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Supplement of

Fog scavenging of organic and inorganic aerosol in the Po Valley

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Supplementary Material to the paper "Fog scavenging of organic and inorganic aerosol in the Po Valley", by Gilardoni et al., ACPD

PMF analysis and results

Figure 1S shows Positive Matrix Factorization (PMF) key diagnostic plots for the HR-TOF-AMS measurements performed in SPC during the period November 15-December 1, 2011. *Q/Qexp* is shown as a function of the number of factors *P* (Fig. 1S, panel a) and fpeak values (Fig. 1S, panel c). Panel b) and d) show, respectively, the distribution of scaled residuals and *Q/Qexp* for each m/z. For this dataset we chose a 4-factor solution (*P* = 4) yielding a HOA, two BBOA and a LVOOA components with a *Q/Qexp* = 4. Even though the *Q/Qexp* for a 3-factor solution is only slightly higher (4.2), a 4-factor solution allowed to separate better the HOA factor from the others. The addition of a factor does not decrease significantly the *Q/Qexp*, meaning that most of the data variability can be explained by four factors. The rotational ambiguity of the 4-factor solution was explored by varying fpeak between -1.0 and +1.0. Since we did not observe significant changes in *Q/Qexp* with fpeak (panel c) and both the mass spectra (MS) and temporal series (TS) did not change with varying fpeak (not shown here), a fpeak = 0 was chosen for this solution.

Figure 2S and 3S show the MS and TS of the 4-factor solution, respectively. Factor 1 has a strong diurnal trend (larger LVOOA during the daytime), whereas factor 2 has a weaker trend, and it is anti-correlated with LVOOA only after November 25. Factor 3 and 4 do not show any diurnal pattern. Factor 3 and factor 4 were recombined into a BBOA component because of the similarities in both TS and MS. In particular, both factor profiles 3 and 4 have relatively higher signals at m/z 29, 60 and 73 (typically present in biomass burning dominated OA). Factor 1 is dominated by m/z 44 (CO_2^+), and it can be easily identified as LVOOA. Factor 2 has also a relatively large amount of signal at m/z 44, but it is the only one for which the signal at m/z 43 is mainly represented by $C_3H_7^+$ and therefore can be distinguished from all the other factors and unequivocally identified as HOA.

Figure 4S presents the high resolution mass spectral profiles (MS) and mass-weighted pie charts of the ion components for the three PMF factors HOA (top panel), BBOA (middle panel) and LVOOA (bottom panel). The HOA spectrum is dominated by the characteristic $C_xH_{2y-1}^+$ and $C_xH_{2y+1}^+$ ion pattern, with $C_3H_5^+$ (m/z=41), $C_3H_7^+$ (m/z=43), $C_4H_7^+$ (m/z=55) and $C_4H_9^+$ (m/z=57) being among the dominant peaks. The pie chart indicates that the $C_xH_y^+$ ions represent, in mass, approximately 2/3 of the total HOA component. The HOA spectrum is overall consistent with previously reported ambient HOA spectra (*Zhang et al.*, 2005a; *Sun et al.*, 2011a; *Ng et al.*, 2011b). The BBOA MS has a significant fraction of hydrocarbon-like $C_xH_y^+$ ions (60% in mass). However, the BBOA factor has a larger fraction of $C_xH_yO_1^+$ ions compared to the HOA MS (25 % vs. 6% respectively), and m/z=43 (mostly $C_2H_3O^+$) and m/z = 29 (mostly CHO^+) are the most abundant peaks. $C_xH_yO_1^+$ ions represent approximately 30-40% of the signal at m/z 55, 57, 69 and 71 as well. The signals at m/z = 60 and m/z = 73 is entirely dominated by $C_2H_4O_2^+$ and $C_3H_5O_2^+$, which are proxies for biomass burning aerosols (likely originating from fragmentation of levoglucosan). Finally, the MS for the BBOA factor is very similar to the one published in Mohr et al. (2012) from PMF analyses performed on the HR-AMS data collected during the DAURE campaign (Spain, 2009). The LVOOA MS shows the typical features of previously published data (*Jimenez et al.*, 2009; *Ng et al.*, 2010), with high m/z = 44 (CO_2^+) and mass dominated by $C_xH_yO_{>1}^+$ ions (45 % for this LVOOA MS). The $C_xH_yO_1^+$ ions (approximately 25% in mass) dominate at m/z 29,41,43,55, 57, 69 and 71.

Figure 5S shows the diurnal trend of the three factors averaged over the entire campaign and over the two days that were not characterized by fog events, here taken as reference period. The presence of fog contributes to the decrease of absolute maxima of BBOA and HOA concentrations in the evenings and the nights.

Supplementary Figures

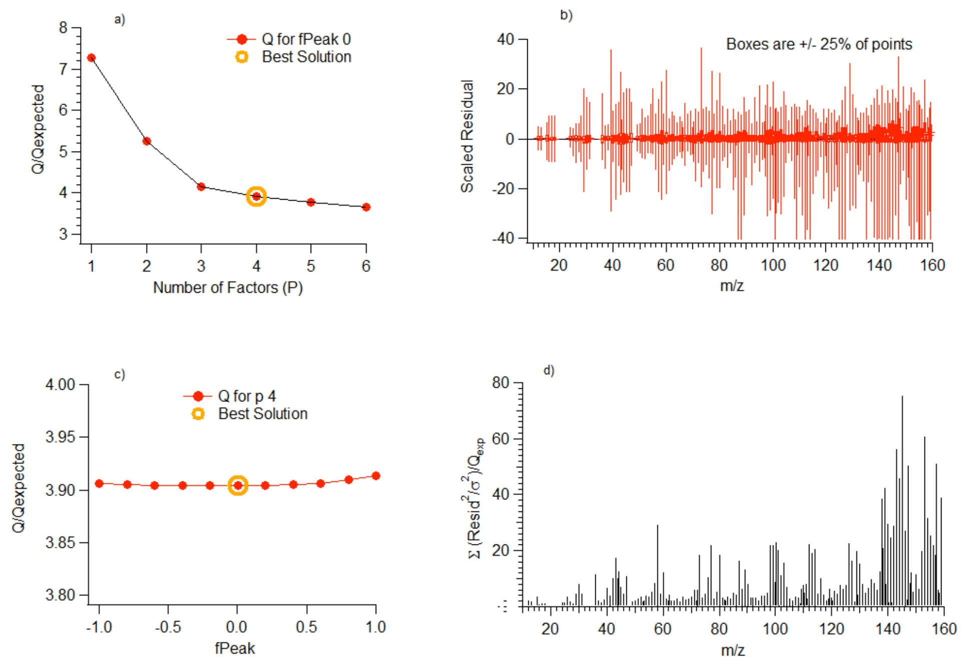

Figure 1S: Summary of PMF key diagnostic plots (panels a, b, c, d) for the HR-TOF-AMS data collected during the SPC campaign in fall 2011. A 4-factor solution with *Q/Qexp* = 4 and fpeak = 0 was chosen for these data. Panel a shows the *Q/Qexp* as a function of the number of factors *P* and panel c shows the *Q/Qexp* as a function of fpeak for the 4-factor solution. Panels b and d show the distribution of scaled residuals and *Q/Qexp* as a function of m/z.

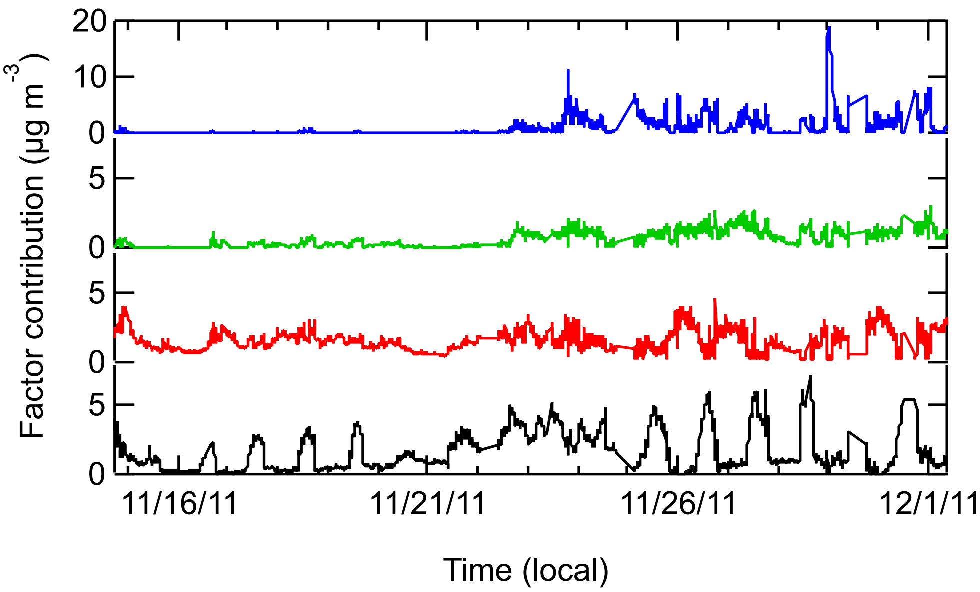

Figure 2S: Temporal series (TS) for the 4-factor solution of the PMF analysis performed on the HR-AMS data collected at the SPC site. Factor 1 has a strong diurnal trend (larger LVOOA during the daytime), whereas factor 2 has a weaker trend, and it is anti-correlated with LVOOA after November 25. Both factor 3 and 4 do not show a clear diurnal pattern.

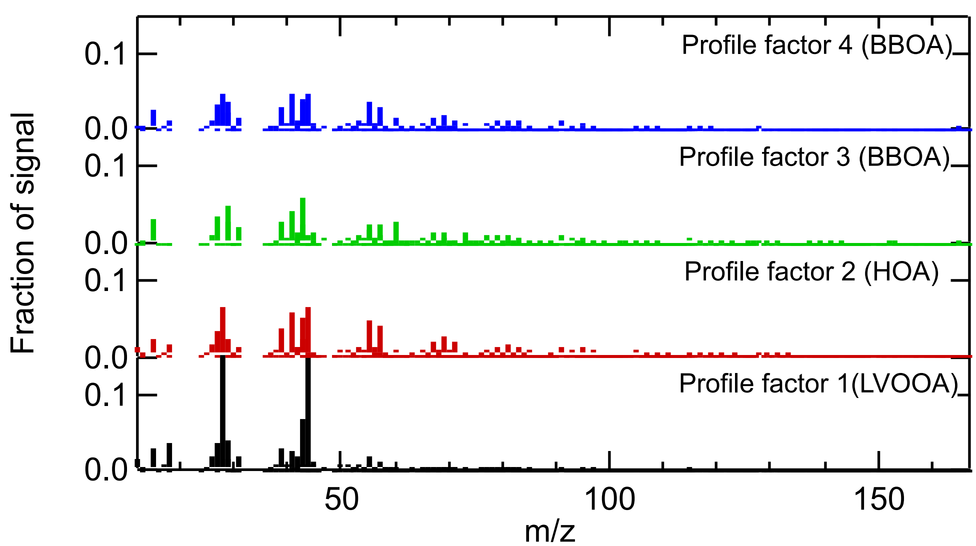

Figure 3S: Mass spectra (MS) of the 4 factors identified by PMF analyses. Factor 1 was identified as LVOOA, whereas factor 2 was identified as HOA. Factor 3 and factor 4 were both identified as BBOA and recombined into one BBOA component.

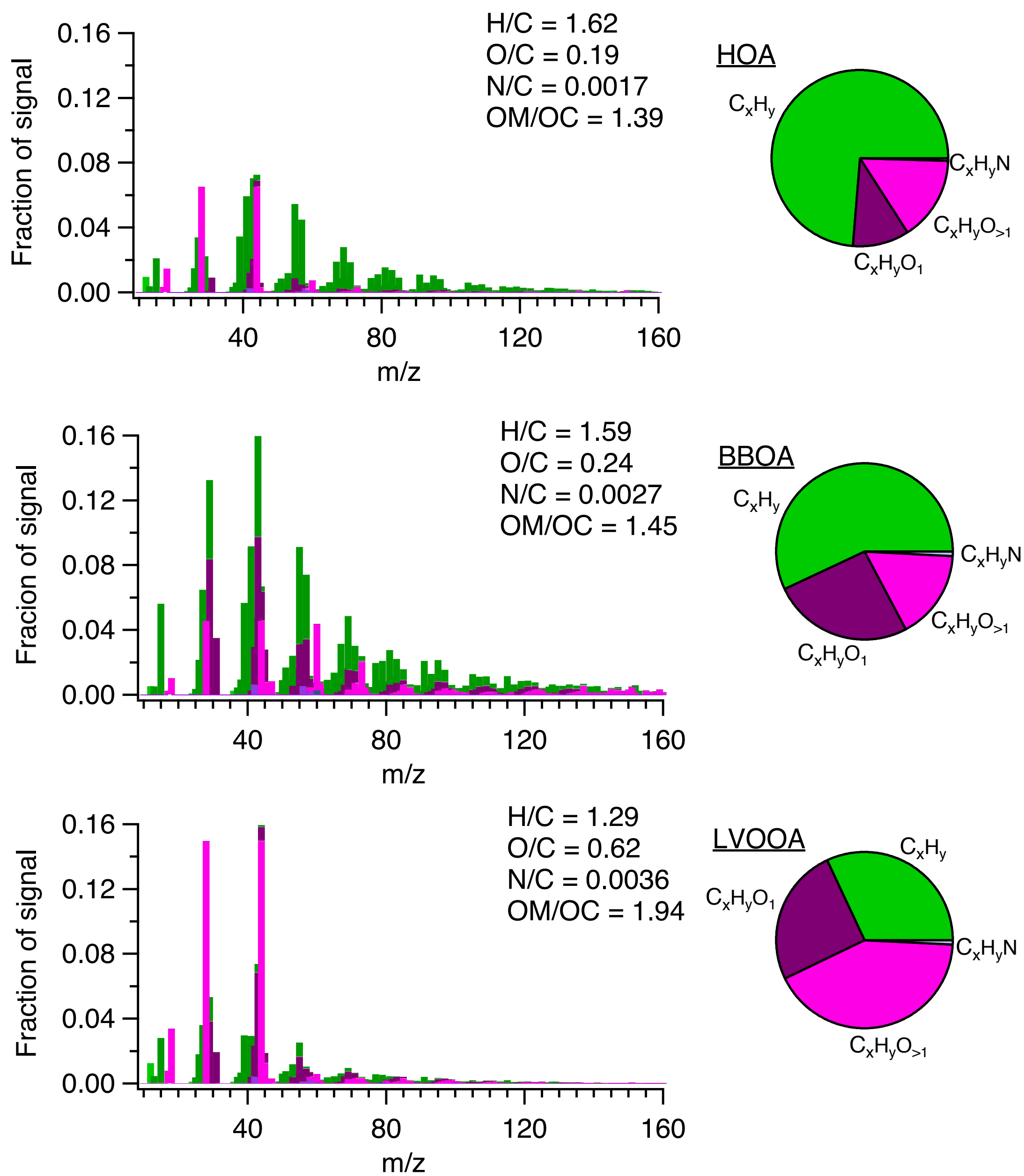

Figure 4S: Summary of PMF results from the combination 2 factors: a. mass spectra and mass weighted pie charts, colored by the ion families CxHy, $CxHyO_1$ and $CxHyO_{>1}$, are shown for HOA, BBOA and LVOOA.

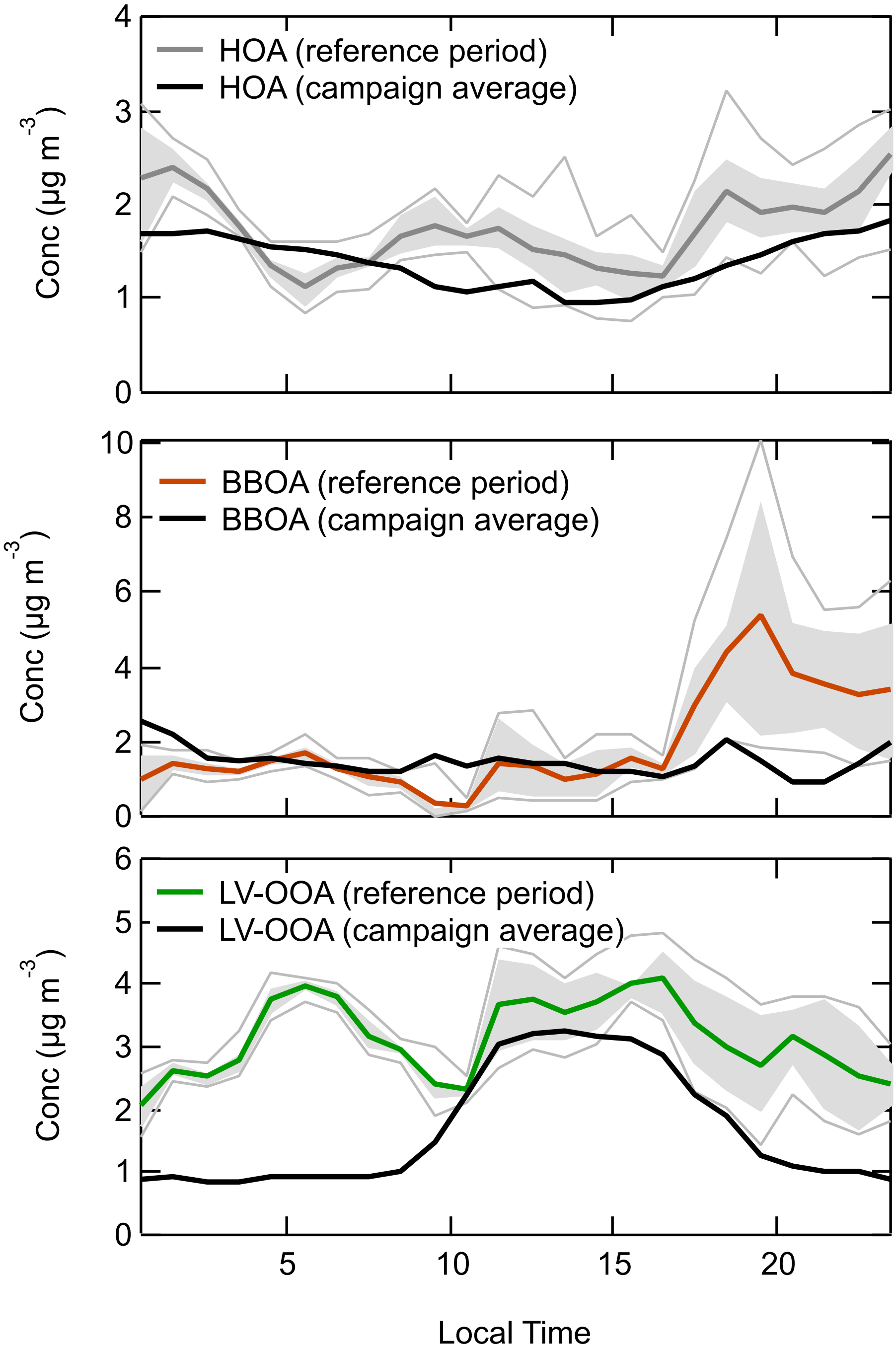

Figure 5S. Comparison between diurnal time trend of HOA, BBOA, and LV-OOA during reference period characterized by the absence of fog events (22 and 23 of November) and over the entire campaign; shadowed gray area corresponds to the 25th – 75th percentile range, grey lines define the 5th-95th percentile range.