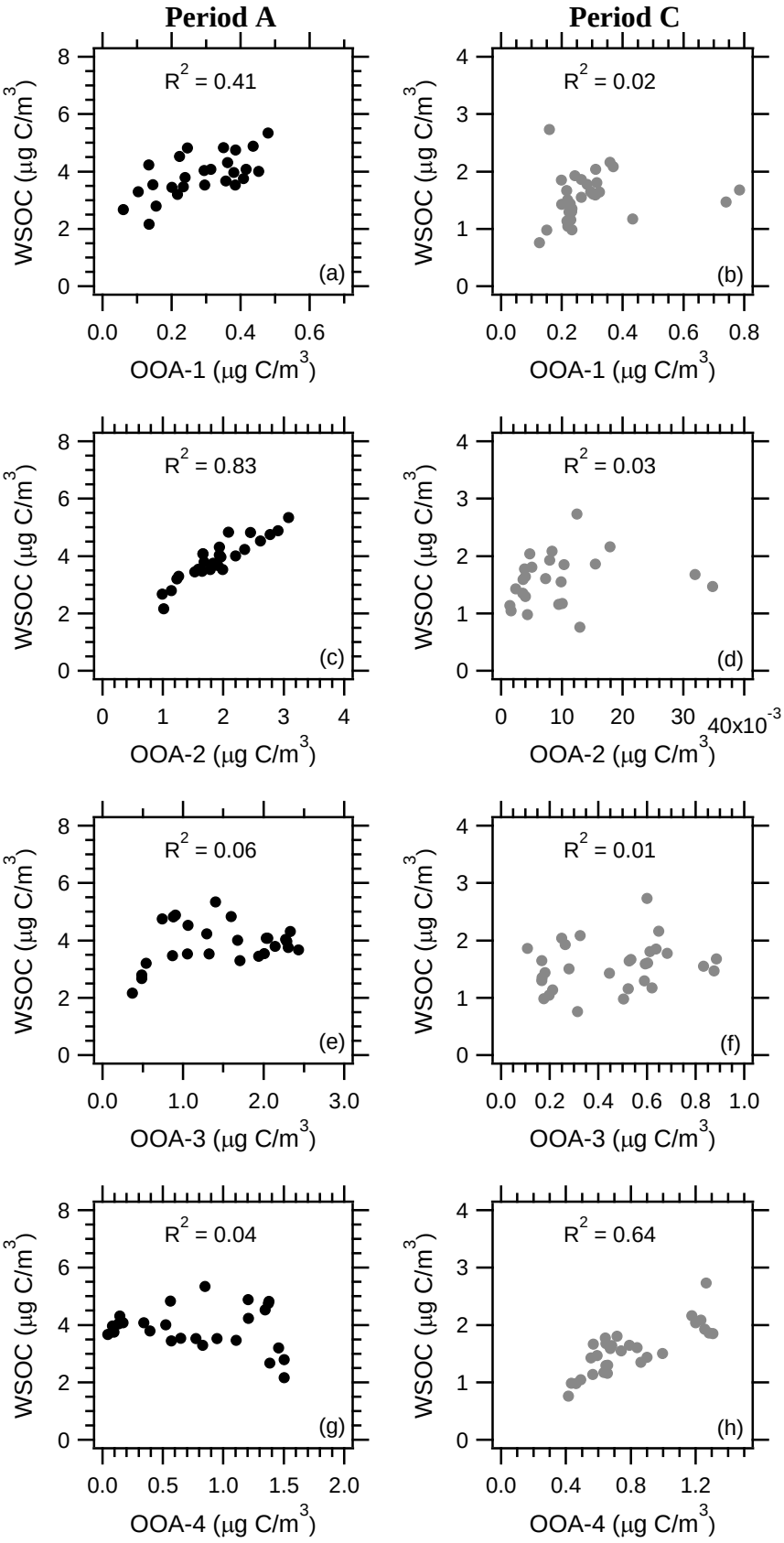

Period A
Period C
R2 = 0.41
R2 = 0.02
R2 = 0.83
R2 = 0.03
R2 = 0.06
R2 = 0.01
R2 = 0.04
R2 = 0.64
(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
WSOC (μg C/m3)
OOA-1 (μg C/m3)
OOA-2 (μg C/m3)
OOA-3 (μg C/m3)
OOA-4 (μg C/m3)
40x10-3

Figure 11

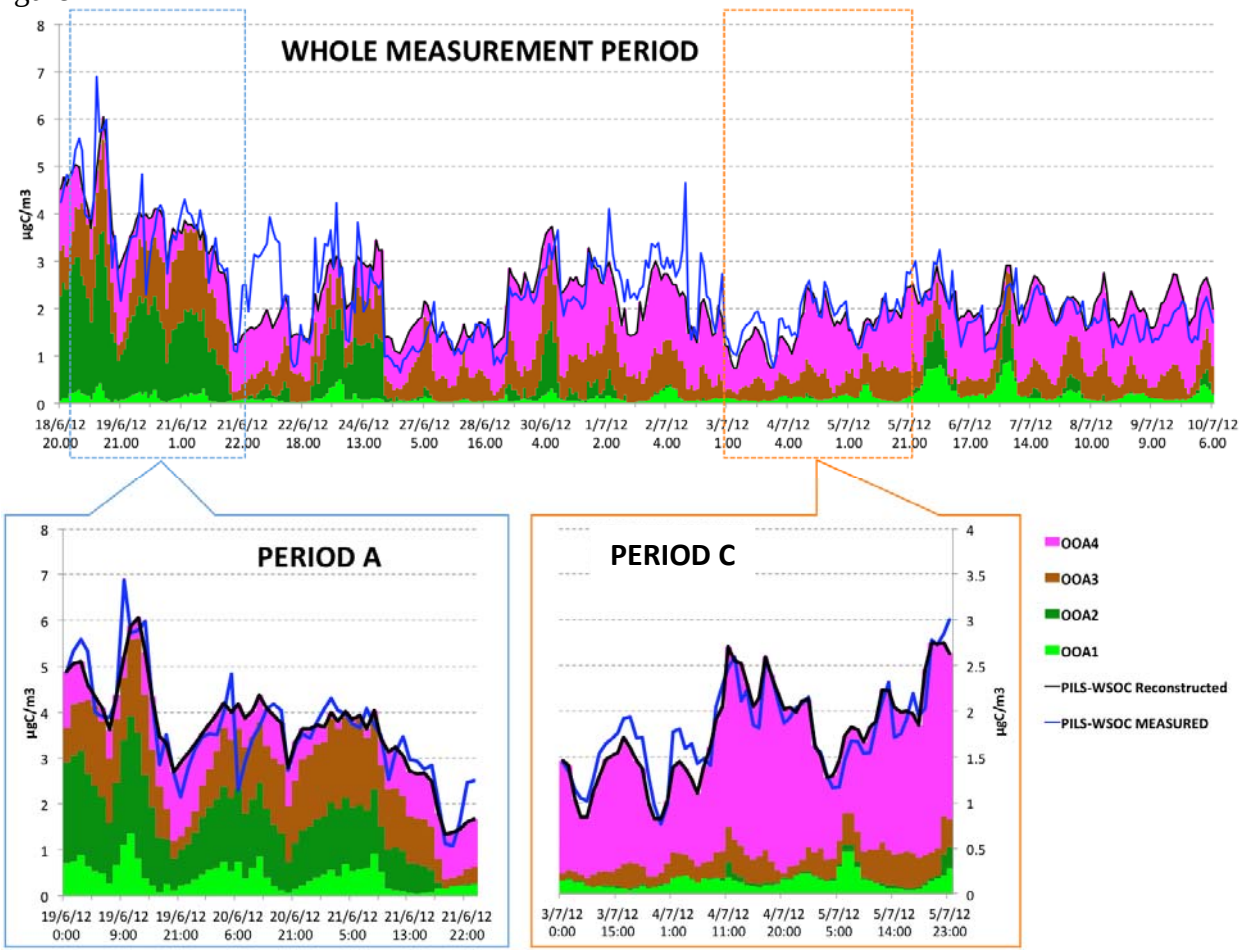

WHOLE MEASUREMENT PERIOD
µgC/m3
PERIOD A
PERIOD C
OOA4
OOA3
OOA2
OOA1
PILS-WSOC Reconstructed
PILS-WSOC MEASURED

Figure 12

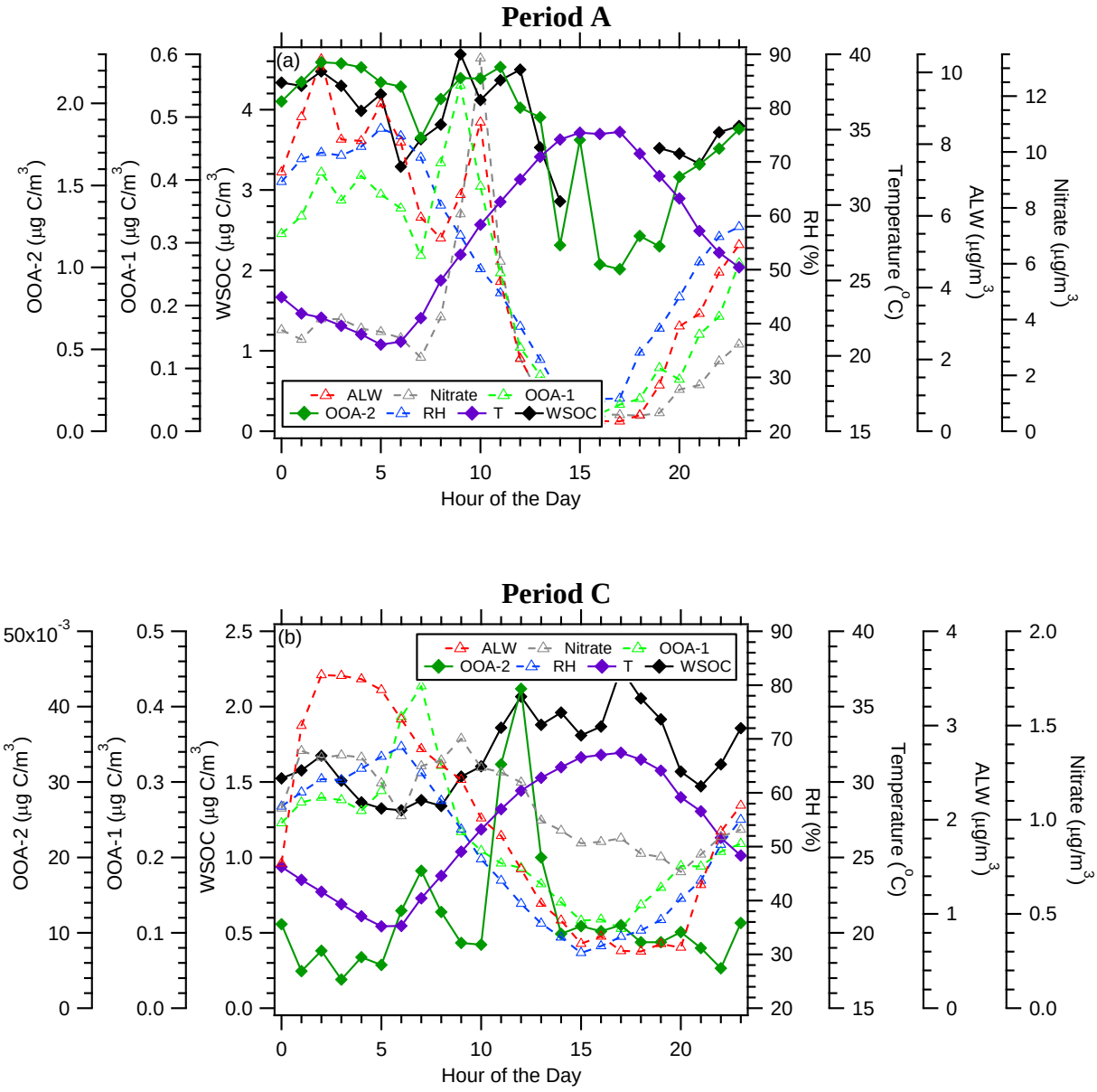
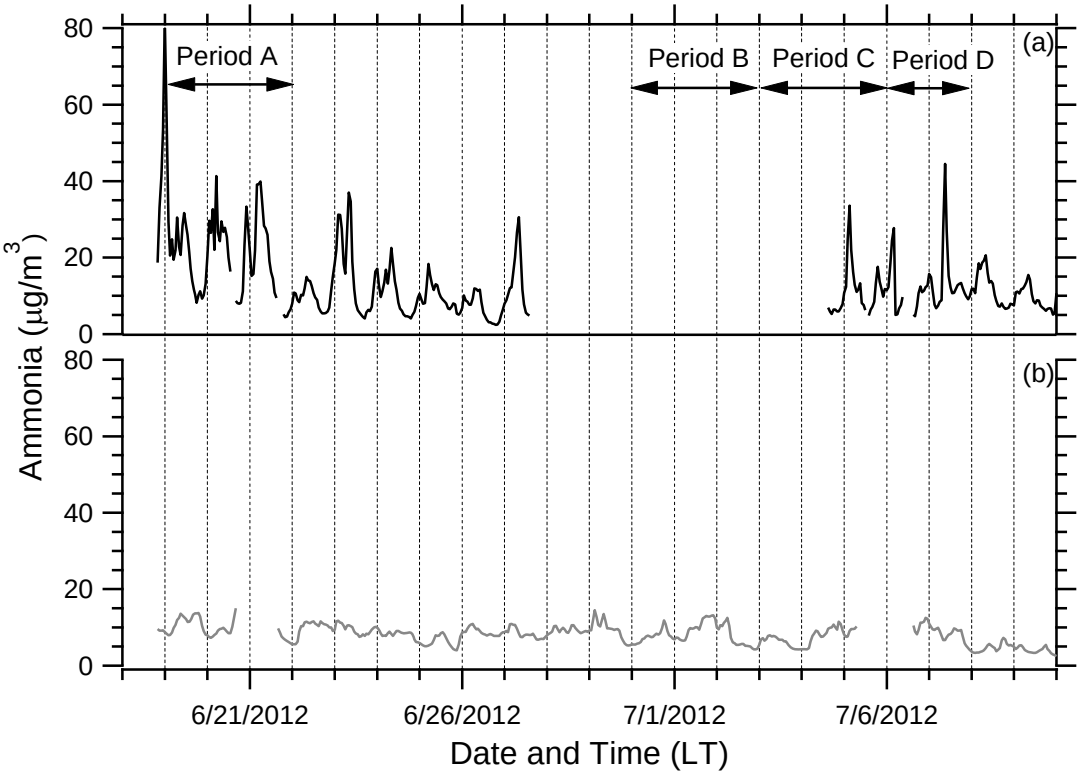

Period A
(a)
ALW
Nitrate
OOA-1
OOA-2
RH
T
WSOC
OOA-2 (µg C/m3)
OOA-1 (µg C/m3)
WSOC (µg C/m3)
RH (%)
Temperature (oC)
ALW (µg/m3)
Nitrate (µg/m3)
Hour of the Day
Period C
(b)
50x10-3
ALW
Nitrate
OOA-1
OOA-2
RH
T
WSOC
OOA-2 (µg C/m3)
OOA-1 (µg C/m3)
WSOC (µg C/m3)
RH (%)
Temperature (oC)
ALW (µg/m3)
Nitrate (µg/m3)
Hour of the Day

Figure 13


Period A
Period B
Period C
Period D
(a)
(b)
Ammonia (μg/m3)
0
20
40
60
80
6/21/2012
6/26/2012
7/1/2012
7/6/2012
Date and Time (LT)

Supporting Information for

# Evidence for Ambient Dark Aqueous SOA Formation in the Po Valley, Italy

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**AMS Organic Aerosol Source Apportionment**

Source apportionment analysis on the high resolution organic aerosol (OA) mass spectra provided by the AMS was made using the Multilinear Engine algorithm (ME-2) developed by *Paatero* [1999] and the interface Solution Finder (SoFi 4.9) [*Canonaco et al.*, 2013]. Prior to analysis, the organic matrix was prepared according to the recommendations of *Ulbrich et al*. [2009]. First, isotope ions were removed and a minimum counting error was applied. Fragments with a signal-to-noise ratio (SNR) below 0.2 were down-weighted by a factor of 10 and fragments with a SNR between 0.2 and 2 were down-weighted by a factor of 2. Finally, the fragments related to ion $CO_2^+$ were also down-weighted since they are calculated as a constant fraction of the ion $CO_2^+$ [*Allan et al.*, 2004]. Elemental analysis on the mass spectra of the identified factors was performed using the Analytic Procedure for Elemental Separation (APES vers. 1.06) based on *Aiken et al.* [2007, 2008] and including the improved estimation from *Canagaratna et al.* [2015].

For the first attempt, a non-constrained approach was investigated using a factor number ranging from 1 to 6 and applying 10 seeds (Figure S1). The best solution was obtained for the 4-factors solution (Figure S2) including 3 different oxygenated OA (OOA-a, OOA-b and OOA-c) and a mixed-sources factor (mix-OA). The mix-OA factor contributes to 16% of the total OA and it has a mass spectrum with ions typically associated with hydrocarbon-like OA and shows the lowest O/C (oxygen/carbon) ratio (0.28) compared to the other factors. Although, it indicates that this factor can be related to primary OA, its elemental ratios are higher than reported Hydrocarbon-like OA (HOA) factors [*Canagaratna et al.*, 2015]. This factor also has a large contribution of oxygenated fragments at *m/z* 43 ($CHO^+$) and 44 ($CO_2^+$) compared to previously reported HOA factors. Regarding its time variation, this factor correlates relatively well with gas-phase primary emissions tracers (e.g., benzene (r=0.35), toluene (r=0.48)) and particulate black carbon (BC, r=0.49) as well as with semi-volatile inorganic compounds (e.g., nitrate (r=0.57)). Therefore, considering the mass spectrum and time series particularities, this factor was identified to represent a mixture of Hydrocarbon-like OA (HOA) and semi-volatile OA (SV-OOA). The three OOA factors have quite similar mass spectra, but they present clear distinct time trends. Therefore, they are considered as separate factors and identified as follows:

- OOA-a (10% of total OA) appears to be specific to a certain time period of the campaign characterized by high temperature, a high pressure system, and stagnant air masses. Therefore, this OOA-a factor can be related to an accumulation of aged particles on the regional background. The OOA-a mass spectrum is dominated by oxygenated ions and shows the highest O/C ratio (1.02) in agreement with aged OA.

- OOA-b (30% of total OA) is the least oxygenated OOA factors (O/C = 0.55). It also correlates well with sulfate (r=0.58), but also with methanesulfonic acid (MSA, r=0.60). Therefore, this suggested that OOA-b might be related to marine OA rather than continental OA. This is in agreement with previous measurements made at the same location by *Saarikoski et al.* [2012], who reported a factor with a source originating from the Mediterranean Sea.

- OOA-c (44% of total OA) correlates with particulate sulfate (r=0.55) but not with MSA, opposite to OOA-b, and therefore can be linked to more “continental” SOA formation.

Increasing the number of factors did not provide a significant change on the mix-OA factor as illustrated in Figure S3 but rather a change in the split of the different OOA factors. Therefore, as a second attempt, the source apportionment was performed in a semi-constrained mode in order to dissociate primary OA from semi-volatile OA more clearly. The principal primary OA source expected is the HOA factor. In contrary to *Saarikoski et al.* [2012] who reported the contribution of a Biomass Burning OA (BBOA) factor in the spring season, here no BBOA is expected since the contribution of the fragment *m/z* 60 (a tracer for BBOA) to total OA was systematically below the background level of 0.3% defined by *Cubison et al.* [2011]. Consequently, a reference HOA mass spectrum corresponding to an average of 2 HOA factors previously identified in this area (M. Rinaldi, personal communication) was used as a priori information to partially constrain the model.

For this approach, the number of factors was varied from 5 to 7 since at least 5 factors are expected based on previous AMS measurements in the Po Valley (HOA and 4 types of OOA). In order to test the sensitivity of the results, the difference in the degree of variation for the various fragments for the output HOA factor to the input reference mass spectra (the so-called a-value) was investigated for a-values ranging from 0.05 (i.e., extremely constrained run where fragments of the resulting HOA factor can only vary from 5% compared to the reference HOA) to 0.5 (50% variation). The contribution of the HOA to the total OA was extremely stable over the investigated a-value range indicating that identification of the HOA factor is quite robust (Figure S4). The 5-factors solution (with an a-value of 0.1) was considered as the final solution (Figure S5). This solution corresponds to better discrimination between HOA and the semi-volatile OA (referred in the following as OOA-1), while the 3 others OOA factors correspond to the previously identified ones in the non-constrained model and here are referred to as OOA-2 (12% of OA), OOA-3 (28% of OA), and OOA-4 (45% of OA) in order to avoid confusion when referring to the first (unconstrained) analysis (Figures S6 and S7). Increasing the number of factors to 6 or 7 solely leads to a further splitting of the OOA factors without a clear identification.

The HOA factor (4% of OA) now better follows the time trend of benzene (r=0.58), while no real improvement of the correlation with BC (r=0.50) and toluene (r=0.49) can be reported. However, the semi-volatile OOA-1 is now better correlated with nitrate (r=0.74) than HOA (r=0.36) confirming the presence of these two factors in the previously identified mix-OA.

Although the OOA-1 factor (12% of total OA) is related to semi-volatile OA, its mass spectrum appears to be more oxygenated (higher contribution of the $CO_2^+$ fragment compared to the $CHO^+$) than classical SV-OOA ($CHO^+ > CO_2^+$). However, this is quite similar to the previously reported semi-volatile OOA measured at SPC by *Saarikoski et al.* [2012].

Although contributions of the 3 others OOA factors (OOA-2, OOA-3, and OOA-4) to the total OA are quite similar to the contribution of their corresponding factors in the non-constrained mode (12%, 28% and 45%, respectively), some small differences can be reported either in terms of their mass spectra (and consequently their elemental ratios) or their time trends. These differences can be explained by a small contribution of the non-constrained OOA factors (i.e., OOA-a, OOA-b, and OOA-c) to OOA-1. The most stable factor is OOA-2 which correlates quite well with the previously identified OOA-a, even if the final factor has a lower oxidation state. Although OOA-2 contributed to 12% over the entire time period, during its prevalent period it accounted for up to more than half of the OA.

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**Figure Captions**

**Figure S1.** Evolution of the $Q/Q_{exp}$ ratio (top) and factor contribution (bottom) over the investigated factor range for the non-constrained model.

**Figure S2.** Time series (top) and mass spectra colored by fragments family (bottom) for the non-constrained 4-factors solution.

**Figure S3.** Evolution of the mix-OA factor time series (top) and mass spectra (bottom) for different factor solutions (from 3 to 6). Numbers in parentheses on the bottom plots (following the number of the factor solution) correspond to the slope of the regression line compare to the selected 4-factors solution.

**Figure S4.** Evolution of the $Q/Q_{exp}$ ratio (top) and factor contribution (bottom) over the investigated factor range for the partially-constrained model.

**Figure S5.** Overview of the partially-constrained factor solution including (a) time series of the factors and corresponding tracers, (b) mass fraction of the different factors to the total OA, and (c) mass spectra of the factors colored by fragment family.

**Figure S6.** Comparison between the time trends of the factors identified for the non-constrained (y-axis) and the ones identified for the partially-constrained (x-axis) analysis.

**Figure S7.** Comparison between the mass spectra of the factors identified for the non-constrained (y-axis) and the ones identified for the partially-constrained (x-axis) analysis.

**Figure S8.** Correlation of hourly averaged WSOC vs. OA for (a) Period B and (b) Period D, ALW for (c) Period B and (d) Period D, and RH for (e) Period B and (f) Period D at SPC. All plots are for during the times of RH increasing.

**Figure S9.** Correlation of hourly averaged WSOC vs. nitrate for (a) Period B and (b) Period D, oxalate for (c) Period B and (d) Period D, and sulfate for (e) Period B and (f) Period D at SPC. All plots are for during the times of RH increasing.

**Figure S10.** Diurnal profile of WSOC, OOA-1, OOA-2, RH, Temperature, ALW, and Nitrate for (a) Period B and (b) Period D at SPC.

**Table S1.** Dates and times for the times of RH increasing and decreasing during Periods A, B, C, and D.

| Period | RH Increasing | RH Decreasing |
|---|---|---|
| A | 18 June at 20:00 – 19 June at 01:00,<br>19 June at 20:00 – 20 June at 06:00,<br>20 June at 21:00 – 21 June at 07:00 | 19 June at 02:00 – 19 June at 12:00,<br>20 June at 03:00 – 20 June at 11:00,<br>21 June at 00:00 – 21 June at 12:00 |
| B | 29 June at 19:00 – 30 June at 06:00,<br>30 June at 19:00 – 1 July at 06:00,<br>1 July at 21:00 – 2 July at 07:00 | 30 June at 04:00 – 1 July at 12:00,<br>1 July at 01:00 – 1 July at 08:00,<br>2 July at 02:00 – 2 July at 10:00 |
| C | 2 July at 21:00 – 3 July at 07:00,<br>3 July at 23:00 – 4 July at 06:00,<br>4 July at 20:00 – 5 July at 07:00 | 3 July at 03:00 – 3 July at 11:00,<br>4 July at 01:00 – 4 July at 12:00,<br>5 July at 05:00 – 5 July at 11:00 |
| D | 5 July at 19:00 – 6 July at 07:00,<br>6 July at 16:00 – 7 July at 03:00 | 6 July at 01:00 – 6 July at 15:00,<br>7 July at 07:00 – 7 July at 14:00 |

**Table S2.** Parameters of the multilinear regression analysis of WSOC. Slope coefficients are reported for the individual AMS ME-2 factors, while y-intercepts are presented in the right column. Numbers in parenthesis refer to the percent contributions of each AMS factors (and of intercepts) to the measured WSOC. See the main text for further explanation.

| | | OOA-1 | OOA-2 | OOA-3 | OOA-4 | Intercept |
|---|---|---|---|---|---|---|
| **Whole campaign** | intercept forced to 0 | 0.56 (7%) | 0.87 (12%) | 0.83 (32%) | 1.00 (49%) | - |
| | unforced | 0.40 (5%) | 0.94 (12%) | 0.63 (24%) | 0.92 (44%) | 0.31 µgC/m$^3$ (15%) |
| **Period A** | intercept forced to 0 | 1.00 (7%) | 0.88 (37%) | 0.77 (32%) | 1.00 (24%) | - |
| | unforced | 0.88 (6%) | 0.92 (38%) | 0.48 (19%) | 0.59 (14%) | 0.72 µgC/m$^3$ (22%) |
| **Period B** | intercept forced to 0 | 0.83 (11%) | 1.00 (1%) | 0.93 (32%) | 1.00 (56%) | - |
| | unforced | 0.27 (4%) | 1.00 (1%) | 0.46 (15%) | 1.00 (53%) | 0.47 µgC/m$^3$ (28%) |

**Figure S1**

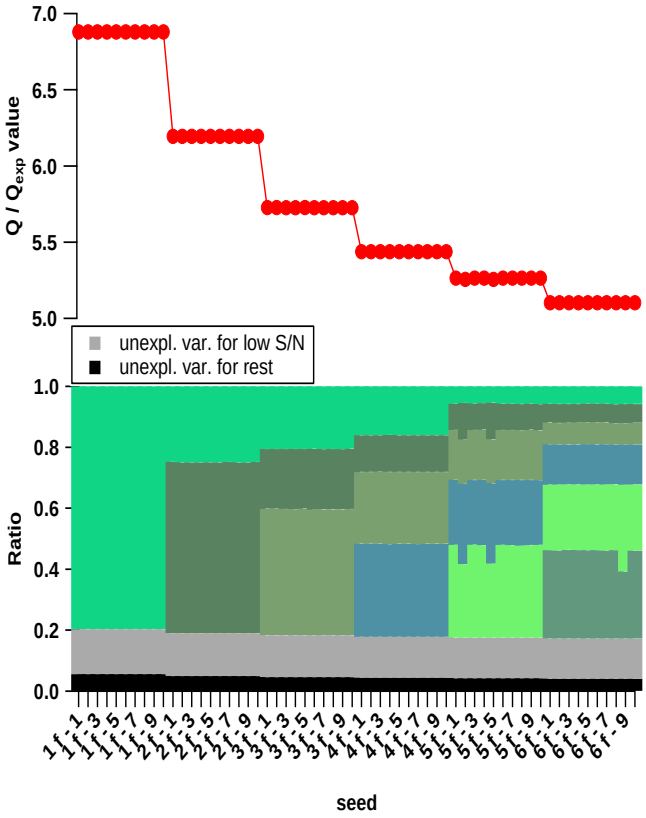
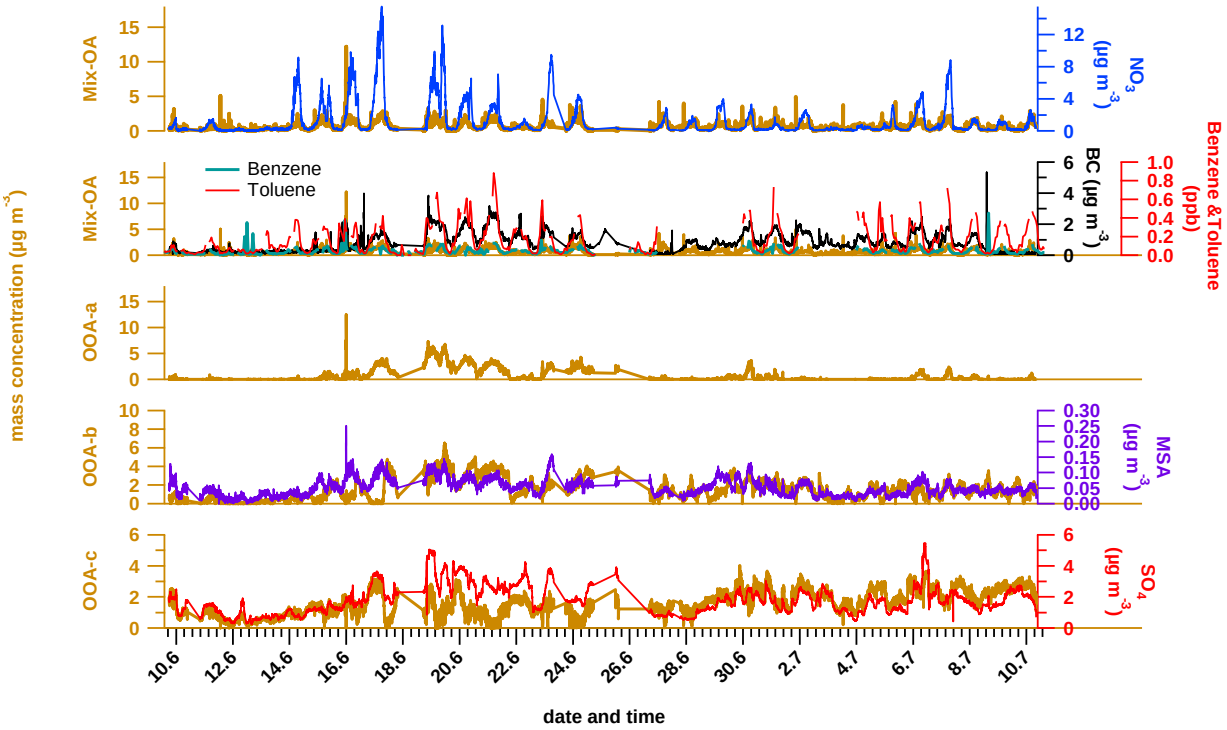

7.0
6.5
6.0
5.5
5.0
Q / Q$_{exp}$ value
unexpl. var. for low S/N
unexpl. var. for rest
1.0
0.8
0.6
0.4
0.2
0.0
Ratio
seed

**Figure S2**


mass concentration (μg m-3)
Mix-OA
NO3 (μg m-3)
Benzene
Toluene
BC (μg m-3)
Benzene &Toluene (ppb)
OOA-a
OOA-b
MSA (μg m-3)
OOA-c
SO4 (μg m-3)
10.6
12.6
14.6
16.6
18.6
20.6
22.6
24.6
26.6
28.6
30.6
2.7
4.7
6.7
8.7
10.7
date and time

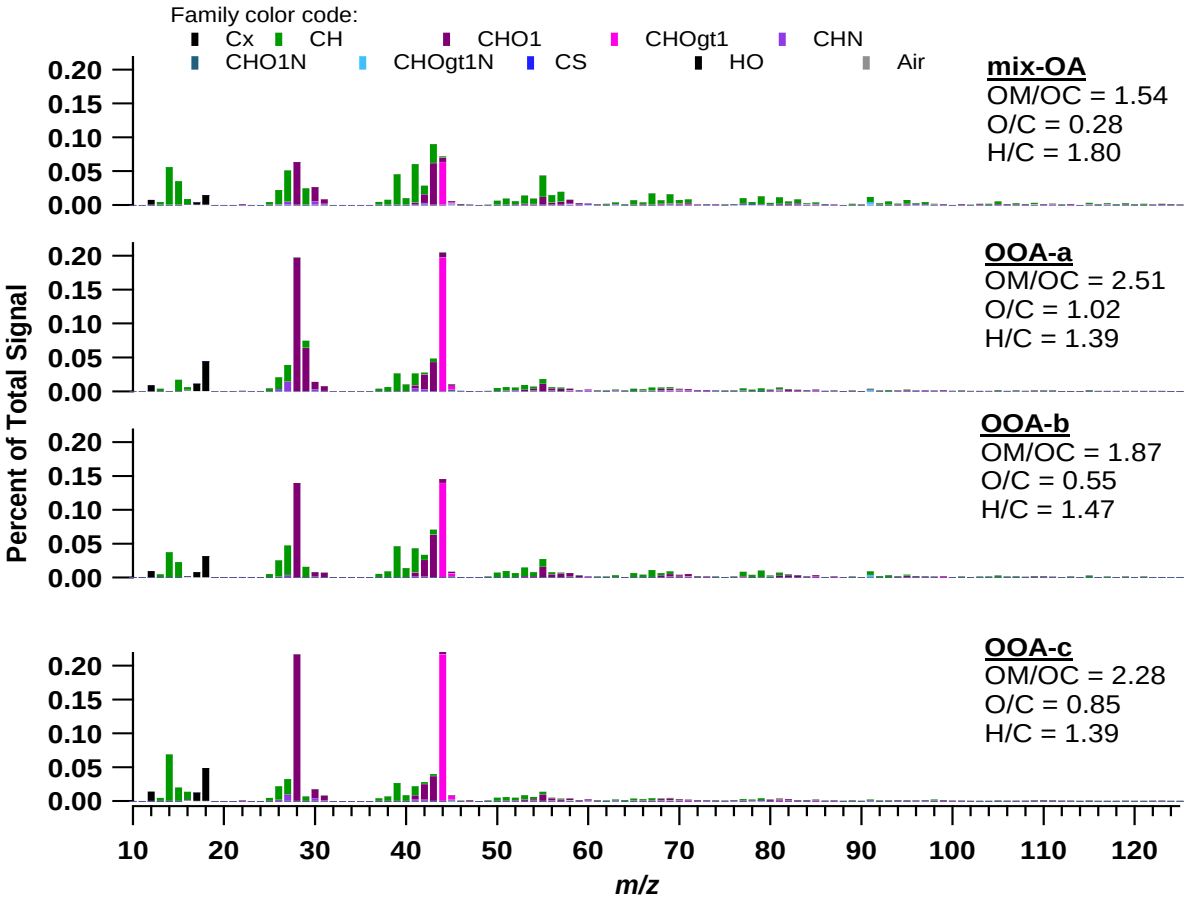
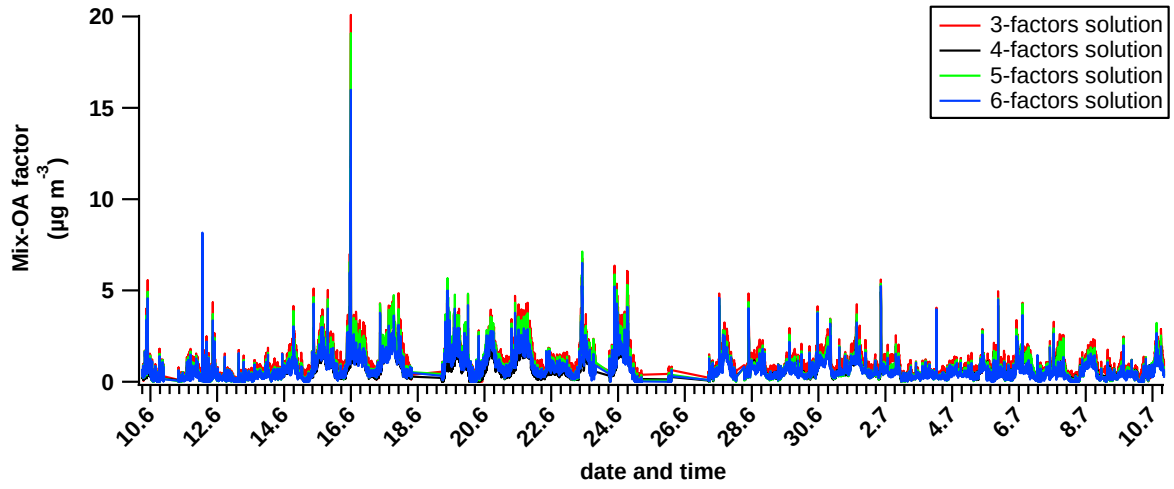

Family color code:
Cx
CH
CHO1
CHOgt1
CHN
CHO1N
CHOgt1N
CS
HO
Air
Percent of Total Signal
mix-OA
OM/OC = 1.54
O/C = 0.28
H/C = 1.80
OOA-a
OM/OC = 2.51
O/C = 1.02
H/C = 1.39
OOA-b
OM/OC = 1.87
O/C = 0.55
H/C = 1.47
OOA-c
OM/OC = 2.28
O/C = 0.85
H/C = 1.39
m/z

**Figure S3**


3-factors solution
4-factors solution
5-factors solution
6-factors solution
Mix-OA factor (µg m-3)
20
15
10
5
0
10.6
12.6
14.6
16.6
18.6
20.6
22.6
24.6
26.6
28.6
30.6
2.7
4.7
6.7
8.7
10.7
date and time

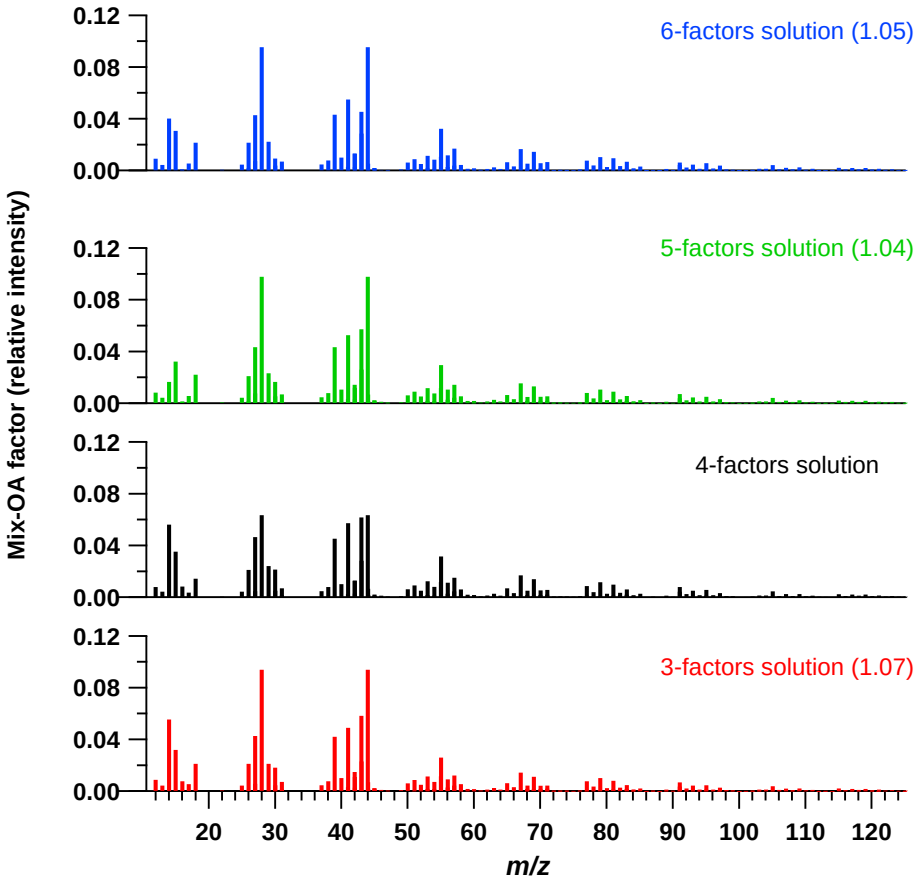

6-factors solution (1.05)
5-factors solution (1.04)
4-factors solution
3-factors solution (1.07)
Mix-OA factor (relative intensity)
0.12
0.08
0.04
0.00
20
30
40
50
60
70
80
90
100
110
120
m/z

**Figure S4**

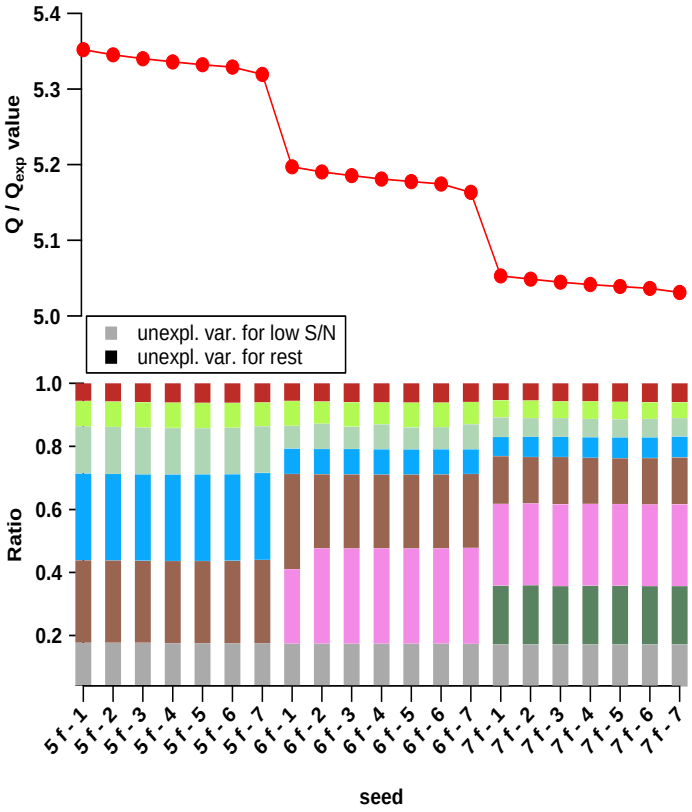
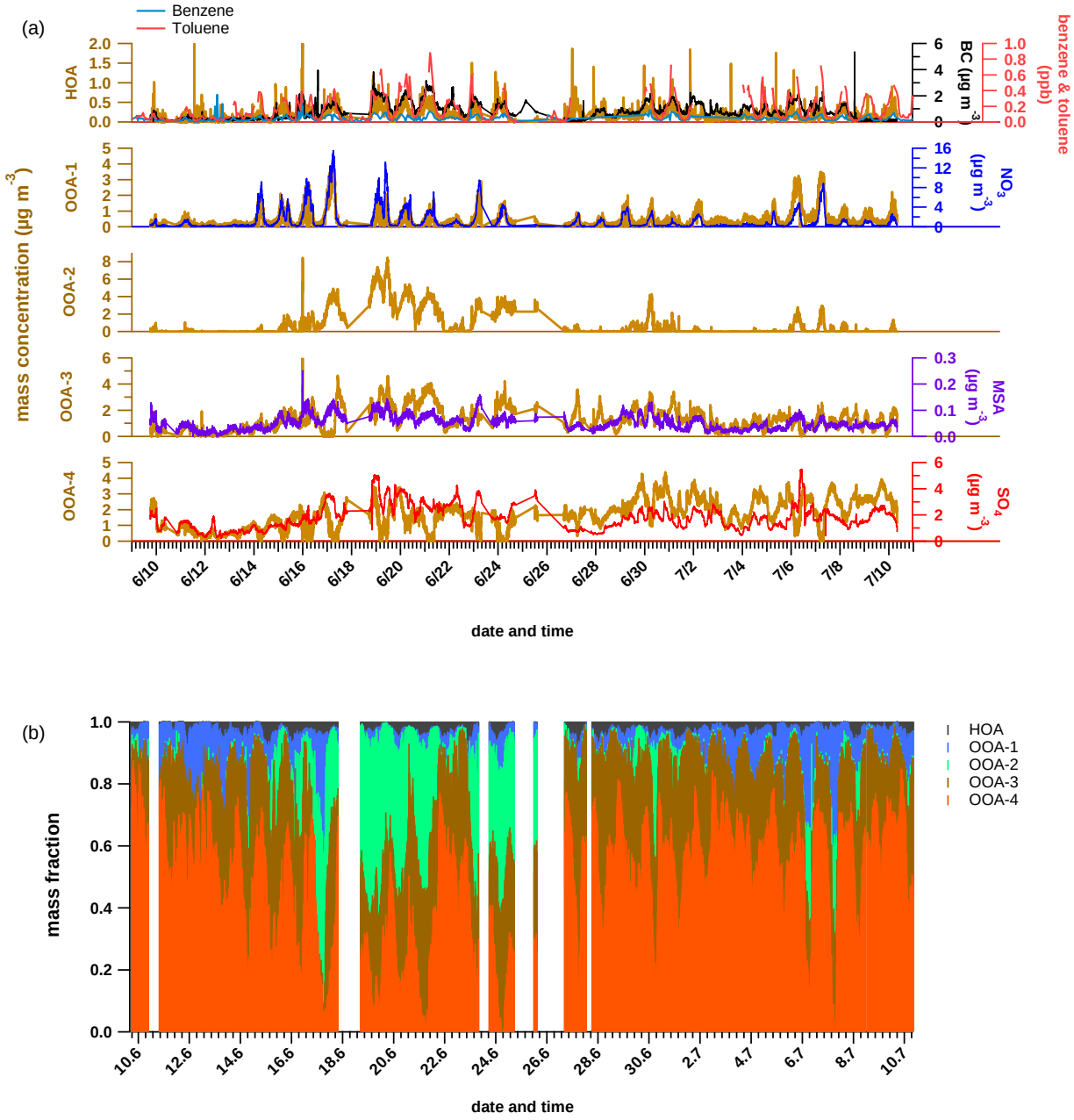

5.4
5.3
5.2
5.1
5.0
Q / Q_exp value
unexpl. var. for low S/N
unexpl. var. for rest
1.0
0.8
0.6
0.4
0.2
Ratio
5f-1
5f-2
5f-3
5f-4
5f-5
5f-6
5f-7
6f-1
6f-2
6f-3
6f-4
6f-5
6f-6
6f-7
7f-1
7f-2
7f-3
7f-4
7f-5
7f-6
7f-7
seed

**Figure S5**


(a)
Benzene
Toluene
HOA
BC (μg m-3)
benzene & toluene (ppb)
mass concentration (μg m-3)
OOA-1
NO3 (μg m-3)
OOA-2
OOA-3
MSA (μg m-3)
OOA-4
SO4 (μg m-3)
6/10
6/12
6/14
6/16
6/18
6/20
6/22
6/24
6/26
6/28
6/30
7/2
7/4
7/6
7/8
7/10
date and time
(b)
mass fraction
HOA
OOA-1
OOA-2
OOA-3
OOA-4
10.6
12.6
14.6
16.6
18.6
20.6
22.6
24.6
26.6
28.6
30.6
2.7
4.7
6.7
8.7
10.7
date and time

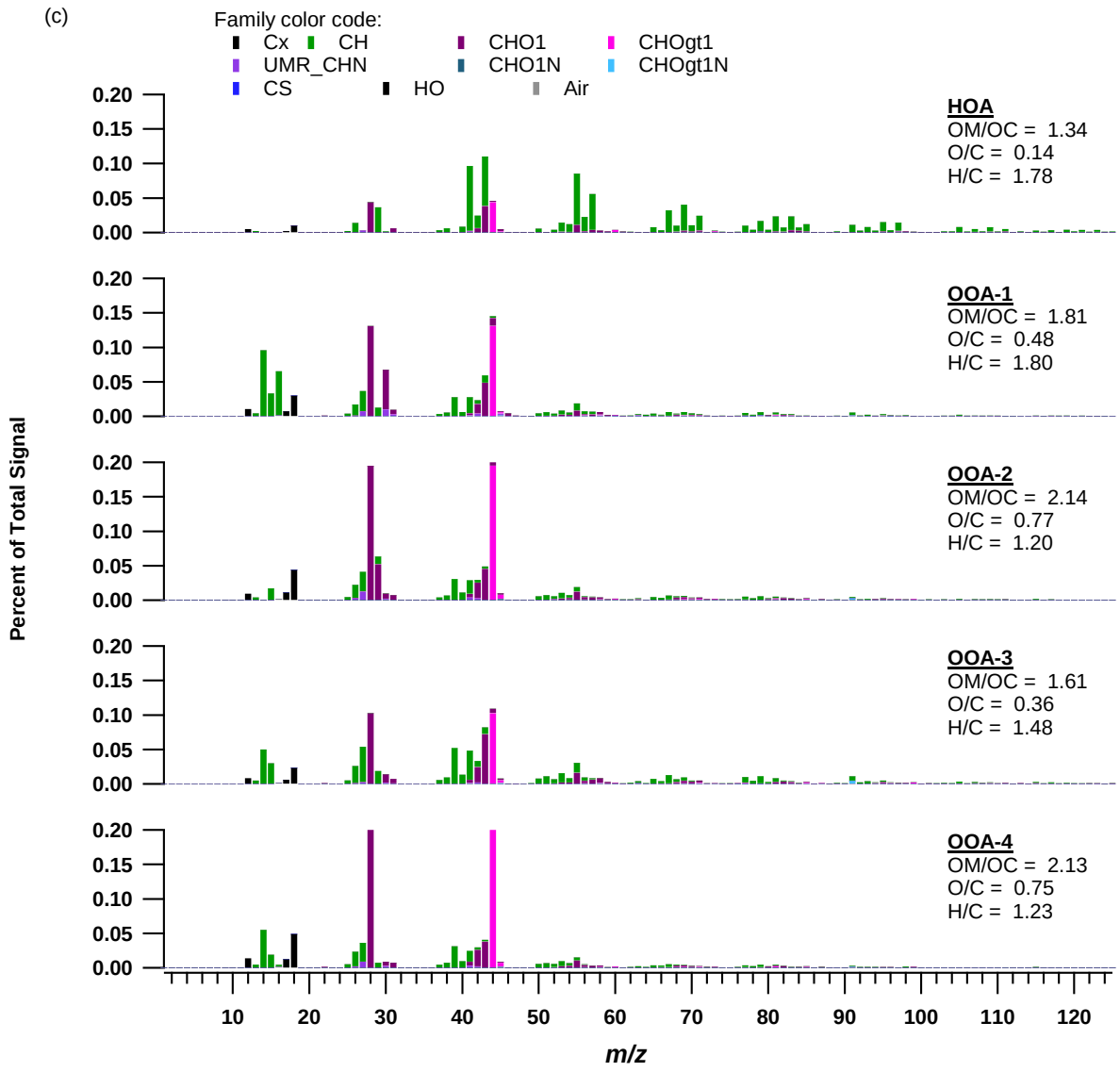

(c)
Family color code:
Cx
CH
CHO1
CHOgt1
UMR_CHN
CHO1N
CHOgt1N
CS
HO
Air
Percent of Total Signal
0.20
0.15
0.10
0.05
0.00
HOA
OM/OC = 1.34
O/C = 0.14
H/C = 1.78
OOA-1
OM/OC = 1.81
O/C = 0.48
H/C = 1.80
OOA-2
OM/OC = 2.14
O/C = 0.77
H/C = 1.20
OOA-3
OM/OC = 1.61
O/C = 0.36
H/C = 1.48
OOA-4
OM/OC = 2.13
O/C = 0.75
H/C = 1.23
10
20
30
40
50
60
70
80
90
100
110
120
m/z

**Figure S6**

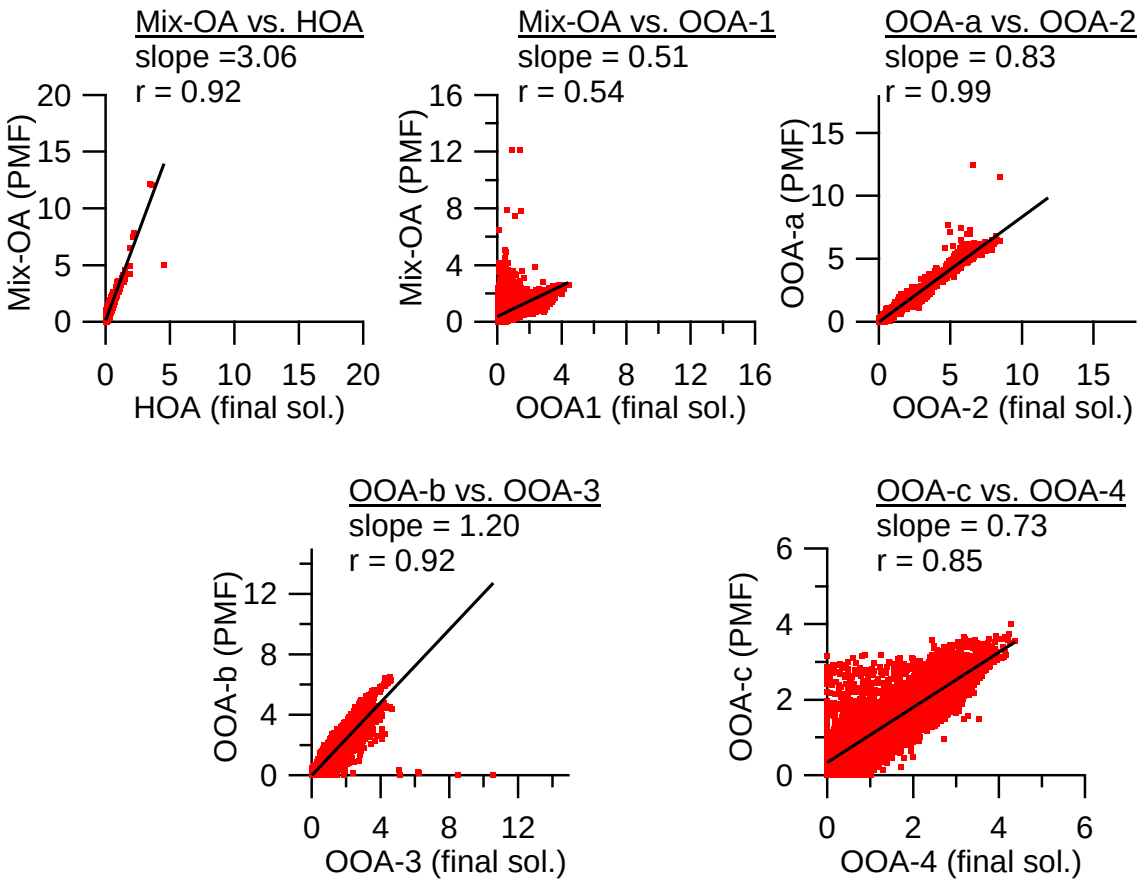

Mix-OA vs. HOA
slope =3.06
r = 0.92
Mix-OA (PMF)
HOA (final sol.)
Mix-OA vs. OOA-1
slope = 0.51
r = 0.54
Mix-OA (PMF)
OOA1 (final sol.)
OOA-a vs. OOA-2
slope = 0.83
r = 0.99
OOA-a (PMF)
OOA-2 (final sol.)
OOA-b vs. OOA-3
slope = 1.20
r = 0.92
OOA-b (PMF)
OOA-3 (final sol.)
OOA-c vs. OOA-4
slope = 0.73
r = 0.85
OOA-c (PMF)
OOA-4 (final sol.)

**Figure S7**

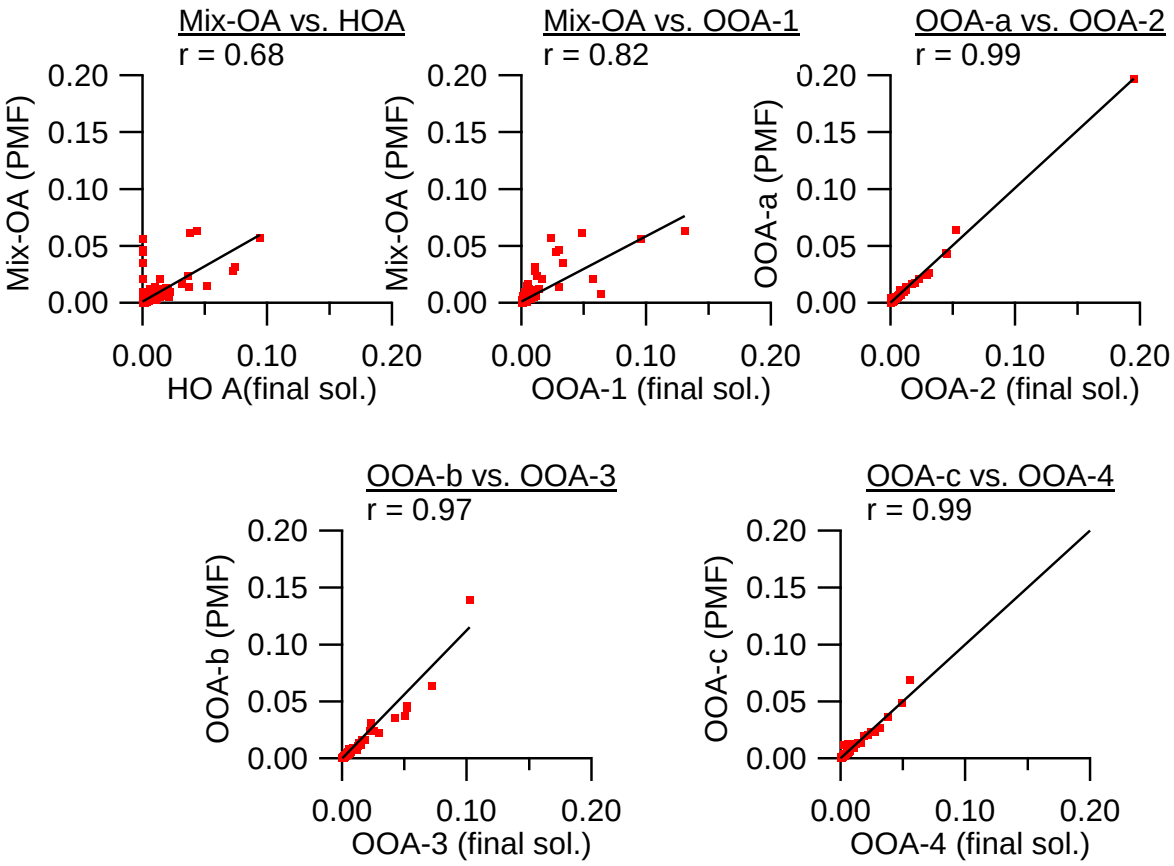

Mix-OA vs. HOA
r = 0.68
Mix-OA (PMF)
HO A(final sol.)
Mix-OA vs. OOA-1
r = 0.82
Mix-OA (PMF)
OOA-1 (final sol.)
OOA-a vs. OOA-2
r = 0.99
OOA-a (PMF)
OOA-2 (final sol.)
OOA-b vs. OOA-3
r = 0.97
OOA-b (PMF)
OOA-3 (final sol.)
OOA-c vs. OOA-4
r = 0.99
OOA-c (PMF)
OOA-4 (final sol.)
0.00
0.05
0.10
0.15
0.20

**Figure S8**

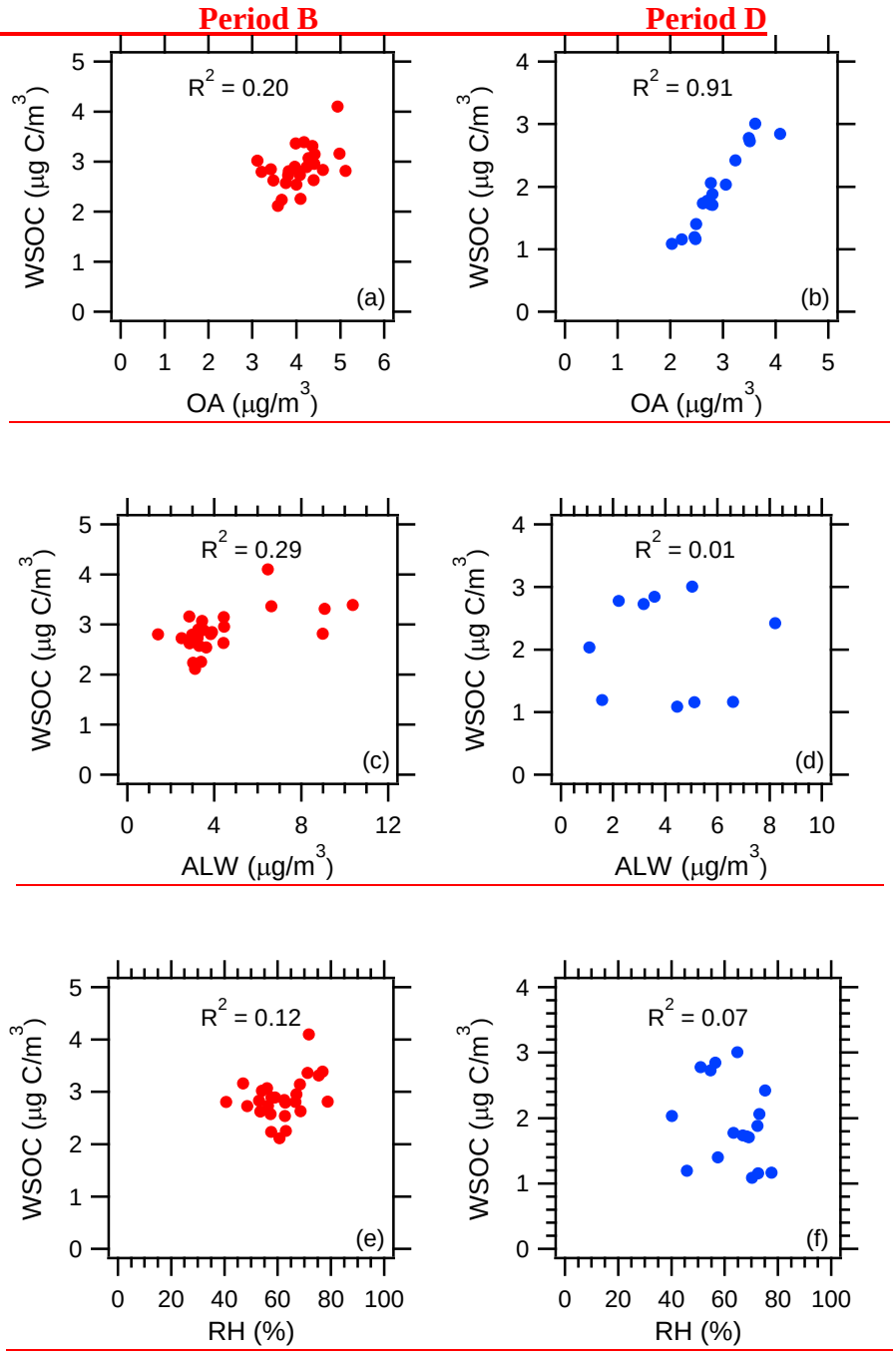

Period B
Period D
R2 = 0.20
R2 = 0.91
R2 = 0.29
R2 = 0.01
R2 = 0.12
R2 = 0.07
WSOC (μg C/m3)
OA (μg/m3)
ALW (μg/m3)
RH (%)
(a)
(b)
(c)
(d)
(e)
(f)

**Figure S9**

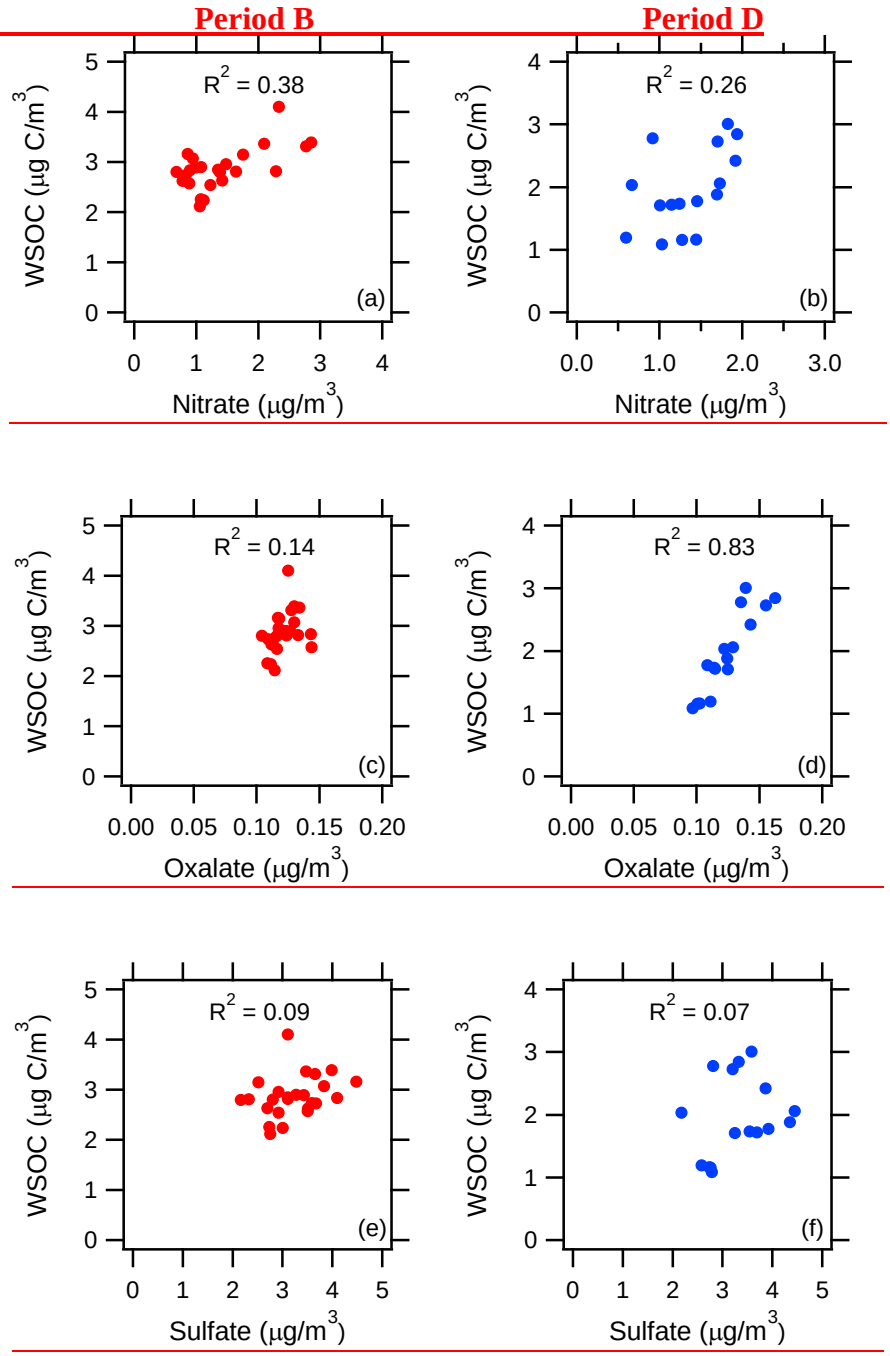
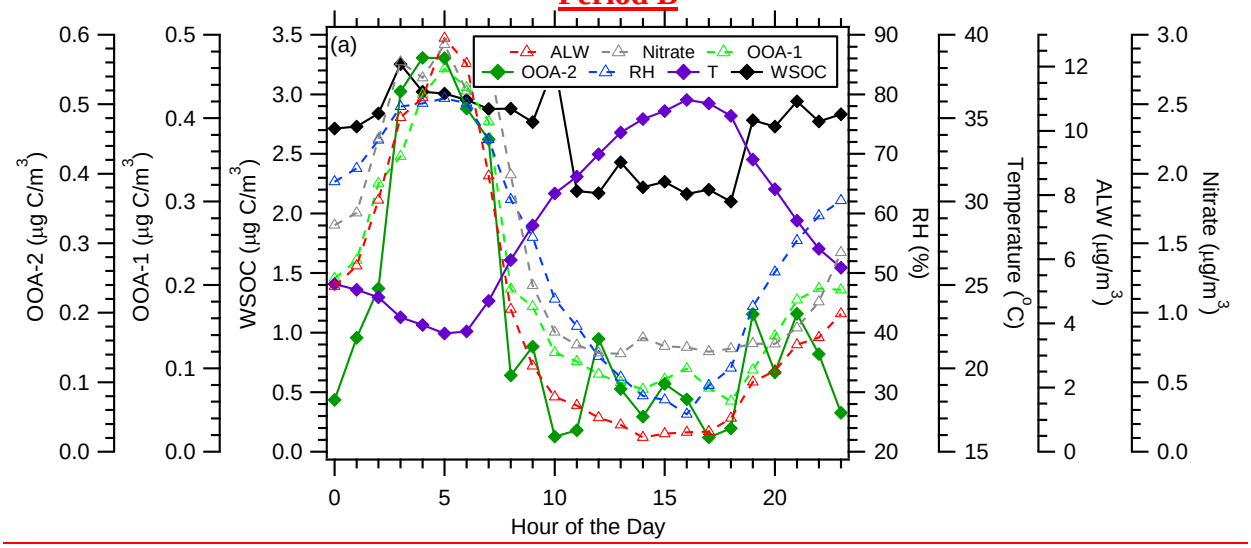

Period B
Period D
R2 = 0.38
R2 = 0.26
R2 = 0.14
R2 = 0.83
R2 = 0.09
R2 = 0.07
WSOC (μg C/m3)
Nitrate (μg/m3)
Oxalate (μg/m3)
Sulfate (μg/m3)
(a)
(b)
(c)
(d)
(e)
(f)

**Figure S10**

**Period B**




**Period D**