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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

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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

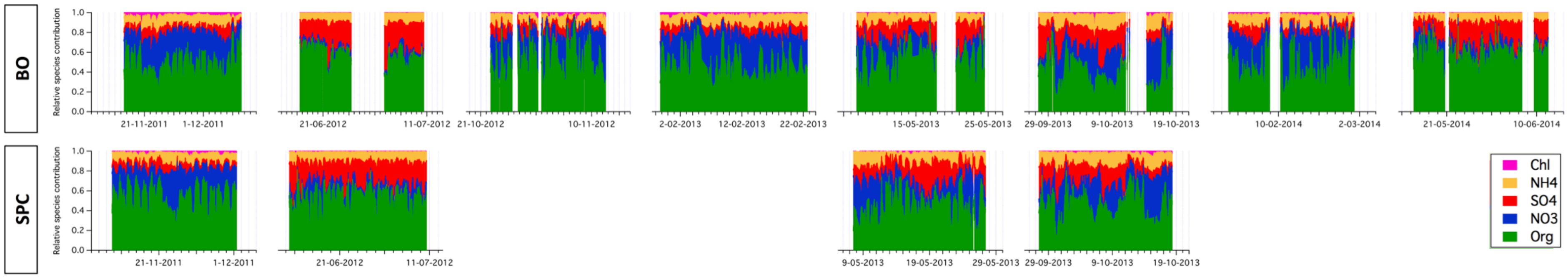


Figure S1: time series of the relative contributions of main NR-PM1 chemical components as measured by AMS in each intensive campaign of Supersito project.

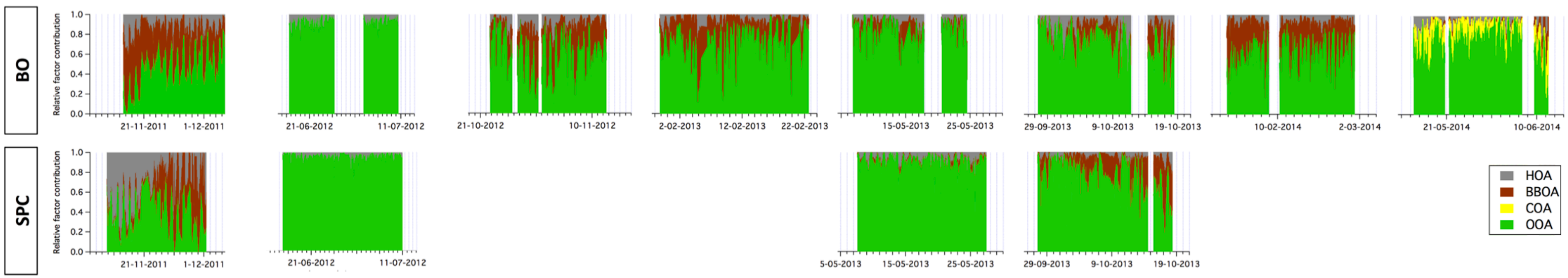


Figure S2: time series of the relative contributions of OA primary and secondary components as calculated by PMF and ME-2

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) following the sequential steps reported below:
1. Unconstrained run (PMF): in a first step, a range of unconstrained runs was examined: solutions from two to eight factors are investigated (applying three pseudo-random starting point -seeds- each, for a total of 21 unconstrained runs) for all the datasets in order to choose the most appropriate number of interpretable 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). The most appropriate number of factors was chosen based on the residual analysis (inspecting and minimizing 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). This means that the best number of factor is established when further increasing the number of factors does not improve the interpretation of the data, as the new factor time series and spectral profiles are highly correlated with those extracted from lower order solutions and cannot be explicitly associated to distinct sources or processes.

2. Constraining only HOA mass spectrum: after the most reasonable number of factors was identified, the HOA mass spectrum was constrained in a range of a-values (i.e., a=0, 0.05, 0.1, 0.3, 0.5) in order to check its attribution and any possible erroneous mixing between sources. Moreover

various numbers of factors close to the optimal were tested: for example if the best number of factors identified was 5, we run solutions with 4, 5 and 6 factors. For every a-value, the model was initiated from three different pseudo-random starting points (seeds), yielding 45 total runs for each reference spectral profile constrained. We tested also different reference HOA factor profiles from ambient deconvolved spectra of the high-resolution aerosol mass spectral database (URL: http://cires.colorado.edu/jimenezgroup/ HRAMSsd/", Ulbrich et al., 2009). In particular, for HOA we employed reference profiles from Mohr et al. (2012) (obtained at Barcelona urban background site) and from Crippa et al. (2013a) (from Paris).
Crippa et al. (2014) (and most of the subsequent literature) suggested low a-values (e.g., a=0.05–0.1) for HOA profiles, given usual low variability of this source profile in most of the studies. Nevertheless applying these low a-values to our datasets resulted often in two split HOA factors with very similar profiles and time series or in additional HOA/BBOA-mixed factors. Moreover solutions with higher a-value associated to HOA (a=0.5) maximized the correlation with external tracers of traffic emissions (i.e., NOx, BC, EC) and minimized the residuals associated with rush hours in the diurnal trend of the residuals (see Table S3 and S4) and for this reason were chosen.

3. Looking for BBOA (if not identified before or mixed with HOA or COA): BBOA reference profiles were constrained when a not clear separation between BBOA and other primary factors (HOA and COA) were found. First of all the BBOA reference spectrum from Mohr et al. (2012) was constrained alternatively alone (in a range of a-values =0, 0.05, 0.1, 0.3, 0.5) and together with the HOA reference profile (always from Mohr et al., 2012). When simultaneous constraining of BBOA and HOA were applied, the a-values were independently varied for HOA and BBOA (a-value =0, 0.05, 0.1, 0.3, 0.5, giving 25 a-value combinations). For every a-value combination the model was initiated from three different pseudo-random starting points (seeds), yielding 75+15=90 total runs.
Again, together with different a-values, various numbers of factors were tested close to the optimal, in order to study any possible improvements of the solution in term of both the analysis of the residuals and the correlation of the factors with each other and with external tracers of traffic (i.e., NOx, BC, EC) and biomass burning (Levoglucosan) emissions.
Actually in our analysis we found an improvement in constraining BBOA only in two cases out of 12: BO_spring 2014 and SPC_spring 2013 campaigns. In these two cases we needed a strong constrain (a-value of 0.05) to see a better separation between BBOA and COA (in the case of BO_spring 2014) and HOA (in the case of SPC_spring 2013). This low a-value is not common for constraining BBOA for which, given the degree of variability that the BBOA spectrum can have depending on the burning material and systems, higher values (a-value = 0.3–0.5) are usually suggested. Anyway, in our cases, applying the suggested values we didn't obtain any significant improvement in the separation between BBOA and HOA or COA factors. Using the selected a-value of 0.05 instead we found a better correlation with external tracers in both cases (see Table S4).

4. Looking for COA: even if not suspected from the initial unconstrained analysis (looking the possible presence of meal hour peaks in the diurnals and inspecting the f55-f57 relative abundance as suggested by Mohr et al. (2012)), in any case an attempt of looking for COA factor was done for each campaign.
COA reference profiles from Mohr et al. (2012) and Crippa et al. (2013a) were alternatively constrained alone (in a range of a-values =0, 0.05, 0.1, 0.3, 0.5). Only when the unconstrained or this first COA constraining resulted in a possible COA contribution, then COA reference profiles were constrained together with HOA and BBOA profiles (always from Mohr et al., 2012).
When simultaneous constraining of COA and HOA were applied, the a-values were independently varied for HOA and COA (a-value =0, 0.05, 0.1, 0.3, 0.5, giving 25 a-value combinations). Also the

same a-values were applied constraining COA together with both HOA and BBOA profiles, varying each independently (giving 105 a-values combinations).
Despite these efforts, in our analysis only in 2 cases out of 12 there was the suspicion of a COA contribution and only in one case (BO_spring 2014) this contribution was considered real in the end (based on its spectral profile similarity with references and on the presence of meal hour peaks). For this campaign actually the chosen solution was leaving COA profile unconstrained because constraining the COA profile (both from Mohr et al, 2012 and Crippa et al., 2013a reference profiles) leaded to split COA factors only with variable amount of m/z 44.
The COA factor identified in BO_spring 2014 campaign shows an early lunch-time peak in the diurnal trend (peaking around 11-12) and an higher than usual contribution of m/z 44, which leave some doubts in the correct quantification of this COA contribution. We considered the hypotheses of a misleading mixing-source between COA and HOA, COA and BBOA and also between COA and OOA: we tested all the possible combination of constraining (only HOA, HOA+BBOA, HOA+COA, HOA+BBOA+COA), a number of a-values (a-value =0, 0.05, 0.1, 0.3, 0.5) for each of this combination and also for different numbers of factors (from 4 to 7), which resulted in strong increases of the residuals with a clear diurnal pattern peaking between 11-12 (in the case of a reduced number of factors) or in split/mixed HOA, BBOA and COA profiles. Eventually we opted for the solution that minimizes the uncertainty in the identification of the other two primary components (HOA and BBOA) and maximizes their correlation with external tracers. This mainly because the focus of our study is on BB-related factors and because COA represents in any case just a minor factor found in only one campaign. We acknowledge this issue, but we leave the deeper investigation of the peculiarity of this COA factor to other possible future studies.

ITERATIVELY. Residual analysis: for each step the residual plots were consulted in order to evaluate whether the constrained profile(s) has (have) caused structures in the residuals. If so, the constrained profiles were tested with a higher a-value or rejected.

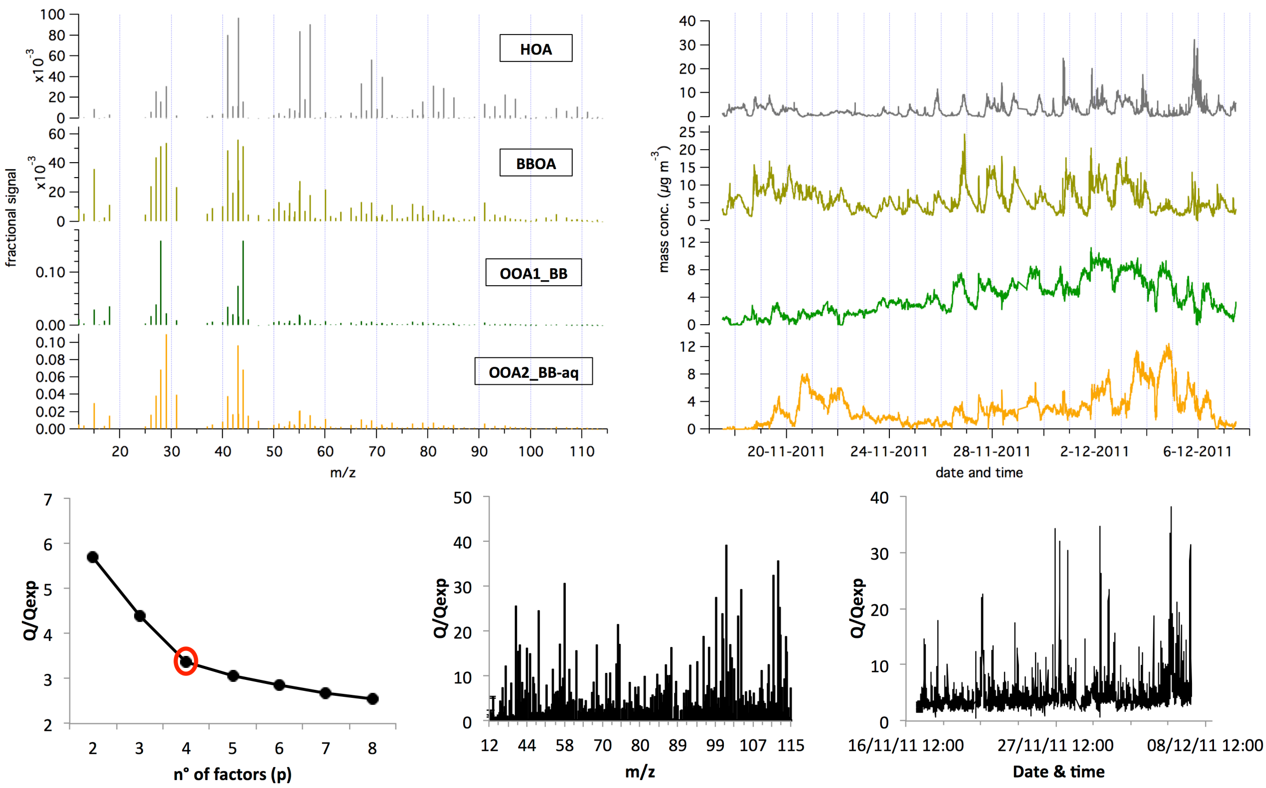
Oxidized organic aerosol components (OOAs) factors were never constrained because their mass spectra are characterized by a greater variability with respect to the POA factors, reflecting the multiplicity of atmospheric secondary formation and transformation processes contributing to SOA formation and composition (Canonaco et al. 2015).
When an unconstrained PMF solution was considered as the optimal one, PMF solutions for multiple values of FPEAK are explored to test the rotational ambiguity of the results. Chosen the best number of factors, variable FPEAKs values (from -0.6 to +0.6, with 0.2 steps) were applied and the resulting Q values, scaled residuals, and factor profiles and time series were examined to select the optimum solution.

Optimum solutions were selected if they satisfied the following set of criteria:
1. fCO2+ <0.04 in HOA and COA factor profiles (HOA based on Aiken et al., 2009; Mohr et al., 2012; Crippa et al., 2013a, 2014 and COA based on Crippa et al., 2013a, 2013b; Mohr et al., 2012), with the exception of SPC_fall 2011 due to the peculiar meteorological conditions further described in section 3.2;
2. HOA correlates significantly with NOx, BC and EC;
3. HOA correlates better with NOx than COA; BBOA correlates significantly with levoglucosan;
4. The concentration ratios between the main POA factors (HOA and BBOA) and tracer compounds (used as source-specific ratios) are in a reasonable range compared with values in literature;
5. COA has a diurnal trend characterized by meal hours peaks (lunch and dinner time).

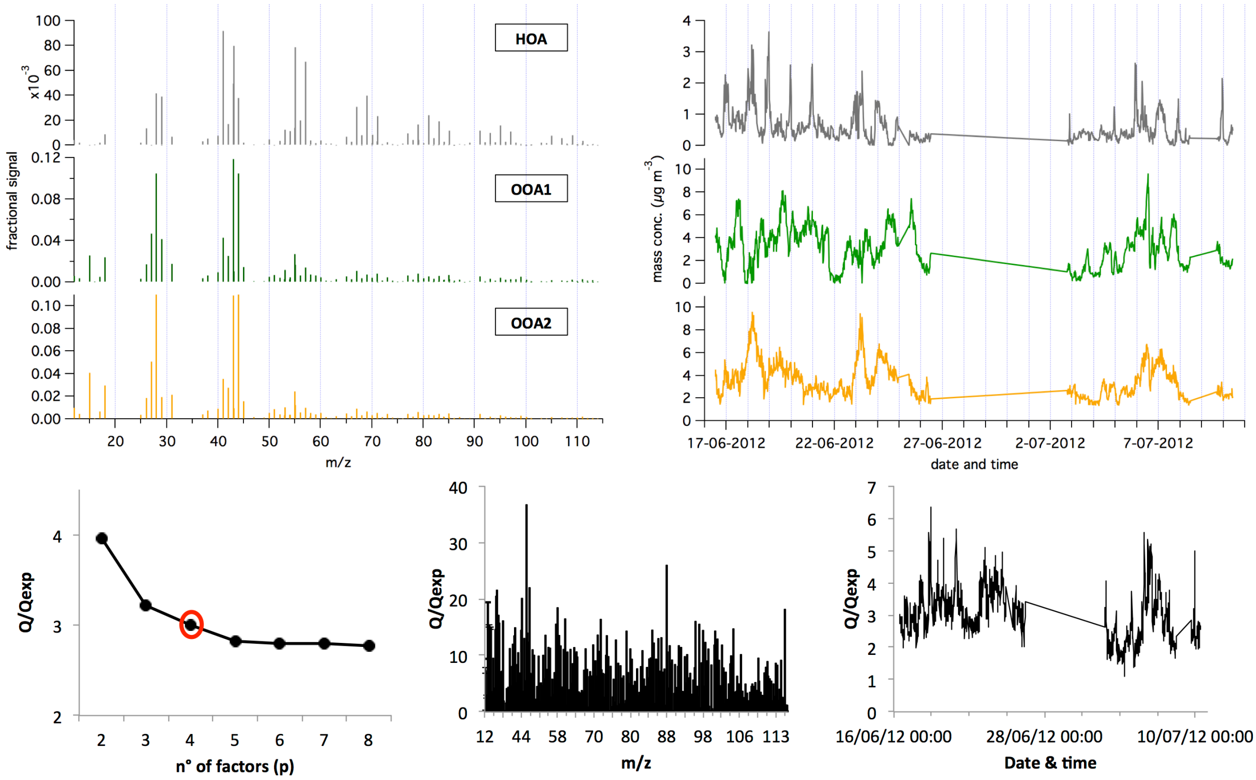
The interpretation of the retrieved source apportionment factors as organic aerosol sources is based on the comparison of their mass spectral profiles with reference ones (Table S5, S6 and S7), on the correlations with external data (see Table S8) and on the investigation of their diurnal trends (see

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.

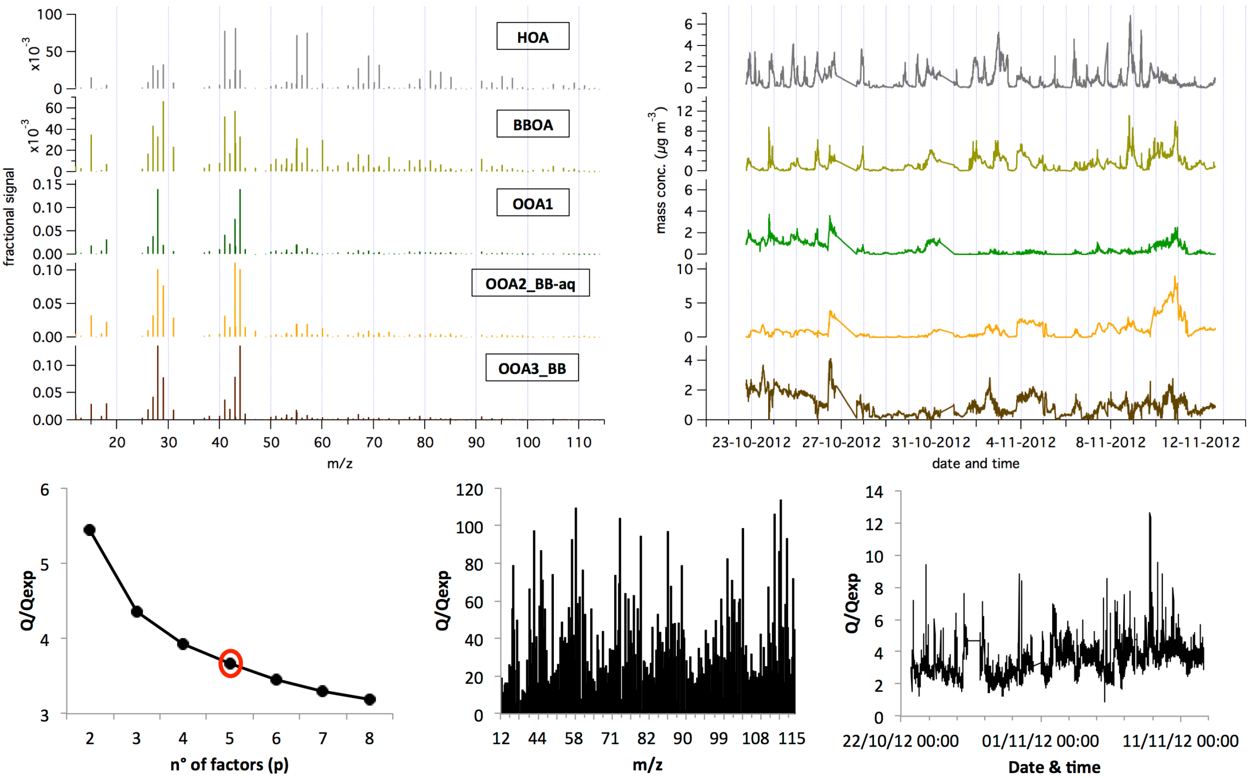
BO_2011fall: p=4; unconstrained PMF



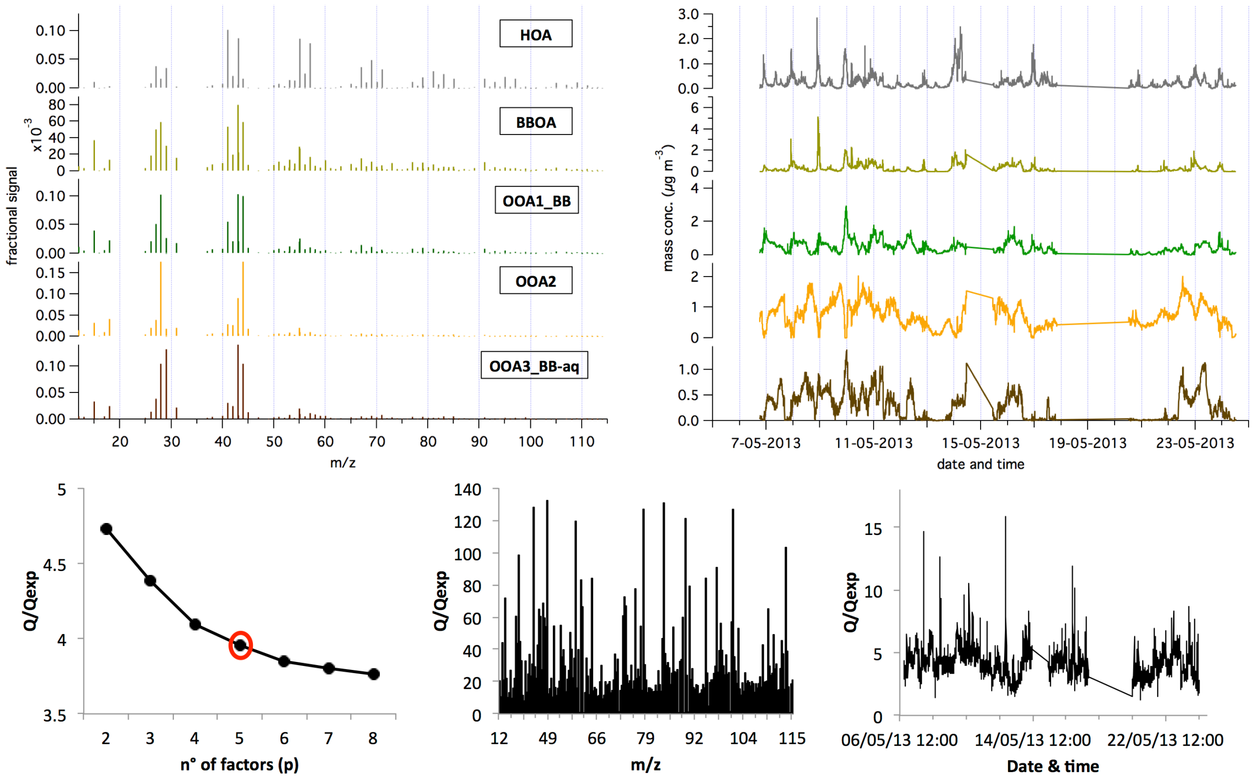
BO_2012summer: p=4; unconstrained PMF; OOA2 recombined



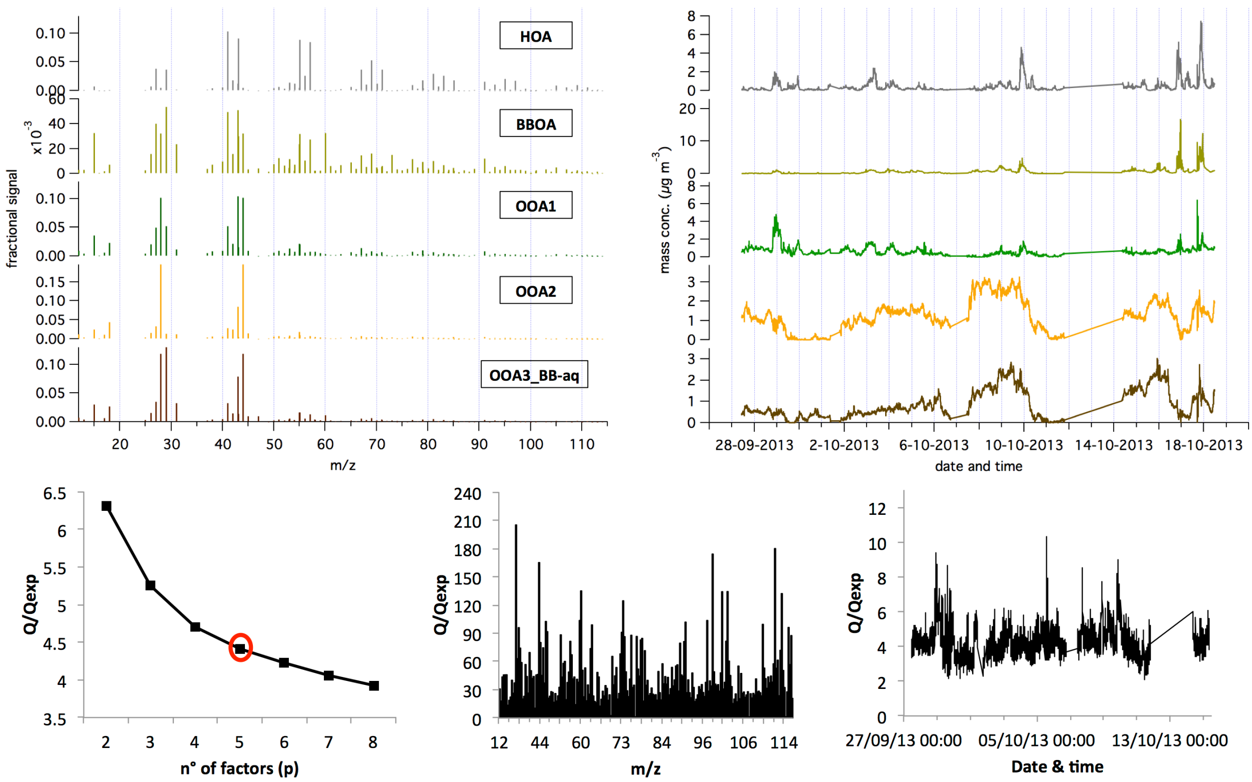
BO_2012fall: p=5; unconstrained PMF



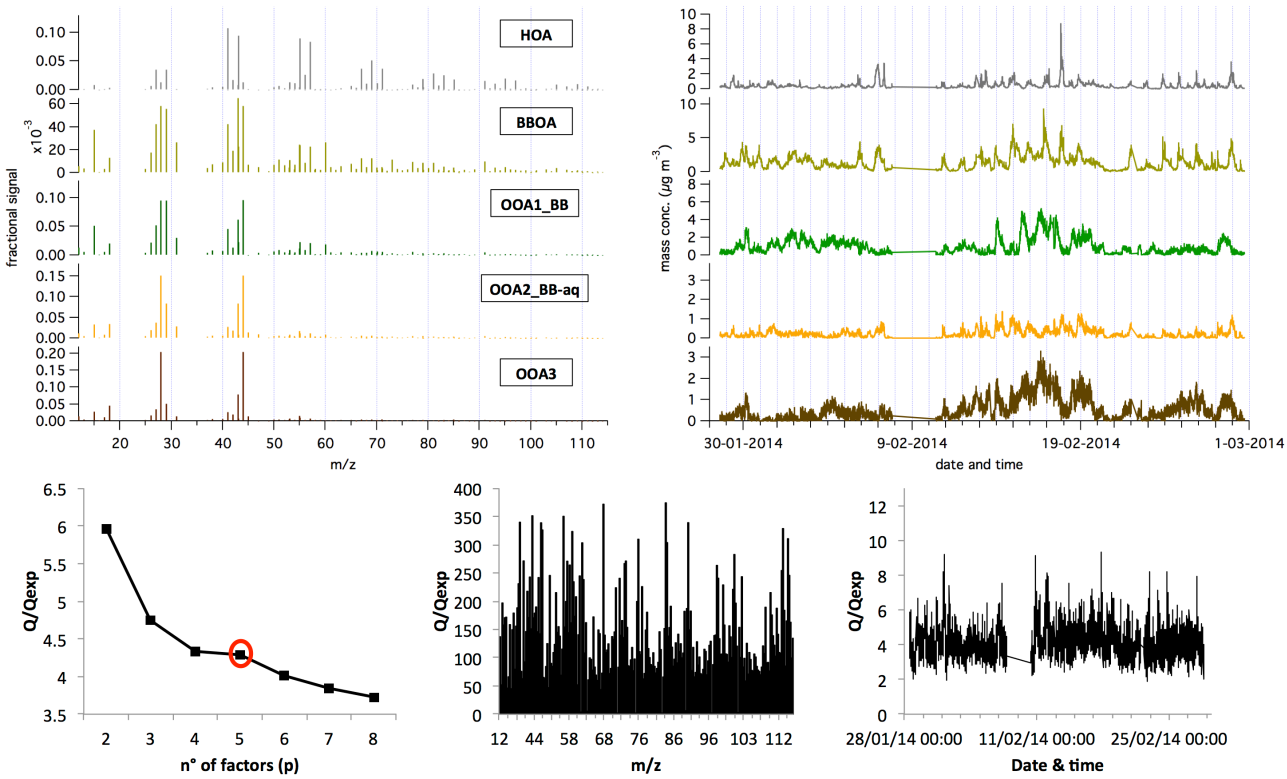
BO_2013spring: p=5 ME-2 HOA Mohr et al. 2012, a-value=0.5



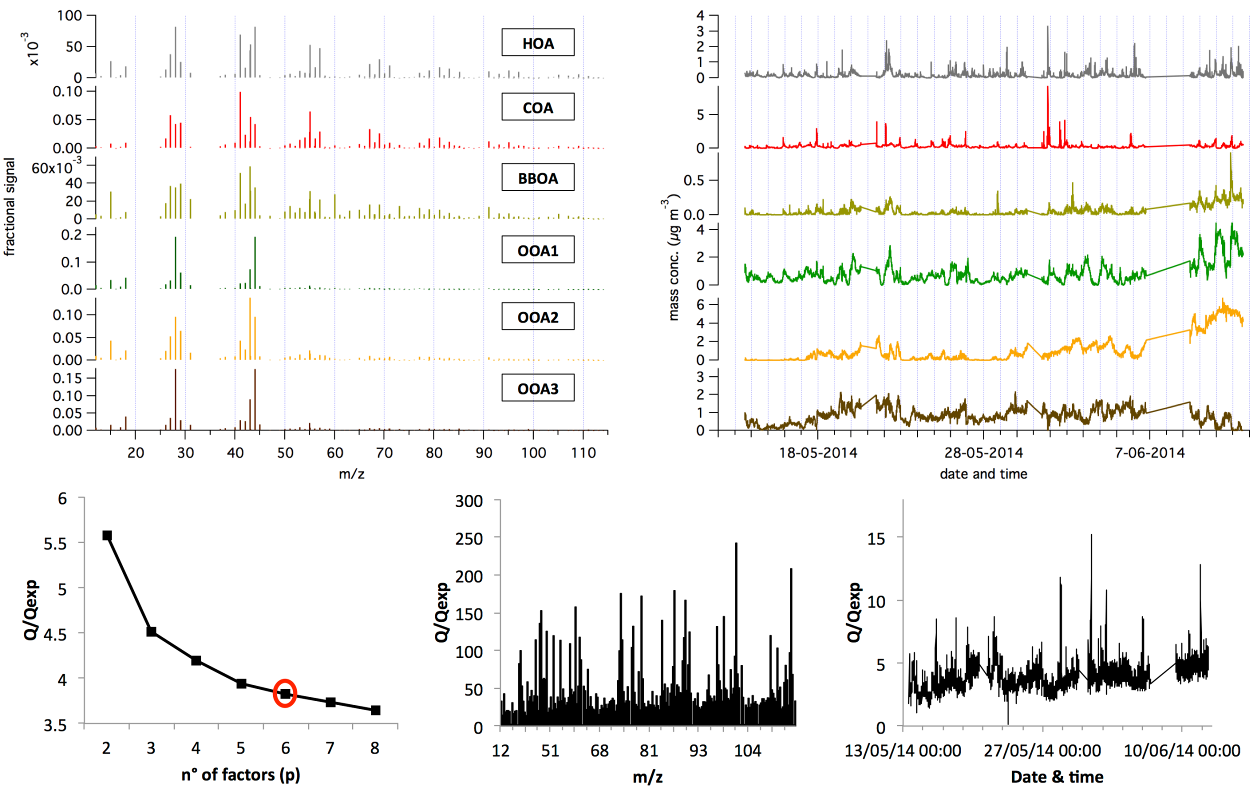
BO_2013fall: p=5; ME-2 HOA Mohr et al. 2012, a-value=0.5



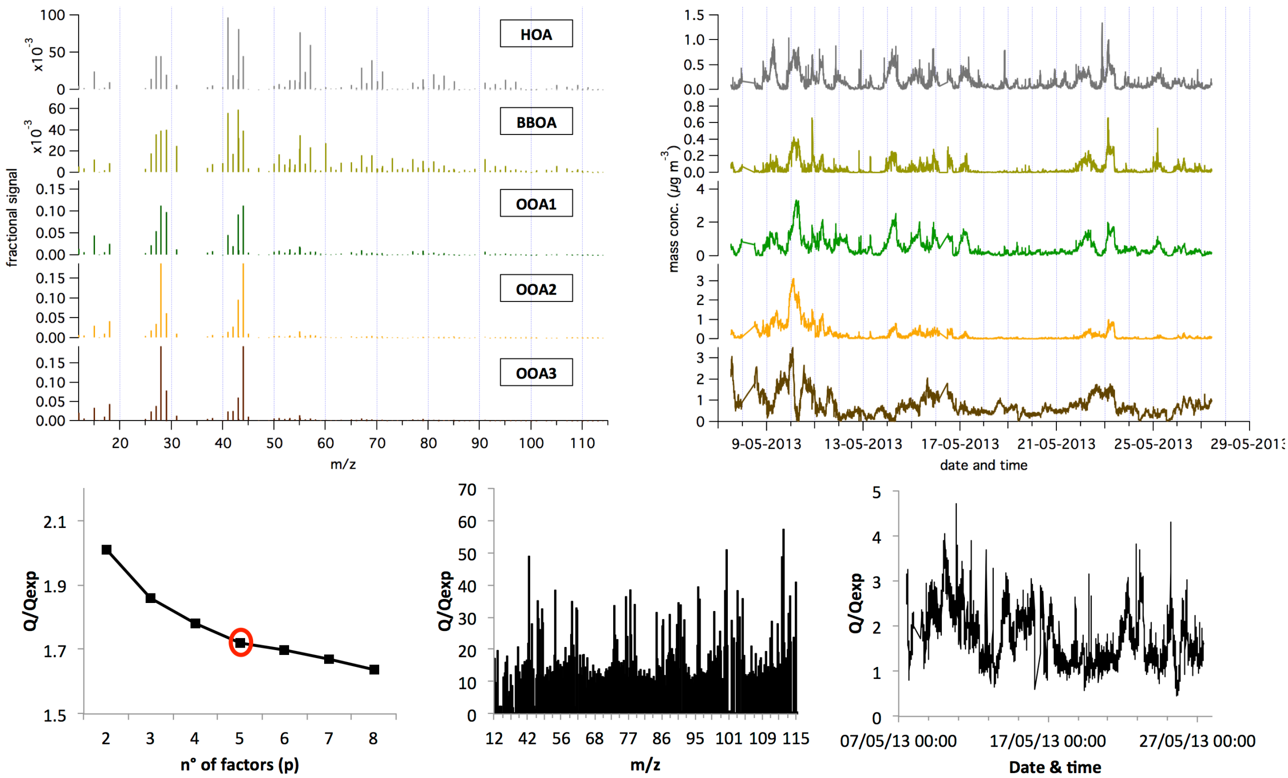
BO_2014winter: p=5; ME-2 HOA Mohr et al. 2012, a-value=0.5



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

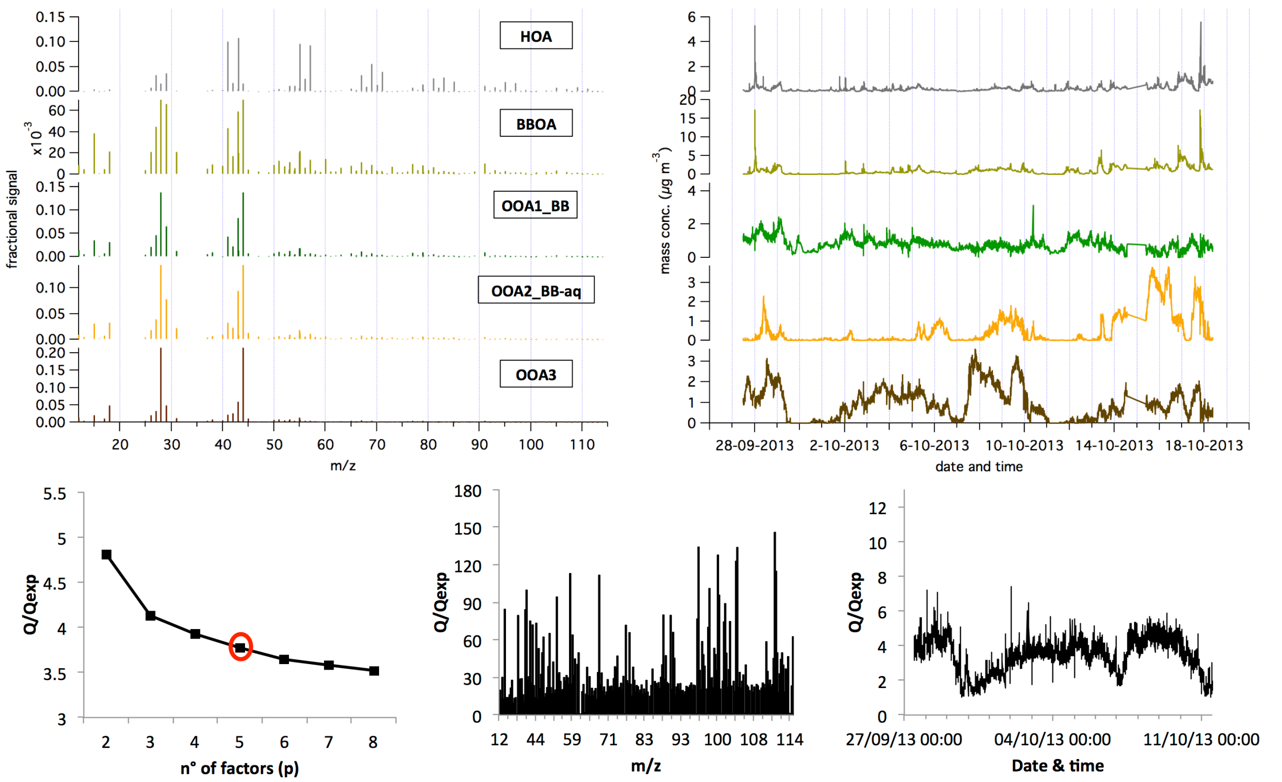


Table S3. summary of the main tests performed on each dataset to identify the optimal number of factors and the best constraints in PMF analysis. In bold the chosen solution.

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.

		BO							SPC			Reference spectra											
Θ (°)	**BBOA**	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.

		BO								SPC				Reference spectra																				
Θ (°)	**OOA_TOT**	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).

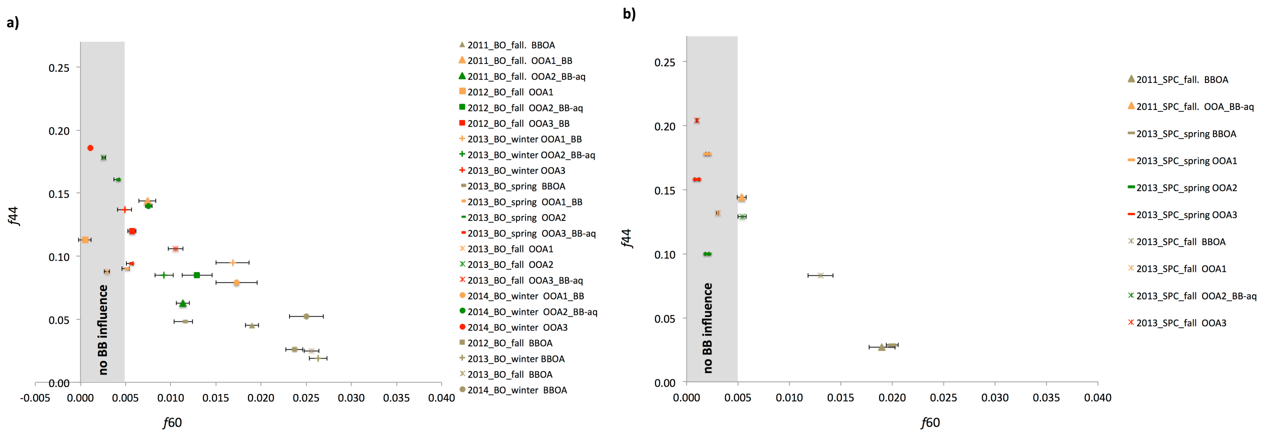


Figure S3: Variability of *f*60 contribution on BBOA and OOAx_BB in different PMF solutions tested to evaluate the rotational ambiguity of the model. The markers in the plots show *f*44 versus *f*60 average values. The error bars represent the *f*60 standard deviation of the different solutions tested. 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**

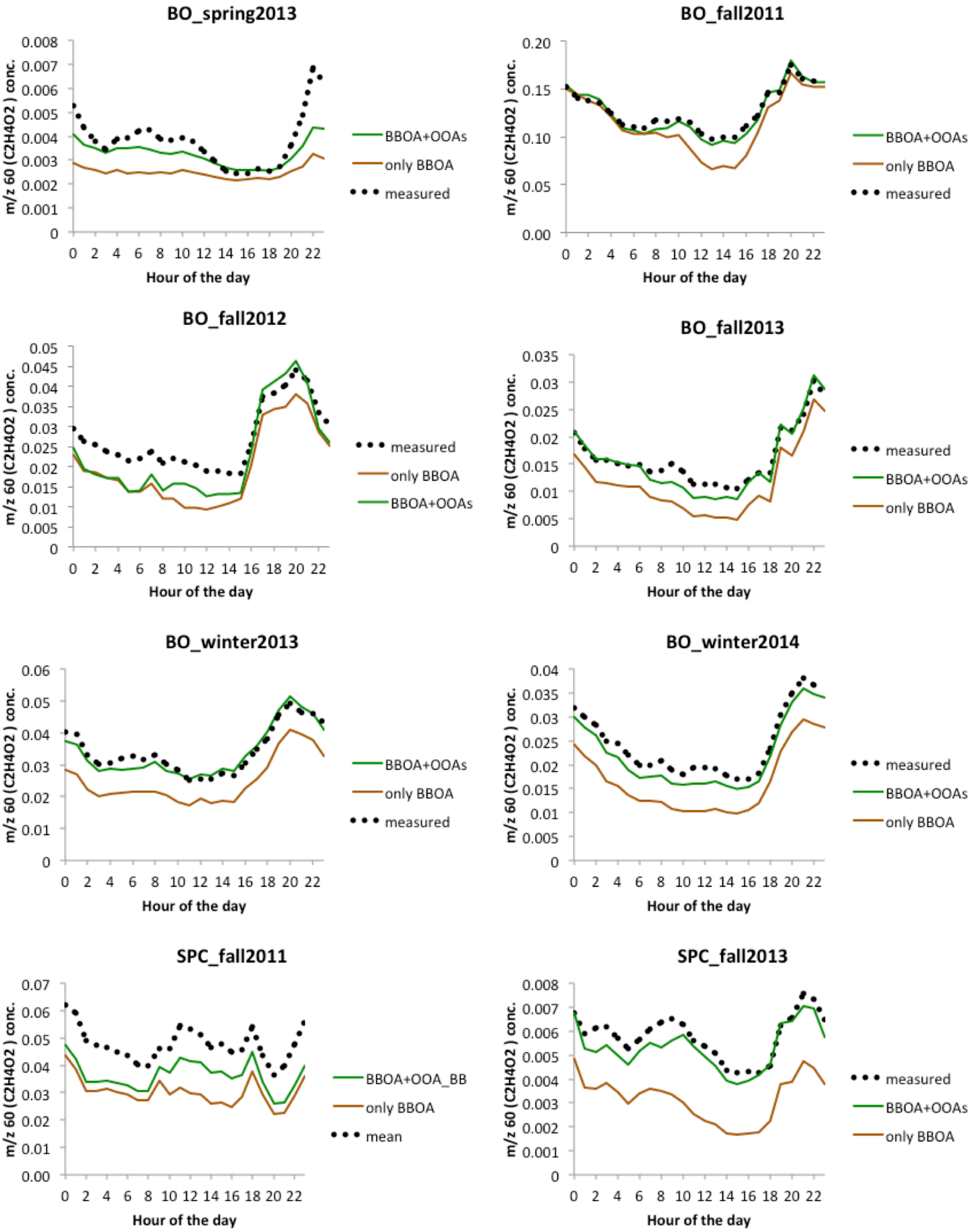


Figure S4: comparison of measured and reconstructed diurnal pattern of concentrations of the AMS mass fragment $C_2H_4O_2^+$ (m/z 60.021) for different PMF solutions considering only the BBOA primary factor or both BBOA and OOAx_BB.

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	0.0057	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	0.0049	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	0.0053	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	0.0054	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	0.0054	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	0.0054	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									

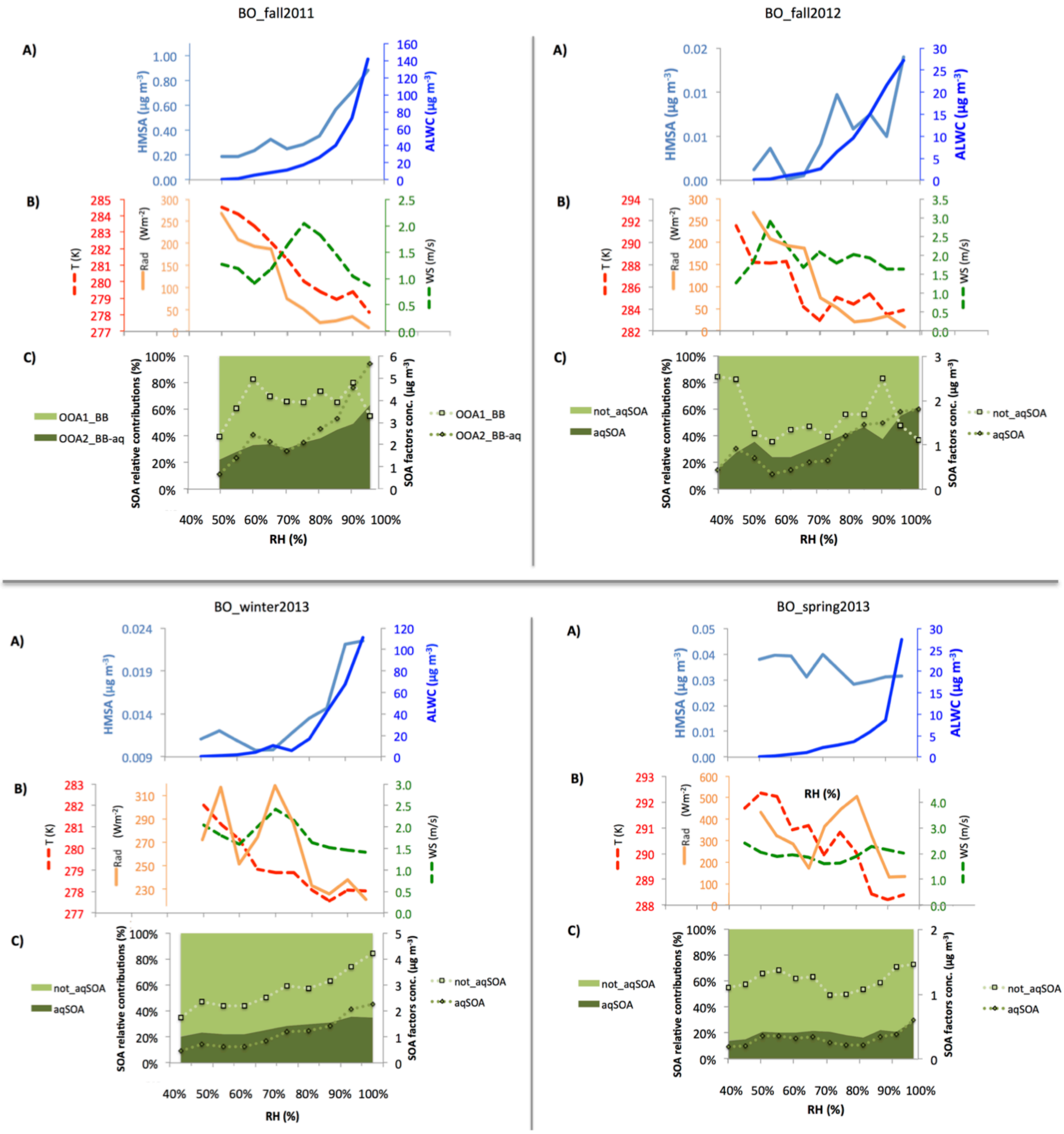


Figure S5.1. variations of meteo and chemical parameters as function of RH during all the SUPERSITO campaigns showing aqSOA formation. The data were binned according to the RH (5% increment), and mean values are shown for each bin. Panels A: Aerosol Liquid Water Content (ALWC) and hydroximethansulfonic 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.

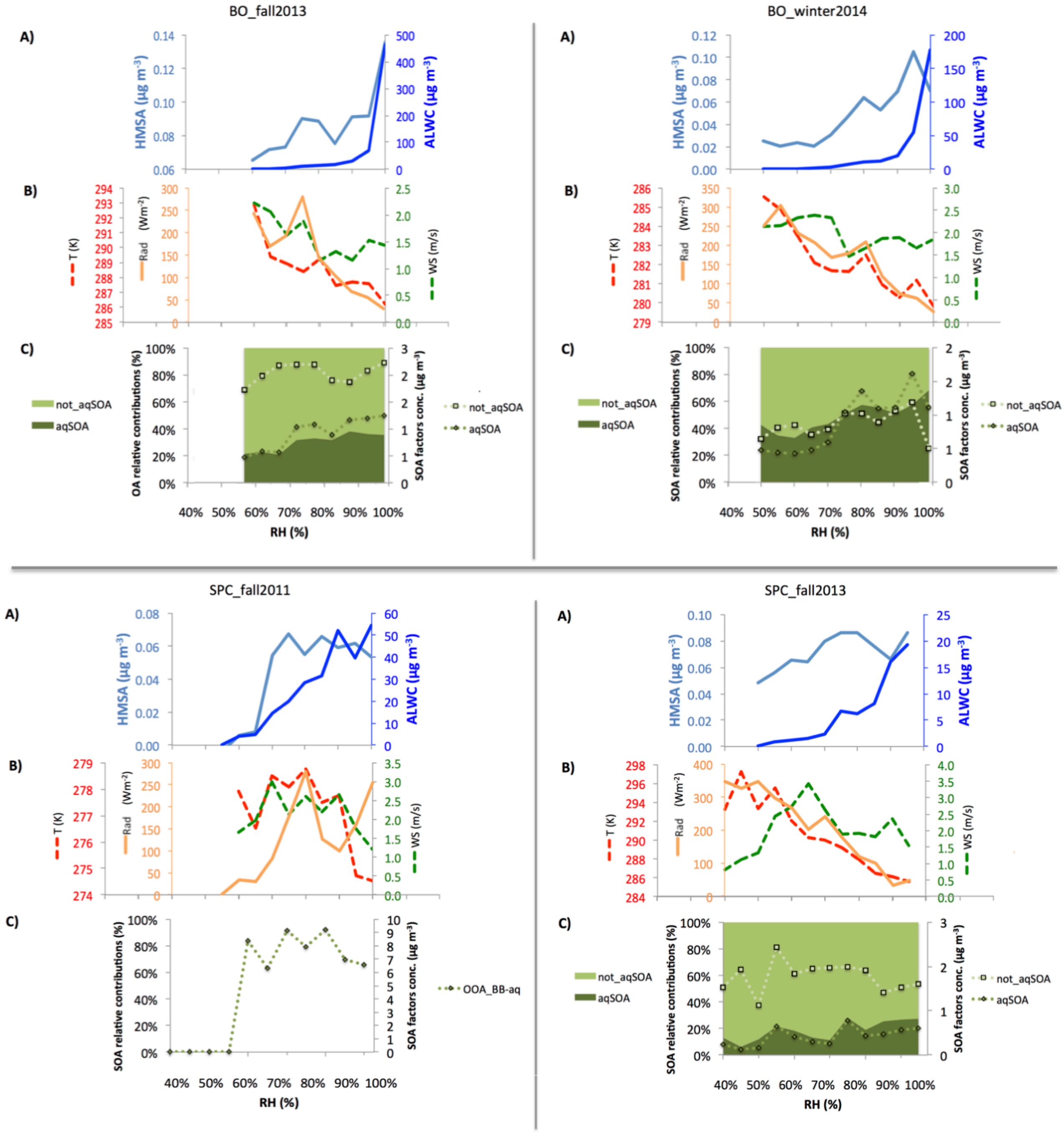


Figure S5.2. variations of meteo and chemical parameters as function of RH during all the SUPERSITO campaigns showing aqSOA formation. The data were binned according to the RH (5% increment), and mean values are shown for each bin. Panels A: Aerosol Liquid Water Content (ALWC) and hydroximethansulfonic 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.

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