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*Supplement of*

## **Organic aerosol evolution and transport observed at Mt. Cimone (2165 m a.s.l.), Italy, during the PEGASOS campaign**

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## Supporting information

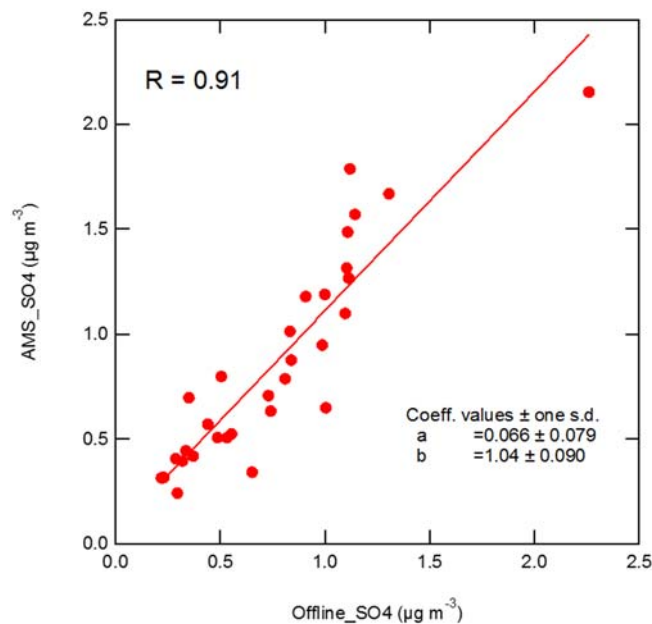


Figure S1. AMS sulphate (after CE correction) vs. offline PM<sub>1</sub> sulphate. R = Pearson's correlation coefficient, a = intercept, b = slope.

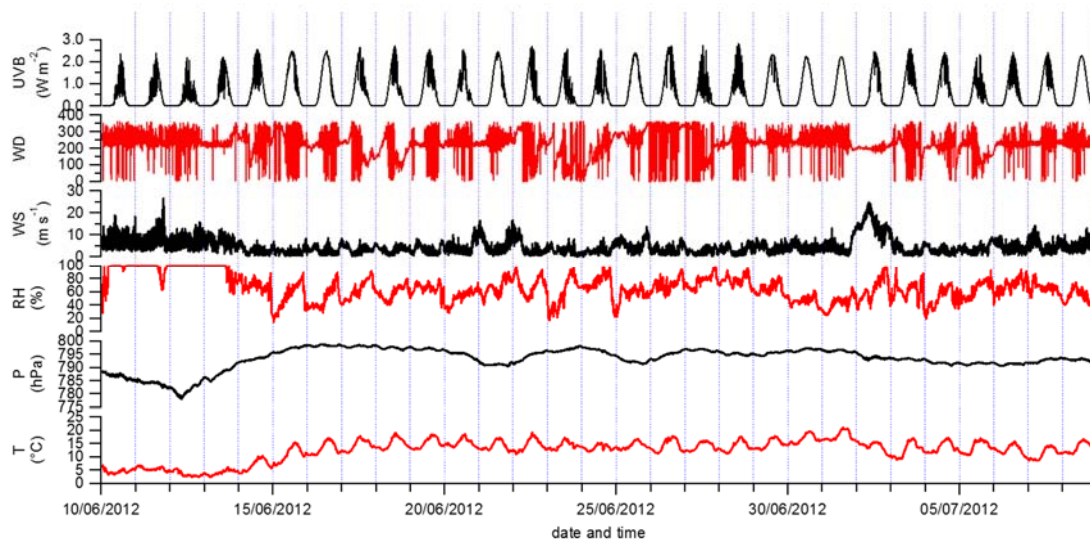


Figure S2. Meteorological parameters measured during the campaign. T = air temperature, P = atmospheric pressure, RH = relative humidity, WS = wind speed, WD = wind direction, UVB = UV-B radiation flux.

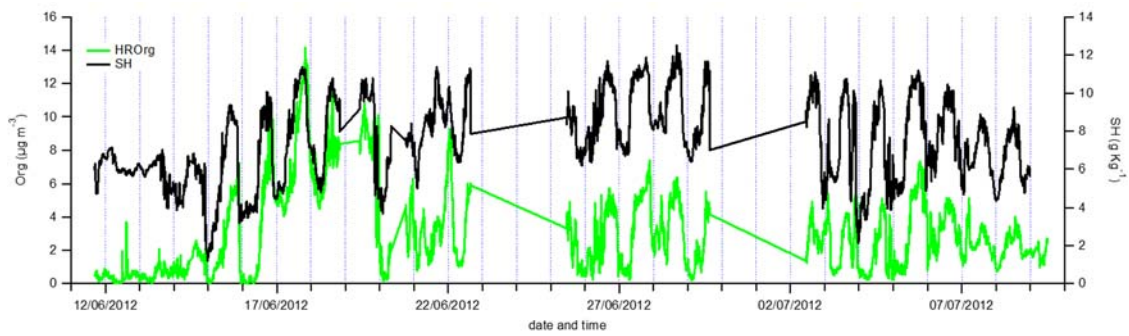


Figure S3. Time trends of AMS organics (green) and specific humidity, SH (black).

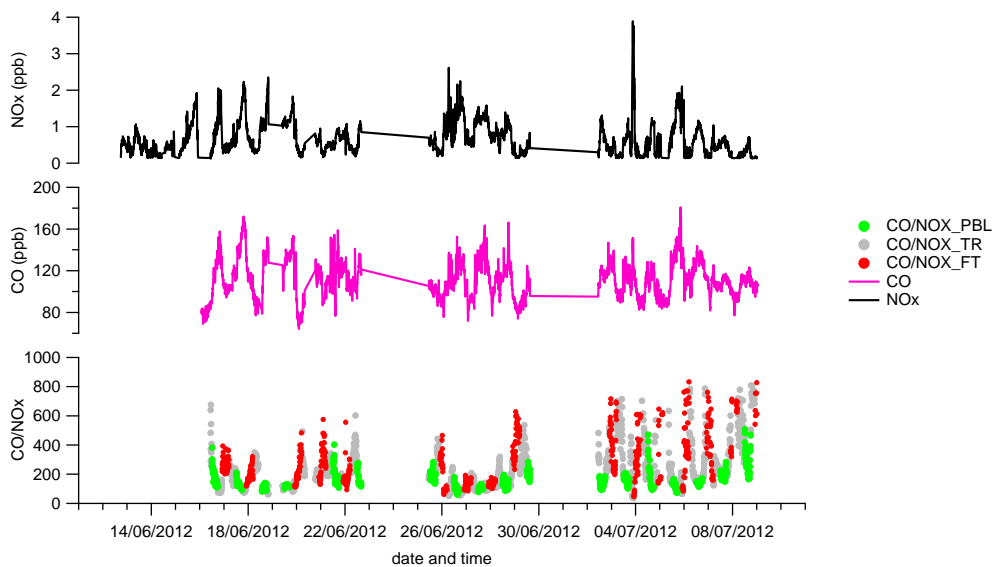


Figure S4: Time series, from top to bottom, of NO<sub>x</sub> (ppb), CO (ppb), and CO/NO<sub>x</sub> ratios color coded for PBL, FT and TR regimes.

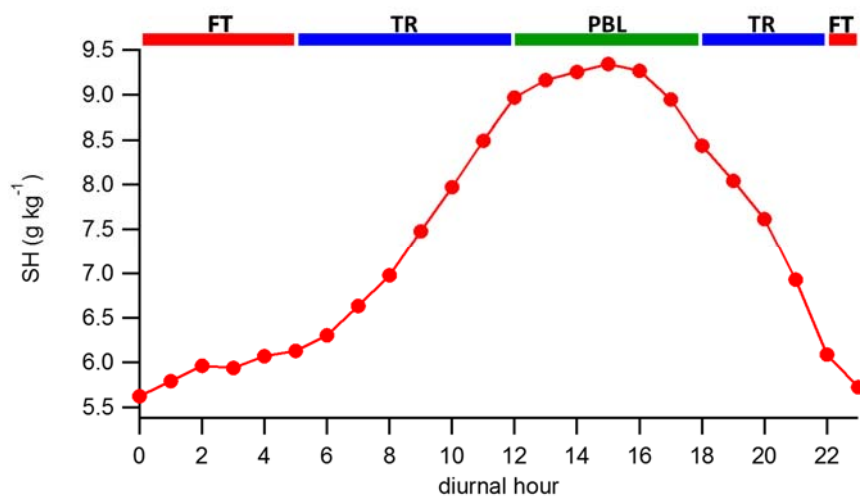


Figure S5. Average daily trend of SH measured at Mt. Cimone. Colored bars indicate the reference periods for the definition of FT, TR and PBL samples.

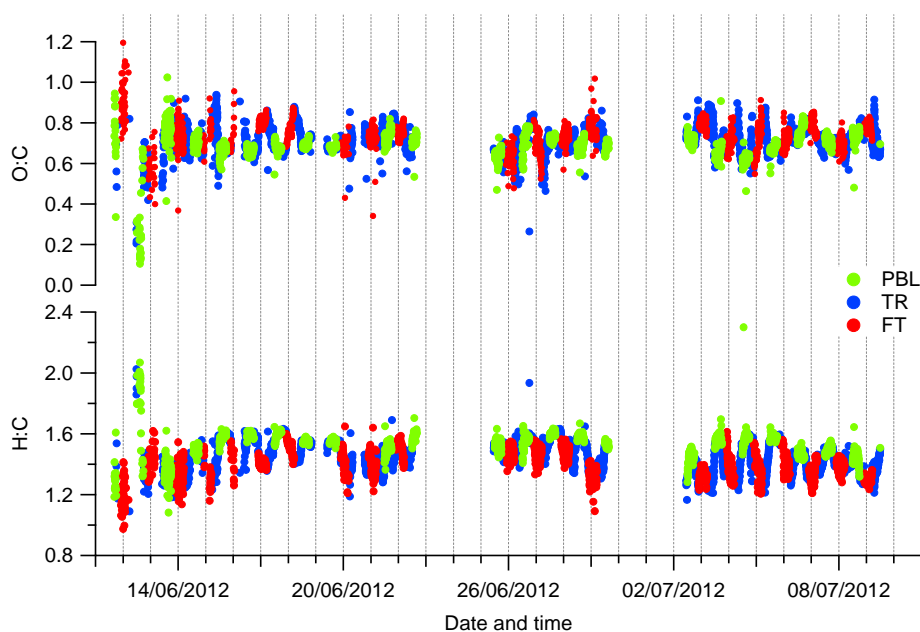


Figure S6. Time series of O:C and H:C colored according to the data classification described in the text.

## PMF analysis

Figure S7 shows Positive Matrix Factorization (PMF) key diagnostic plots for the HR-ToF-AMS measurements performed at Mt. Cimone during the PEGASOS campaign (June-July 2012).  $Q/Q_{exp}$  is shown as a function of the number of factors  $P$  (Figure S7, panel a) and  $f_{peak}$  values (Figure S7, panel c). Panel b) and d) show the distribution of scaled residuals and  $Q/Q_{exp}$  for each  $m/z$ , respectively. For this dataset we chose a 4-factor solution ( $P=4$ ) yielding four different OOAs, with  $Q/Q_{exp} = 2.3$ . Two of the OOAs (Factor 1 and Factor 4 in Figure S8) were recombined into one factor, because of coincident time series and profiles, yielding to the factor labelled OOAa in the paper. This solution was chosen instead of the 3-factor solution ( $P=3$ ) because it reduced  $Q/Q_{exp}$  and residuals. The addition of a factor ( $P=5$ ) does not further decrease significantly the  $Q/Q_{exp}$  (2.2), meaning that most of the data variability can be explained by the selected solution.

The rotational ambiguity of the 4-factor solution was explored by varying  $f_{peak}$  between -1.0 and +1.0. Tables S1 and S2 show a systematic comparison between the solutions obtained with  $f_{peak}$  values of 0,  $\pm 0.2$  and  $\pm 1$ . Excellent correlations were observed between homologous factors (as both time trends and profiles) at different  $f_{peak}$  values. It is worth noting that all the solutions maintain the internal correlation of time series and profile between Factor 1 and Factor 4, further justifying our decision of merging the two factors. To further explore the solution dependency according to the  $f_{peak}$  parameter, the variability of the time series and the fractional contribution of the PMF factors with varying  $f_{peak}$  have been compared (Figures S9 and S10). The highest deviation from the mean is observed for  $f_{peak}=1$ , particularly for the factor profiles. The solution with  $f_{peak}=1$  was considered the less realistic as, although not modifying substantially the fractional contribution of the factors, conversely to the other solutions, it yielded at least one factor that was hardly reconcilable with OOA spectra published in the literature. According to Figure S10, the changes in the fractional contribution of the PMF factors were small,  $\pm 5\%$ ,  $\pm 2\%$  and  $\pm 4\%$ , for OOAa, OOAb and OOAc, respectively, indicating that changing  $f_{peak}$  away from 0 didn't affect the overall PMF results. Therefore we decided to adopt the solution that minimizes the residuals, that is the one with  $f_{peak}=0$  (Figure S7c).

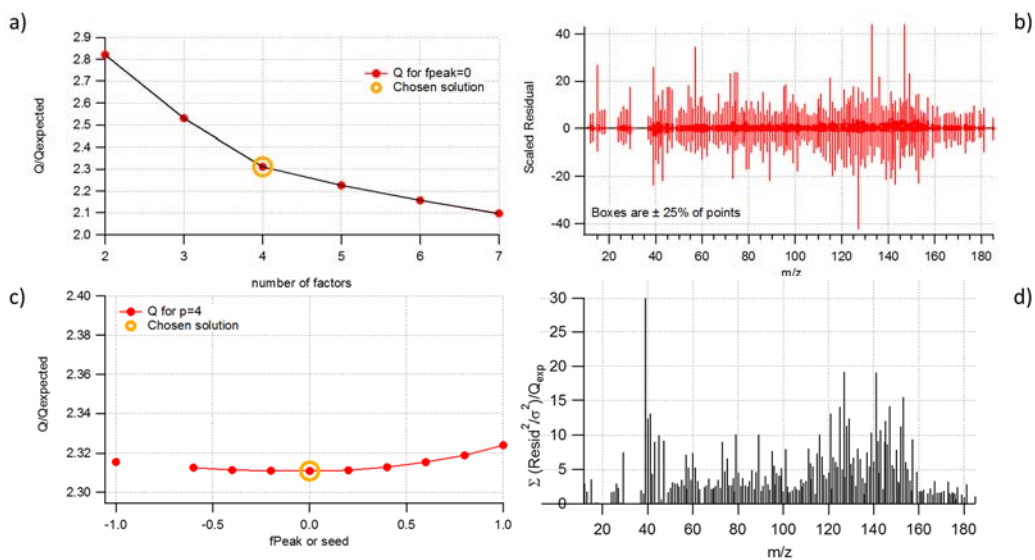


Figure S7. Summary of PMF key diagnostic plots (panels a, b, c, d) for the HR-ToF-AMS data collected during the campaign. Panel a) shows the  $Q/Q_{exp}$  as a function of the number of factors  $P$  and panel c) shows the  $Q/Q_{exp}$  as a function of  $f_{peak}$  for the 4-factor solution. Panels b) and d) show the distribution of scaled residuals and  $Q/Q_{exp}$  as a function of  $m/z$ .

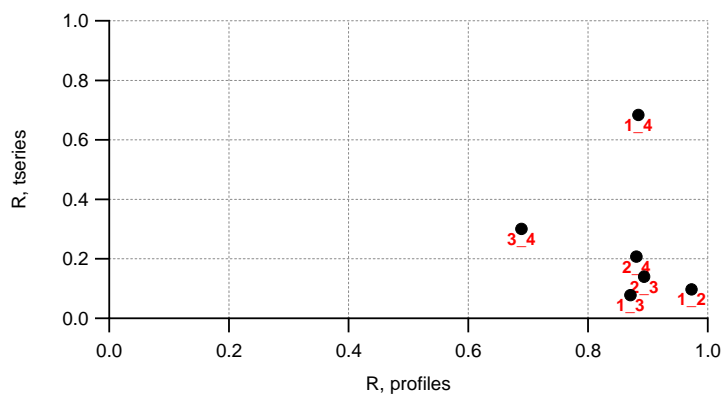


Figure S8. Comparison of time series and profile between the factors resulting from the  $P=4$  solution. The plot shows high similarity for both time series and profile between Factor 1 and Factor 4.

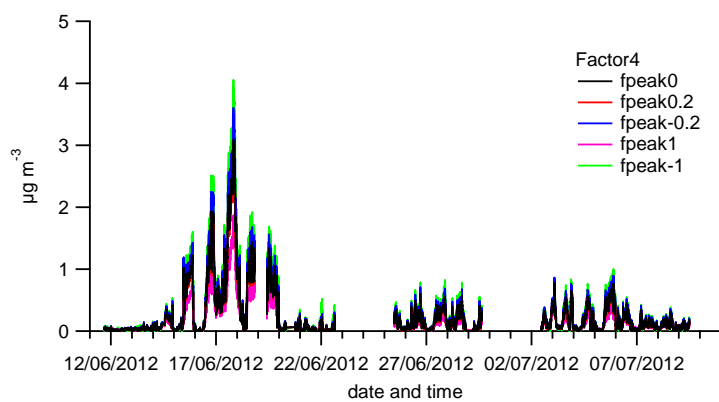
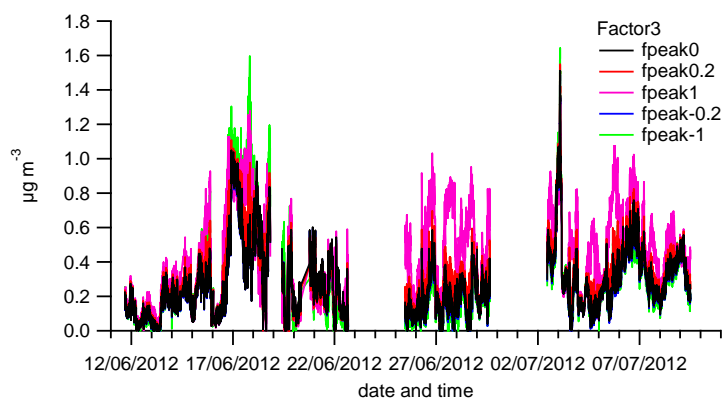
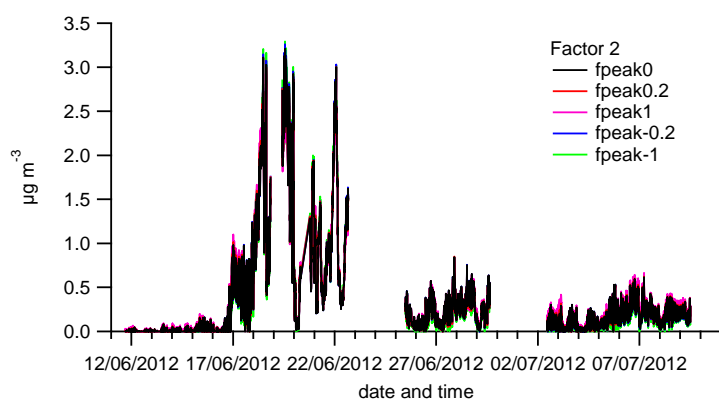
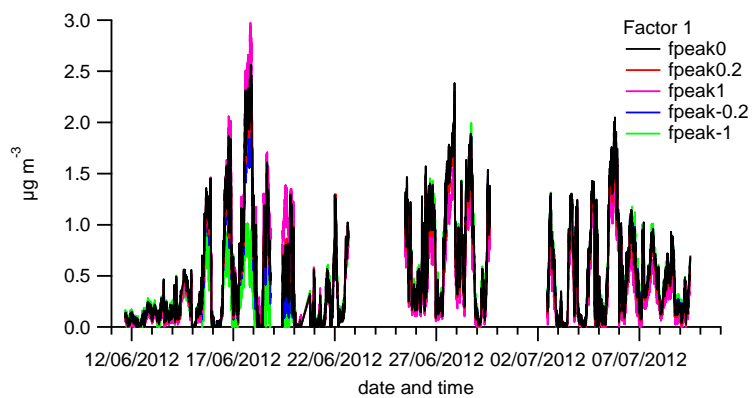


Figure S9. Time series of the PMF factors obtained with  $f_{\text{peak}} = 0, \pm 0.2$  and  $\pm 1$ . No CE applied.

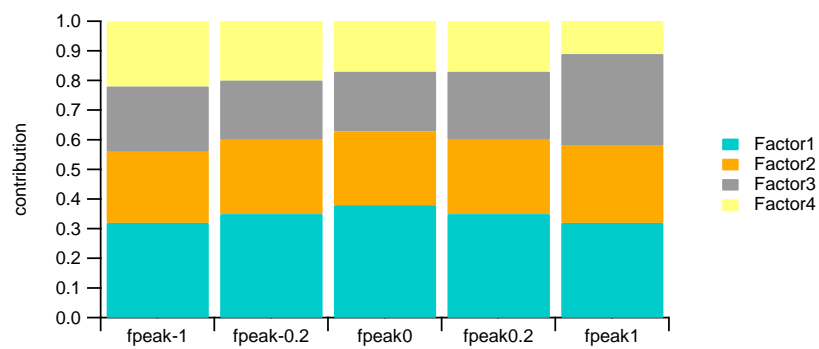


Figure S10. Contribution of the PMF factors at varying fpeak for the 4-factor solution.



Table S1. Correlation coefficients (r) between the time series of the factors obtained with different fpeak values. The solution obtained with fpeak=0 is used as the reference.

		fpeak = 0			
		F1	F2	F3	F4
fpeak = 0.2	F1	<b>0.999</b>	0.129	0.065	0.690
	F2	0.084	<b>1.000</b>	0.155	0.201
	F3	0.321	0.076	<b>0.965</b>	0.473
	F4	0.674	0.216	0.303	<b>1.000</b>
fpeak = 1	F1	<b>0.943</b>	0.263	0.106	0.862
	F2	0.071	<b>0.995</b>	0.212	0.192
	F3	0.736	-0.011	<b>0.700</b>	0.570
	F4	0.653	0.211	0.362	<b>0.997</b>
fpeak = -0.2	F1	<b>0.994</b>	0.065	0.058	0.599
	F2	0.096	<b>1.000</b>	0.135	0.207
	F3	0.067	0.143	<b>1.000</b>	0.307
	F4	0.689	0.207	0.293	<b>1.000</b>
fpeak = -1	F1	<b>0.875</b>	0.004	-0.030	0.253
	F2	0.064	<b>0.999</b>	0.135	0.191
	F3	0.299	0.109	<b>0.884</b>	0.685
	F4	0.699	0.223	0.263	<b>0.998</b>

Table S2. Correlation coefficients (r) between the mass spectral profiles of the factors obtained with different fpeak values. The solution obtained with fpeak=0 is used as the reference.

		fpeak = 0			
		F1	F2	F3	F4
fpeak = 0.2	F1	<b>0.997</b>	0.965	0.831	0.901
	F2	0.972	<b>1.000</b>	0.906	0.871
	F3	0.874	0.895	<b>1.000</b>	0.691
	F4	0.870	0.865	0.660	<b>0.999</b>
fpeak = 1	F1	<b>0.895</b>	0.907	0.998	0.708
	F2	0.865	<b>0.815</b>	0.522	0.918
	F3	0.965	0.994	<b>0.934</b>	0.842
	F4	0.904	0.932	0.922	<b>0.892</b>
fpeak = -0.2	F1	<b>1.000</b>	0.973	0.877	0.878
	F2	0.973	<b>1.000</b>	0.893	0.882
	F3	0.868	0.892	<b>1.000</b>	0.687
	F4	0.909	0.902	0.716	<b>0.998</b>
fpeak = -1	F1	<b>0.998</b>	0.977	0.902	0.865
	F2	0.971	<b>0.999</b>	0.910	0.872
	F3	0.872	0.896	<b>1.000</b>	0.692
	F4	0.865	0.839	0.586	<b>0.982</b>

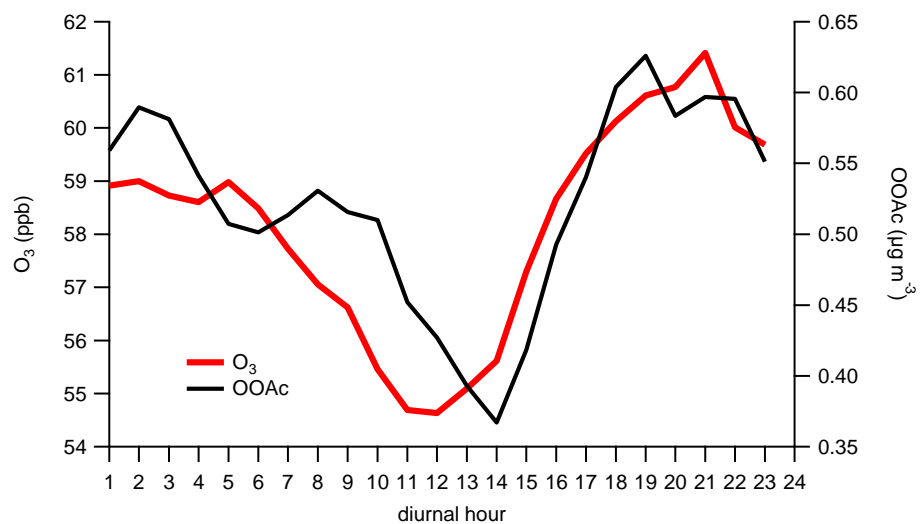


Figure S11. Average daily trend of ozone and OOAAc at Mt. Cimone during the campaign.