**Supplement of:**

# The impact of biomass burning and aqueous-phase processing on air quality: a multi-year source apportionment study in the Po Valley, Italy

Marco Paglione et al.

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## S1. Overall characterization of SUPERSITO dataset

**Table S1: average concentrations (µg m$^{-3}$ ±standard deviation) of main NR-PM1 components Organics (Org), Nitrate ($NO_3^-$), Sulfate ($SO_4^{2-}$), Ammonium ($NH_4^+$) and Chloride ($Cl^-$) for all the considered campaigns. BO = Bologna, SPC = San Pietro Capofiume.**

| | | | Org | | $NO_3^-$ | | $SO_4^{2-}$ | | $NH_4^+$ | | $Cl^-$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BO | SPRING | 2013 | 2.1 | ±1.2 | 1.2 | ±1.6 | 0.8 | ±0.4 | 0.6 | ±0.5 | 0.1 | ±0.2 |
| | | 2014 | 3.3 | ±2.3 | 0.7 | ±1.1 | 1.5 | ±1.0 | 0.6 | ±0.5 | 0.0 | ±0.1 |
| | SUMMER | 2012 | 7.1 | ±2.8 | 0.7 | ±0.9 | 3.3 | ±1.3 | 1.2 | ±0.6 | 0.0 | ±0.0 |
| | FALL | 2011 | 18 | ±9.2 | 12.2 | ±6.8 | 3.3 | ±2.4 | 4.5 | ±2.4 | 1.2 | ±1.0 |
| | | 2012 | 5.0 | ±4.1 | 3.4 | ±3.5 | 0.9 | ±0.7 | 1.3 | ±1.2 | 0.3 | ±0.4 |
| | | 2013 | 4.6 | ±2.8 | 4.5 | ±4.8 | 2.4 | ±1.5 | 2.1 | ±1.7 | 0.3 | ±0.8 |
| | WINTER | 2013 | 8.5 | ±5.3 | 6.9 | ±5.7 | 1.7 | ±1.2 | 2.5 | ±1.9 | 0.4 | ±0.5 |
| | | 2014 | 4.1 | ±2.6 | 3.8 | ±3.2 | 0.9 | ±0.7 | 1.4 | ±1.1 | 0.2 | ±0.3 |
| | | | | | | | | | | | | |
| SPC | SPRING | 2013 | 1.8 | ±1.4 | 1.7 | ±2.5 | 0.7 | ±0.5 | 0.8 | ±0.9 | 0.0 | ±0.1 |
| | SUMMER | 2012 | 4.2 | ±2.6 | 1.3 | ±2.2 | 2.0 | ±1.0 | 1.0 | ±0.8 | 0.0 | ±0.1 |
| | FALL | 2011 | 9.9 | ±6.1 | 6.2 | ±5.5 | 1.2 | ±0.7 | 2.3 | ±1.8 | 0.3 | ±0.4 |
| | | 2013 | 3.6 | ±2.3 | 2.7 | ±3.1 | 1.3 | ±0.9 | 1.3 | ±1.1 | 0.1 | ±0.1 |

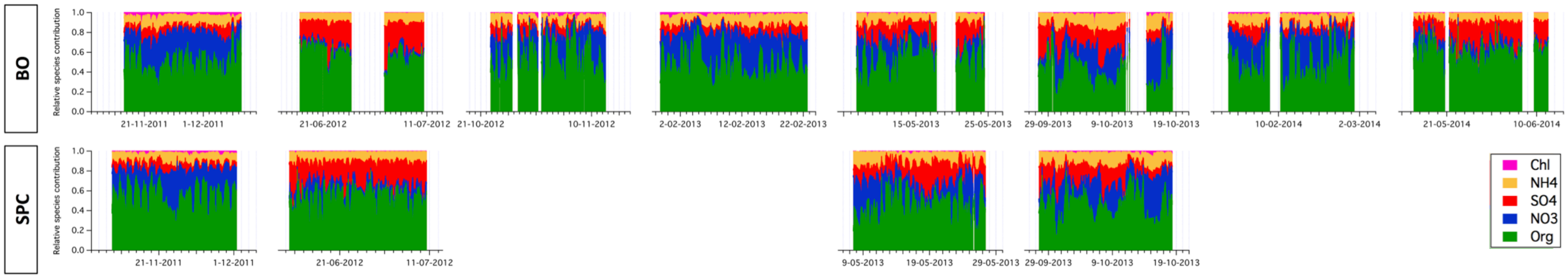



**Figure S1**: time series of the relative contributions of main NR-PM1 chemical components as measured by AMS in each intensive campaign of Supersito project.

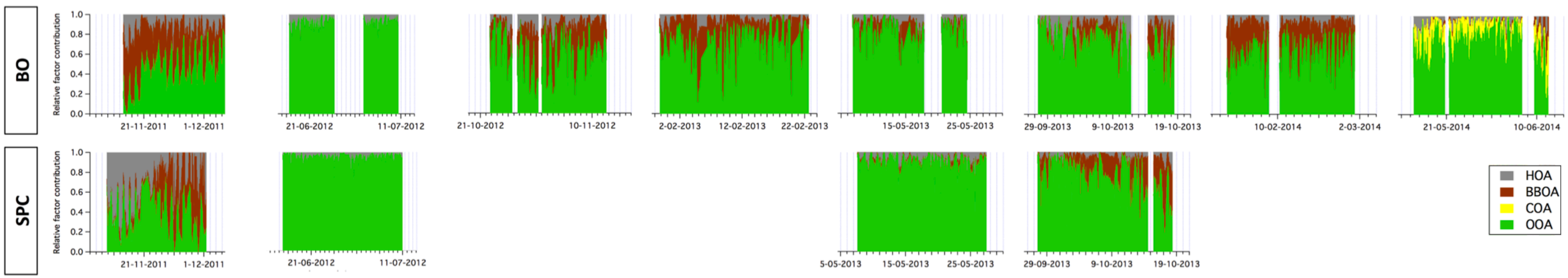



**Figure S2**: time series of the relative contributions of OA primary and secondary components as calculated by PMF and ME-2

**Table S2: Comparison (Pearson's Coefficient R) between time series of the main PM1 components as measured by AMS and by other independent parallel measurements. OC stands for Organic Carbon (by thermo-optical measurements, Sunset); WSOC stands for Water Soluble Organic Carbon (by elemental C evolved gas analysis, Analytik Jena).**

| | | | AMS vs filters | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Sunset | Berner | | | | | Berner | Beta attenuation |
| | | R | Org vs OC | Org vs WSOC | $NO_3^-$ | $SO_4^{2-}$ | $NH_4^+$ | $Cl^-$ | PM1 | PM2.5 |
| BO | SPRING | 2013 | 0.91 | 0.65 | 0.87 | 0.72 | 0.83 | - | 0.90 | 0.76 |
| | | 2014 | 0.84 | 0.59 | 0.73 | 0.55 | 0.68 | 0.83 | 0.83 | 0.86 |
| | SUMMER | 2012 | 0.86 | 0.72 | 0.93 | 0.65 | 0.81 | 0.9 | 0.83 | 0.60 |
| | FALL | 2011 | - | 0.44 | 0.85 | 0.76 | 0.81 | 0.63 | 0.74 | 0.78 |
| | | 2012 | 0.83 | - | - | - | - | - | - | 0.85 |
| | | 2013 | 0.87 | 0.85 | 0.97 | 0.97 | 0.99 | 0.98 | 0.99 | 0.85 |
| | WINTER | 2013 | 0.79 | 0.84 | 0.93 | 0.85 | 0.94 | 0.88 | 0.96 | 0.87 |
| | | 2014 | 0.92 | 0.88 | 0.84 | 0.41 | 0.82 | - | 0.94 | 0.87 |
| | | | | | | | | | | |
| SPC | SPRING | 2013 | 0.98 | 0.86 | 0.97 | 0.67 | 0.94 | 0.72 | 0.97 | 0.91 |
| | SUMMER | 2012 | 0.80 | 0.83 | 0.91 | 0.82 | 0.89 | 0.81 | 0.90 | 0.77 |
| | FALL | 2011 | - | 0.85 | 0.96 | 0.92 | 0.97 | 0.96 | 0.95 | 0.92 |
| | | 2013 | 0.92 | 0.84 | 0.8 | 0.93 | 0.78 | 0.89 | 0.91 | 0.95 |

## S2. Source apportionment configuration and evaluation

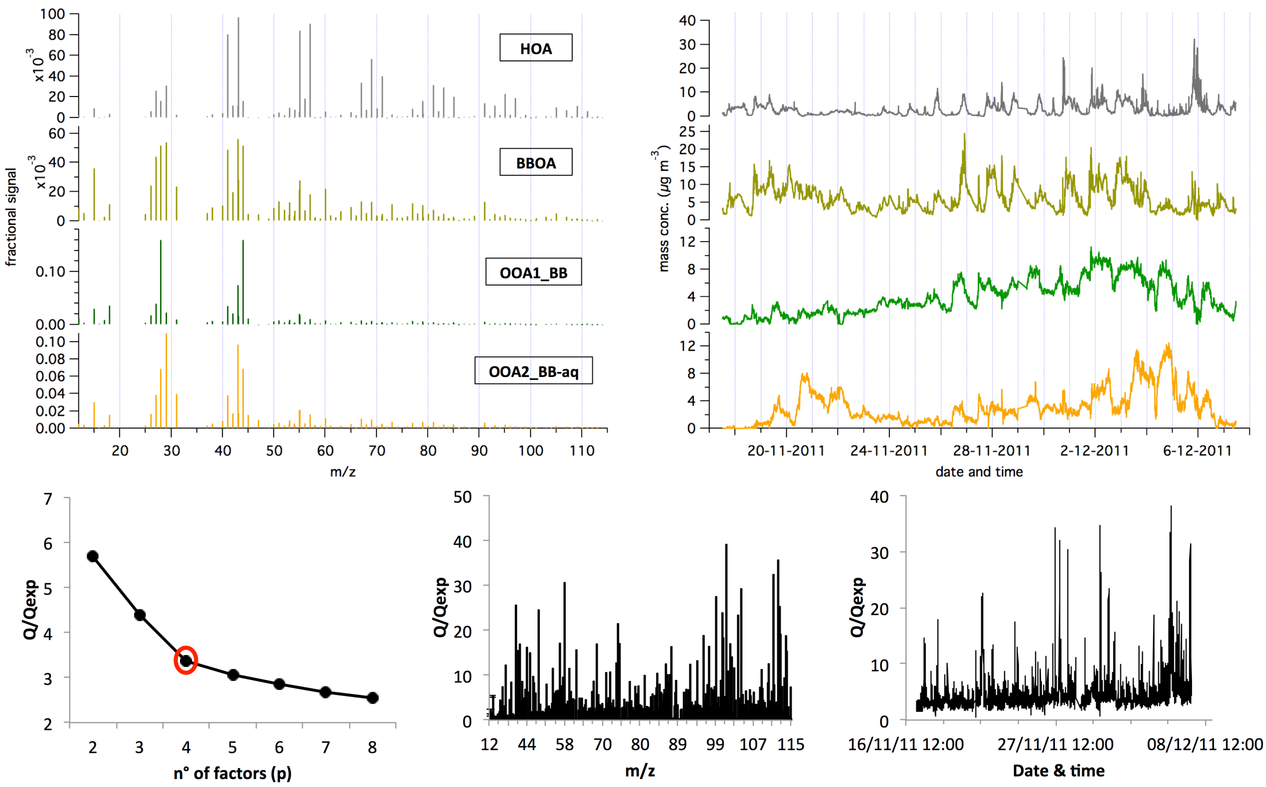
Source apportionment analysis on the HR-TOF-AMS high resolution OA mass spectra was performed using the Multilinear Engine 2 solver (ME-2, Paatero, 1999) controlled within the Source Finder software (SoFi v4.8, Canonaco et al. 2013; Crippa et al., 2014). Prior to factor analysis, the organic data matrix was arranged according to the Ulbrich et al. (2009) recommendations. First of all, 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).
The standardized source apportionment strategy introduced in Crippa et al. (2014) is systematically applied to the 12 available HR-TOF-AMS datasets (8 from BO and 4 from SPC), consisting of the organic mass spectra over time and the corresponding errors. Before selecting the most appropriate solution we performed a sequence of runs from the unconstrained PMF to the sequential constraint of all the possible OA primary sources (Hydrocarbon-like OA or HOA + Biomass Burning OA or BBOA + Cooking OA or COA) if not identified (or uncertainly identified) by the unconstrained runs. Solutions from two to eight factors (applying 3 seeds each) are investigated for all the datasets in order to choose the most appropriate number of factors, that resulted to be campaign-specific and ranged from 3 up to 6 (depending on the season, the site and the number of interpretable OOA factors). In general the appropriate number of factor was chosen based on the residual analysis (inspecting both the Q-value and the possible presence of structure in the residual diurnal trends) together with the correlation analysis of the factors with each other both in terms of mass-spectral and time-dependent similarities (Ulbrich et al., 2009).
Solutions applying various numbers of factors and constraining different factor profiles for each campaign are summarized in Table S3. The influence of different a-values on the OA apportionment has been investigated and some of these data are summarized in Table S4.
A range of *a*-values was tested applying the recommendations of Crippa et al. (2014) and comparing the results with independent measurements (e.g. NOx, BC, organic tracers, etc., see Table S4). We tested various reference factor profiles (RFPs) from ambient deconvolved spectra of

the high-resolution aerosol mass spectral database (URL: http://cires.colorado.edu/jimenez-group/HRAMSsd/", Ulbrich et al., 2009). In particular, we employed the HOA, BBOA and COA reference profiles from Mohr et al. (2012) (obtained at Barcelona urban background site) and from Crippa et al. (2013) (HOA and COA from a Paris summer campaign). Oxidized organic aerosol components (OOAs) factors were never constrained because their mass spectra are characterized by a greater variability with respect to the POA factors, reflecting the multiplicity of atmospheric secondary formation and transformation processes contributing to SOA formation and composition (Canonaco et al. 2015).

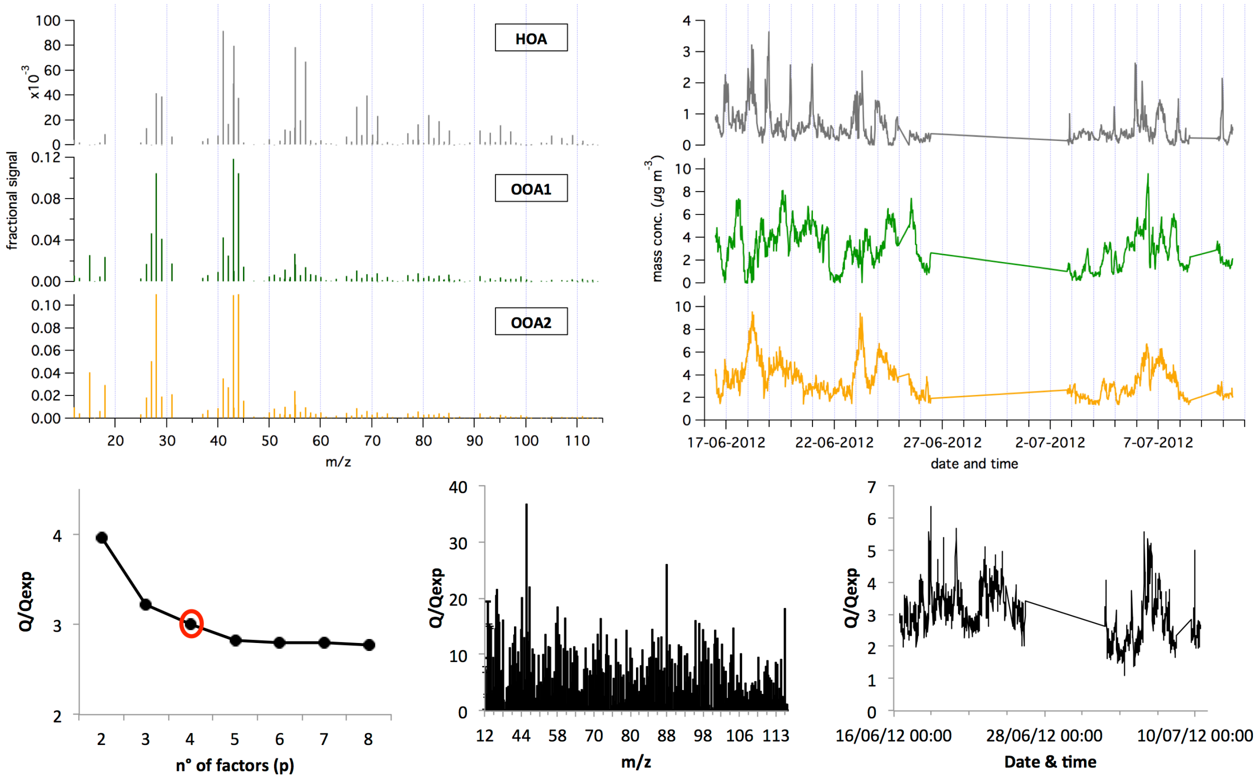
The interpretation of the retrieved source apportionment factors as organic aerosol sources is based on the comparison of their mass spectral profiles with reference ones (Table S5, S6 and S7), on the correlations with external data (see Table S8) and on the investigation of their diurnal trends (see Figure 3 of the main text).

For the PMF-results already discussed in other papers (i.e., BO_2013winter and SPC_2011fall, and SPC_2012summer campaigns) we refer the reader to the corresponding publications (i.e, Gilardoni et al., 2014 & 2016 and Sullivan et al., 2016).
Regarding the other datasets, details of the best solution chosen for each campaign are reported in the following figures.

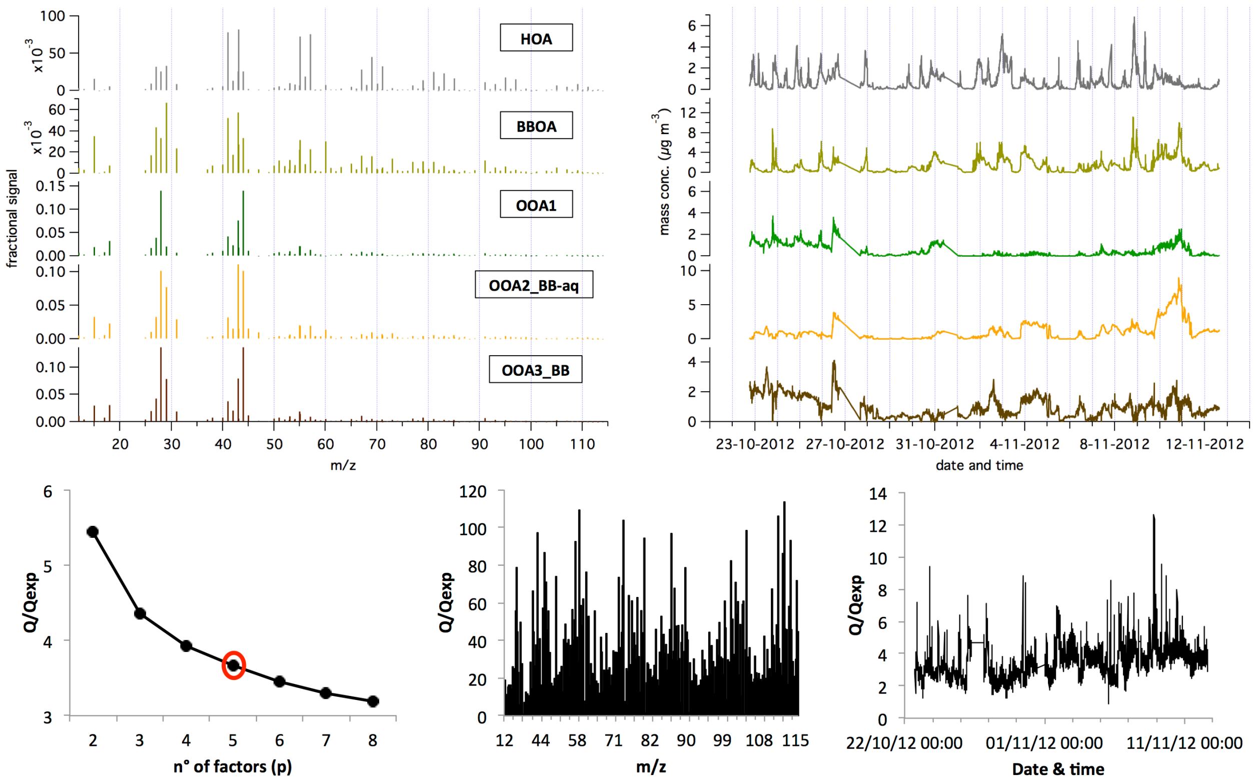
**BO_2011fall: p=4; unconstrained PMF**



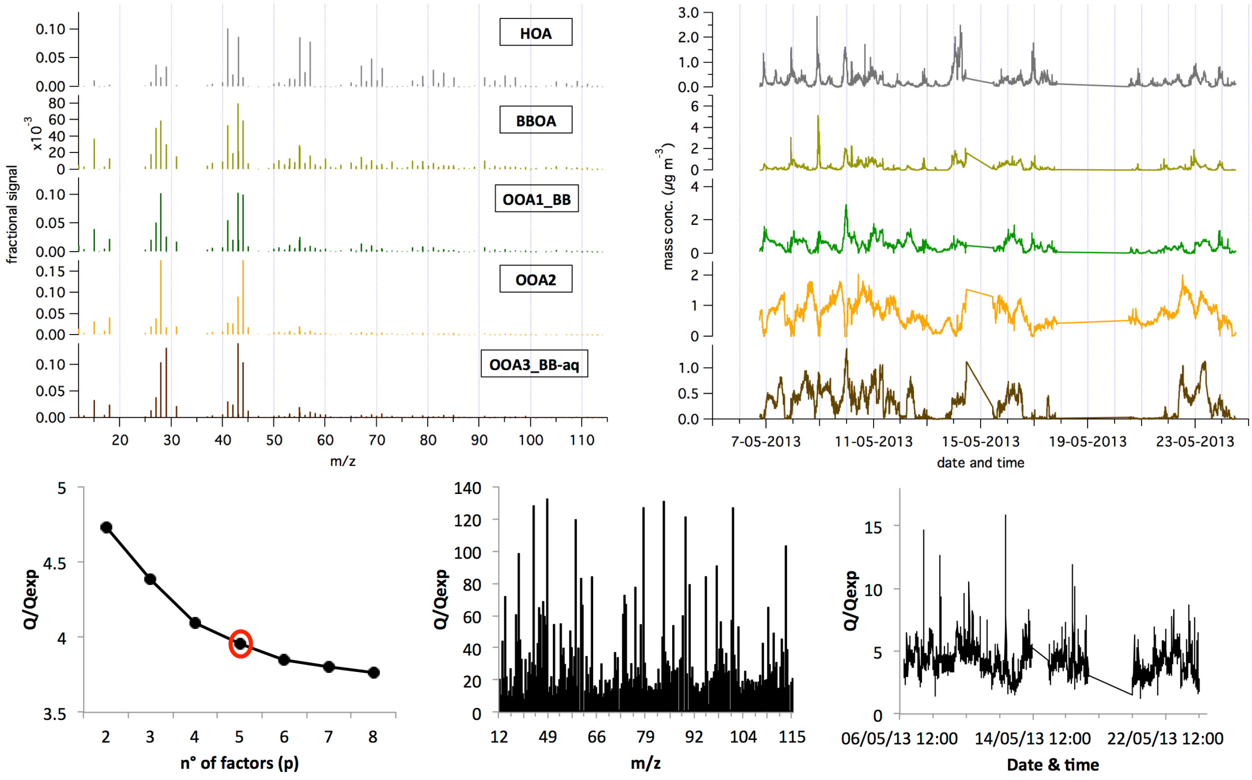
## BO_2012summer: p=4; unconstrained PMF; OOA2 recombined



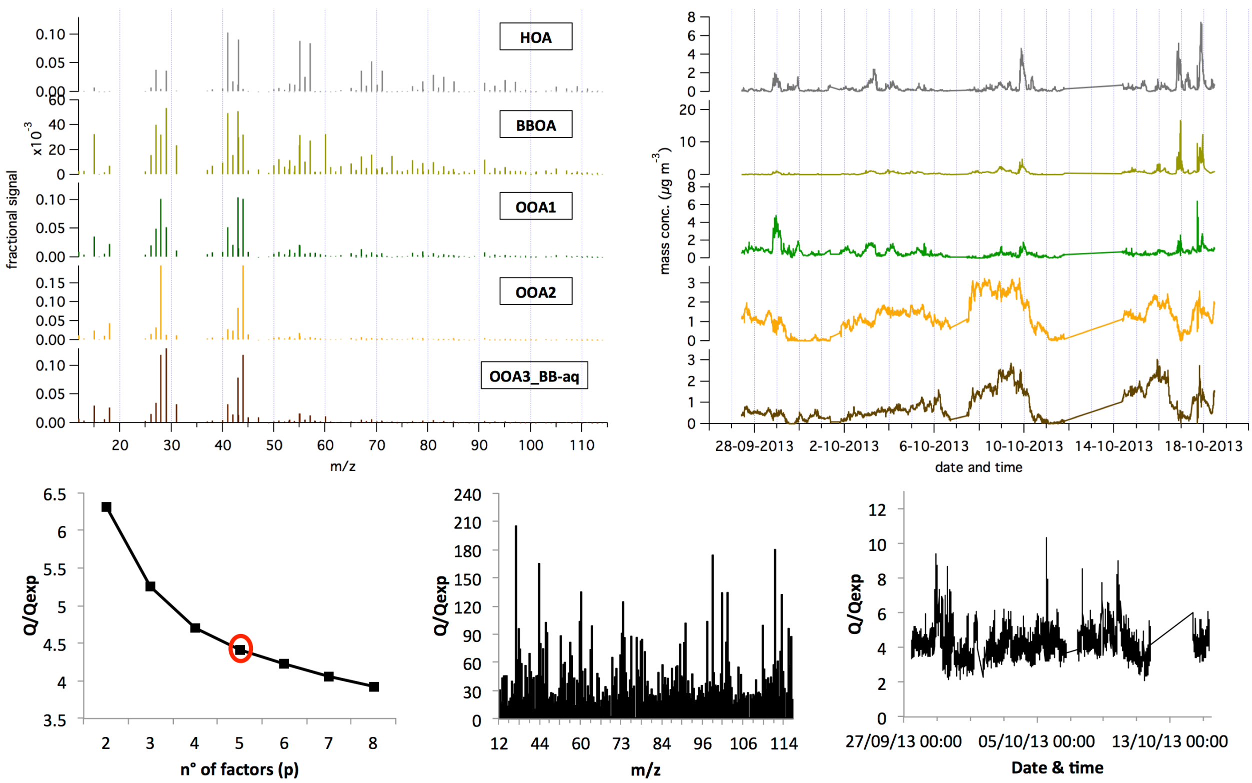

## BO_2012fall: p=5; unconstrained PMF



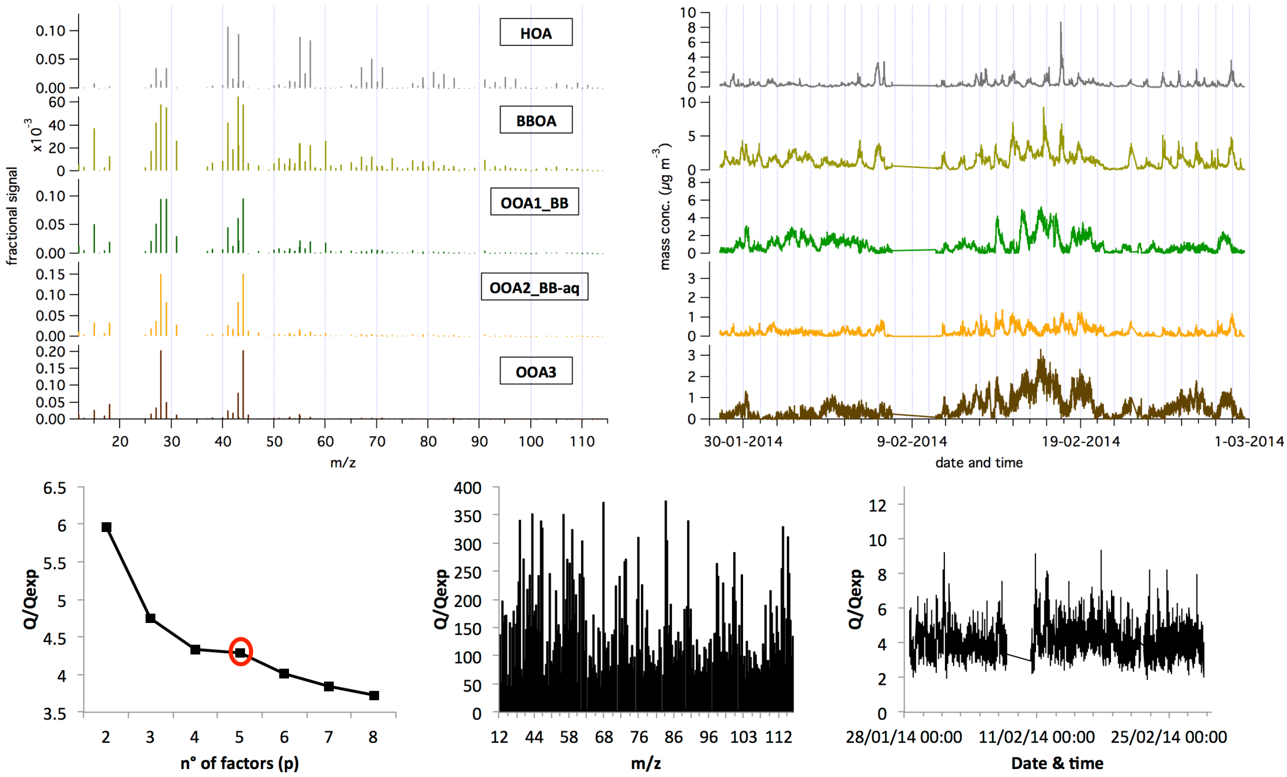
**BO_2013spring: p=5 ME-2 HOA Mohr et al. 2012, a-value=0.5**



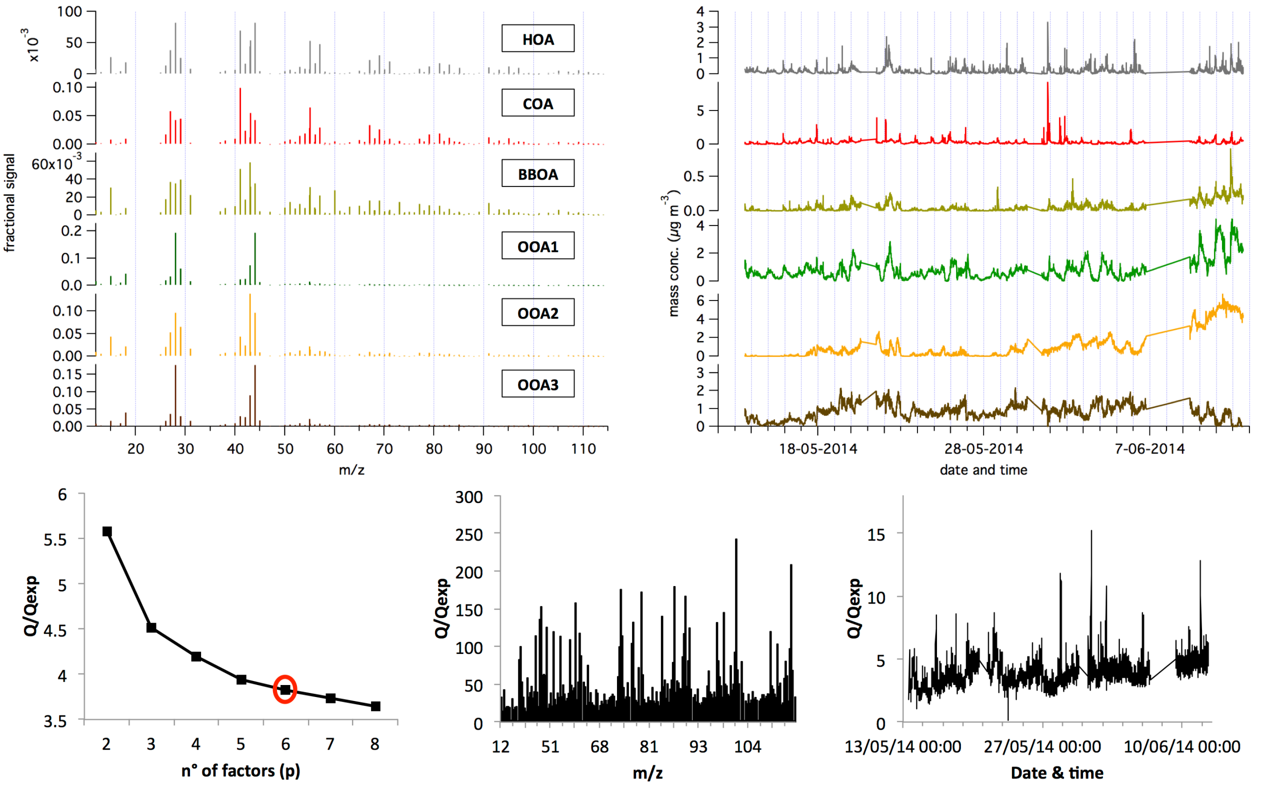

**BO_2013fall: p=5; ME-2 HOA Mohr et al. 2012, a-value=0.5**



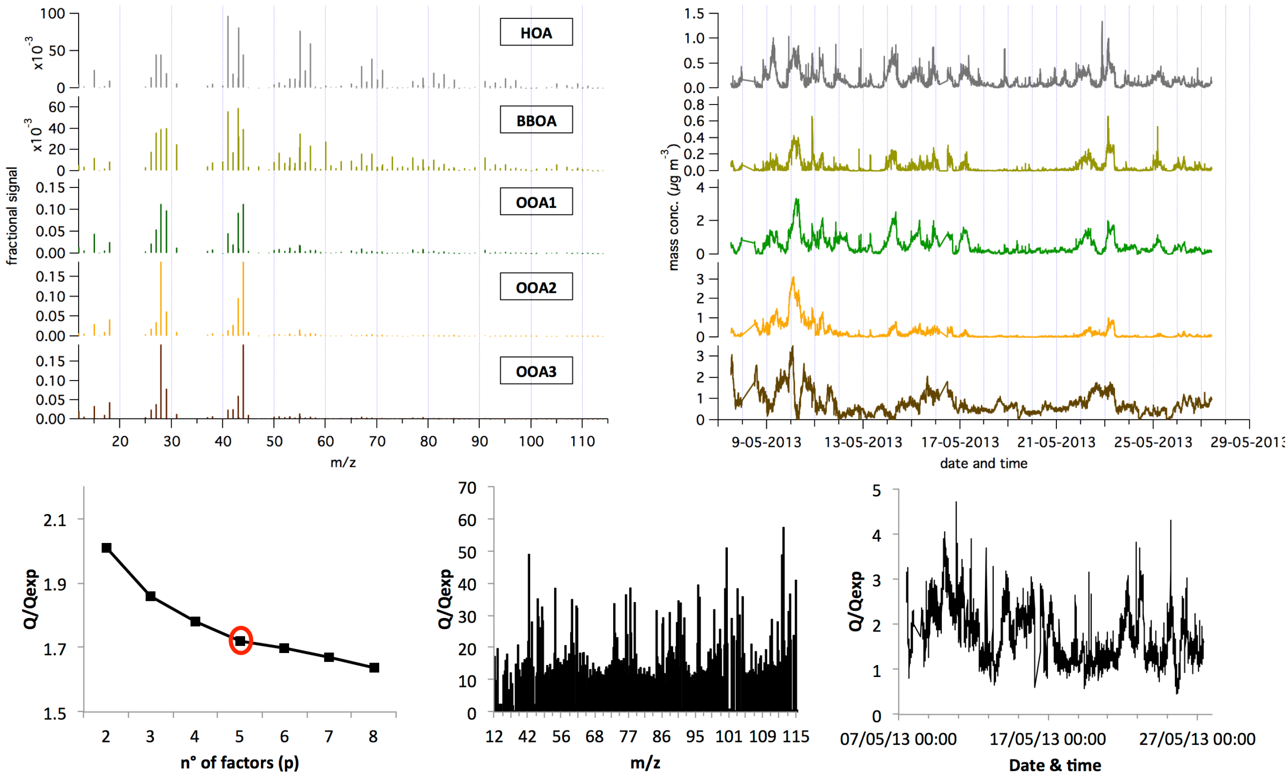
## BO_2014winter: p=5; ME-2 HOA Mohr et al. 2012, a-value=0.5




## BO_2014spring: p=6; ME-2 HOA Mohr et al. 2012, a-value=0.5 + BBOA Mohr et al. 2012, a-value=0.05



## SPC_2013spring: p=5; ME-2 HOA Mohr et al. 2012, a-value=0.5 + BBOA Mohr et al. 2012, a-value=0.05




## SPC_2013fall: p=5; ME-2 HOA Mohr et al. 2012, a-value=0.5

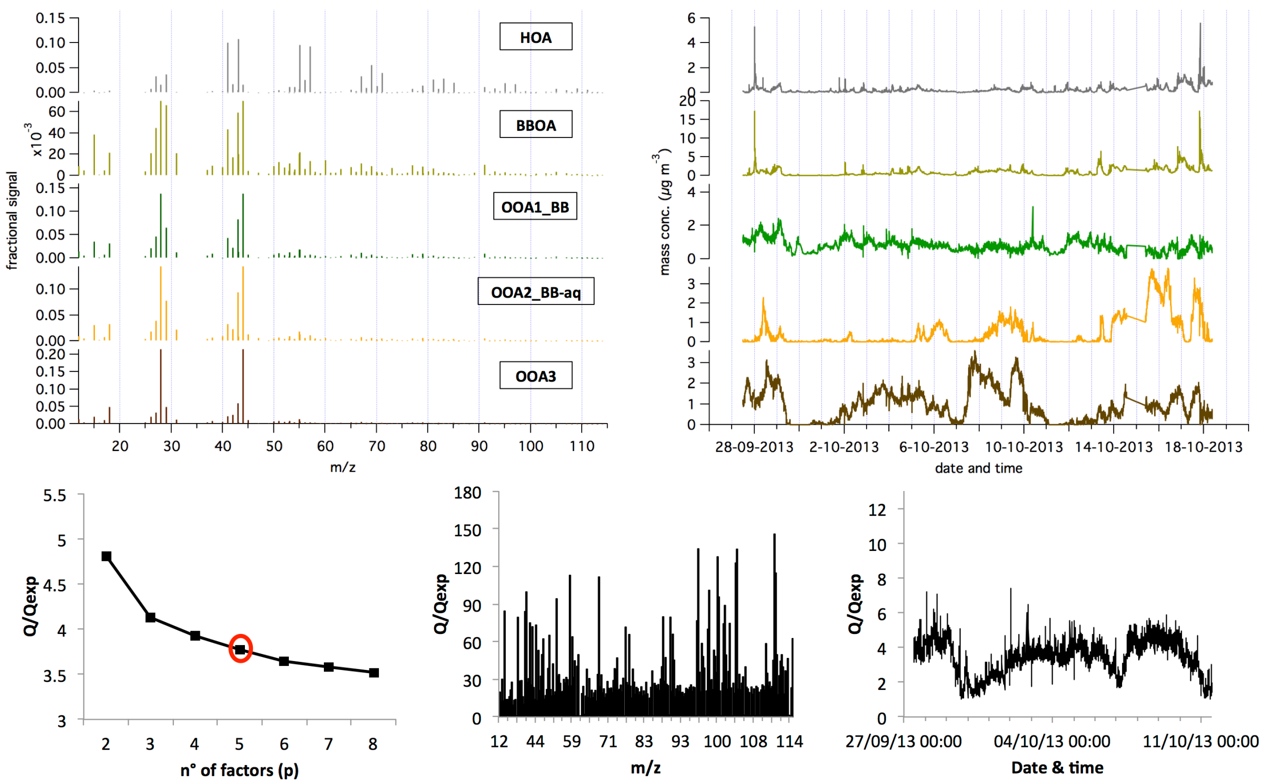


**Table S3. summary of the main tests performed on each dataset to identify the optimal number of factors and the best constraints in PMF analysis. In bold the chosen solution.**

| Site | | Campaign | n° of factors | Factors fixed (a-values tested) | Factors identified | Q/Qexp & residuals structure | Comments |
|---|---|---|---|---|---|---|---|
| **BO** | **SPRING** | **2013** | 2 | unconstrain PMF | HOA, OOA | Q/Qexp=5.3; very high residuals | HOA very oxidized, OOA mixed with BBOA |
| | | | 3 | unconstrain PMF | HOA, 2-OOAs mixed | Q/Qexp=4.6; high residuals for m/z 29, 44 & 60; higher residuals during evening (18-21) | high seed variability, BBOA mixed with OOAs and HOA |
| | | | 4 | unconstrain PMF | HOA, BBOA, OOA1, OOA2 | Q/Qexp=4.3; high residuals for m/z44 & 60; higher residuals during evening (16-21) | HOA very oxidized, BBOA without any m/z 29 & 44, OOA1&OOA2 mixed with BBOA |
| | | | 5 | unconstrain PMF | HOA, BBOA, OOA1, OOA2, OOA3 | Q/Qexp=4.1; good residuals distribution | **Optimal n°of factors**; HOA still oxidized --> try to fix HOA |
| | | | 6 | unconstrain PMF | Factors split | Q/Qexp=3.9; good residuals distribution | High correlations between factor profiles and time series |
| | | | **5** | **HOA (0, 0.05, 0.1, 0.3, 0.5)** | **HOA, BBOA, OOA1, OOA2, OOA3** | **Q/Qexp=4.1 (4.14-4.09)** | **Optimal solution (a=0.5)** |
| | | | 5 | HOA, BBOA (0, 0.05, 0.1, 0.3, 0.5) | HOA, BBOA, OOA1, OOA2, OOA3 | Q/Qexp=3.8 (4.03-3.65); higher residuals during early morning (6-10) | HOA not well represented; BBOA split in two factors |
| | | | 5 | HOA, BBOA, COA (0, 0.05, 0.1, 0.3, 0.5) | HOA, BBOA, COA, OOA1, OOA2 | Q/Qexp=4.4 (4.46-4.43); high residuals for m/z 29, 44 & 60; higher residuals during early morming (6-10) | HOA not well represented and mixed with COA; COA contr. negligible and with flat diurnal trend; BBOA split |
| | | | 6 | HOA, BBOA, COA (0, 0.05, 0.1, 0.3, 0.5) | Factors split | Q/Qexp=4.1 (4.19-4.09); high residuals for m/z 29, 44 & 60; higher residuals during early morming (6-10) | HOA not well represented and mixed with COA; COA contr. negligible and with flat diurnal trend; BBOA split |
| | | **2014** | 2 | unconstrain PMF | HOA/BBOAmixed, OOA | Q/Qexp=3.6; very high residuals | HOA mixed with BBOA, OOA with high m/z fragments |
| | | | 3 | unconstrain PMF | HOA, 2-OOAs mixed | Q/Qexp=3.2; high residuals for m/z 44, 55 & 60; higher residuals during morning (10-13) | HOA very oxidized, OOA mixed with BBOA |
| | | | 4 | unconstrain PMF | HOA, BBOA, OOA1, OOA2 | Q/Qexp=3.1; high residuals for m/z 44, 55 & 60; higher residuals during morning (10-13) | HOA very oxidized, BBOA mixed with OOAs |
| | | | 5 | unconstrain PMF | HOA, BBOA, COA/OOA1 mixed, OOA2, OOA3 | Q/Qexp=3; high residuals for m/z 44 & 60; residual diurnal trend with 2 maxima (early morning and evening) | BBOA with very poor m/z 60 (split in all the factors), possible COA mixed with OOA (diurnal maximum at 12-13) |
| | | | 6 | unconstrain PMF | HOA, BBOA, COA, OOA1, OOA2, OOA3 | Q/Qexp=2.9; good residuals distribution | **Optimal n°of factors**; BUT BBOA still mixed with OOAs --> try to fix BBOA |
| | | | 7 | unconstrain PMF | Factors split | Q/Qexp=2.8; good residuals distribution | High correlations between factor profiles and time series |
| | | | 6 | BBOA (0, 0.05, 0.1, 0.3, 0.5) | HOA, BBOA, COA, OOA1, OOA2, OOA3 | Q/Qexp=2.9 (2.9-2.8); good residuals distribution | HOA very oxidized, high contributions |
| | | | 6 | HOA, BBOA (0, 0.05, 0.1, 0.3, 0.5) | HOA, BBOA, COA, OOA1, OOA2, OOA3 | Q/Qexp=3.8 (3.84-3.82); good residuals distribution | Promising solution, but overlapping between BBOA and COA |
| | | | 6 | HOA, BBOA, COA (0, 0.05, 0.1, 0.3, 0.5) | HOA, BBOA, COA, OOA1, OOA2, OOA3 | Q/Qexp=3.7; good residuals distribution | HOA not well represented and mixed with COA; COA contr. Very high; BBOA contr. negligible |
| | | | **6** | **HOA (0.5), BBOA (0.05)** | **HOA, BBOA, COA, OOA1, OOA2, OOA3** | **Q/Qexp=3.8** | **Optimal solution (HOA a=0.5, BBOA a=0.05)** |
| | **SUMMER** | **2012** | 2 | unconstrain PMF | OOA1_A, OOA1_B | Q/Qexp=3.6; high residuals for m/z 43 & 44, higher during rush hours | OOAs spectra highly correlated, OOAs contribution split in the two periods of the campaign (probably due to a new calibration after an instrumental problem) |
| | | | 3 | unconstrain PMF | HOA, OOA1_A, OOA1_B | Q/Qexp=3; high residuals for m/z 43 & 44 | HOA very oxidized |
| | | | **4** | **unconstrain PMF** | **HOA, OOA1_A, OOA1_B, OOA2** | **Q/Qexp=2.8; good residuals distribution** | **Optimal n°of factors**; OOA1_A and OOA1_B recombined because considered same factor in two different period of the campaign (2 different calibrations) |
| | | | 5 | unconstrain PMF | Factors split | Q/Qexp=2.7; good residuals distribution | HOA split and mixed with OOAs; High correlations between time series |
| | | | 4 | HOA (0, 0.05, 0.1, 0.3, 0.5) | HOA, OOA1_A, OOA1_B, OOA2 | Q/Qexp=2.9; good residuals distribution | HOA split and mixed with OOAs (m/z 41, 55 & 57 in the OOAs) |
| | | | 4 | COA (0, 0.05, 0.1, 0.3, 0.5) | COA, OOA1_A, OOA1_B, OOA2 | Q/Qexp=2.9; good residuals distribution | HOA mixed with OOAs; COA contr. negligible and with flat diurnal trend |
| | | | 5 | COA (0, 0.05, 0.1, 0.3, 0.5) | HOA, COA, OOA1_A, OOA1_B, OOA2 | Q/Qexp=2.7; good residuals distribution | HOA not well represented and mixed with COA; COA contr. negligible and with flat diurnal trend |
| | **FALL** | **2011** | 2 | unconstrain PMF | HOA/BBOA mixed, OOA | Q/Qexp=5.7; high residuals for m/z 43, 44 & 60, higher during night | HOA mixed with BBOA, OOA with high-mass fragments (m/z>60) |
| | | | 3 | unconstrain PMF | HOA, BBOA/OOA mixed, OOA mixed | Q/Qexp=4.4; high residuals for m/z 43, 44 | Reasonable HOA, BBOA mixed with OOAs (with high m/z29 & 60 fragments) |
| | | | **4** | **unconstrain PMF** | **HOA, BBOA, OOA1, OOA2** | **Q/Qexp=3.4; good residuals distribution** | **Optimal n°of factors & solution** |
| | | | 5 | unconstrain PMF | Factors split | Q/Qexp=3.1; good residuals distribution | High correlations between factor profiles and OOAs time series |
| | | | 4 | COA (0, 0.05, 0.1, 0.3, 0.5) | COA, BBOA, OOA1, OOA2 | Q/Qexp=4.2; high residuals for m/z 57, higher during rush hours | HOA not represented; COA contr. very low and with flat diurnal trend |
| | | | 5 | COA (0, 0.05, 0.1, 0.3, 0.5) | HOA, COA, BBOA, OOA1, OOA2 | Q/Qexp=3.3; good residuals distribution | HOA still not well represented and COA contr. very low and with flat diurnal trend |
| | | **2012** | 2 | unconstrain PMF | HOA/BBOAmixed, OOA | Q/Qexp=5.4; high residuals for m/z 29, 43, 44 & 60; higher residuals during night | HOA mixed with BBOA, OOA with high m/z fragments |
| | | | 3 | unconstrain PMF | HOA, BBOA, OOA | Q/Qexp=4.4; high residuals for m/z 29, 43, 44 & 60 | HOA oxidized, high residuals for m/z 43, 44 and 60. |
| | | | 4 | unconstrain PMF | HOA, BBOA, OOA1, OOA2 | Q/Qexp=3.9; residuals for m/z 29, 43, 44 & 60; higher residuals during night | high seed variability, BBOA mixed with OOAs |
| | | | **5** | **unconstrain PMF** | **HOA, BBOA, OOA1, OOA2, OOA3** | **Q/Qexp=3.6; good residuals distribution** | **Optimal n°of factors & solution** |
| | | | 6 | unconstrain PMF | Factors split | Q/Qexp=3.5; good residuals distribution | High correlations between factor profiles and time series |
| | | | 5 | HOA (0, 0.05, 0.1, 0.3, 0.5) | HOA, BBOA, OOA1, OOA2, OOA3 | Q/Qexp=3.6 (3.7-3.5) | Results very similar to unconstrained runs: slight variability of HOA contributions and correlation with tracers |
| | | | 5 | HOA+COA (0, 0.05, 0.1, 0.3, 0.5) | HOA, COA/BBOAmixed, OOA1, OOA2, OOA3 | Q/Qexp=3.7; high residuals for m/z 29, 43, 44 & 60 | not convergent for a-values<0.5; for a=0.5 COA profile mixed with BBOA (high m/z 60 and diurnal trend with night-time maximum) |
| | | | 6 | HOA+COA (0, 0.05, 0.1, 0.3, 0.5) | Factors split | Q/Qexp=3.5 (3.7-3.5) | HOA split in 2 factors; COA spectrum not reasonable (very high m/z28 and 44); COA contr. very low and with flat diurnal trend |
| | | **2013** | 2 | unconstrain PMF | HOA/BBOAmixed, OOA | Q/Qexp=5.8; high residuals for m/z 60 & 73; higher residuals during night and rush hours | HOA&BBOA mixed; high residuals |
| | | | 3 | unconstrain PMF | HOA, BBOA, OOA | Q/Qexp=4.9; high residuals for m/z 43, 44 & 60; higher residuals during night | HOA very oxidized, BBOA mixed with OOAs |
| | | | 4 | unconstrain PMF | HOA, BBOA, OOA1, OOA2 | Q/Qexp=4.5; high residuals for m/z44 & 60; higher residuals during night | BBOA mixed with OOAs (high m/z 55 & 57); HOA oxidized |
| | | | 5 | unconstrain PMF | HOA, BBOA, OOA1, OOA2, OOA3 | Q/Qexp=4.3; good residuals distribution | **Optimal n°of factors**; HOA still oxidized --> try to fix HOA |
| | | | 6 | unconstrain PMF | Factors split | Q/Qexp=4.1; good residuals distribution | High correlations between factor profiles and time series |
| | | | **5** | **HOA (0, 0.05, 0.1, 0.3, 0.5)** | **HOA, BBOA, OOA1, OOA2, OOA3** | **Q/Qexp=4.3; good residuals distribution** | **Optimal solution (a=0.5); not convergent for a-values<0.1; for a=0.1-0.5 results very similar to unconstrained runs: slight variability of HOA contributions and correlation with tracers** |
| | | | 5 | HOA, BBOA, COA (0, 0.05, 0.1, 0.3, 0.5) | - | - | not convergent |
| | | | 6 | HOA, BBOA, COA (0, 0.05, 0.1, 0.3, 0.5) | HOA, BBOA, COA, OOA1, OOA2, OOA3 | Q/Qexp=4.4; good residuals distribution | BBOA split in 2 factors; COA contr. very low and with flat diurnal trend |
| | **WINTER** | **2014** | 2 | unconstrain PMF | HOA/BBOAmixed, OOA | Q/Qexp=4.9 | HOA&BBOA mixed; high residuals |
| | | | 3 | unconstrain PMF | HOA, BBOA, OOA | Q/Qexp=4.3; high residuals for m/z 43, 44 & 60; higher residuals during night | HOA very oxidized, BBOA mixed with OOAs |
| | | | 4 | unconstrain PMF | HOA, BBOA, OOA1, OOA2 | Q/Qexp=4.0; high residuals for m/z 43, 44 & 60; higher residuals during night | HOA very oxidized, BBOA mixed with OOAs |
| | | | 5 | unconstrain PMF | HOA, BBOA, OOA1, OOA2, OOA3 | Q/Qexp=3.8; good residuals distribution | **Optimal n°of factors**; HOA still oxidized --> try to fix HOA |
| | | | 6 | unconstrain PMF | Factors split | Q/Qexp=3.7; good residuals distribution | High correlations between factor profiles and time series |
| | | | **5** | **HOA (0, 0.05, 0.1, 0.3, 0.5)** | **HOA, BBOA, OOA1, OOA2, OOA3** | **Q/Qexp=4.3; good residuals distribution** | **Optimal solution (a=0.5)** |
| | | | 5 | HOA, COA (0, 0.05, 0.1, 0.3, 0.5) | HOA, BBOA, COA, OOA1, OOA2 | Q/Qexp=4.2; good residuals distribution | BBOA mixed with HOA; COA correlating with BBOA time series; COA contr. very low and maximum during night |
| | | | 6 | HOA, COA (0, 0.05, 0.1, 0.3, 0.5) | HOA, BBOA, COA, OOA1, OOA2, OOA3 | Q/Qexp=4.1; good residuals distribution | COA correlating with BBOA time series; COA contr. very low and maximum during night |
| **SPC** | **SPRING** | **2013** | 2 | unconstrain PMF | HOA/BBOAmixed, OOA | Q/Qexp=1.9; high residuals; residuals maximum at early-morning/night | HOA&BBOA mixed and highly oxidized; high residuals |
| | | | 3 | unconstrain PMF | HOA, BBOA/OOAmixed, OOA | Q/Qexp=1.8; high residuals for m/z 43, 44 & 60; higher residuals durning early morning/night | HOA very oxidized, BBOA mixed with OOAs |
| | | | 4 | unconstrain PMF | HOA, HOA/BBOAmixed, OOA1, OOA2 | Q/Qexp=1.75; high residuals for m/z 41, 44 & 60; higher residuals during early morning/night | HOA very oxidized, BBOA mixed with HOA |
| | | | 5 | unconstrain PMF | HOA, BBOA, OOA1, OOA2, OOA3 | Q/Qexp=1.7; good residuals distribution | **Optimal n°of factors**; HOA still oxidized and mixed with BBOA --> try to fix HOA & BBOA |
| | | | 6 | unconstrain PMF | Factors split | Q/Qexp=1.65; good residuals distribution | High correlations between factor profiles and time series |
| | | | 5 | HOA (0, 0.05, 0.1, 0.3, 0.5) | HOA, HOA/BBOAmixed, OOA1, OOA2, OOA3 | Q/Qexp=1.7; good residuals distribution | HOA split in two factors, one good the other mixed with BBOA |
| | | | **5** | **HOA, BBOA (0, 0.05, 0.1, 0.3, 0.5)** | **HOA, BBOA, OOA1, OOA2, OOA3** | **Q/Qexp=1.7; good residuals distribution** | **Optimal solution (HOA a=0.5, BBOA a=0.05)** |
| | | | 6 | HOA, BBOA, COA (0, 0.05, 0.1, 0.3, 0.5) | HOA, BBOA, COA, OOA1, OOA2, OOA3 | Q/Qexp=1.7; good residuals distribution | HOA not well represented; COA correlating with BBOA time series; COA contr. very low and maximum during night |
| | **FALL** | **2013** | 2 | unconstrain PMF | HOA, OOA | Q/Qexp=4.5; high residuals for m/z 43, 44 & 60; higher residuals durning early morning/night | HOA&BBOA mixed and highly oxidized; high residuals |
| | | | 3 | unconstrain PMF | HOA, OOA1, OOA2 | Q/Qexp=4; high residuals for m/z 43, 44 & 60; higher residuals durning night | HOA very oxidize and mixed with BBOA |
| | | | 4 | unconstrain PMF | HOA/BBOAmixed, OOA1, OOA2 | Q/Qexp=3.8; high residuals for m/z 43, 44 & 60; higher residuals during night | HOA very oxidized, BBOA mixed with HOA |
| | | | 5 | unconstrain PMF | HOA, BBOA, OOA1, OOA2, OOA3 | Q/Qexp=3.7; good residuals distribution | **Optimal n°of factors**; HOA still oxidized --> try to fix HOA |
| | | | 6 | unconstrain PMF | Factors split | Q/Qexp=3.6; good residuals distribution | High correlations between factor profiles and time series |
| | | | **5** | **HOA (0, 0.05, 0.1, 0.3, 0.5)** | **HOA, BBOA, OOA1, OOA2, OOA3** | **Q/Qexp=3.6; good residuals distribution** | **Optimal solution (a=0.5)** |

**Table S4: Influences of constraints and a-values on the agreement (expressed as Pearson correlation coefficient, R) of PMF factors with specific independent measurements.**

| | | | | | Correlations (R) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | HOA | | BBOA | | OOA | |
| Site | | Campaign | n° of factors | Factors fixed (reference; a-value) | NOx | BC | EC | Levo | NO3 | SO4 | NH4 |
| BO | SPRING | 2013 | 5 | unconstrain PMF | 0.6 | - | 0.76 | 0.43 | 0.66 | 0.75 | 0.73 |
| | | | 5 | HOA (Mohr, 2012; a=0.05) | 0.57 | - | 0.74 | 0.44 | 0.67 | 0.73 | 0.71 |
| | | | 5 | HOA (Mohr, 2012; a=0.1) | 0.59 | - | 0.76 | 0.49 | 0.65 | 0.73 | 0.72 |
| | | | **5** | **HOA (Mohr, 2012; a=0.5)** | **0.62** | **-** | **0.77** | **0.57** | **0.68** | **0.73** | **0.73** |
| | | 2014 | 6 | unconstrain PMF | 0.5 | - | 0.46 | 0.71 | 0.38 | 0.81 | 0.7 |
| | | | 6 | BBOA (Mohr, 2012; a=0.1) | 0.45 | - | 0.51 | 0.7 | 0.35 | 0.85 | 0.68 |
| | | | 6 | HOA, BBOA, COA (Mohr, 2012; a=0.1) | 0.21 | - | 0.32 | 0.53 | 0.32 | 0.67 | 0.54 |
| | | | **6** | **HOA (Mohr, 2012; 0.5), BBOA (Mohr, 2012; 0.05)** | **0.48** | **-** | **0.56** | **0.77** | **0.21** | **0.87** | **0.66** |
| | SUMMER | 2012 | **4** | **unconstrain PMF** | **0.49** | **0.69** | **0.6** | | **0.49** | **0.39** | **0.55** |
| | | | 4 | HOA (Mohr, 2012; a=0.5) | 0.43 | 0.3 | 0.5 | | 0.48 | 0.35 | 0.53 |
| | | | 5 | HOA, COA (Mohr, 2012; a=0.5) | 0.45 | 0.65 | 0.53 | | 0.49 | 0.37 | 0.53 |
| | FALL | 2011 | **4** | **unconstrain PMF** | **0.58** | **-** | **-** | **0.67** | **0.92** | **0.77** | **0.92** |
| | | | 4 | COA (Mohr, 2012; a=0.5) | | | | 0.65 | 0.9 | 0.76 | 0.91 |
| | | | 5 | COA (Mohr, 2012; a=0.5) | 0.53 | - | - | 0.66 | 0.91 | 0.77 | 0.92 |
| | | 2012 | **5** | **unconstrain PMF** | **0.58** | **0.78** | **0.8** | **-** | **0.86** | **0.67** | **0.89** |
| | | | 5 | HOA (Mohr, 2012; a=0.05) | 0.59 | 0.76 | 0.77 | - | 0.85 | 0.69 | 0.82 |
| | | | 5 | HOA (Mohr, 2012; a=0.5) | 0.58 | 0.78 | 0.8 | - | 0.86 | 0.67 | 0.88 |
| | | | 5 | HOA, COA (Mohr, 2012; a=0.5) | 0.57 | 0.75 | 0.73 | - | 0.83 | 0.65 | 0.85 |
| | | 2013 | 5 | unconstrained PMF | 0.41 | - | 0.77 | 0.71 | 0.73 | 0.75 | 0.85 |
| | | | 5 | HOA (Mohr, 2012; a=0.05) | 0.43 | - | 0.79 | 0.7 | 0.71 | 0.73 | 0.82 |
| | | | **5** | **HOA (Mohr, 2012; a=0.5)** | **0.46** | **-** | **0.81** | **0.7** | **0.72** | **0.76** | **0.83** |
| | | | 6 | HOA, BBOA, COA (Mohr, 2012; a=0.5) | 0.07 | - | 0.3 | 0.42 | 0.67 | 0.69 | 0.72 |
| | WINTER | 2014 | 5 | unconstrained PMF | 0.27 | - | 0.7 | 0.72 | 0.89 | 0.77 | 0.92 |
| | | | 5 | HOA (Mohr, 2012; a=0.05) | 0.3 | - | 0.71 | 0.73 | 0.88 | 0.75 | 0.9 |
| | | | **5** | **HOA (Mohr, 2012; a=0.5)** | **0.35** | **-** | **0.79** | **0.75** | **0.9** | **0.79** | **0.94** |
| | | | 6 | HOA, COA (Mohr, 2012; a=0.5) | 0.34 | - | 0.79 | 0.35 | 0.86 | 0.76 | 0.92 |
| SPC | SPRING | 2013 | 5 | unconstrained PMF | 0.55 | - | 0.71 | 0.49 | 0.8 | 0.79 | 0.85 |
| | | | 5 | HOA (Mohr, 2012; a=0.5) | 0.59 | - | 0.73 | 0.43 | 0.81 | 0.79 | 0.86 |
| | | | **5** | **HOA (Mohr, 2012; 0.5), BBOA (Mohr, 2012; 0.05)** | **0.59** | **-** | **0.73** | **0.51** | **0.82** | **0.81** | **0.88** |
| | | | 6 | HOA, COA (Mohr, 2012; a=0.5) | 0.27 | - | 0.35 | 0.32 | 0.79 | 0.77 | 0.83 |
| | FALL | 2013 | 5 | unconstrained PMF | 0.45 | - | 0.75 | 0.56 | 0.65 | 0.77 | 0.81 |
| | | | 5 | HOA (Mohr, 2012; a=0.05) | 0.49 | - | 0.76 | 0.64 | 0.64 | 0.75 | 0.79 |
| | | | **5** | **HOA (Mohr, 2012; 0.5)** | **0.55** | **-** | **0.79** | **0.66** | **0.66** | **0.78** | **0.82** |

## S2.1 Evaluation of the factor spectra

The subsequent tables (S5, S6 and S7) report the comparison between factor spectral profiles from SUPERSITO campaigns and other correspondent reference profiles from literature and from ambient deconvolved spectra of the HR- and UMR-AMS database (URL: http://cires.colorado.edu/jimenez-group/HRAMSsd/"): the comparison is expressed in term of theta-angle (θ) between the spectra (Kostenidou et al., 2009). In shaded red spectra that exhibit angles less than 15° (very similar to each other), in orange spectra with angles between 15° and 30° (some similarity but also some differences), in green spectra with θ larger than 30° (do not compare well).

**Table S5**.

| | | Reference spectra | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | BO | | | | | | | | SPC | | | | HOA | | | | | | | | | | | | | COA | | | | | | | |
| Θ (°) | **HOA** | 2011_fall. (nov.-dec.) | 2012_summer (jun-jul.) | 2012_fall (oct.-nov.) | 2013_winter (jan.-feb.) | 2013_spring (may) | 2013_fall (oct.) | 2014_winter (jan.-feb.) | 2014_spring (may) | 2011_fall. (nov.-dec.) | 2012_summer (jun.-jul.) | 2013_spring (may) | 2013_fall (oct.) | HOA_Crippa2013s | HOA_Mohr2012 | HOA_Elser2016 | HOA_Setyan2012 | HOA_Aiken2006 | HOA_EUCAARImean | HOA_Crippa2013w | HOAmean_Ng2011 | HOA_Saarikoski2012 | HOA_Stuckmeier2016 | HOA_Athens_Florou2017 | HOA_Patras_Florou2017 | HOA_Stavroulas_2018 | COA_Crippa2013s | COA_Mohr2012 | COA_Elser2016 | COA_Crippa2013w | COA_Stuckmeier2016 | COA_Athens_Florou2017 | COA_Patras_Florou2017 | COA_Stavroulas_2018 |
| BO | **2011_fall. (nov.-dec.)** | 0 | | | | | | | | | | | | 21 | 6 | 13 | 25 | 17 | 11 | 10 | 9 | 33 | 21 | 22 | 11 | 12 | 35 | 48 | 36 | 29 | 20 | 29 | 26 | 35 |
| | **2012_summer (jun-jul.)** | 21 | 0 | | | | | | | | | | | 22 | 25 | 17 | 28 | 18 | 18 | 16 | 18 | 27 | 16 | 19 | 16 | 18 | 33 | 38 | 32 | 28 | 21 | 28 | 23 | 35 |
| | **2012_fall (oct.-nov.)** | 13 | 18 | 0 | | | | | | | | | | 12 | 16 | 8 | 19 | 12 | 12 | 10 | 12 | 27 | 17 | 18 | 10 | 12 | 31 | 39 | 31 | 24 | 17 | 25 | 21 | 30 |
| | **2013_winter (jan.-feb.)** | 6 | 22 | 10 | 0 | | | | | | | | | 19 | 8 | 12 | 24 | 16 | 11 | 9 | 10 | 33 | 21 | 22 | 11 | 12 | 35 | 48 | 36 | 29 | 20 | 29 | 25 | 34 |
| | **2013_spring (may)** | 10 | 21 | 13 | 12 | 0 | | | | | | | | 22 | 14 | 15 | 21 | 14 | 10 | 10 | 11 | 30 | 21 | 20 | 14 | 12 | 30 | 44 | 29 | 21 | 13 | 23 | 20 | 26 |
| | **2013_fall (oct.)** | 10 | 22 | 15 | 11 | 5 | 0 | | | | | | | 23 | 12 | 17 | 20 | 14 | 8 | 9 | 9 | 33 | 24 | 23 | 15 | 10 | 30 | 46 | 30 | 24 | 15 | 25 | 23 | 28 |
| | **2014_winter (jan.-feb.)** | 9 | 21 | 14 | 11 | 4 | 4 | 0 | | | | | | 22 | 12 | 15 | 21 | 14 | 9 | 9 | 9 | 31 | 22 | 21 | 14 | 10 | 30 | 46 | 30 | 23 | 14 | 24 | 22 | 28 |
| | **2014_spring (may)** | 9 | 22 | 14 | 11 | 6 | 3 | 5 | 0 | | | | | 22 | 11 | 16 | 21 | 14 | 8 | 8 | 8 | 33 | 24 | 23 | 14 | 9 | 32 | 46 | 31 | 25 | 16 | 26 | 24 | 29 |
| SPC | **2011_fall. (nov.-dec.)** | 38 | 31 | 29 | 36 | 37 | 41 | 38 | 40 | 0 | | | | 26 | 42 | 28 | 36 | 33 | 33 | 31 | 34 | 19 | 19 | 21 | 29 | 33 | 40 | 32 | 39 | 27 | 30 | 31 | 25 | 35 |
| | **2012_summer (jun.-jul.)** | 23 | 6 | 20 | 24 | 22 | 24 | 22 | 24 | 29 | 0 | | | 24 | 27 | 19 | 29 | 20 | 21 | 19 | 21 | 25 | 15 | 19 | 18 | 20 | 32 | 38 | 31 | 27 | 21 | 27 | 21 | 33 |
| | **2013_spring (may)** | 20 | 20 | 15 | 20 | 16 | 20 | 18 | 20 | 24 | 18 | 0 | | 18 | 25 | 15 | 23 | 16 | 19 | 18 | 19 | 19 | 12 | 14 | 17 | 19 | 29 | 36 | 28 | 20 | 16 | 21 | 17 | 27 |
| | **2013_fall (oct.)** | 7 | 21 | 14 | 8 | 8 | 7 | 5 | 7 | 39 | 23 | 19 | 0 | 22 | 10 | 14 | 24 | 15 | 8 | 7 | 8 | 32 | 21 | 21 | 13 | 10 | 33 | 48 | 33 | 26 | 16 | 26 | 23 | 30 |
| | HOA_median | 8 | 19 | 11 | 9 | 4 | 5 | 4 | 37 | 5 | 36 | 20 | 16 | 6 | 20 | 12 | 13 | 12 | 9 | 7 | 9 | 28 | 18 | 18 | 11 | 9 | 30 | 44 | 30 | 22 | 14 | 24 | 20 | 28 |
| | **COA** | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| BO | **2014_spring (may)** | 41 | 31 | 33 | 40 | 36 | 40 | 38 | 40 | 21 | 28 | 24 | 39 | 34 | 46 | 34 | 36 | 32 | 32 | 31 | 33 | 18 | 22 | 22 | 30 | 32 | 29 | 26 | 27 | 19 | 23 | 24 | 19 | 25 |

**Table S6.**

| Θ (°) | BBOA | BO | | | | | | | SPC | | | Reference spectra | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 2011_fall. (nov.-dec.) | 2012_fall (oct.-nov.) | 2013_winter (jan.-feb.) | 2013_spring (may) | 2013_fall (oct.) | 2014_winter (jan.-feb.) | 2014_spring (may) | 2011_fall. (nov.-dec.) | 2013_spring (may) | 2013_fall (oct.) | BBOA_Mohr2012 | BBOA_Elser2016 | BBOA_Aiken2006 | BBOA_EUCAARImean | BBOA_Crippa2013w | BBOAmean_Ng2011 | BBOA_Saarikoski2012 | BBOA_Stuckmeier2016 | BBOA_Athens_Florou2017 | BBOA_Patras_Florou2017 | BBOA_Bougiatioti_2014 | BBOA_Stavroulas_2018 |
| BO | 2011_fall. (nov.-dec.) | 0 | | | | | | | | | | 28 | 35 | 14 | 24 | 25 | 22 | 34 | 15 | 21 | 19 | 31 | 24 |
| | 2012_fall (oct.-nov.) | 12 | 0 | | | | | | | | | 26 | 28 | 8 | 21 | 32 | 18 | 31 | 22 | 19 | 16 | 23 | 20 |
| | 2013_winter (jan.-feb.) | 19 | 13 | 0 | | | | | | | | 21 | 19 | 13 | 27 | 38 | 20 | 36 | 27 | 25 | 18 | 23 | 20 |
| | 2013_spring (may) | 20 | 27 | 25 | 0 | | | | | | | 23 | 39 | 27 | 34 | 30 | 29 | 44 | 22 | 31 | 26 | 37 | 30 |
| | 2013_fall (oct.) | 13 | 6 | 10 | 26 | 0 | | | | | | 26 | 26 | 7 | 23 | 33 | 18 | 31 | 23 | 20 | 16 | 24 | 21 |
| | 2014_winter (jan.-feb.) | 8 | 15 | 21 | 19 | 16 | 0 | | | | | 27 | 39 | 16 | 27 | 25 | 23 | 37 | 18 | 22 | 19 | 33 | 25 |
| | 2014_spring (may) | 28 | 26 | 20 | 23 | 25 | 27 | 0 | | | | 2 | 29 | 27 | 31 | 41 | 25 | 42 | 30 | 29 | 22 | 25 | 23 |
| SPC | 2011_fall. (nov.-dec.) | 15 | 9 | 10 | 27 | 10 | 19 | 26 | 0 | | | 26 | 23 | 12 | 24 | 35 | 19 | 34 | 24 | 22 | 17 | 23 | 21 |
| | 2013_spring (may) | 14 | 14 | 12 | 22 | 12 | 17 | 25 | 14 | 0 | | 25 | 27 | 13 | 27 | 35 | 23 | 35 | 23 | 24 | 18 | 25 | 25 |
| | 2013_fall (oct.) | 19 | 29 | 36 | 25 | 30 | 17 | 41 | 31 | 29 | 0 | 40 | 52 | 30 | 34 | 19 | 34 | 42 | 18 | 31 | 31 | 44 | 38 |
| | BBOA_median | 6 | 9 | 14 | 20 | 9 | 9 | 25 | 11 | 12 | 22 | 25 | 31 | 11 | 24 | 28 | 20 | 34 | 19 | 21 | 17 | 28 | 23 |

**Table S7.**

| Θ (°) | OOA_TOT | BO | | | | | | | | SPC | | | | Reference spectra | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 2011_fall. (nov.-dic.) | 2012_summer (jun-jul.) | 2012_fall (oct.-nov.) | 2013_winter (jan.-feb.) | 2013_spring (may) | 2013_fall (oct.) | 2014_winter (jan.-feb.) | 2014_spring (may) | 2011_fall. (nov.-dic.) | 2012_summer (jun.-jul.) | 2013_spring (may) | 2013_fall (oct.) | SV_OOA_Crippa2013s | LV_OOA_Crippa2013s | SV_OOA_Mohr2012 | LV_OOA_Mohr2012 | OOA_Elser2016 | LO_OOA_Setyan2012 | MO_OOA_Setyan2012 | OOA1_Aiken2006 | OOA2_Aiken2006 | SV_OOA_EUCAARImean | LV_OOA_EUCAARImean | LV_OOA_Crippa2013w | OOA2_BBCrippa2013w | SV_OOAmean_Ng2011 | LV_OOAmean_Ng2011 | OOAmean_Ng2011 | OOAa_Saarikoski2012 | OOAb_Saarikoski2012 | OOAc_Saarikoski2012 | SV_OOA_Stuckmeier2016 | LV_OOA_Stuckmeier2016 |
| BO | 2011_fall. (nov.-dic.) | 0 | | | | | | | | | | | | 28 | 15 | 24 | 18 | 11 | 18 | 17 | 20 | 8 | 38 | 49 | 19 | 18 | 39 | 45 | 43 | 21 | 17 | 26 | 23 | 27 |
| | 2012_summer (jun-jul.) | 11 | 0 | | | | | | | | | | | 24 | 18 | 30 | 24 | 16 | 20 | 16 | 27 | 8 | 38 | 50 | 24 | 24 | 37 | 45 | 43 | 22 | 20 | 28 | 19 | 28 |
| | 2012_fall (oct.-nov.) | 5 | 12 | 0 | | | | | | | | | | 26 | 15 | 26 | 18 | 7 | 21 | 14 | 19 | 8 | 38 | 49 | 19 | 17 | 39 | 45 | 43 | 22 | 18 | 28 | 23 | 28 |
| | 2013_winter (jan.-feb.) | 5 | 9 | 5 | 0 | | | | | | | | | 27 | 15 | 28 | 19 | 9 | 21 | 14 | 21 | 8 | 39 | 49 | 19 | 19 | 40 | 45 | 43 | 21 | 17 | 27 | 23 | 27 |
| | 2013_spring (may) | 9 | 7 | 12 | 9 | 0 | | | | | | | | 30 | 14 | 28 | 19 | 17 | 16 | 19 | 22 | 11 | 41 | 49 | 19 | 25 | 42 | 45 | 43 | 17 | 16 | 23 | 25 | 22 |
| | 2013_fall (oct.) | 8 | 14 | 7 | 8 | 10 | 0 | | | | | | | 32 | 9 | 27 | 12 | 11 | 17 | 17 | 14 | 12 | 42 | 48 | 13 | 21 | 45 | 45 | 44 | 15 | 13 | 21 | 29 | 21 |
| | 2014_winter (jan.-feb.) | 11 | 18 | 10 | 11 | 14 | 5 | 0 | | | | | | 35 | 10 | 29 | 9 | 12 | 20 | 19 | 10 | 16 | 43 | 48 | 11 | 20 | 47 | 45 | 45 | 15 | 12 | 21 | 32 | 20 |
| | 2014_spring (may) | 9 | 12 | 9 | 8 | 8 | 4 | 7 | 0 | | | | | 32 | 9 | 29 | 13 | 13 | 18 | 17 | 16 | 12 | 49 | 48 | 8 | 29 | 55 | 47 | 47 | 9 | 12 | 16 | 39 | 12 |
| SPC | 2011_fall. (nov.-dic.) | 12 | 19 | 11 | 13 | 15 | 6 | 3 | 8 | 0 | | | | 37 | 9 | 30 | 7 | 13 | 20 | 20 | 9 | 17 | 44 | 48 | 8 | 21 | 49 | 45 | 45 | 15 | 12 | 20 | 34 | 19 |
| | 2012_summer (jun.-jul.) | 21 | 23 | 23 | 22 | 17 | 16 | 17 | 15 | 16 | 0 | | | 46 | 13 | 32 | 14 | 27 | 14 | 31 | 17 | 25 | 51 | 50 | 13 | 34 | 57 | 49 | 48 | 9 | 15 | 13 | 42 | 6 |
| | 2013_spring (may) | 13 | 20 | 12 | 14 | 16 | 7 | 5 | 9 | 4 | 17 | 0 | | 36 | 11 | 29 | 9 | 13 | 20 | 19 | 9 | 17 | 43 | 48 | 9 | 21 | 48 | 45 | 45 | 15 | 12 | 19 | 33 | 19 |
| | 2013_fall (oct.) | 13 | 19 | 13 | 14 | 13 | 6 | 6 | 7 | 5 | 11 | 6 | 0 | 38 | 8 | 29 | 7 | 17 | 17 | 22 | 10 | 18 | 45 | 48 | 7 | 25 | 50 | 46 | 45 | 10 | 11 | 17 | 35 | 14 |
| | OOA_median | 8 | 14 | 9 | 9 | 9 | 3 | 6 | 3 | 6 | 14 | 8 | 6 | 34 | 8 | 28 | 11 | 13 | 17 | 18 | 14 | 13 | 42 | 48 | 12 | 22 | 45 | 45 | 44 | 14 | 12 | 20 | 29 | 20 |

## S2.2 Evaluation of POA and SOA factors apportionment

### *S2.2.1 Correlation with external tracers*

**Table S8: Comparison (Pearson's Coefficient R) between source apportionment factors, independent species and organic m/z tracers time series. BC stands for Black Carbon (from optical measurement, PSAP or MAAP; EC stands for Elemental Carbon (from thermo-optical measurements, Sunset); Org_i means AMS spectral organic signal at m/z i (i=43, 44, 60, 73)**

| | | | HOA | | | BBOA | | | | SOA | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | R | NOx | BC | EC | Levo (NMR) | Levo (GC/MS) | Org_60 | Org_73 | NO3 | SO4 | NH4 | Org_43 | Org_44 |
| BO | SPRING | 2013 | 0.62 | - | 0.48 | - | 0.57 | 0.85 | 0.86 | 0.68 | 0.73 | 0.73 | 0.94 | 0.92 |
| | | 2014 | 0.48 | - | 0.56 | - | 0.77 | 0.87 | 0.87 | 0.21 | 0.87 | 0.66 | 0.99 | 0.99 |
| | SUMMER | 2012 | 0.49 | 0.69 | 0.60 | | | | | 0.49 | 0.39 | 0.55 | 0.82 | 0.74 |
| | FALL | 2011 | 0.58 | - | - | - | 0.67 | 0.71 | 0.70 | 0.92 | 0.77 | 0.92 | 0.93 | 0.92 |
| | | 2012 | 0.58 | 0.78 | 0.80 | - | 0.83 | 0.93 | 0.90 | 0.86 | 0.67 | 0.89 | 0.94 | 0.98 |
| | | 2013 | 0.46 | - | 0.81 | 0.85 | 0.70 | 0.93 | 0.90 | 0.72 | 0.76 | 0.83 | 0.94 | 0.93 |
| | WINTER | 2013 | 0.57 | 0.77 | 0.82 | 0.84 | 0.81 | 0.83 | 0.80 | 0.90 | 0.84 | 0.93 | 0.94 | 0.95 |
| | | 2014 | 0.35 | - | 0.79 | 0.59 | 0.75 | 0.93 | 0.91 | 0.90 | 0.79 | 0.94 | 0.94 | 0.97 |
| SPC | SPRING | 2013 | 0.59 | - | 0.73 | - | 0.51 | 0.84 | 0.82 | 0.82 | 0.81 | 0.88 | 0.96 | 0.97 |
| | SUMMER | 2012 | 0.43 | 0.52 | 0.53 | | | | | 0.56 | 0.70 | 0.73 | - | - |
| | FALL | 2011 | 0.59 | 0.42 | - | 0.69 | 0.81 | 0.94 | 0.95 | 0.90 | 0.75 | 0.90 | 0.81 | 0.91 |
| | | 2013 | 0.55 | - | 0.79 | 0.74 | 0.66 | 0.88 | 0.89 | 0.66 | 0.78 | 0.82 | 0.86 | 0.94 |

### *S2.2.2 Source-specific ratios for POA components*

The concentration ratios between the main POA factors (HOA and BBOA) and tracer compounds are used here as source-specific ratios to confirm our apportionment of the main primary components. Table S9 reports these ratios and a comparison with available literature ranges.

Average concentrations of NOx, BC and EC_ff (=Elemental Carbon from fossil fuel, calculated from thermo-optical measurements, Sunset, following the suggestions of Gilardoni et al., 2011) are used to validate HOA. BBOA is instead compared with concentrations of Levoglucosan and $C_2H_4O_2^+$ AMS mass fragment (Org_60).

The HOA/NOx ratios are pretty variable and often lower than what reported by Allan et al., 2004. This discrepancy may depend on the fact that the NOx data come from the monitoring network of the Regional Environmental Protection Agency of Emilia Romagna (ARPAE), which measurement sites are not exactly co-located with those of the AMS and are more impacted by traffic.

Nevertheless the overall good agreement between the other source-specific ratios (based on co-located measurements) and the literature ranges supports our apportionment of POA components.

**Table S9: Source-specific ratios for the POA factors identified. Literature ranges comes from: (1) Allan et al., 2010; (2) Gilardoni et al., 2011; (3) Cubison et al., 2011.**

| | | | HOA/NOx | HOA/BC | HOA/EC_ff | BBOA/Levo | Org_60/BBOA |
|---|---|---|---|---|---|---|---|
| | | Literature range | (26-31)[1] | (0.3-1.2)[2] | (0.3-1.2)[2] | (4-13)[2] | (0.01-0.04)[3] |
| BO | SPRING | 2013 | 14 | - | 0.3 | 8 | 0.013 |
| | | 2014 | 8 | - | 0.3 | 9 | 0.071 |
| | SUMMER | 2012 | 39 | 0.4 | 0.6 | | |
| | FALL | 2011 | 22 | - | - | 6 | 0.021 |
| | | 2012 | 11 | 0.7 | 0.4 | 5 | 0.020 |
| | | 2013 | 11 | - | 0.3 | 17 | 0.026 |
| | WINTER | 2013 | 13 | 0.7 | 0.8 | 9 | 0.015 |
| | | 2014 | 8 | - | 0.8 | 5 | 0.091 |
| | | | | | | | |
| SPC | SPRING | 2013 | 24 | - | 0.5 | 13 | 0.042 |
| | SUMMER | 2012 | 14 | 0.4 | 0.3 | | |
| | FALL | 2011 | 35 | 1.2 | - | 3 | 0.016 |
| | | 2013 | 35 | - | 0.4 | 24 | 0.011 |

**Table S10: Correlation (Pearson coefficient, R) between the OA components and the main aerosol species as measured by HR-TOF-AMS in each campaign. The shaded cells highlight the highest correlations with a color scale ranging from less to more intense as the R value increases. Each season has a specific color-code: green for spring, yellow for summer, brown for fall and blue for winter.**

| | | | BO | | | | | SPC | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Org | NO3 | SO4 | NH4 | Chl | Org | NO3 | SO4 | NH4 | Chl |
| SPRING | 2013_spring (may) | HOA | 0.64 | 0.08 | 0.06 | 0.08 | 0.07 | 0.72 | 0.58 | 0.37 | 0.58 | 0.57 |
| | | BBOA | 0.81 | 0.15 | 0.20 | 0.17 | 0.09 | 0.80 | 0.67 | 0.46 | 0.68 | 0.55 |
| | | SOA | 0.84 | 0.68 | 0.73 | 0.73 | 0.18 | 0.99 | 0.82 | 0.81 | 0.88 | 0.53 |
| | 2014_spring (may) | HOA | 0.39 | 0.25 | 0.17 | 0.27 | 0.22 | | | | | |
| | | BBOA | 0.89 | 0.21 | 0.68 | 0.55 | 0.12 | | | | | |
| | | COA | 0.32 | 0.12 | 0.09 | 0.13 | 0.09 | | | | | |
| | | SOA | 0.97 | 0.21 | 0.87 | 0.66 | 0.07 | | | | | |
| | | | | | | | | | | | | |
| SUMMER | 2012_summer (jun-jul.) | HOA | 0.51 | 0.26 | 0.10 | 0.22 | 0.24 | 0.58 | 0.40 | 0.27 | 0.44 | 0.50 |
| | | SOA | 0.97 | 0.49 | 0.39 | 0.55 | 0.33 | 0.97 | 0.56 | 0.70 | 0.73 | 0.26 |
| | | | | | | | | | | | | |
| FALL | 2011_fall. (nov.-dic.) | HOA | 0.68 | 0.12 | 0.02 | 0.08 | 0.13 | 0.23 | -0.02 | -0.02 | -0.02 | 0.08 |
| | | BBOA | 0.72 | 0.26 | 0.14 | 0.25 | 0.30 | 0.92 | 0.55 | 0.40 | 0.55 | 0.65 |
| | | SOA | 0.67 | 0.92 | 0.77 | 0.92 | 0.40 | 0.48 | 0.90 | 0.75 | 0.90 | 0.39 |
| | 2012_fall (oct.-nov.) | HOA | 0.39 | 0.08 | 0.12 | 0.10 | 0.18 | | | | | |
| | | BBOA | 0.63 | 0.49 | 0.14 | 0.46 | 0.48 | | | | | |
| | | SOA | 0.71 | 0.86 | 0.67 | 0.89 | 0.45 | | | | | |
| | 2013_fall (oct.) | HOA | 0.70 | 0.15 | -0.02 | 0.20 | 0.57 | 0.72 | 0.35 | 0.01 | 0.30 | 0.36 |
| | | BBOA | 0.85 | 0.36 | 0.14 | 0.40 | 0.51 | 0.88 | 0.52 | 0.19 | 0.51 | 0.52 |
| | | SOA | 0.80 | 0.72 | 0.76 | 0.83 | 0.26 | 0.77 | 0.66 | 0.78 | 0.82 | 0.38 |
| | | | | | | | | | | | | |
| WINTER | 2013_winter (jan.-feb.) | HOA | 0.67 | 0.21 | 0.18 | 0.22 | 0.32 | | | | | |
| | | BBOA | 0.78 | 0.20 | 0.11 | 0.20 | 0.21 | | | | | |
| | | SOA | 0.75 | 0.90 | 0.84 | 0.93 | 0.56 | | | | | |
| | 2014_winter (jan.-feb.) | HOA | 0.58 | 0.13 | 0.02 | 0.13 | 0.27 | | | | | |
| | | BBOA | 0.88 | 0.47 | 0.36 | 0.49 | 0.53 | | | | | |
| | | SOA | 0.80 | 0.90 | 0.79 | 0.94 | 0.60 | | | | | |

### *S2.2.3 Validation of by Biomass Burning influenced OOAs*

In the main text *f*60 is used as synthetic parameter for the determination of the influence of biomass burning on OOAx_BB components. However, in order to validate the attribution of the $C_2H_4O_2^+$ fragment (corresponding to the *f*60) to the OOA factors, we report here additional tests on the rotational ambiguity and the allocation of the model residuals in different solutions.

Results from different PMF solutions with different seeds, FPEAKs and a-values are compared for each campaign and OA factor. Chosen the best number of factors, the results from three random seeds are tested. Subsequently different FPEAKs (variable from -0.6 to +0.6, with 0.2 steps), for the unconstrained solutions, and different a-values (ranging from 0 to 0.5), for the constrained ones, are compared. The comparison shows substantial similarities in term of the attribution of m/z 60 to the BBOA and OOAx_BB factors. The variable contribution of *f*60 on each factor for each campaign is showed in Figure S3 by the points and the error bars, representing, in the *f*44 vs *f*60 space (Cubison et al., 2011), the average values and the standard deviation of the tested solutions, respectively. Factors considered as OOAx_BB are only those for which both average values and error bars are located out of the gray shaded area indicating no influence of biomass burning.

To further evaluate the validity of the OOAx_BB factors identification, the mass concentration time series of the single BBOA and of the sum of BBOA and OOAx_BB factors were compared with specific measurements: Org_60 and Org_73 (the concentrations in time of the AMS fragments $C_2H_4O_2^+$ and $C_3H_5O_2^+$, respectively at m/z 60 and 73), representing the total anhydrosugars, and Levoglucosan (as independently measured by GC/MS). Table S11 reports the correlation coefficients of this comparison. Correlation with levoglucosan is always better when we compare it with the BBOA factor alone. This is expected considering levoglucosan as a better tracer of fresh emissions (due to its atmospheric degradation over time) and confirms the robustness of the distinction between OOA factors and primary BBOA. Correlation with the $C_2H_4O_2^+$ and $C_3H_5O_2^+$ fragments (Org_60 and Org_73) instead is always better adding the OOAx_BB fractions, indicating the importance of these secondary components in explaining the measurements.

This is further highlighted in Figure S4 where the diurnal pattern of the measured Org_60 are compared with those of the Org_60 reconstructed starting by the results of different PMF solutions: one considering only the BBOA factor and the other including also the OOAx_BBs. The addition of OOAx_BB factors always improves the fitting with the measured Org_60. This is especially true during day-time (10-18) when the primary BBOA factor tends to its minimum, while Org_60 is often higher and better reconstructed adding secondary factors (OOAx_BB).

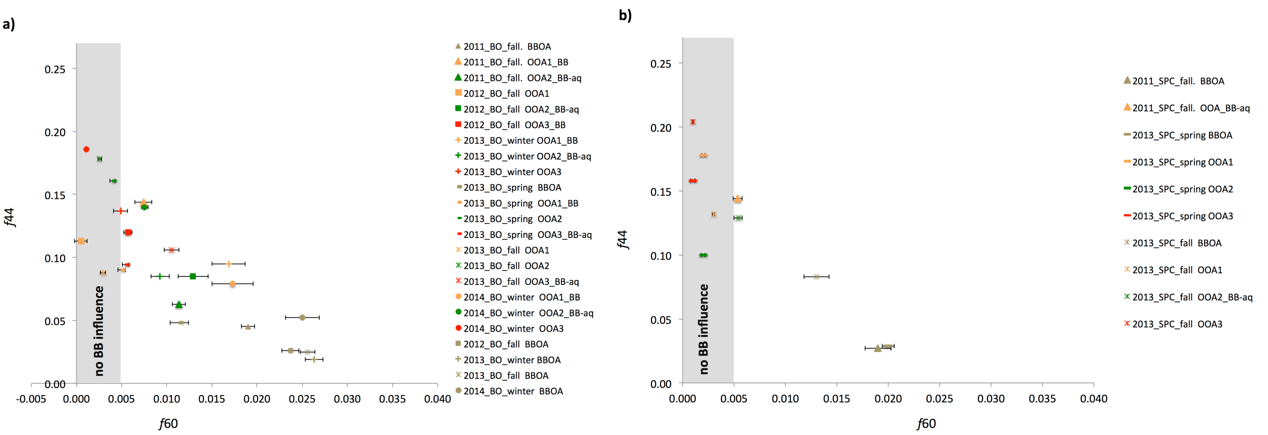



**Figure S3: Variability of *f*60 contribution on BBOA and OOAx_BB in different PMF solutions tested to evaluate the rotational ambiguity of the model. The markers in the plots show *f*44 versus *f*60 average values. The error bars represent the *f*60 standard deviation of the different solutions tested. Different shapes of the markers identify different SUPERSITO campaigns. Different colors represents the different kind of PMF-factors: gold-green identifies BBOA primary factors, yellow, green and red the OOAs numerically ordered based on their O:C ratios. Gray areas correspond to *f*60 0.003 ± 0.002 representing the Cubison et al. 2010 threshold of BB influence.**

**Table S11: Effect of the addition of the BB-influenced OOA factors on the agreement (expressed as Pearson correlation coefficient, R) of PMF solutions with specific measurements: Org_60 and Org_73 (the concentrations in time of the AMS fragments $C_2H_4O_2^+$ and $C_3H_5O_2^+$, respectively at m/z 60 and 73) and Levoglucosan (as measured by GC/MS).**

| | | | R (pearson) | Org_60 | Org_73 | levoglucosan |
|---|---|---|---|---|---|---|
| BO | SPRING | 2013 | only BBOA | 0.85 | 0.86 | 0.57 |
| | | | **BBOA+OOAx_BB** | **0.89** | **0.87** | **0.46** |
| | FALL | 2011 | only BBOA | 0.71 | 0.70 | 0.67 |
| | | | **BBOA+OOAx_BB** | **0.91** | **0.93** | **0.69** |
| | | 2012 | only BBOA | 0.93 | 0.90 | 0.83 |
| | | | **BBOA+OOAx_BB** | **0.98** | **0.99** | **0.65** |
| | | 2013 | only BBOA | 0.93 | 0.90 | 0.70 |
| | | | **BBOA+OOAx_BB** | **0.96** | **0.90** | **0.70** |
| | WINTER | 2013 | only BBOA | 0.83 | 0.80 | 0.81 |
| | | | **BBOA+OOAx_BB** | **0.92** | **0.94** | **0.73** |
| | | 2014 | only BBOA | 0.93 | 0.91 | 0.75 |
| | | | **BBOA+OOAx_BB** | **0.95** | **0.96** | **0.69** |
| | | | | | | |
| SPC | FALL | 2011 | only BBOA | 0.94 | 0.95 | 0.81 |
| | | | **BBOA+OOAx_BB** | **0.91** | **0.93** | **0.74** |
| | | 2013 | only BBOA | 0.88 | 0.89 | 0.54 |
| | | | **BBOA+OOAx_BB** | **0.94** | **0.95** | **0.54** |

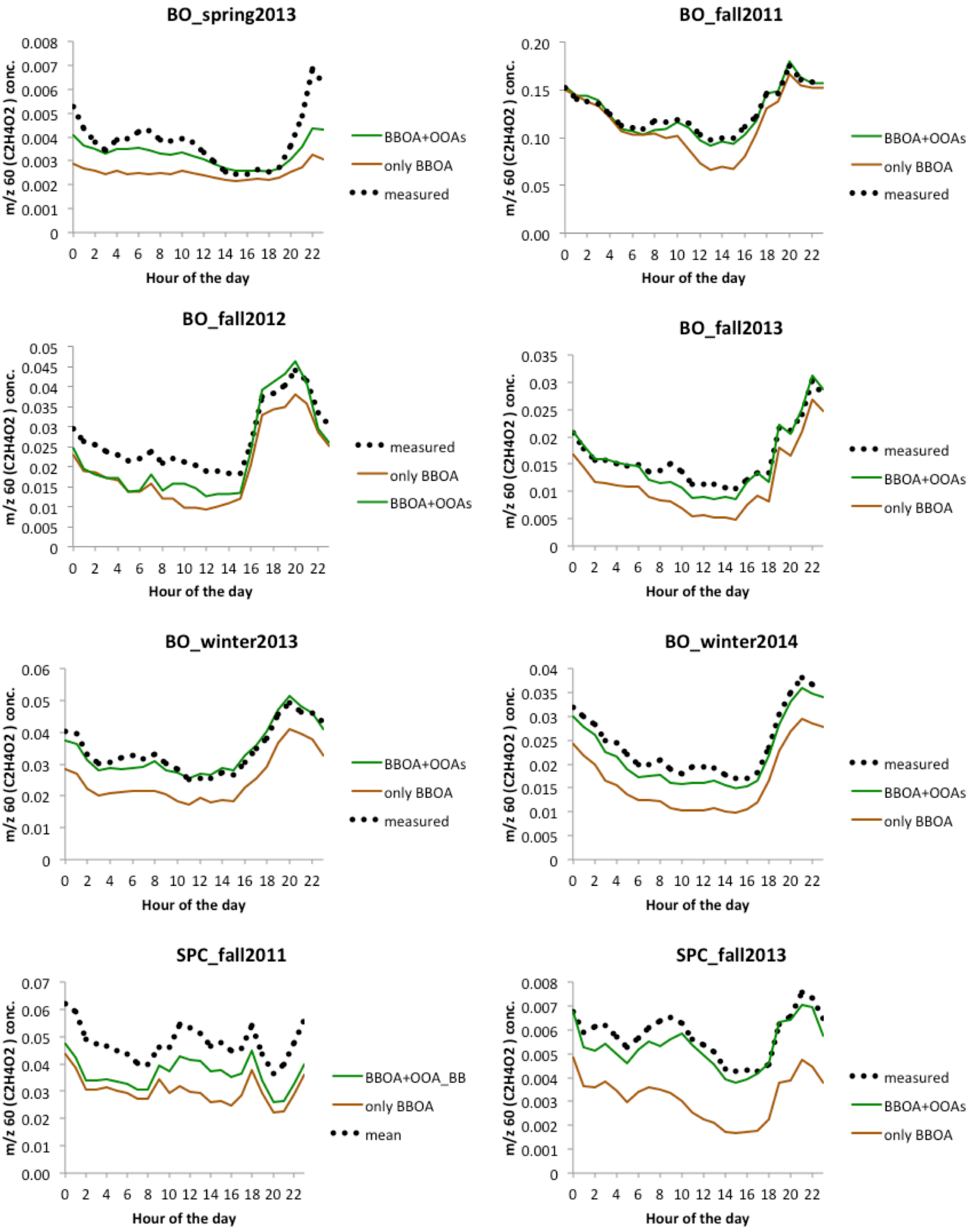



**Figure S4: comparison of measured and reconstructed diurnal pattern of concentrations of the AMS mass fragment $C_2H_4O_2^+$ (m/z 60.021) for different PMF solutions considering only the BBOA primary factor or both BBOA and OOAx_BB.**

**Table S12: Elemental ratios and fractional abundances of characteristic ions for all the components of organic aerosols identified by the PMF of the AMS data for the Bologna site. The fractions (f) of the ions 43, 44 and 60 of the mass spectra are calculated as the ratio between the intensity of those ions and the sum of the intensity of the whole spectrum. The oxidation state (OSc) is instead calculated following Kroll et al. (2006) as OSc=2*O:C-H:C. Shaded cells highlight influence of anhydrosugars (shaded orange) and of aqueous-phase processing (shaded blue).**

| | | Ambient Improved (Canagaratna et al., 2014) | | | | $CHO^+$ | $C_2H_3O^+$ | $CO_2^+$ | $C_2H_4O_2^+$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | OM/OC | O/C | H/C | OSc | f29 | f43 | f44 | f60 | conc. mean (ug/m3) | % of OA |
| 2011_BO_fall. (nov.-dec.) | HOA | 1.27 | 0.07 | 2.02 | -1.88 | 0.000 | 0.010 | 0.015 | 0.005 | 2.80 | 18% |
| | BBOA | 1.66 | 0.38 | 1.69 | -0.93 | 0.047 | 0.049 | 0.045 | 0.019 | 6.05 | 38% |
| | OOA1_BB | 2.02 | 0.65 | 1.52 | -0.22 | 0.003 | 0.067 | 0.144 | 0.007 | 3.91 | 25% |
| | OOA2_BB-aq | 2.08 | 0.69 | 1.74 | -0.46 | 0.100 | 0.088 | 0.063 | 0.011 | 3.08 | 19% |
| 2012_BO_summer (jun.-jul.) | HOA | 1.38 | 0.16 | 1.91 | -1.58 | 0.000 | 0.044 | 0.034 | 0.003 | 0.58 | 8% |
| | OOA1 | 1.96 | 0.61 | 1.62 | -0.39 | 0.036 | 0.102 | 0.091 | 0.004 | 3.05 | 43% |
| | OOA2 | 2.02 | 0.65 | 1.56 | -0.26 | 0.014 | 0.091 | 0.110 | 0.004 | 3.52 | 49% |
| 2012_BO_fall (oct.-nov.) | HOA | 1.36 | 0.15 | 2.00 | -1.70 | 0.023 | 0.021 | 0.021 | 0.006 | 0.74 | 16% |
| | BBOA | 1.62 | 0.35 | 1.76 | -1.05 | 0.052 | 0.044 | 0.026 | 0.023 | 1.37 | 30% |
| | OOA1 | 1.90 | 0.57 | 1.50 | -0.35 | 0.016 | 0.061 | 0.113 | 0.000 | 0.48 | 10% |
| | OOA2_BB-aq | 2.12 | 0.72 | 1.80 | -0.36 | 0.065 | 0.093 | 0.085 | 0.012 | 1.04 | 23% |
| | OOA3_BB | 2.11 | 0.73 | 1.55 | -0.09 | 0.069 | 0.070 | 0.120 | 0.005 | 0.98 | 21% |
| 2013_BO_winter (jan.-feb.) | HOA | 1.31 | 0.10 | 2.01 | -1.80 | 0.013 | 0.007 | 0.014 | 0.009 | 0.88 | 11% |
| | BBOA | 1.55 | 0.30 | 1.76 | -1.16 | 0.030 | 0.049 | 0.019 | 0.023 | 2.35 | 28% |
| | OOA1_BB | 1.84 | 0.54 | 1.53 | -0.46 | 0.001 | 0.078 | 0.095 | 0.016 | 1.66 | 20% |
| | OOA2_BB-aq | 2.19 | 0.77 | 1.79 | -0.25 | 0.078 | 0.094 | 0.085 | 0.009 | 1.95 | 23% |
| | OOA3 | 2.27 | 0.84 | 1.53 | 0.16 | 0.048 | 0.075 | 0.137 | 0.005 | 1.53 | 18% |
| 2013_BO_spring (may) | HOA | 1.23 | 0.05 | 1.94 | -1.84 | 0.002 | 0.005 | 0.014 | 0.001 | 0.25 | 12% |
| | BBOA | 1.61 | 0.35 | 1.63 | -0.93 | 0.008 | 0.066 | 0.048 | 0.011 | 0.29 | 14% |
| | OOA1_BB | 1.73 | 0.44 | 1.65 | -0.77 | 0.000 | 0.093 | 0.090 | 0.005 | 0.47 | 23% |
| | OOA2 | 2.12 | 0.75 | 1.41 | 0.08 | 0.000 | 0.083 | 0.161 | 0.004 | 0.74 | 36% |
| | OOA3_BB-aq | 2.32 | 0.88 | 1.77 | -0.02 | 0.118 | 0.127 | 0.094 | 0.005 | 0.29 | 14% |
| 2013_BO_fall (oct.) | HOA | 1.21 | 0.03 | 1.97 | -1.91 | 0.002 | 0.011 | 0.004 | 0.001 | 0.43 | 11% |
| | BBOA | 1.61 | 0.34 | 1.72 | -1.04 | 0.041 | 0.039 | 0.025 | 0.025 | 0.64 | 17% |
| | OOA1 | 1.84 | 0.52 | 1.67 | -0.63 | 0.045 | 0.090 | 0.088 | 0.003 | 1.25 | 33% |
| | OOA2 | 2.16 | 0.78 | 1.35 | 0.22 | 0.001 | 0.077 | 0.178 | 0.002 | 0.86 | 23% |
| | OOA3_BB-aq | 2.46 | 0.96 | 1.83 | 0.08 | 0.143 | 0.071 | 0.106 | 0.010 | 0.63 | 17% |
| 2014_BO_winter (jan.-feb.) | HOA | 1.23 | 0.04 | 2.01 | -1.93 | 0.003 | 0.008 | 0.012 | 0.001 | 0.43 | 12% |
| | BBOA | 1.78 | 0.47 | 1.76 | -0.81 | 0.050 | 0.064 | 0.052 | 0.024 | 1.37 | 38% |
| | OOA1_BB | 1.93 | 0.55 | 1.93 | -0.82 | 0.079 | 0.051 | 0.079 | 0.016 | 0.24 | 7% |
| | OOA2_BB-aq | 2.34 | 0.90 | 1.57 | 0.23 | 0.078 | 0.078 | 0.140 | 0.007 | 1.00 | 28% |
| | OOA3 | 2.43 | 0.97 | 1.43 | 0.51 | 0.047 | 0.072 | 0.186 | 0.001 | 0.55 | 15% |
| 2014_BO_spring (may) | HOA | 1.21 | 0.03 | 1.97 | -1.90 | 0.002 | 0.015 | 0.005 | 0.001 | 0.18 | 6% |
| | BBOA | 1.56 | 0.31 | 1.63 | -1.01 | 0.017 | 0.062 | 0.013 | 0.009 | 0.06 | 2% |
| | COA | 1.49 | 0.26 | 1.75 | -1.24 | 0.011 | 0.018 | 0.059 | 0.006 | 0.28 | 9% |
| | OOA1 | 1.95 | 0.61 | 1.68 | -0.46 | 0.059 | 0.120 | 0.091 | 0.004 | 0.84 | 26% |
| | OOA2 | 2.19 | 0.80 | 1.47 | 0.13 | 0.033 | 0.084 | 0.149 | 0.003 | 1.08 | 33% |
| | OOA3 | 2.44 | 0.98 | 1.43 | 0.54 | 0.058 | 0.067 | 0.184 | 0.004 | 0.80 | 25% |

**Table S13: Elemental ratios and fractional abundances of characteristic ions for all the components of organic aerosols identified by the PMF of the AMS data for the San Pietro Capofiume site. The fractions (f) of the ions 43, 44 and 60 of the mass spectra are calculated as the ratio between the intensity of those ions and the sum of the intensity of the whole spectrum. The oxidation state (OSc) is instead calculated following Kroll et al. (2006) as OSc=2*O:C-H:C. Shaded cells highlight influence of anhydrosugars (shaded orange) and of aqueous-phase processing (shaded blue).**

| | | Ambient Improved (Canagaratna et al., 2014) | | | | $CHO^+$ | $C_2H_3O^+$ | $CO_2^+$ | $C_2H_4O_2^+$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | OM/OC | O/C | H/C | OSc | f29 | f43 | f44 | f60 | conc. mean (ug/m3) | % of OA |
| **2011_SPC_fall. (nov.-dec.)** | HOA | 1.54 | 0.29 | 1.80 | -1.22 | 0.041 | 0.020 | 0.062 | 0.007 | 2.93 | 32% |
| | BBOA | 1.59 | 0.33 | 1.79 | -1.13 | 0.048 | 0.046 | 0.027 | 0.019 | 3.07 | 33% |
| | OOA_BB-aq | 2.26 | 0.85 | 1.48 | 0.22 | 0.068 | 0.066 | 0.144 | 0.005 | 3.29 | 35% |
| **2012_SPC_summer (jun.-jul.)** | HOA | 1.33 | 0.12 | 1.90 | -1.65 | 0.000 | 0.04 | 0.05 | 0.004 | 0.20 | 4% |
| | OOA1 | 1.68 | 0.34 | 1.66 | -0.97 | 0.000 | 0.07 | 0.19 | 0.002 | 1.49 | 28% |
| | OOA2 | 1.90 | 0.43 | 1.88 | -1.02 | 0.013 | 0.05 | 0.22 | 0.002 | 0.55 | 10% |
| | OOA3 | 1.90 | 0.50 | 1.48 | -0.48 | 0.000 | 0.09 | 0.12 | 0.002 | 1.21 | 23% |
| | OOA4 | 2.00 | 0.55 | 1.48 | -0.38 | 0.000 | 0.04 | 0.26 | 0.002 | 1.82 | 35% |
| **2013_SPC_spring (may)** | HOA | 1.35 | 0.14 | 1.90 | -1.62 | 0.009 | 0.012 | 0.039 | 0.003 | 0.15 | 9% |
| | BBOA | 1.58 | 0.33 | 1.63 | -0.98 | 0.030 | 0.044 | 0.029 | 0.020 | 0.05 | 3% |
| | OOA1 | 1.99 | 0.64 | 1.61 | -0.34 | 0.072 | 0.055 | 0.178 | 0.002 | 0.53 | 31% |
| | OOA2 | 2.38 | 0.91 | 1.46 | 0.36 | 0.088 | 0.082 | 0.100 | 0.002 | 0.24 | 14% |
| | OOA3 | 2.41 | 0.96 | 1.37 | 0.55 | 0.053 | 0.081 | 0.158 | 0.001 | 0.76 | 44% |
| **2013_SPC_fall (oct.)** | HOA | 1.25 | 0.05 | 2.05 | -1.95 | 0.002 | 0.005 | 0.014 | 0.001 | 0.23 | 7% |
| | BBOA | 1.87 | 0.54 | 1.64 | -0.57 | 0.058 | 0.052 | 0.083 | 0.013 | 0.95 | 28% |
| | OOA1 | 2.07 | 0.70 | 1.54 | -0.14 | 0.062 | 0.079 | 0.132 | 0.003 | 0.79 | 23% |
| | OOA2_BB-aq | 2.25 | 0.82 | 1.74 | -0.10 | 0.069 | 0.084 | 0.129 | 0.005 | 0.47 | 14% |
| | OOA3 | 2.46 | 1.00 | 1.30 | 0.71 | 0.045 | 0.056 | 0.204 | 0.001 | 0.94 | 28% |

**Table S14: Comparison between OOAs factor spectral profiles from SUPERSITO campaigns and other correspondent reference profiles from literature: the comparison is expressed in term of theta-angle (θ) between the spectra (Kostenidou et al., 2009). In shaded red spectra that exhibit angles less than 15° (very similar to each other), in orange spectra with angles between 15° and 30° (some similarity but also some differences), in green spectra with θ larger than 30° (do not compare well).**

| Θ (°) | OOAs | | Reference spectra | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | SV_OOA_Crippa2013s | SV_OOA_Mohr2012 | OOA1_Aiken2006 | SV_OOA_EUCAARImean | SV_OOAmean_Ng2011 | SV_OOA_Stuckmeier2016 | LV_OOA_Crippa2013s | LV_OOA_Mohr2012 | OOA2_Aiken2006 | LV_OOA_EUCAARImean | LV_OOA_Crippa2013w | LV_OOAmean_Ng2011 | LV_OOA_Stuckmeier2016 | OOAa_Saarikoski2012 | OOAb_Saarikoski2012 | OOAc_Saarikoski2012 | OOA_Elser2016 | OOA2_BBCrippa2013w | LO_OOA_Setyan2012 | MO_OOA_Setyan2012 | OOA_Athens_Florou2017 | aBBOA_Patras_Florou2017 | OOA_Patras_Florou2017 | OOA-BB_Bougiatioti_2014 | OOA_Bougiatioti_2014 | SV-OOA(BB)_Stavroulas_2018 | LV-OOA_Stavroulas_2018 |
| BO | 2011_fall. (nov.-dec.) | OOA1_BB | 40 | 28 | 21 | 46 | 49 | 34 | 13 | 17 | 20 | 49 | 16 | 47 | 14 | 11 | 15 | 17 | 24 | 31 | 12 | 28 | 16 | 42 | 12 | 51 | 56 | 52 | 50 |
| | | OOA2_BB-aq | 22 | 35 | 38 | 37 | 32 | 23 | 37 | 38 | 25 | 55 | 39 | 49 | 50 | 44 | 37 | 47 | 21 | 19 | 41 | 23 | 38 | 37 | 39 | 60 | 68 | 27 | 52 |
| | 2012_summer (jun-jul.) | OOA1 | 19 | 30 | 30 | 36 | 33 | 15 | 23 | 28 | 7 | 51 | 27 | 46 | 34 | 28 | 24 | 33 | 16 | 22 | 24 | 14 | 22 | 37 | 24 | 54 | 62 | 37 | 50 |
| | | OOA2 | 29 | 30 | 25 | 40 | 40 | 24 | 16 | 22 | 12 | 50 | 22 | 46 | 24 | 19 | 18 | 24 | 18 | 27 | 18 | 19 | 16 | 38 | 17 | 52 | 59 | 45 | 50 |
| | 2012_fall (oct.-nov.) | OOA1 | 35 | 24 | 20 | 42 | 45 | 30 | 13 | 18 | 16 | 49 | 17 | 46 | 19 | 15 | 16 | 20 | 21 | 27 | 11 | 24 | 16 | 40 | 14 | 51 | 57 | 48 | 50 |
| | | OOA2_BB-aq | 21 | 31 | 28 | 38 | 35 | 20 | 24 | 27 | 12 | 52 | 29 | 47 | 38 | 32 | 27 | 37 | 11 | 19 | 30 | 14 | 27 | 38 | 28 | 55 | 63 | 33 | 50 |
| | | OOA3_BB | 31 | 27 | 14 | 40 | 43 | 29 | 13 | 14 | 12 | 48 | 14 | 44 | 25 | 20 | 15 | 24 | 8 | 16 | 20 | 16 | 20 | 36 | 16 | 51 | 57 | 43 | 46 |
| | 2013_winter (jan.-feb.) | OOA1_BB | 31 | 30 | 30 | 40 | 38 | 24 | 22 | 27 | 17 | 51 | 26 | 46 | 27 | 23 | 20 | 27 | 23 | 27 | 19 | 24 | 17 | 35 | 20 | 53 | 61 | 44 | 51 |
| | | OOA2_BB-aq | 22 | 33 | 29 | 37 | 35 | 21 | 26 | 28 | 15 | 51 | 29 | 46 | 39 | 33 | 27 | 38 | 10 | 15 | 33 | 14 | 28 | 36 | 29 | 56 | 63 | 33 | 49 |
| | | OOA3 | 36 | 31 | 14 | 45 | 49 | 33 | 8 | 12 | 16 | 49 | 13 | 46 | 19 | 13 | 15 | 21 | 16 | 26 | 20 | 21 | 20 | 43 | 13 | 51 | 56 | 49 | 48 |
| | 2013_spring (may) | OOA1_BB | 26 | 26 | 35 | 38 | 33 | 18 | 27 | 33 | 17 | 53 | 31 | 48 | 34 | 29 | 27 | 32 | 26 | 29 | 21 | 26 | 21 | 37 | 26 | 55 | 64 | 41 | 53 |
| | | OOA2 | 41 | 33 | 21 | 48 | 52 | 36 | 13 | 17 | 21 | 50 | 16 | 48 | 11 | 10 | 15 | 17 | 25 | 33 | 15 | 27 | 17 | 44 | 12 | 51 | 55 | 55 | 51 |
| | | OOA3_BB | 22 | 39 | 32 | 38 | 36 | 21 | 31 | 32 | 20 | 52 | 33 | 47 | 44 | 37 | 32 | 42 | 16 | 19 | 39 | 14 | 34 | 40 | 34 | 57 | 65 | 34 | 50 |
| | 2013_fall (oct.) | OOA1 | 19 | 25 | 29 | 34 | 32 | 15 | 23 | 27 | 8 | 50 | 27 | 45 | 35 | 29 | 24 | 32 | 15 | 19 | 23 | 14 | 22 | 34 | 25 | 54 | 63 | 36 | 50 |
| | | OOA2 | 44 | 34 | 20 | 51 | 56 | 40 | 12 | 16 | 24 | 50 | 16 | 49 | 9 | 9 | 17 | 16 | 27 | 36 | 16 | 30 | 20 | 47 | 13 | 51 | 55 | 59 | 51 |
| | | OOA3_BB-aq | 34 | 35 | 26 | 41 | 44 | 33 | 30 | 28 | 26 | 52 | 29 | 48 | 42 | 36 | 30 | 40 | 17 | 15 | 38 | 24 | 35 | 40 | 33 | 57 | 62 | 37 | 48 |
| | 2014_winter (jan.-feb.) | OOA1_BB | 30 | 25 | 28 | 37 | 37 | 27 | 30 | 29 | 22 | 52 | 30 | 46 | 41 | 36 | 28 | 38 | 16 | 11 | 31 | 24 | 31 | 32 | 31 | 57 | 63 | 34 | 49 |
| | | OOA2_BB-aq | 34 | 29 | 12 | 42 | 46 | 31 | 12 | 11 | 15 | 48 | 13 | 45 | 23 | 18 | 14 | 23 | 9 | 18 | 22 | 17 | 20 | 38 | 15 | 51 | 56 | 45 | 47 |
| | | OOA3 | 42 | 33 | 11 | 49 | 55 | 39 | 8 | 8 | 21 | 49 | 9 | 47 | 11 | 8 | 13 | 16 | 21 | 30 | 18 | 26 | 20 | 45 | 11 | 50 | 54 | 56 | 49 |
| | 2014_spring (may) | OOA1 | 15 | 32 | 32 | 35 | 31 | 11 | 27 | 30 | 11 | 52 | 31 | 46 | 38 | 32 | 27 | 36 | 15 | 20 | 30 | 10 | 25 | 35 | 28 | 55 | 64 | 36 | 50 |
| | | OOA2 | 36 | 30 | 16 | 44 | 48 | 32 | 8 | 13 | 15 | 48 | 12 | 46 | 16 | 11 | 13 | 18 | 18 | 27 | 15 | 21 | 17 | 42 | 10 | 50 | 55 | 50 | 49 |
| | | OOA3 | 42 | 33 | 9 | 49 | 55 | 39 | 9 | 6 | 22 | 48 | 8 | 47 | 12 | 9 | 12 | 16 | 20 | 29 | 20 | 25 | 20 | 44 | 11 | 50 | 54 | 55 | 48 |
| SPC | 2011_fall. (nov.-dec.) | OOA_BB-aq | 37 | 30 | 9 | 44 | 49 | 34 | 9 | 7 | 17 | 48 | 8 | 45 | 19 | 15 | 12 | 20 | 13 | 21 | 20 | 20 | 20 | 39 | 13 | 50 | 55 | 49 | 47 |
| | 2012_summer (jun.-jul.) | OOA1 | 32 | 27 | 29 | 40 | 41 | 26 | 22 | 26 | 18 | 50 | 24 | 46 | 25 | 22 | 21 | 23 | 25 | 29 | 13 | 26 | 17 | 35 | 20 | 52 | 60 | 48 | 51 |
| | | OOA2 | 44 | 31 | 20 | 49 | 54 | 39 | 15 | 17 | 24 | 50 | 16 | 48 | 10 | 10 | 15 | 15 | 27 | 34 | 15 | 31 | 18 | 44 | 13 | 51 | 55 | 58 | 51 |
| | | OOA3 | 47 | 34 | 10 | 52 | 59 | 45 | 12 | 9 | 27 | 49 | 9 | 49 | 10 | 12 | 16 | 16 | 25 | 33 | 19 | 30 | 24 | 46 | 15 | 50 | 53 | 59 | 49 |
| | | OOA4 | 53 | 38 | 20 | 57 | 65 | 51 | 18 | 17 | 33 | 52 | 18 | 53 | 7 | 14 | 22 | 17 | 33 | 42 | 21 | 38 | 27 | 52 | 19 | 52 | 53 | 67 | 53 |
| | 2013_spring (may) | OOA1 | 24 | 28 | 24 | 35 | 36 | 21 | 23 | 24 | 15 | 49 | 24 | 44 | 34 | 28 | 22 | 31 | 10 | 13 | 28 | 13 | 24 | 33 | 24 | 53 | 61 | 38 | 47 |
| | | OOA2 | 38 | 33 | 13 | 46 | 51 | 35 | 9 | 10 | 18 | 48 | 10 | 46 | 19 | 14 | 13 | 20 | 17 | 24 | 20 | 22 | 21 | 43 | 14 | 50 | 55 | 51 | 47 |
| | | OOA3 | 43 | 32 | 6 | 48 | 55 | 40 | 11 | 5 | 23 | 48 | 6 | 47 | 12 | 11 | 12 | 16 | 20 | 27 | 21 | 25 | 21 | 43 | 12 | 50 | 54 | 55 | 48 |
| | 2013_fall (oct.) | OOA1_BB | 30 | 25 | 16 | 40 | 42 | 27 | 13 | 15 | 12 | 48 | 15 | 44 | 22 | 17 | 14 | 21 | 12 | 20 | 18 | 16 | 16 | 36 | 14 | 51 | 57 | 45 | 48 |
| | | OOA2_BB-aq | 30 | 29 | 15 | 40 | 43 | 27 | 12 | 14 | 11 | 48 | 15 | 45 | 25 | 19 | 15 | 24 | 8 | 18 | 21 | 15 | 20 | 38 | 16 | 51 | 57 | 43 | 47 |
| | | OOA3 | 46 | 34 | 11 | 52 | 58 | 44 | 11 | 8 | 26 | 49 | 9 | 49 | 8 | 10 | 15 | 15 | 25 | 33 | 19 | 30 | 23 | 47 | 13 | 50 | 53 | 59 | 50 |
| | OOA_median | | 34 | 28 | 14 | 42 | 45 | 29 | 8 | 11 | 13 | 48 | 12 | 45 | 20 | 14 | 12 | 20 | 13 | 22 | 17 | 18 | 17 | 39 | 12 | 50 | 56 | 47 | 47 |

**Table S15: Comparison, expressed in term of theta-angle (θ), between each aqSOA spectral profile identified during the SUPERSITO campaigns and the other and between them and the aqSOA after Fog spectra reported by Gilardoni et al. (2016).**

| Θ (°) | OOAs | | BO | | | | | | SPC | | Reference spectra | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 2011_BO_fall. (nov.-dic.) | 2012_BO_fall (oct.-nov.) | 2013_BO_winter (jan.-feb.) | 2013_BO_spring (may) | 2013_BO_fall (oct.) | 2014_BO_winter (jan.-feb.) | 2011_SPC_fall. (nov.-dic.) | 2013_SPC_fall (oct.) | aqSOA_AfterFog1 (Gilardoni et al., 2016) | aqSOA_AfterFog2 (Gilardoni et al., 2016) | aqSOA_AfterFog3 (Gilardoni et al., 2016) | aqSOA_AfterFog9 (Gilardoni et al., 2016) | aqSOA_AfterFog_mean (Gilardoni et al., 2016) |
| | | | OOA2_BB-aq | OOA2_BB-aq | OOA2_BB-aq | OOA3_BB-aq | OOA3_BB-aq | OOA2_BB-aq | OOA_BB-aq | OOA2_BB-aq | | | | | |
| BO | 2011_BO_fall. (nov.-dic.) | OOA2_BB-aq | 0 | | | | | | | | 30 | 27 | 30 | 32 | 30 |
| | 2012_BO_fall (oct.-nov.) | OOA2_BB-aq | 16 | 0 | | | | | | | 7 | 8 | 7 | 7 | 7 |
| | 2013_BO_winter (jan.-feb.) | OOA2_BB-aq | 14 | 8 | 0 | | | | | | 20 | 19 | 20 | 21 | 20 |
| | 2013_BO_spring (may) | OOA3_BB-aq | 14 | 14 | 11 | 0 | | | | | 25 | 22 | 24 | 26 | 24 |
| | 2013_BO_fall (oct.) | OOA3_BB-aq | 18 | 20 | 18 | 17 | 0 | | | | 21 | 17 | 20 | 23 | 20 |
| | 2014_BO_winter (jan.-feb.) | OOA2_BB-aq | 28 | 17 | 18 | 23 | 20 | 0 | | | 5 | 6 | 4 | 5 | 4 |
| SPC | 2011_SPC_fall. (nov.-dic.) | OOA_BB-aq | 32 | 21 | 22 | 27 | 23 | 5 | 0 | | 5 | 8 | 5 | 2 | 4 |
| | 2013_SPC_fall (oct.) | OOA2_BB-aq | 27 | 15 | 16 | 21 | 21 | 4 | 7 | 0 | 8 | 9 | 7 | 7 | 7 |

**Table S16: Correlation (Pearson coefficient, R) between the OOA components and specific fragment ions of aqueous-phase products of phenol and guaiacol emitted during the biomass burning (namely PhOH-OH, $C_6H_6O_2^+$, m/z 110.037; PhOH-2OH, $C_6H_6O_3^+$ at m/z 126.032; GUA-OH, $C_7H_8O_3^+$ at m/z 140.047; GUA-2OH, $C_7H_8O_4^+$ at m/z 156.042), as already identified in previous studies from laboratory experiments (Yu et al., 2014). The shaded cells highlight the highest correlations with a color scale ranging from less to more intense as the R value increases. Gray cells correspond to missing values.**

| | | BO | | | | | | | | | SPC | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Gly+MethylGly | | | Phenols | | Guaiacols | | | | Gly+MethylGly | | | Phenols | | | |
| | | | | | | | PhOH-OH | PhOH-2OH | GUA-OH | GUA-2OH | | | | | | PhOH-OH | PhOH-2OH | GUA-OH | GUA-2OH |
| | | | 29.0027 | 46.0055 | 55.9898 | 58.0055 | 110.037 | 126.032 | 140.047 | 156.042 | | 29.0027 | 46.0055 | 55.9898 | 58.0055 | 110.037 | 126.032 | 140.047 | 156.042 |
| | | | $CHO^+$ | $CH_2O_2^+$ | $C_2O_2^+$ | $C_2H_2O_2^+$ | $C_6H_6O_2^+$ | $C_6H_6O_3^+$ | $C_7H_8O_3^+$ | $C_7H_8O_4^+$ | | $CHO^+$ | $CH_2O_2^+$ | $C_2O_2^+$ | $C_2H_2O_2^+$ | $C_6H_6O_2^+$ | $C_6H_6O_3^+$ | $C_7H_8O_3^+$ | $C_7H_8O_4^+$ |
| SPRING | 2013_spring (may) | OOA1_BB | 0.62 | 0.39 | 0.51 | 0.55 | 0.60 | - | 0.51 | 0.41 | OOA1 | 0.76 | - | 0.64 | 0.65 | 0.74 | - | - | 0.58 |
| | | OOA2 | 0.41 | 0.32 | 0.63 | 0.65 | 0.44 | - | 0.36 | 0.19 | OOA2 | 0.90 | - | 0.90 | 0.90 | 0.90 | - | - | 0.73 |
| | | OOA3_BB-aq | 0.97 | 0.66 | 0.88 | 0.90 | 0.83 | - | 0.70 | 0.48 | OOA3 | 0.59 | - | 0.65 | 0.72 | 0.63 | - | - | 0.46 |
| | 2014_spring (may) | OOA1 | 0.84 | - | 0.69 | 0.76 | 0.81 | - | 0.73 | 0.59 | | | | | | | | | |
| | | OOA2 | 0.88 | - | 0.82 | 0.94 | 0.95 | - | 0.88 | 0.66 | | | | | | | | | |
| | | OOA3 | 0.11 | - | 0.26 | 0.15 | 0.01 | - | -0.02 | 0.01 | | | | | | | | | |
| SUMMER | 2012_summer (jun-jul.) | OOA1 | 0.69 | 0.29 | 0.62 | 0.61 | 0.72 | 0.65 | 0.50 | 0.69 | OOA1 | - | - | - | - | - | - | - | - |
| | | OOA2 | 0.51 | 0.30 | 0.62 | 0.47 | 0.50 | 0.57 | 0.36 | 0.57 | OOA2 | - | - | - | - | - | - | - | - |
| | | | | | | | | | | | OOA3 | - | - | - | - | - | - | - | - |
| | | | | | | | | | | | OOA4 | - | - | - | - | - | - | - | - |
| FALL | 2011_fall. (nov.-dic.) | OOA1_BB | 0.64 | 0.84 | - | 0.77 | 0.74 | 0.50 | 0.69 | 0.84 | OOA_BB-aq | 0.76 | - | - | 0.81 | 0.66 | 0.30 | 0.39 | 0.49 |
| | | OOA2_BB-aq | 0.79 | 0.68 | - | 0.83 | 0.53 | 0.51 | 0.51 | 0.61 | | | | | | | | | |
| | 2012_fall (oct.-nov.) | OOA1 | 0.55 | - | - | 0.59 | 0.59 | 0.63 | - | 0.61 | | | | | | | | | |
| | | OOA2_BB-aq | 0.92 | - | - | 0.93 | 0.89 | 0.81 | - | 0.89 | | | | | | | | | |
| | | OOA3_BB | 0.51 | - | - | 0.54 | 0.39 | 0.45 | - | 0.38 | | | | | | | | | |
| | 2013_fall (oct.) | OOA1 | 0.16 | -0.02 | -0.02 | 0.03 | 0.34 | 0.09 | 0.35 | 0.27 | OOA1_BB | -0.08 | - | -0.15 | -0.20 | -0.03 | -0.11 | - | -0.09 |
| | | OOA2 | 0.68 | 0.44 | 0.76 | 0.80 | 0.63 | 0.65 | 0.58 | 0.63 | OOA2_BB-aq | 0.82 | - | 0.81 | 0.85 | 0.69 | 0.44 | - | 0.60 |
| | | OOA3_BB-aq | 0.90 | 0.78 | 0.94 | 0.94 | 0.70 | 0.72 | 0.64 | 0.71 | OOA3 | 0.47 | - | 0.56 | 0.54 | 0.50 | 0.26 | - | 0.41 |
| WINTER | 2013_winter (jan.-feb.) | OOA1_BB | 0.81 | - | 0.77 | 0.81 | 0.73 | 0.82 | 0.79 | 0.79 | | | | | | | | | |
| | | OOA2_BB-aq | 0.89 | - | 0.92 | 0.91 | 0.61 | 0.67 | 0.56 | 0.58 | | | | | | | | | |
| | | OOA3 | 0.35 | - | 0.32 | 0.32 | 0.34 | 0.34 | 0.32 | 0.39 | | | | | | | | | |
| | 2014_winter (jan.-feb.) | OOA1_BB | 0.52 | - | 0.38 | 0.42 | 0.57 | - | 0.49 | 0.45 | | | | | | | | | |
| | | OOA2_BB-aq | 0.84 | - | 0.90 | 0.88 | 0.66 | - | 0.58 | 0.47 | | | | | | | | | |
| | | OOA3 | 0.74 | - | 0.77 | 0.76 | 0.69 | - | 0.70 | 0.56 | | | | | | | | | |

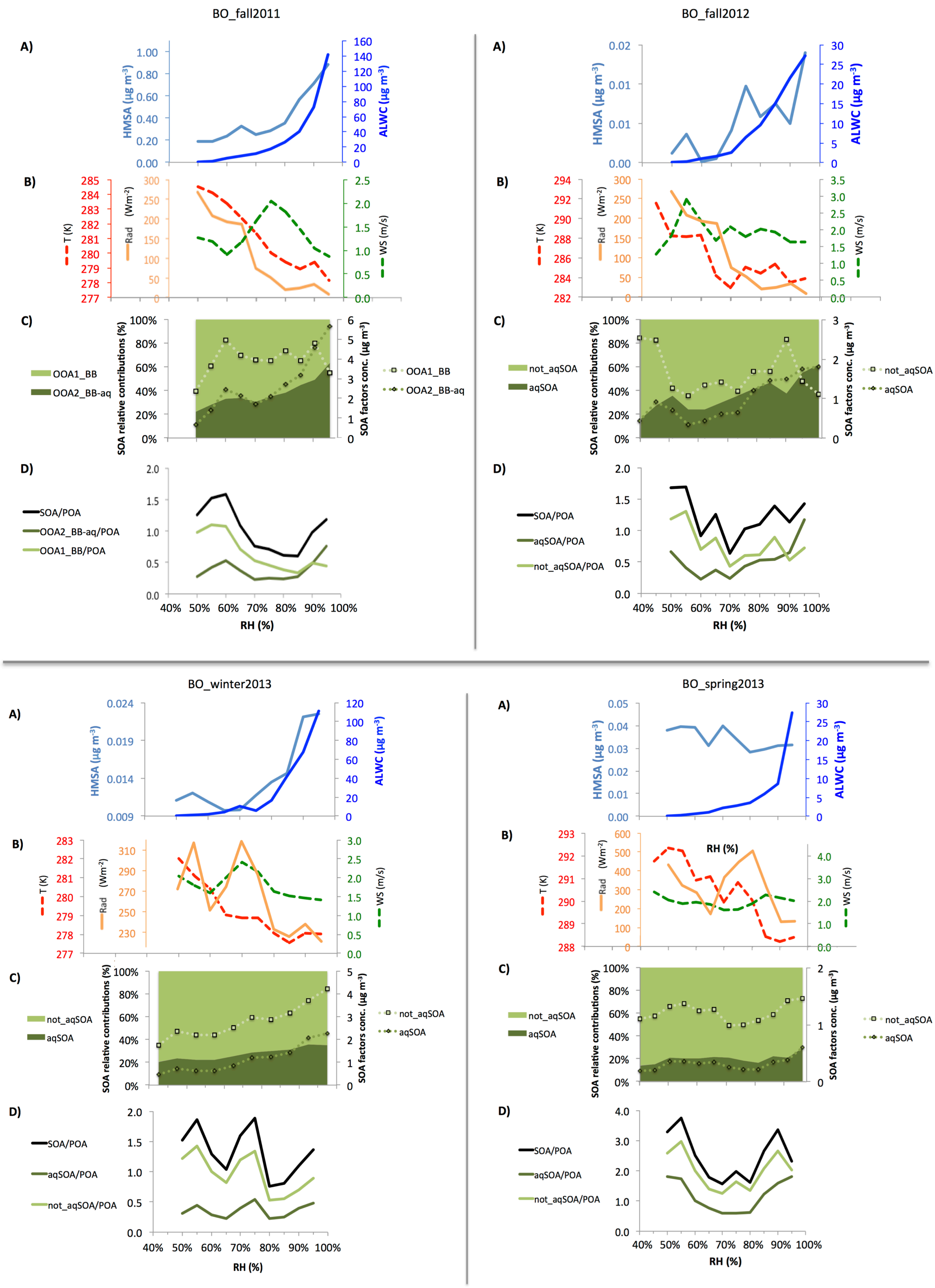



**Figure S5.1. variations of meteo and chemical parameters as function of RH during all the SUPERSITO campaigns showing aqSOA formation. The data were binned according to the RH (10% increment), and mean values are shown for each bin. Panels A: Aerosol Liquid Water Content (ALWC) and hydroximethansulfonic acid (HMSA). Panels B: air temperature together with solar radiation and wind speed (WS) measured at ground level. Panels C: variations in contributions of the OOA factors identified both in absolute (μg m-3) and relative (% of OOA) terms. Panels D: different SOA categories excluding the effects of planetary boundary layer height (PBL) using the total POA as a surrogate.**

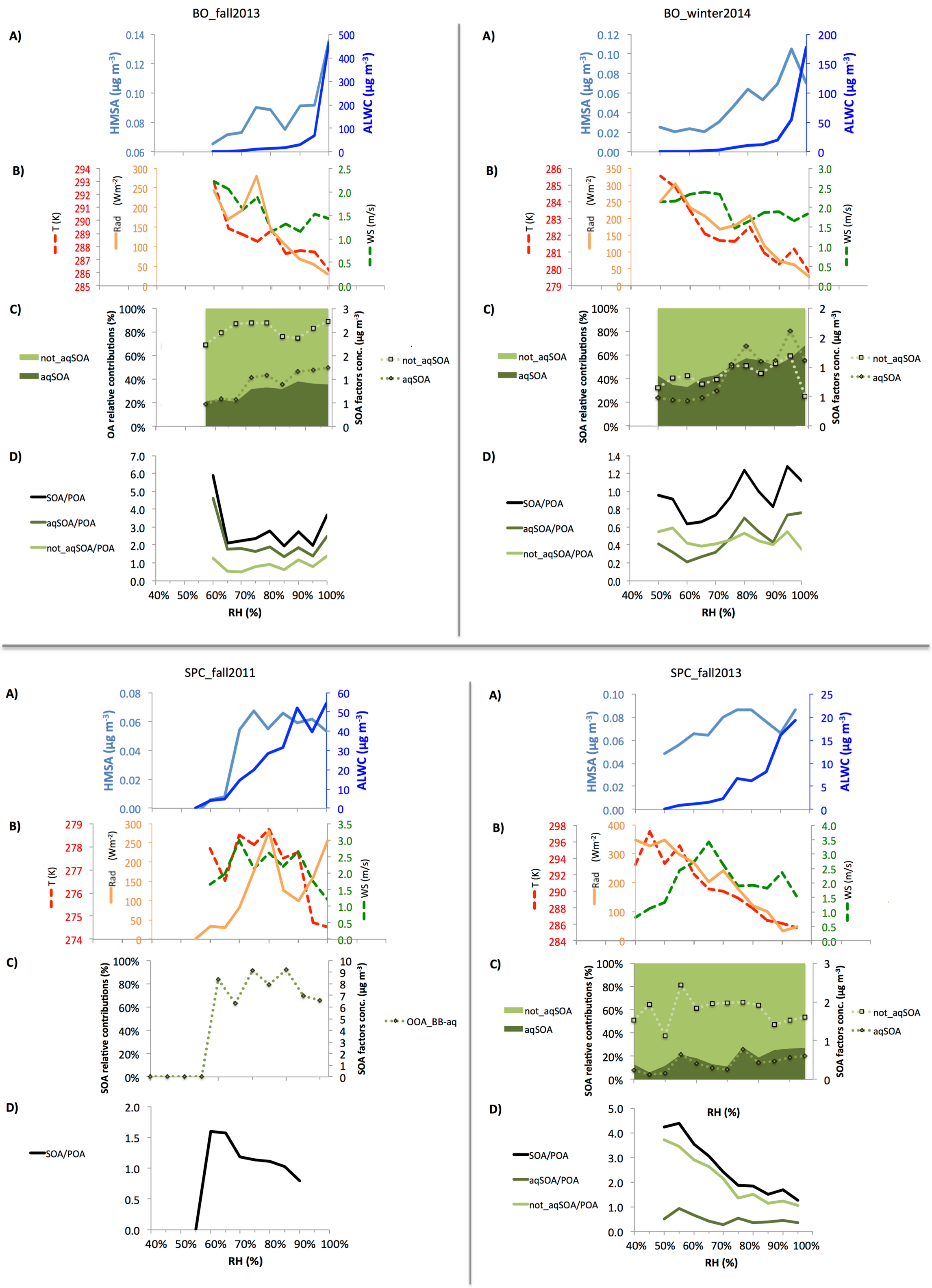



**Figure S5.2. variations of meteo and chemical parameters as function of RH during all the SUPERSITO campaigns showing aqSOA formation. The data were binned according to the RH (10% increment), and mean values are shown for each bin. Panels A: Aerosol Liquid Water Content (ALWC) and hydroximethansulfonic acid (HMSA). Panels B: air temperature together with solar radiation and wind speed (WS) measured at ground level. Panels C: variations in contributions of the OOA factors identified both in absolute (µg m-3) and relative (% of OOA) terms. Panels D: different SOA categories excluding the effects of planetary boundary layer height (PBL) using the total POA as a surrogate.**

**References**

Allan, J., A.E. Delia, H. Coe, K.N. Bower, R.M. Alfarra, J.L. Jimenez, A.M. Middlebrook, F. Drewnick, T.B. Onasch, M.R. Canagaratna, J.T. Jayne, and D.R. Worsnop, A generalised method for the extraction of chemically resolved mass spectra from Aerodyne aerosol mass spectrometer data, J. Aerosol Sci., 35, 909 - 922, doi:10.1016/j.jaerosci.2004.02.007, 2004.

Canonaco, F., Crippa, M., Slowik, J. G., Baltensperger, U., and Prévôt, A. S. H.: SoFi, an IGOR-based interface for the efficient use of the generalized multilinear engine (ME-2) for the source apportionment: ME-2 application to aerosol mass spectrometer data, Atmos. Meas. Tech., 6, 3649–3661, doi:10.5194/amt-6-3649-2013, 2013.

Crippa, M., Canonaco, F., Lanz, V. A., Äijälä, M., Allan, J. D., Carbone, S., Capes, G., Ceburnis, D., Dall'Osto, M., Day, D. A., DeCarlo, P. F., Ehn, M., Eriksson, A., Freney, E., Hildebrandt Ruiz, L., Hillamo, R., Jimenez, J. L., Junninen, H., Kiendler-Scharr, A., Kortelainen, A.-M., Kulmala, M., Laaksonen, A., Mensah, A. A., Mohr, C., Nemitz, E., O'Dowd, C., Ovadnevaite, J., Pandis, S. N., Petäjä, T., Poulain, L., Saarikoski, S., Sellegri, K., Swietlicki, E., Tiitta, P., Worsnop, D. R., Baltensperger, U., and Prévôt, A. S. H.: Organic aerosol components derived from 25 AMS datasets across Europe using a consistent ME-2 based source apportionment approach, Atmos. Chem. Phys., 14, 6159-6176, https://doi.org/10.5194/acp-14-6159-2014, 2014.

Paatero, P., The multilinear engine - A table-driven, least squares program for solving multilinear problems, including the n-way parallel factor analysis model, Journal of Computational and Graphical Statistics, 8, 854-888, doi:10.2307/1390831, 1999.

Paatero, P.: User's guide for the multilinear engine program "ME2" for fitting multilinear and quasimultilinear models, University of Helsinki, Finland, 2000.

Ulbrich, I. M., M.R. Canagaratna, Q. Zhang, D.R. Worsnop, and J.L. Jimenez, Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data, Atmos. Chem. Phys., 9, 2891-2918, doi:10.5194/acp-9-2891-2009, 2009.