1. Criteria for factor selection (Zhang et al., 2011)

-Uncentered correlation coefficients of factor at selection (say, p) with the factors at p−1
-Improvement in the solution's ability to explain residual structure with the addition of a factor
-Ensuring the 25–75th percentiles of scaled residuals for all m/zs are between ± 3
-Changing FPEAK value (−1 to +1) allows exploring rotations of solutions of a given number of factors
-Changing SEED value (0 to 10) allows exploring solutions with different initial conditions
-Changes in the fraction of variance explained by different factors, correlations of factors' mass spectra with reference mass spectra and factors' time series correlations with the time series of external tracers
- m/z 12 not considered due to negative signals; this has been observed elsewhere as well (Fröhlich et al., 2015, Schlag et al., 2016)

- Winter 2017 organic-only PMF (two-factor solution selected)
    - Conducting PMF analysis using different SEEDs at FPEAK zero
        - solutions between 2 to 5 factors achieve convergence; steep drop from 1 to 2 factors implies solution likely has at least 2 factors; 3 factor solution and large SEED values generate unreasonable MS; at low SEEDs, factor splitting occurs, so those solutions are rejected; based on MS and TS correlations, no new solutions different from SEED zero at low SEED; 4 and 5 factor solution generates unreasonable MS at all SEEDs; multiple solutions with reasonable MS could exist at 2 factors; however, minimal variation in fraction of variance explained and MS and TS correlations at the 2 factor selection; so, fixing SEED as zero.
    - Conducting PMF analysis using different FPEAKs between −1 and 1 at SEED zero
        - Uncentered correlation coefficients between factors at a number of factors (say, p) and p−1 do not reject the possibility of 2, 3 or 5 factors (no convergence at 4 factors); 25th–75th scaled residuals for all m/zs are within ±3, even at 2 factors; negligible improvement in residual structure going from 2 to 3 factors; a mass spectral profile at 5 factors is not associated with any reference factor type; going from 3 to 5 factors lowers the separated BBOA factor R with reference BBOA; there is seemingly an unmixing of MS profiles OOA, BBOA, and HOA at 3 factors, but also unreasonable BBOA MS generated; HOA factor R with reference BBOA MS is higher than the BBOA factor and the TS of biomass burning tracers, ΔC and BC_{BB}, also correlate more strongly with HOA factor; thus, going back to 2 factors; pulling profile towards positive FPEAKs has a minimal effect whereas pulling towards the negative FPEAKs generates nearly zero midday concentrations in the POA factor, which is not feasible; thus no reason FPEAK other than zero preferable

- Winter 2017 organic-inorganic combined PMF (four-factor solution selected)
    - Conducting PMF analysis using different SEEDs at FPEAK zero
        - Solutions between 2 to 6 factors achieve convergence; steep drop from 1 to 2 factors implies solution likely has at least 2 factors; 5 and 6 factor solutions have factor(s) that show weak correlations with tracers; 2 and 3 factor solutions' scaled residuals at inorganic m/zs exceeding ± 5; 4 factor

solution shows scaled residual exceedance of ±3 at only one nitrate m/z, m/z 46; 4 factor solutions show minimal variation in fraction of variance explained and MS and TS correlations with changing SEED; so, fixing SEED as zero.
- o Conducting PMF analysis using different FPEAKs between −1 and 1 at SEED zero
  - 25th–75th scaled residuals for sulfate and nitrate m/zs exceed ±4 for 2 and 3 factors but reduces dramatically for sulfate (within ±3) and partially for nitrate (within ± 4) at 4 factors; structure in residual changes dramatically from 2 to 3 but marginally afterward; 5 and 6 factor solutions have factor(s) that show weak correlations with tracers; Uncentered correlation coefficients between factors at number of factors (say, p) and p−1 show no evidence of factor splitting from 3 to 4 factors; 4 factor solutions show minimal variation with FPEAKs in fraction of variance explained and TS correlations; positive FPEAKs pulls profiles towards zero and leads to decreasing MS correlations with reference MS; observe stable MS correlations with negative FPEAKs; thus no reason FPEAK other than zero preferable.

- Spring 2017 organic-only PMF (two-factor solution selected)
  - o Conducting PMF analysis using different SEEDs at FPEAK zero
    - solutions between 2 to 6 factors achieve convergence; steep drop from 1 to 2 factors implies solution likely has at least 2 factors; 3–6 factor solutions show signs of factor "splitting", weak MS and TS correlations; 2 factor solution generates a stable solution, with minimal changes in the fraction of variance explained, and MS and TS correlations; so, fixing SEED as zero
  - o Conducting PMF analysis using different FPEAKs between −1 and 1 at SEED zero
    - 25th–75th scaled residuals for all m/zs are within ±3, even at 2 factors; negligible improvement in residual structure going from 2 to 3 factors; 4–6 factor solutions do not achieve convergence criteria; going back to two factors; pulling profile towards large positive FPEAKs creates unreasonable zeros in MS whereas pulling towards large negative FPEAKs generates zero midday concentrations for the POA factor, which is not feasible; no reason FPEAK other than zero preferable

- Spring 2017 organic-inorganic combined PMF (four-factor solution selected)
  - o Conducting PMF analysis using different SEEDs at FPEAK zero
    - Solutions between 2 to 6 factors achieve convergence; steep drop from 1 to 4 factors and dramatic changes in residual structure implies solution likely has at least 4 factors; 25th–75th scaled residuals for multiple m/zs below ± 3 only starting with 4 factor solutions; 5 and 6 factor solutions have factor(s) that show factor splitting; 4 factor solutions show only 1 solution at SEEDs explored based on the fraction of variance explained and MS and TS correlations at the 4 factor selection; so, fixing SEED as zero.
  - o Conducting PMF analysis using different FPEAKs between −1 and 1 at SEED zero
    - Explanation of residual structure suggests at least 4 factors; weak MS and TS correlations at 5 and 6 factor solutions; at negative FPEAKs, 4 factor solutions show low TS correlations for the AS-OOA factor; minimal variation with FPEAKs in fraction of variance explained and MS and TS correlations for positive FPEAKs; no reason FPEAK other than zero preferable.

- Summer 2017 organic-only PMF (two-factor solution selected)
  - o Conducting PMF analysis using different SEEDs at FPEAK zero
    - ▪ Solutions between 2 to 6 factors achieve convergence; steep drop from 1 to 2 factors implies solution likely has at least 2 factors; 3–6 factor solutions at different SEEDs generate "mixed" solutions, factors with unreasonable MS, weak MS and TS correlations or mismatch between MS and TS correlations for multiple factors (e.g., weaker correlation with CO for POA-associated factors than OOA-associated factors); also, beyond 2 factors, minimal changes in the residual structure to warrant additional factors; multiple solutions with reasonable MS could exist at 2 factors; however, minimal variation with SEEDs in fraction of variance explained and MS and TS correlations at the 2 factor selection; so, fixing SEED as zero.
  - o Conducting PMF analysis using different FPEAKs at SEED zero
    - ▪ 25th–75th scaled residuals for all m/zs are within ±3, even at 2 factors; negligible improvement in residual structure going from 2 to 3 factors and beyond; 3 factor solution shows weak MS and TS correlations at explored FPEAKs; 4 factor solutions either have "mixing" or weak tracer TS correlations; cannot have 5 or 6 factor solutions because independent tracers needed for factor interpretation; going back to two factors; pulling profile towards positive FPEAKs forces contributions at few m/zs closer to zero whereas pulling towards the negative FPEAKs generates nearly zero midday concentrations in the POA factor, which is not feasible; residuals, MS and TS correlations of the two factors do not change with changing FPEAKs; fraction variance explained by one of the factors varies between 39–46% with varying FPEAKS, indicating minimal rotational ambiguity; thus no reason FPEAK other than zero preferable

- Summer 2017 organic-inorganic combined PMF (three-factor solution selected)
  - o Conducting PMF analysis using different SEEDs at FPEAK zero
    - ▪ Solutions between 2 to 6 factors achieve convergence; steep drop from 1 to 2 factors implies solution likely has at least 2 factors; structure of residual seems to stagnate after 5 factors; scaled residuals between ±3 at 3 factors and beyond; too low concentrations of a factor in 5 and 6 factor solutions; uncentered correlations indicate splitting of one factor in 3 factor solution to 2 factors in 4 factor solution, both with an identical tracer nitrate; 3 factor solution show minimal variation with SEEDs in fraction of variance explained and MS and TS correlations at the 3 factor selection; so, fixing SEED as zero.
  - o Conducting PMF analysis using different FPEAKs between −1 and 1 at SEED zero
    - ▪ Structure in residual changes dramatically from 2 to 3 but marginally afterward; uncentered correlation coefficients between factors at number of factors (say, p) and p−1 show no evidence of factor splitting from 2 to 3 but evidence from 3 to 4 factors; 5 and 6 factor solutions have factor(s) that show low concentrations or unreasonable MS; 3 factor solutions show minimal variation with FPEAKs in fraction of variance explained; MS and TS correlations of the factors do not change with changing FPEAKs; fraction variance explained by two of the factors varies between 27–30% and 33–39% with varying FPEAKS, indicating that the solutions have minimal rotational ambiguity; thus no reason FPEAK other than zero preferable

- Monsoon 2017 organic-only PMF (two-factor solution selected)
    - Conducting PMF analysis using different SEEDs at FPEAK zero
        - Solutions between 2 to 6 factors achieve convergence; steep drop from 1 to 2 factors implies solution likely has at least 2 factors; scaled residuals within ±3 even at 2 factors; 3–6 factor solutions at different SEEDs generate "mixed" solutions, factors with unreasonable MS, weak MS and TS correlations; beyond 2 factors, minimal changes in the residual structure to warrant additional factors; multiple solutions with reasonable MS could exist at 2 factors; however, minimal variation with SEEDs in fraction of variance explained and MS and TS correlations at the 2 factor selection; so, fixing SEED as zero.
    - Conducting PMF analysis using different FPEAKs at SEED zero
        - 25th–75th scaled residuals for all m/zs are within ±3, even at 2 factors; negligible improvement in residual structure going from 2 to 3 factors and beyond; 3–6 factor solutions show factor splitting, unrealistic MS or weak tracer TS correlations; going back to two factors; pulling profile towards positive FPEAKs forces contributions at few m/zs to go closer to zero whereas pulling towards the negative FPEAKs generates nearly zero midday concentrations in the POA factor, which is not feasible; MS and TS correlations of the two factors do not change significantly with changing FPEAKs; fraction variance explained by one of the factors varies between 58–66% with varying FPEAKS, indicating that the solutions have minimal rotational ambiguity; thus no reason FPEAK other than zero preferable

- Monsoon 2017 organic-inorganic combined PMF (three-factor solution selected)
    - Conducting PMF analysis using different SEEDs at FPEAK zero
        - Solutions between 2 to 6 factors achieve convergence; steep drop of residual from 1 to 3 factors implies solution likely has at least 3 factors; structure of residual seems to stagnate after 3 factors; scaled residuals between ±3 at 3 factors and beyond; too low concentrations of a factor in 5 and 6 factor solutions; uncentered correlations indicate splitting of one factor in 3 factor solution to 2 factors in 4 factor solution, both with an identical tracer nitrate; 3 factor solution shows minimal variation with SEEDs in fraction of variance explained and MS and TS correlations at the 3 factor selection; so, fixing SEED as zero.
    - Conducting PMF analysis using different FPEAKs between −1 and 1 at SEED zero
        - Structure in residual changes dramatically from 2 to 3 factors but marginally afterward; uncentered correlation coefficients between factors at number of factors (say, p) and p−1 show no evidence of factor splitting from 2 to 3 factors but show evidence of splitting from 3 to 4 factors; 5 and 6 factor solutions have factor(s) that show low concentrations or unreasonable MS; 3 factor solutions show minimal variation with FPEAKs in fraction of variance explained; MS and TS correlations of the factors do not change with changing FPEAKs; fraction variance explained by two of the factors varies between 31–38% and 38–41% with varying FPEAKS, indicating that the solutions have minimal rotational ambiguity; thus no reason FPEAK other than zero preferable

- Winter 2018 organic-only PMF (two-factor solution selected)
    - Conducting PMF analysis using different SEEDs at FPEAK zero

- ▪ solutions between 2 to 6 factors achieve convergence; steep drop from 1 to 2 factors implies solution likely has at least 2 factors; 3–5 factor solution and large SEED values generate unreasonable MS; however, minimal variation with SEEDs in fraction of variance explained and MS and TS correlations at the 2 factor selection; so, fixing SEED as zero.
  - o Conducting PMF analysis using different FPEAKs between −1 and 1 at SEED zero
    - ▪ 25th–75th scaled residuals for all m/zs are within ±3, even at 2 factors; negligible improvement in residual structure going from 2 to 3 factors; Uncentered correlation coefficients between factors at a number of factors (say, p) and p−1 reject the possibility of some of the 3–6 factors; some mass spectral profiles at 3–6 factors not associated with any reference factor type; some have weak TS correlations with tracers; going back to two factors; pulling profile towards positive FPEAKs creates unreasonable zeros in MS whereas pulling towards the negative FPEAKs generates nearly zero midday concentrations in the POA factor, which is not feasible; thus no reason FPEAK other than zero preferable

- Winter 2018 organic-inorganic combined PMF (four-factor solution selected)
  - o Conducting PMF analysis using different SEEDs at FPEAK zero
    - ▪ Solutions between 2 to 6 factors achieve convergence; steep drop from 1 to 3 factors implies solution likely has at least 3 factors; 5 and 6 factor solutions have factor(s) that show unrealistic MS; 2 and 3 factor solutions' scaled residuals at inorganic m/zs exceeding ± 5; 4 factor solution shows scaled residual exceedance of ±3 at only 1 m/z nitrate 46; 4 factor solutions shows 2 solutions at SEEDs explored based on the fraction of variance explained and MS and TS correlations at the 4 factor selection; however, weak TS correlations at one of the solutions at a non-zero SEED; so, fixing SEED as zero.
  - o Conducting PMF analysis using different FPEAKs between −1 and 1 at SEED zero
    - ▪ 25th–75th scaled residuals for sulfate, and nitrate m/zs exceed ±4 for 2 and 3 factors but reduces dramatically for sulfate (within ± 3) and partially for nitrate (within ± 4) at 4 factors; 5 and 6 factor solutions have unrealistic MS; 4 factor solutions show variation with FPEAKs in fraction of variance explained and TS correlations only at extreme positive FPEAKs; high positive FPEAKs results in unrealistic MS; going towards negative FPEAKs reduces TS correlations due to unrealistically low concentrations; thus, no reason FPEAK other than zero preferable.

- Spring 2018 organic-only PMF (three-factor solution selected)
  - o Conducting PMF analysis using different SEEDs at FPEAK zero
    - ▪ solutions between 2 to 6 factors achieve convergence; steep drop from 1 to 2 factors implies solution likely has at least 2 factors; 2 factor solutions are invariant across varying SEEDs; 4–6 factor solutions generate unreasonable MS and show signs of factor "splitting"; 3 factor solution generates two solutions, one of which at a non-zero SEED has low TS correlations; so, fixing SEED as zero
  - o Conducting PMF analysis using different FPEAKs between −1 and 1 at SEED zero
    - ▪ 25th–75th scaled residuals for all m/zs are within ±3, even at 2 factors; negligible improvement in residual structure going from 2 to 3 factors; separation justified due to improvement in MS and TS correlations; 4–6 factor solutions are "split" factors based on the uncentered correlation

coefficients between factors at a number of factors (say, p) and p−1 and identical TS correlations; some mass spectral profiles at 5–6 factors not associated with any reference factor type; some have weak TS correlations with tracers; at three factors, pulling profile towards large positive FPEAKs creates unreasonable zeros in MS resulting in apparent similarity of the HOA and BBOA profiles whereas pulling towards large negative FPEAKs generates very low TS correlations with tracers sulfate and nitrate for the OOA factor, which is not feasible; no reason FPEAK other than zero preferable

- Spring 2018 organic-inorganic combined PMF (four-factor solution selected)
    - o Conducting PMF analysis using different SEEDs at FPEAK zero
        - ▪ Solutions between 2 to 6 factors achieve convergence; steep drop from 1 to 3 factors implies solution likely has at least 3 factors; 25th–75th scaled residuals for multiple m/zs exceeding ± 3 in 3 factor solutions; 4 factor solution shows no such exceedance; 5 and 6 factor solutions have factor(s) that show factor splitting; 4 factor solutions show only 1 solution at SEEDs explored based on the fraction of variance explained and MS and TS correlations at the 4 factor selection; so, fixing SEED as zero.
    - o Conducting PMF analysis using different FPEAKs between −1 and 1 at SEED zero
        - ▪ Scaled residuals dictate at least 4 factors; 5 and 6-factor solutions show signs of factor splitting; at negative FPEAKs, 4-factor solutions show low TS correlations for the AS-OOA factor; minimal variation with FPEAKs in the fraction of variance explained and TS correlations for positive FPEAKs; no reason FPEAK other than zero preferable.

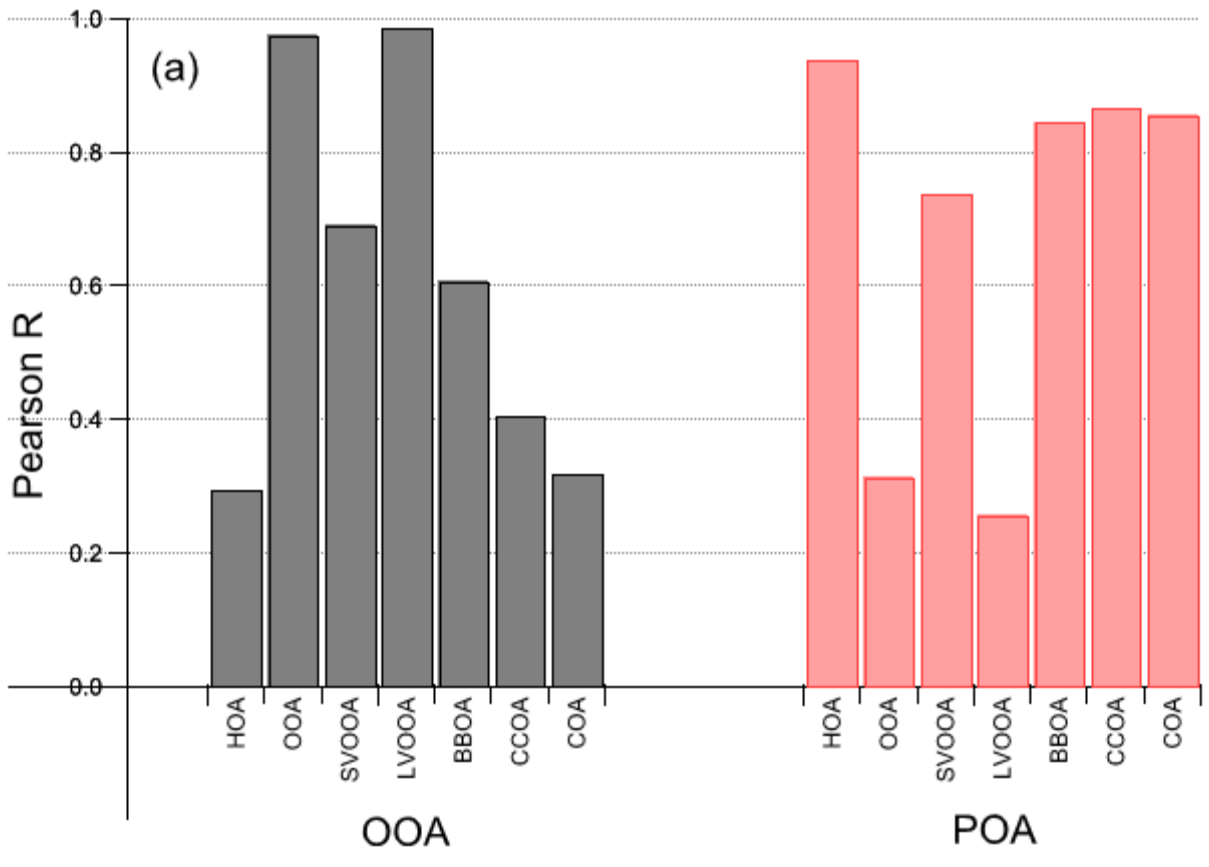
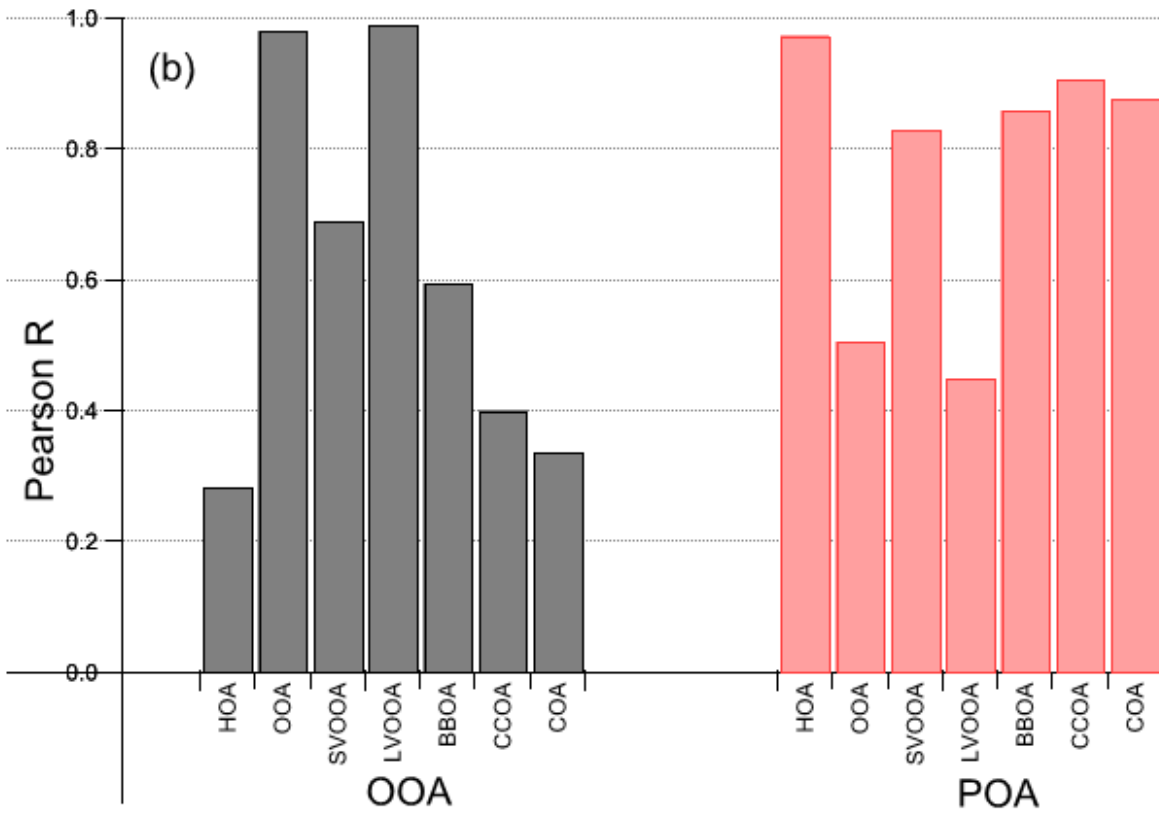
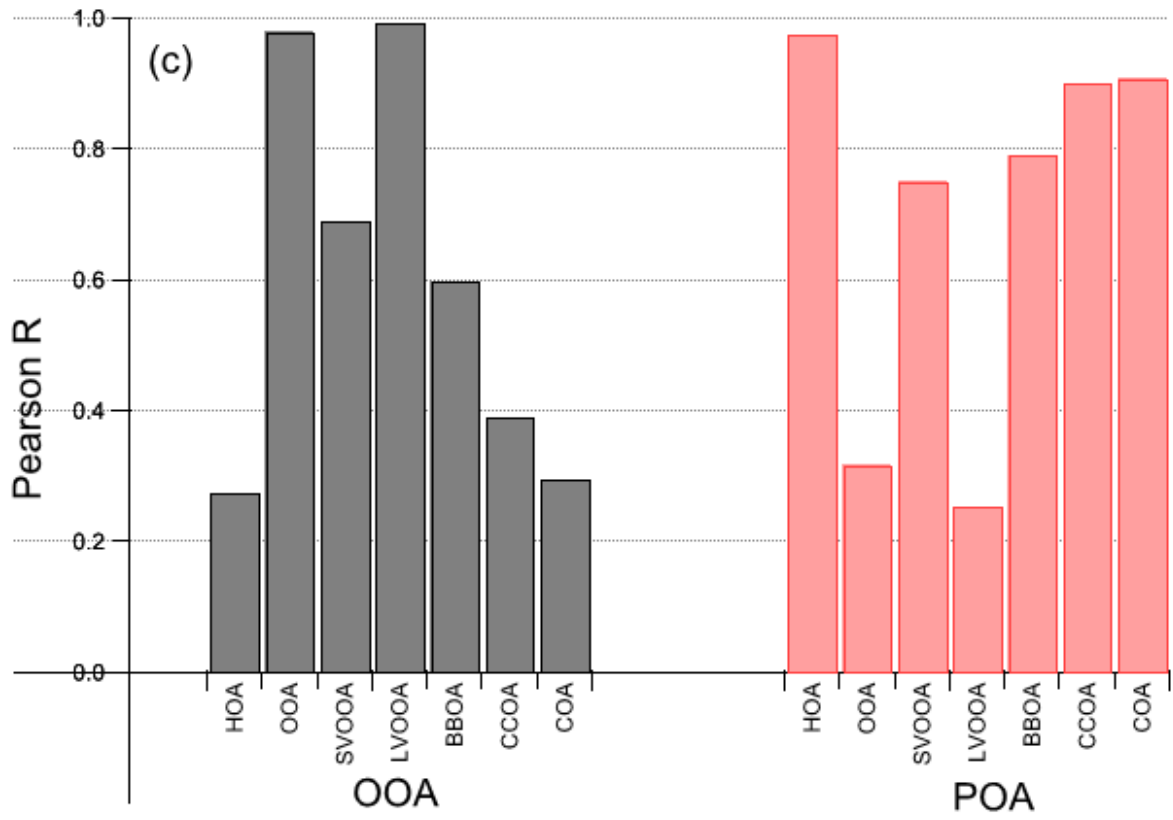
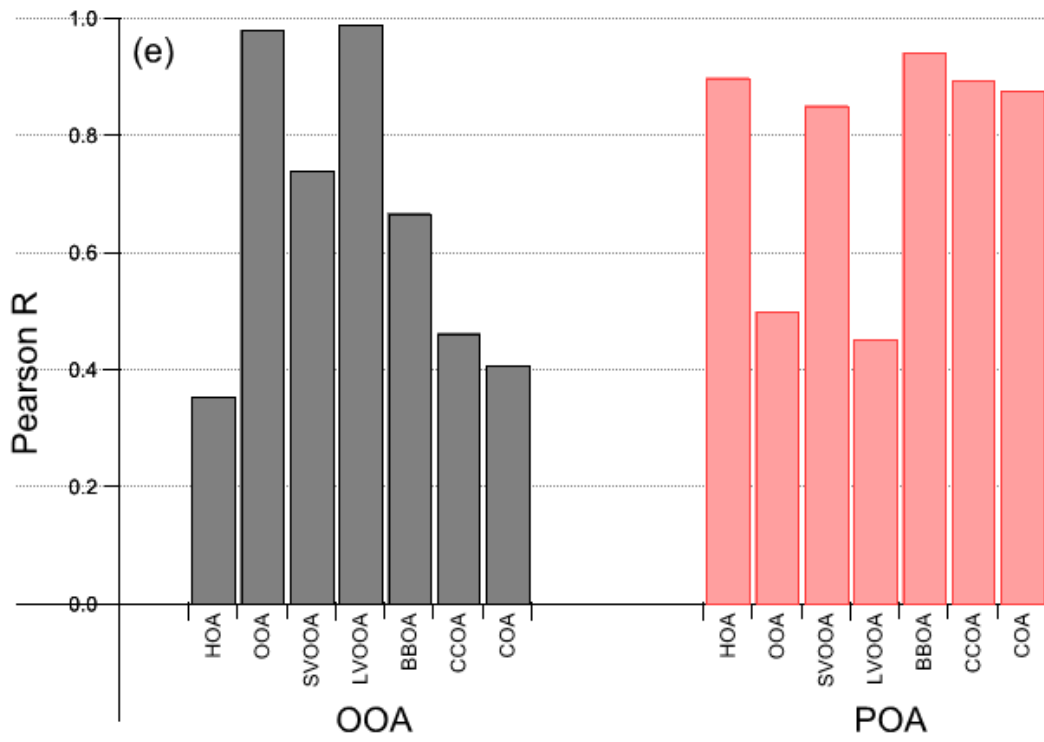
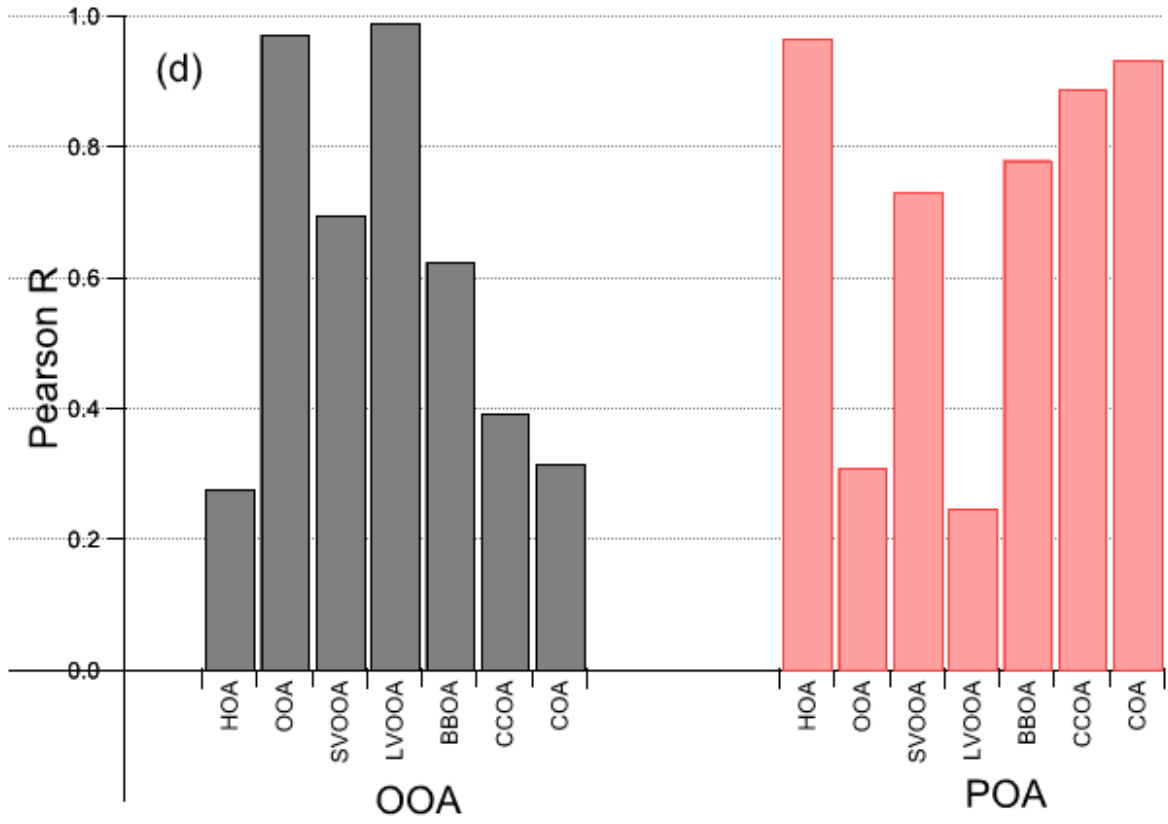
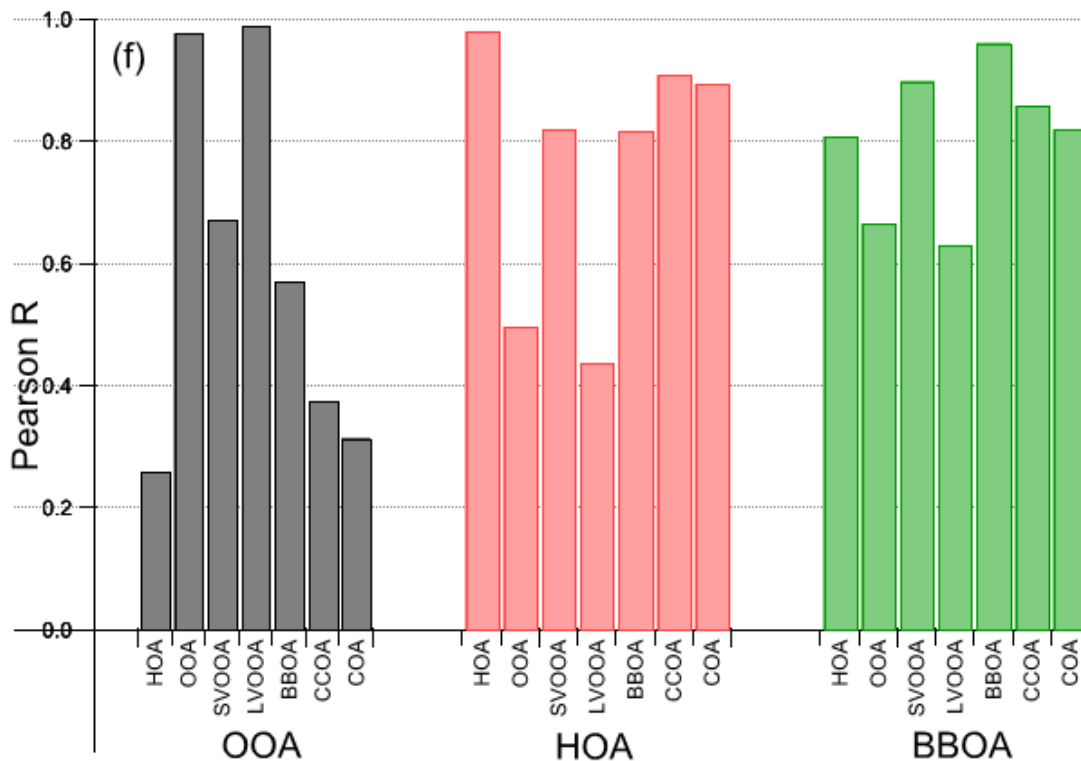



Figure S1 shows the organic-only PMF factors' MS correlations with reference profiles in the order: (a) winter 2017, (b) spring 2017, (c) summer 2017, (d) monsoon 2017, (e) winter 2018, and (f) spring 2018. Clearly, all organic-only PMF factors show strong correlations with at least one reference profile.

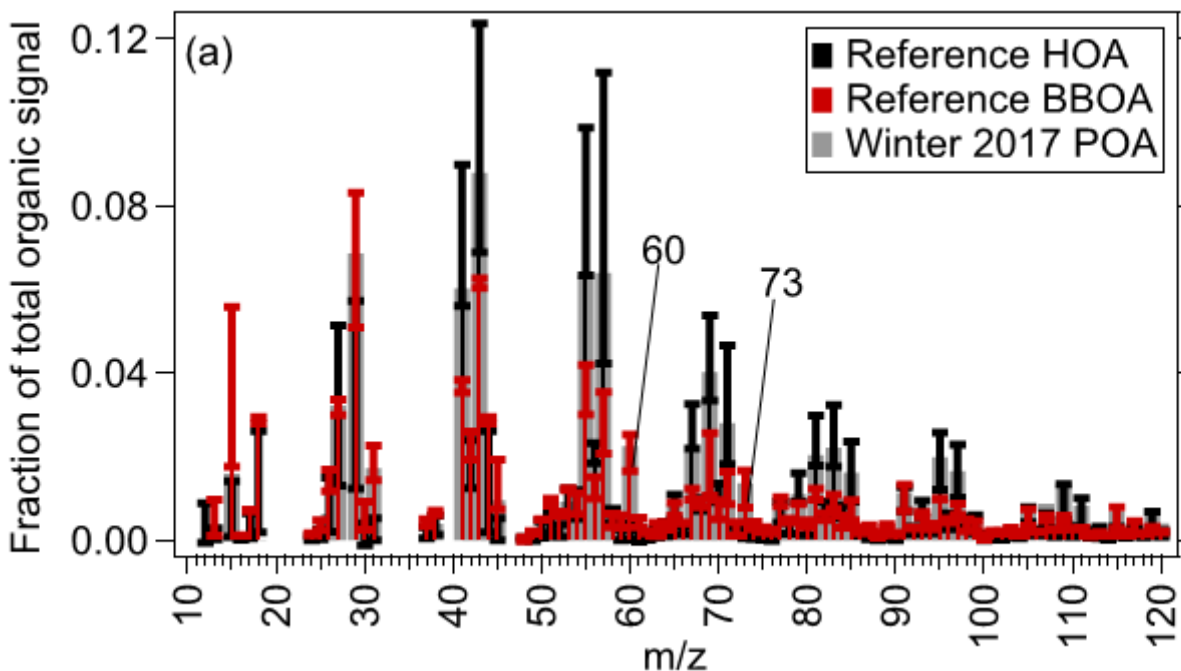
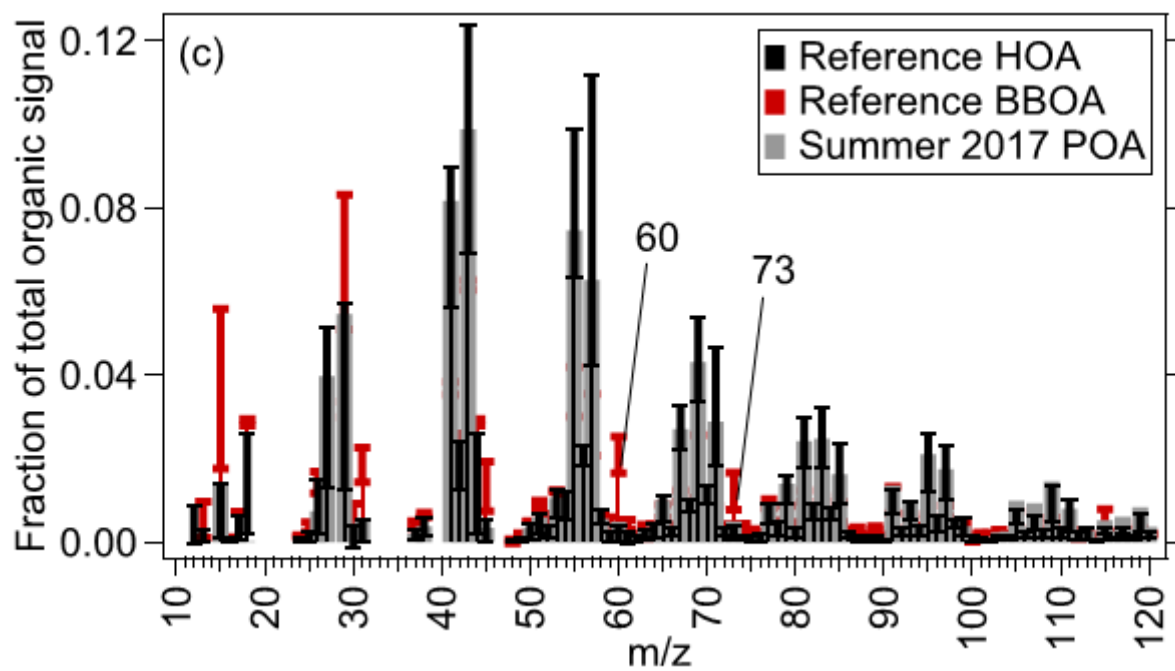
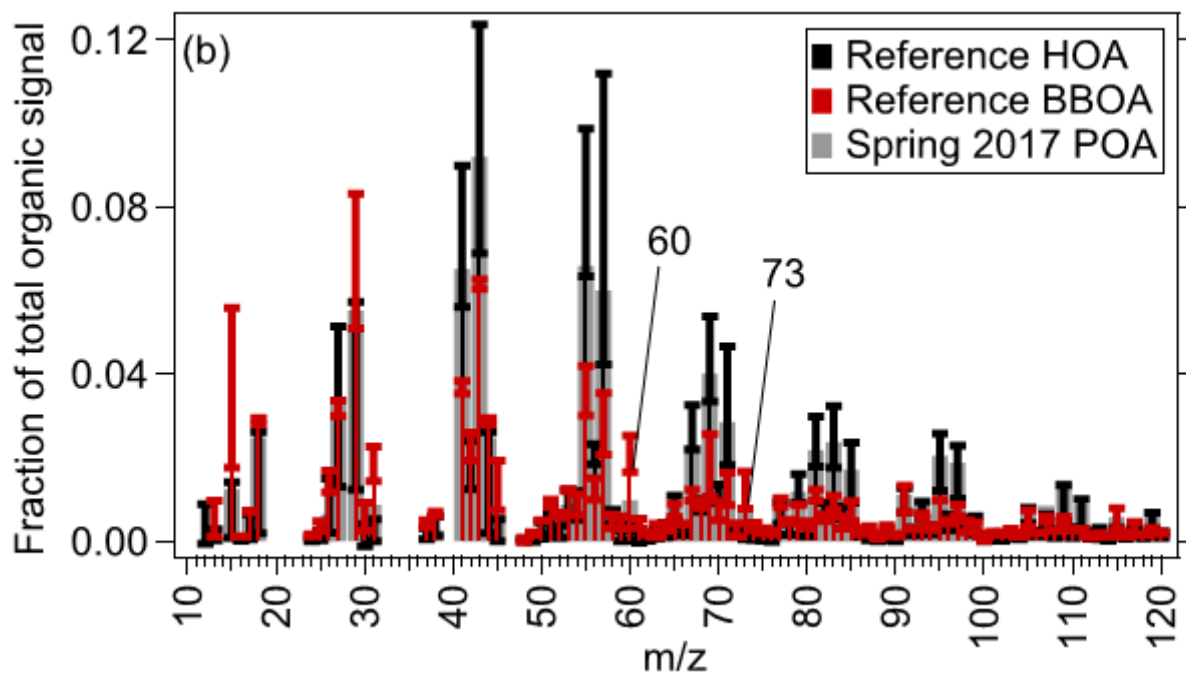
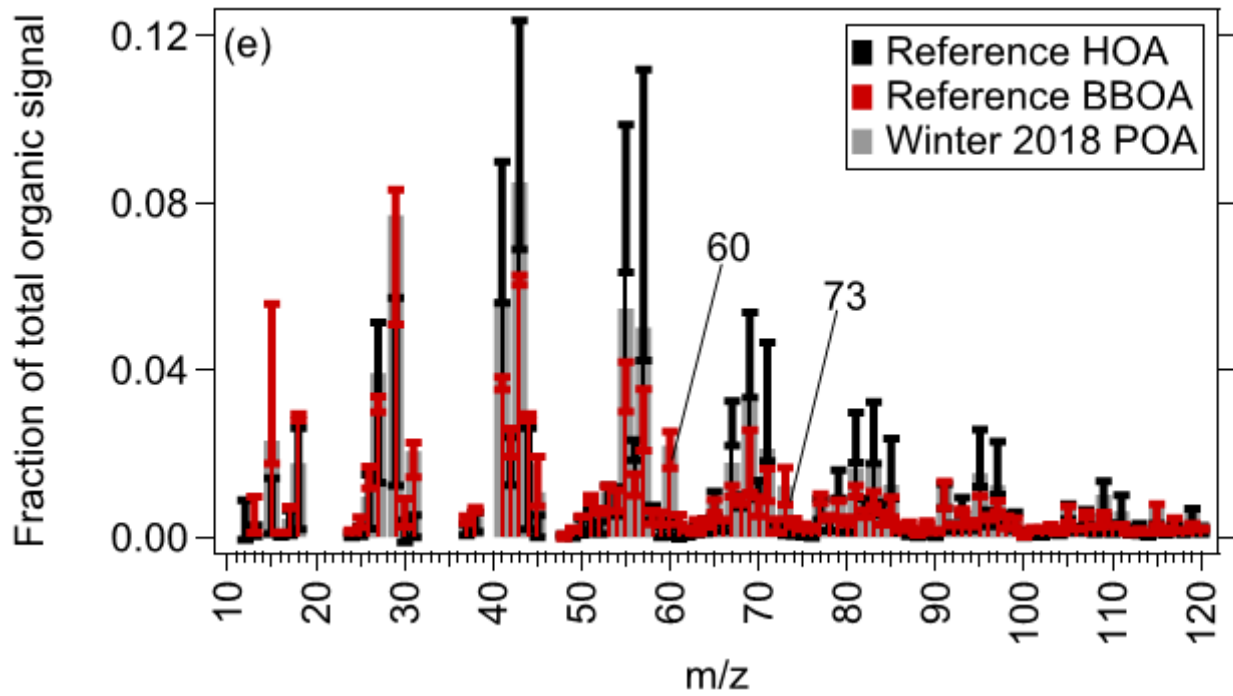
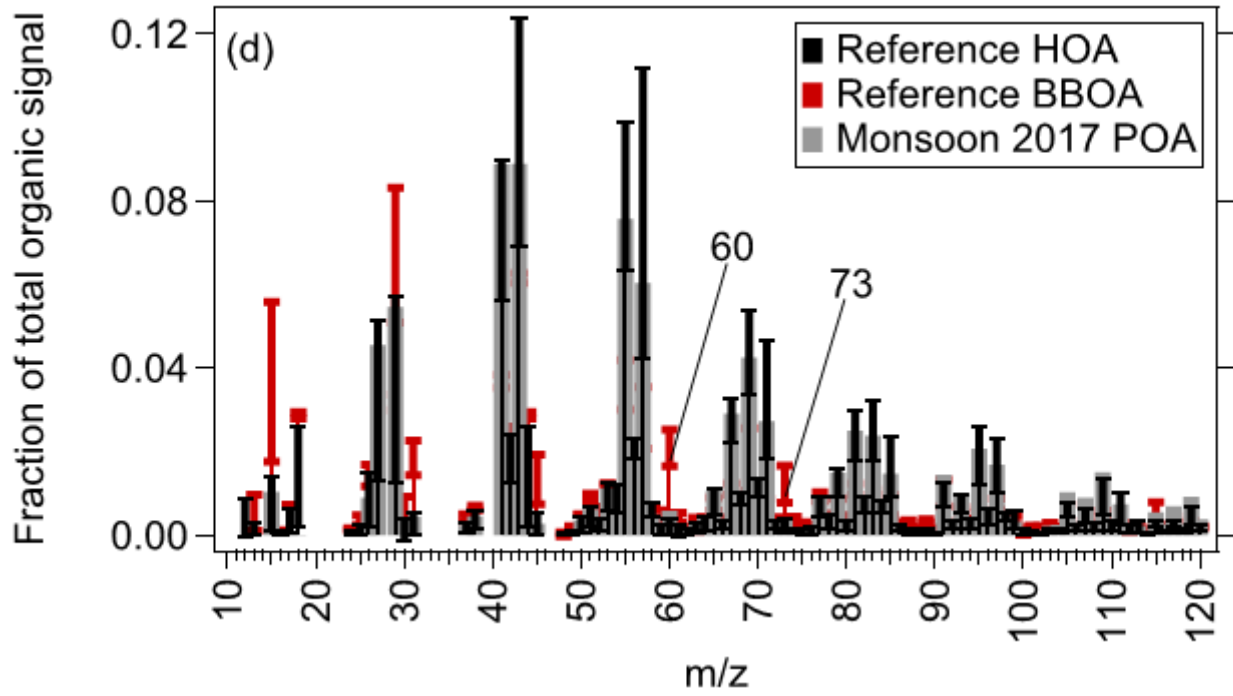
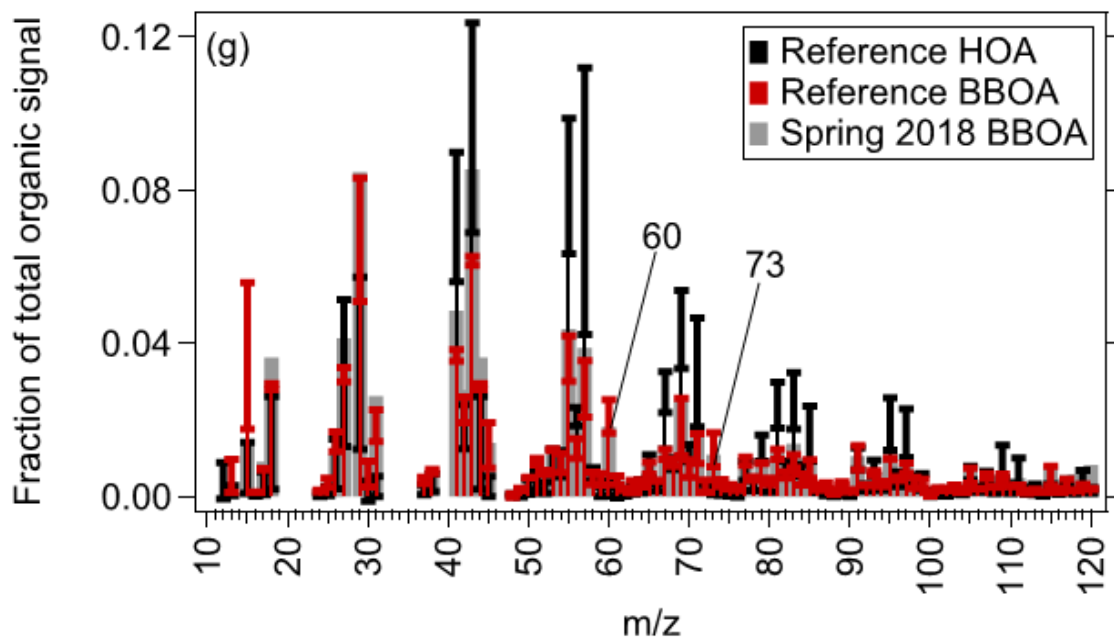
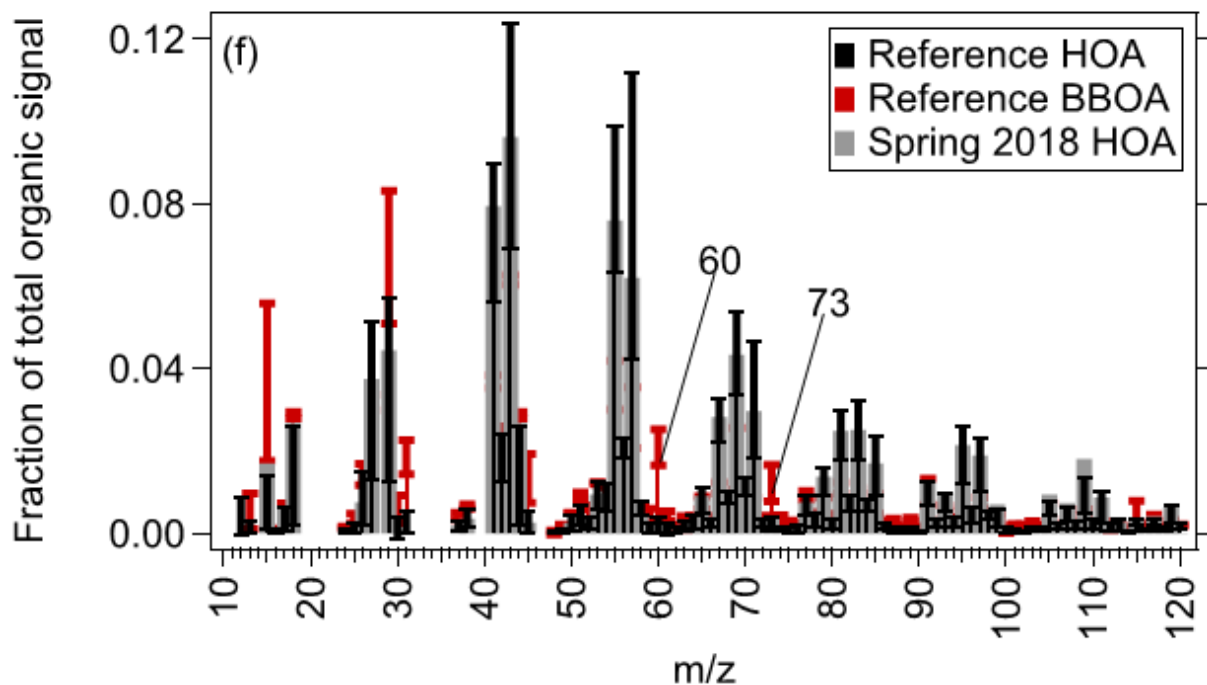



Figure S2 shows the average mass spectrum of organic-only PMF mixed hydrocarbon-like organic aerosol (HOA)-biomass burning organic aerosol (BBOA) (POA) factor in different seasons, which is similar to the reference HOA and BBOA factors. The whiskers in the graphs represent ±1 standard deviation of the reference spectra. The comparison of PMF factor MS with reference profiles is shown in the order: (a) winter 2017 POA, (b) spring 2017 POA, (c) summer 2017 POA, (d) monsoon 2017 POA, (e) winter 2018 POA, (f) spring 2018 HOA, and (g) spring 2018 BBOA. The profiles show the influence of both HOA and BBOA aerosols.

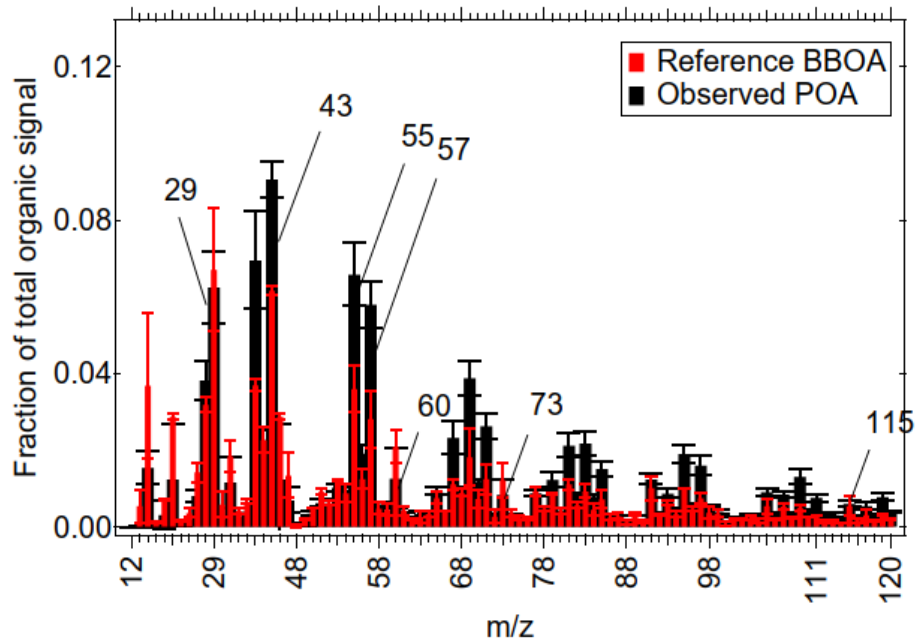



Figure S3 This figure shows the average mass spectrum of the organic-only PMF primary organic aerosol (POA) factor. At m/z 29, 60, 73 and 115, observed POA signals are in line with the reference biomass burning organic aerosol (BBOA) factor.

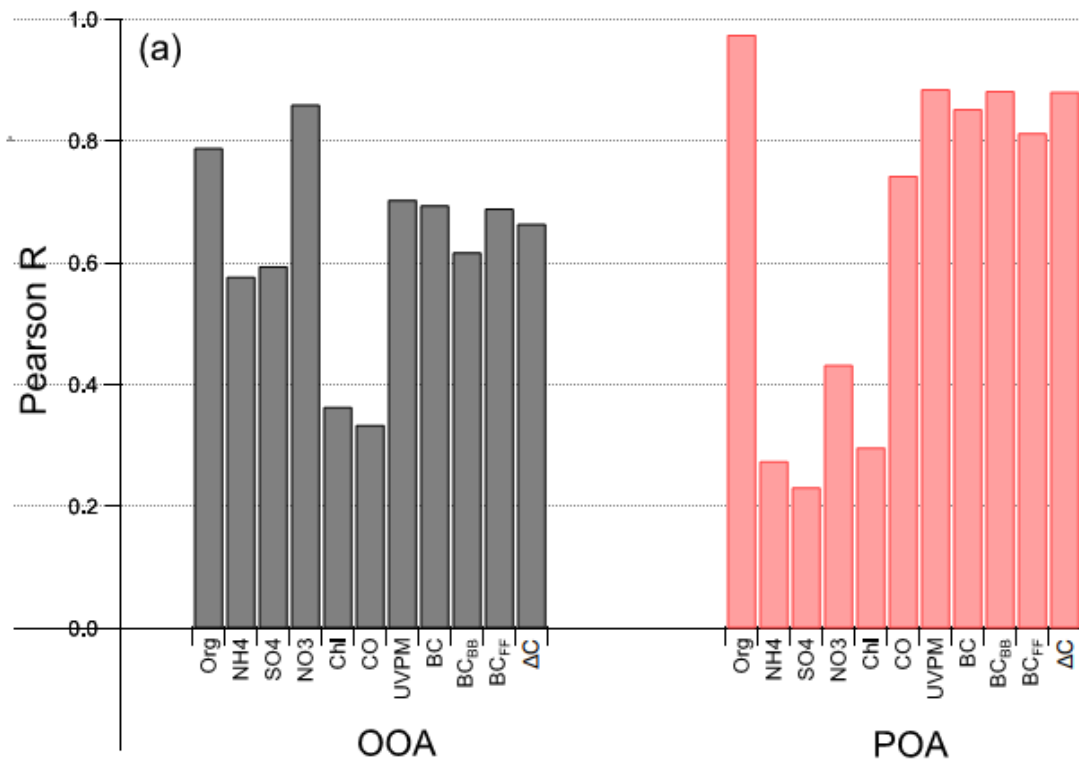
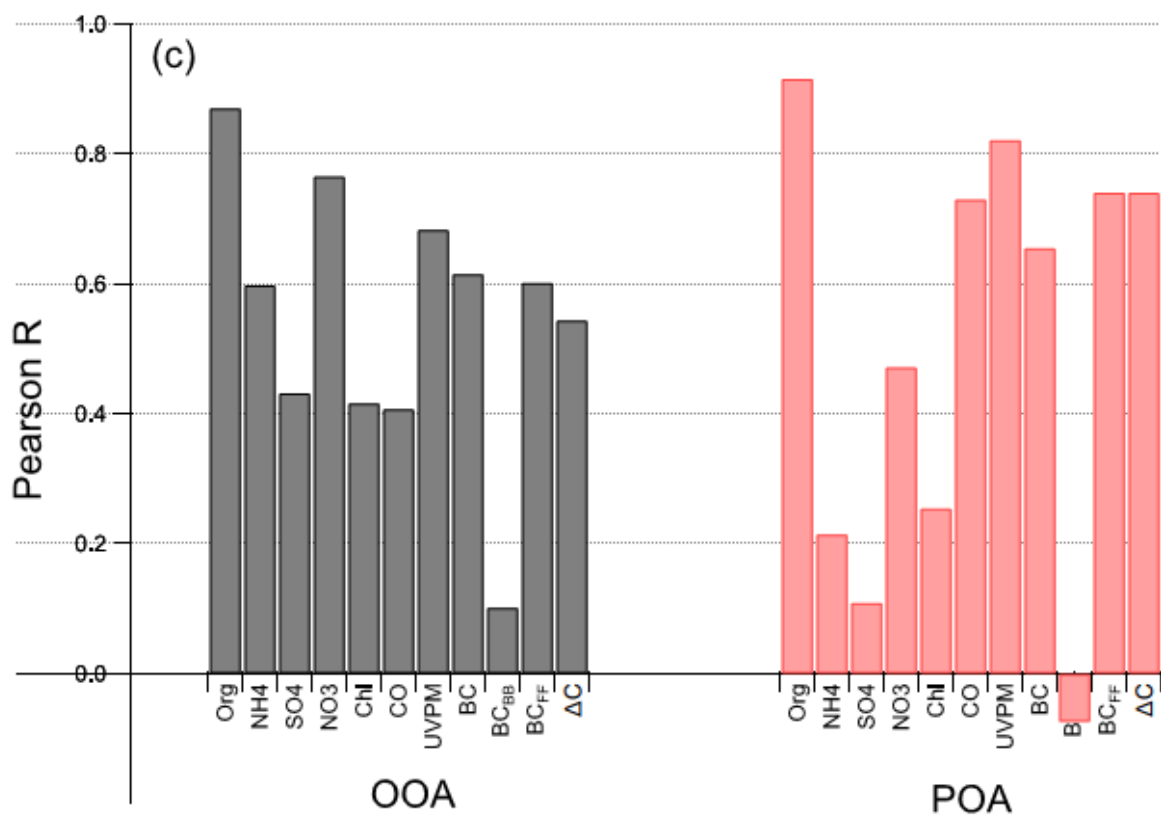
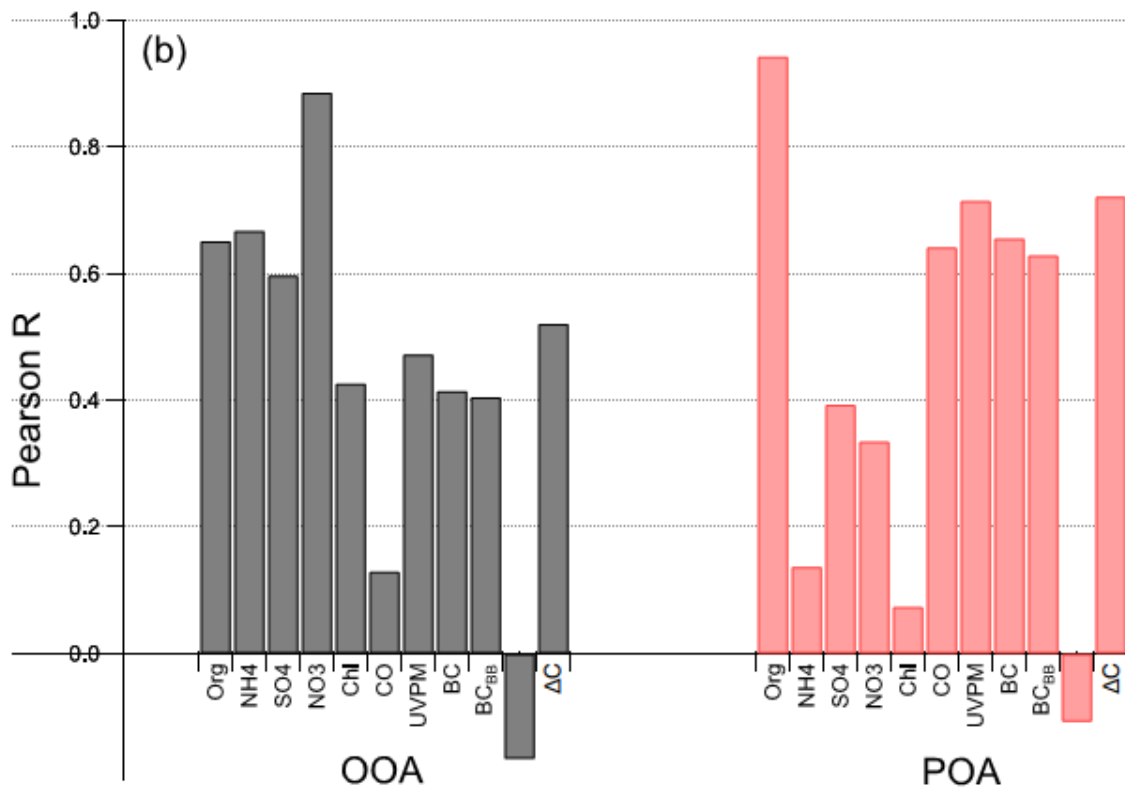
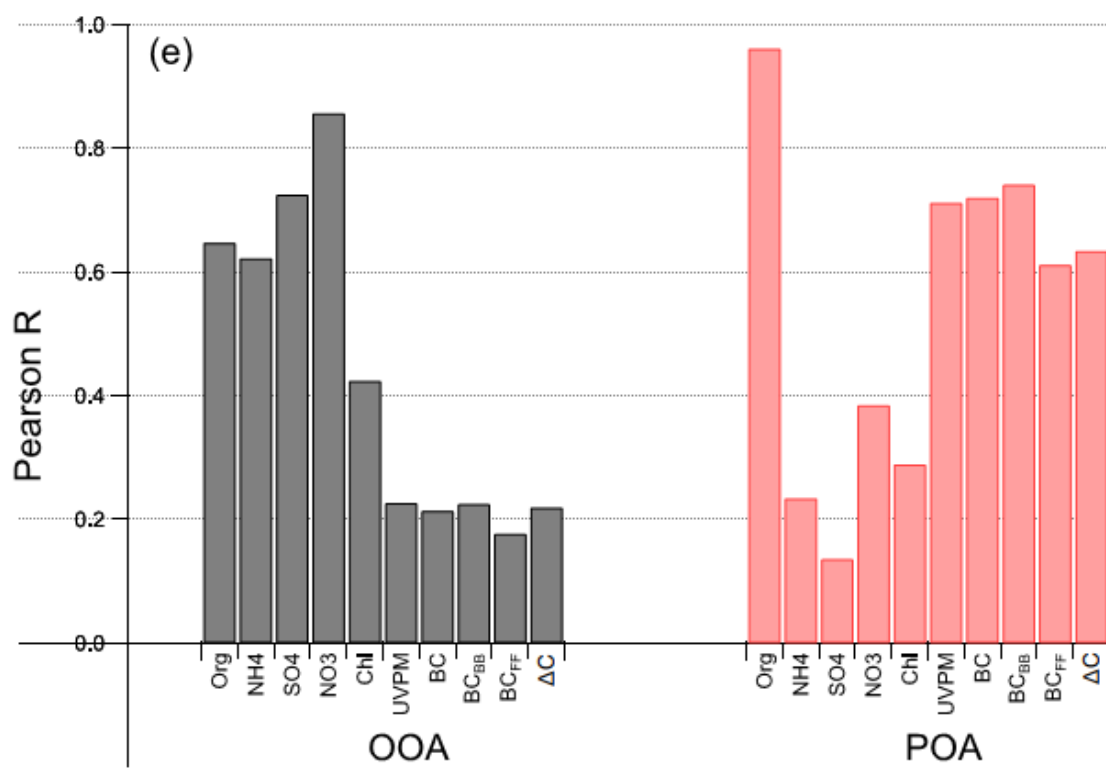
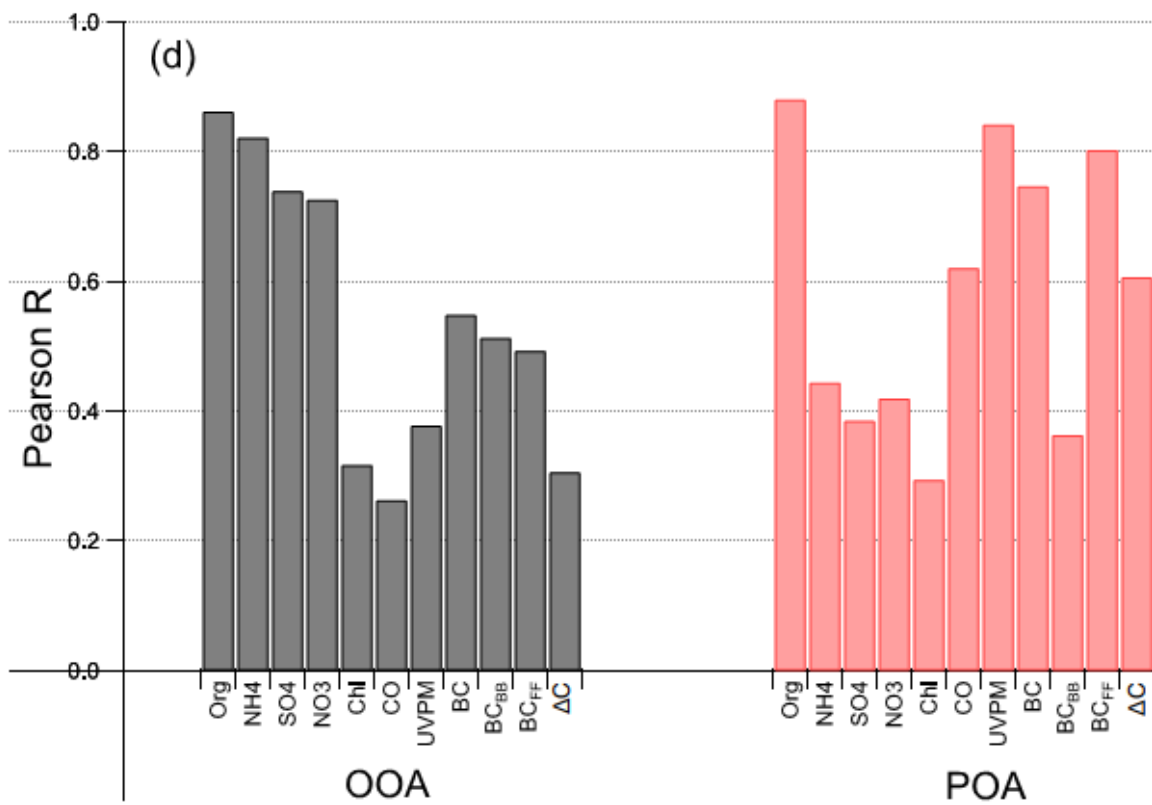
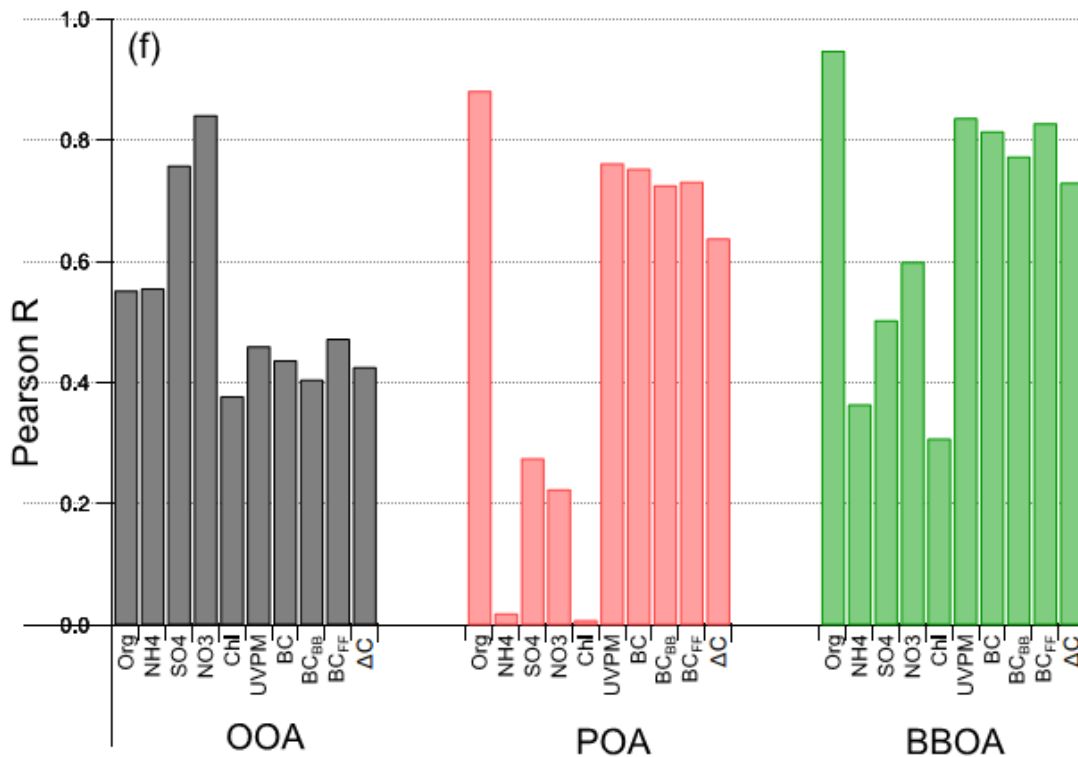



Figure S4 shows the time series correlations of organic-only PMF factors with tracer species in different seasons. The comparison of PMF factors with tracers is shown in the order: (a) winter 2017, (b) spring 2017, (c) summer 2017, (d) monsoon 2017, (e) winter 2018, and (f) spring 2018.

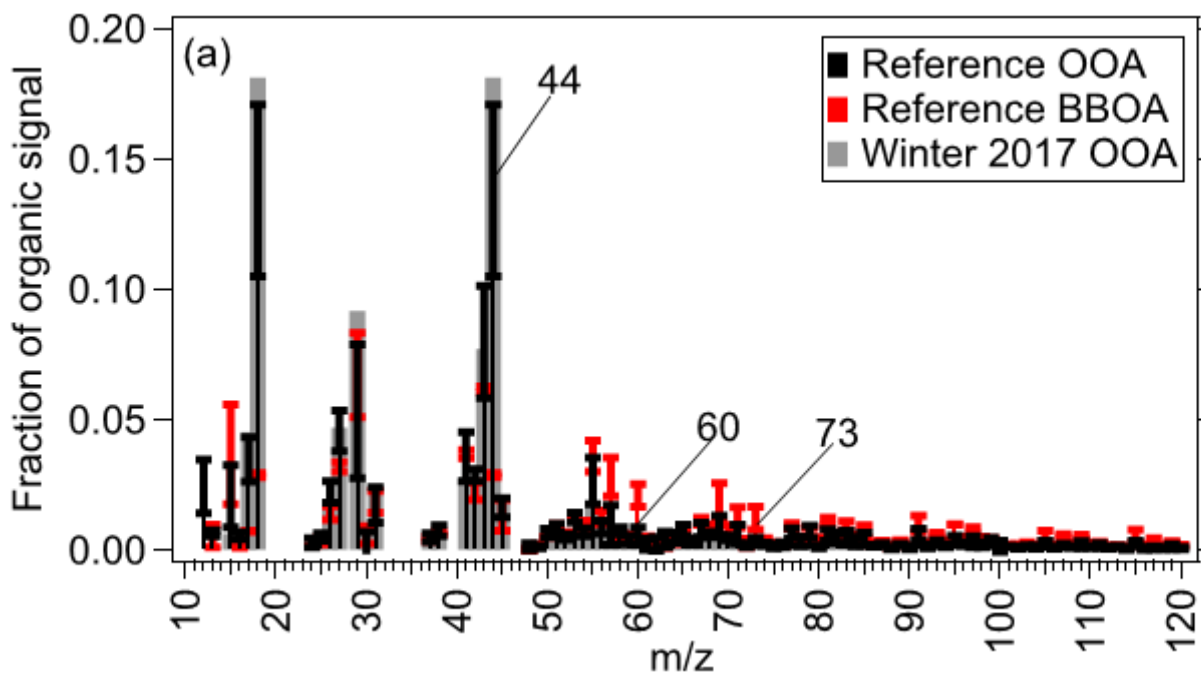
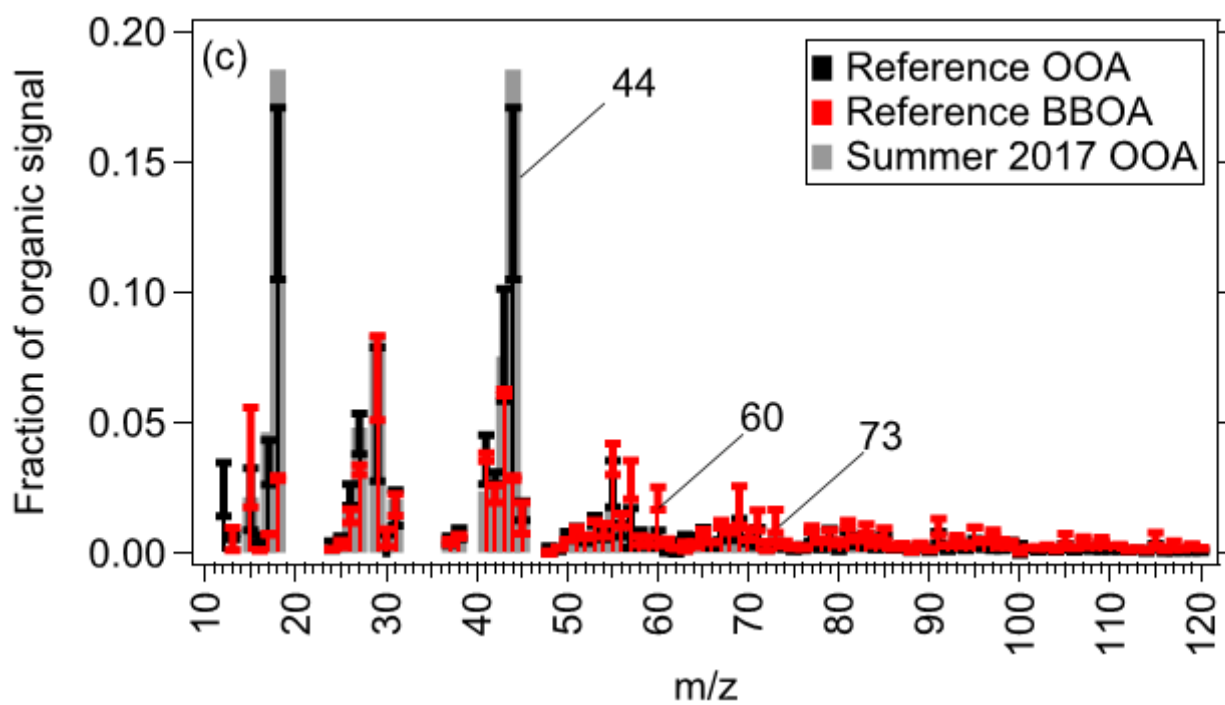
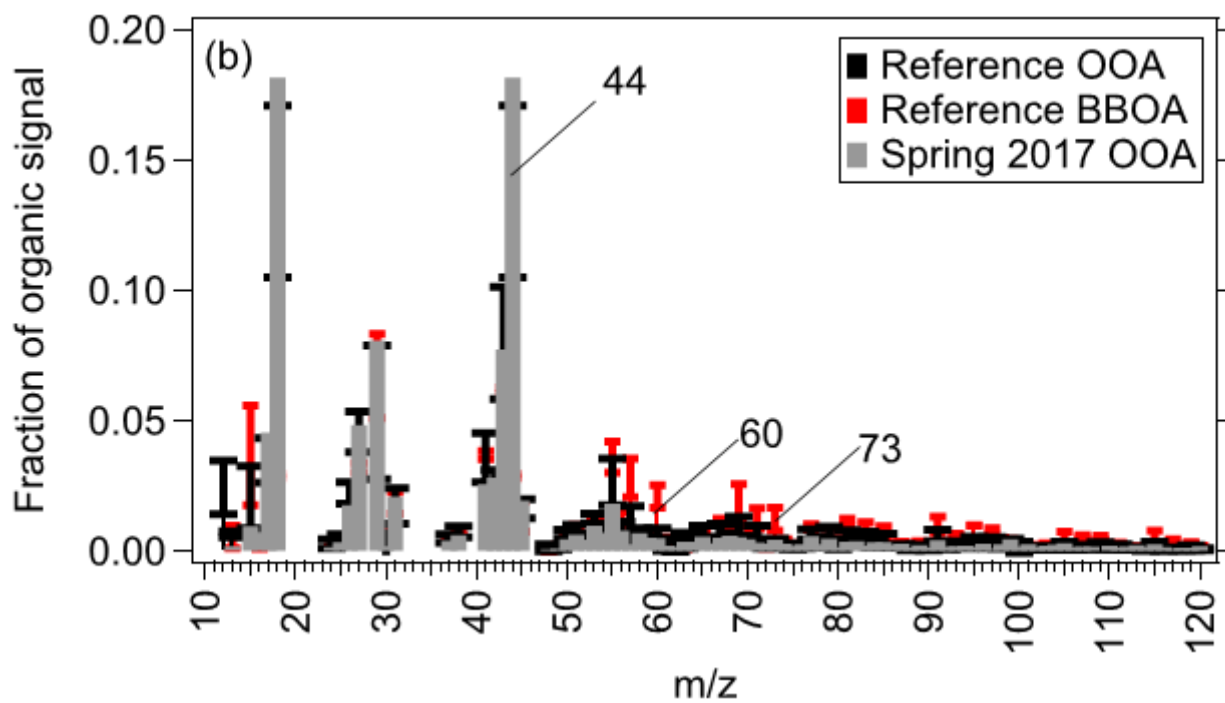
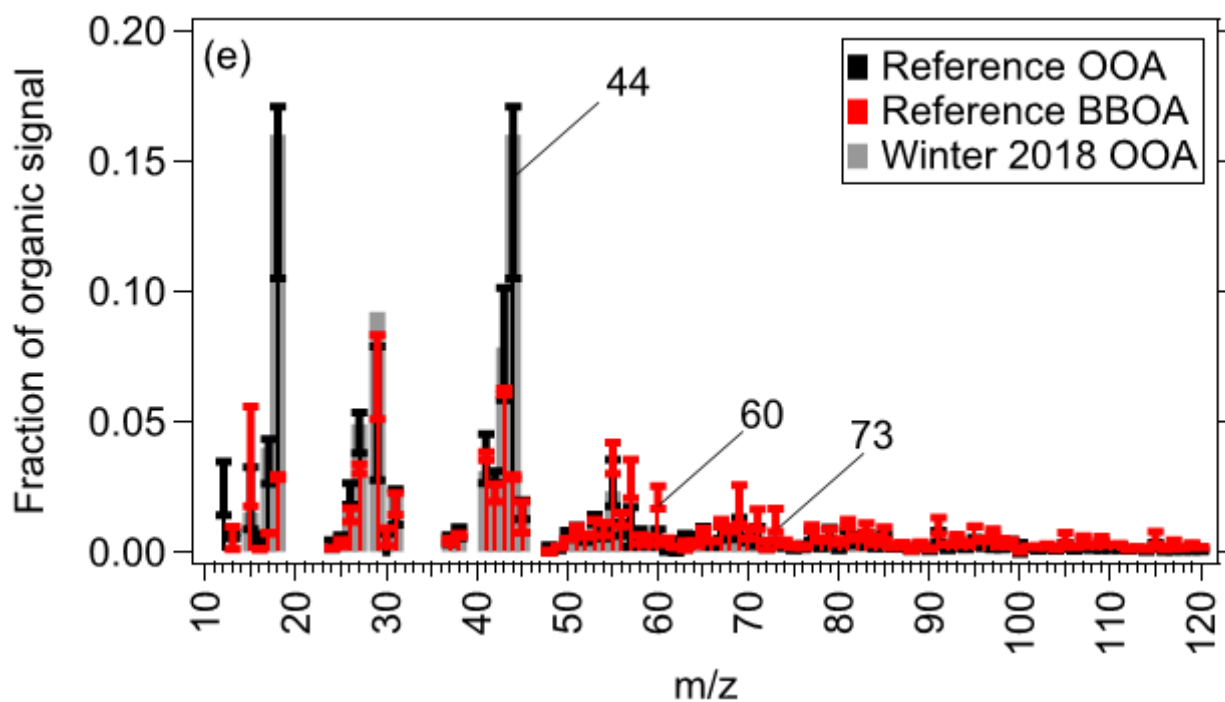
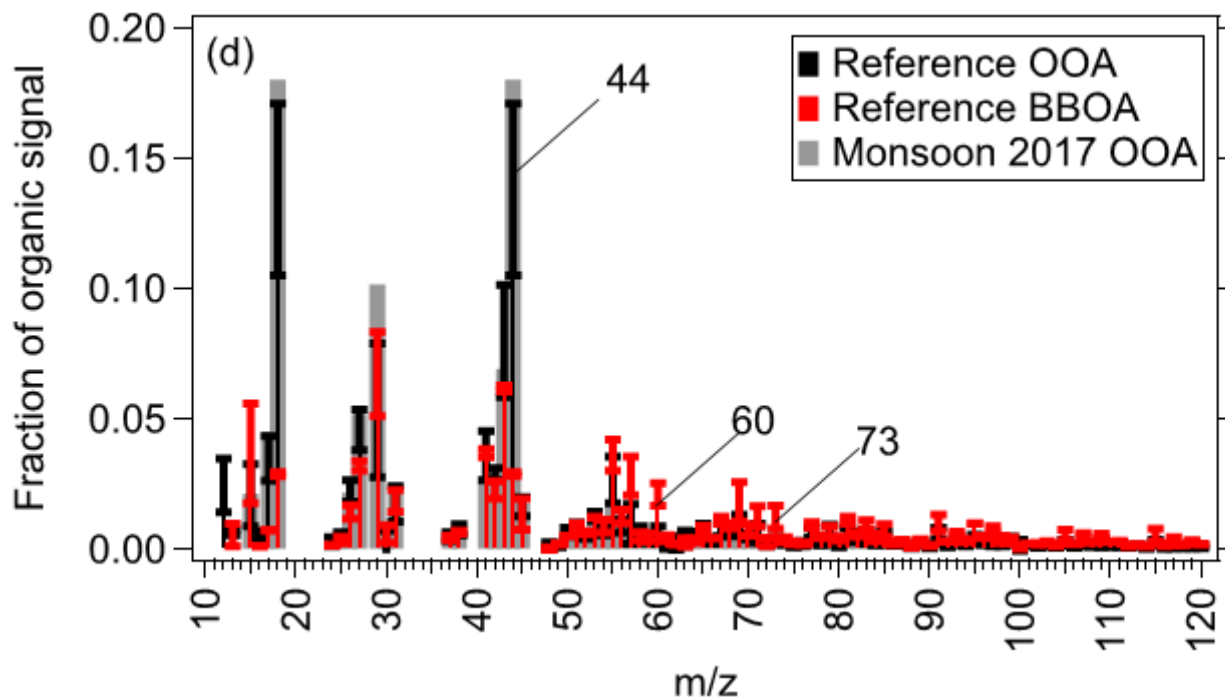
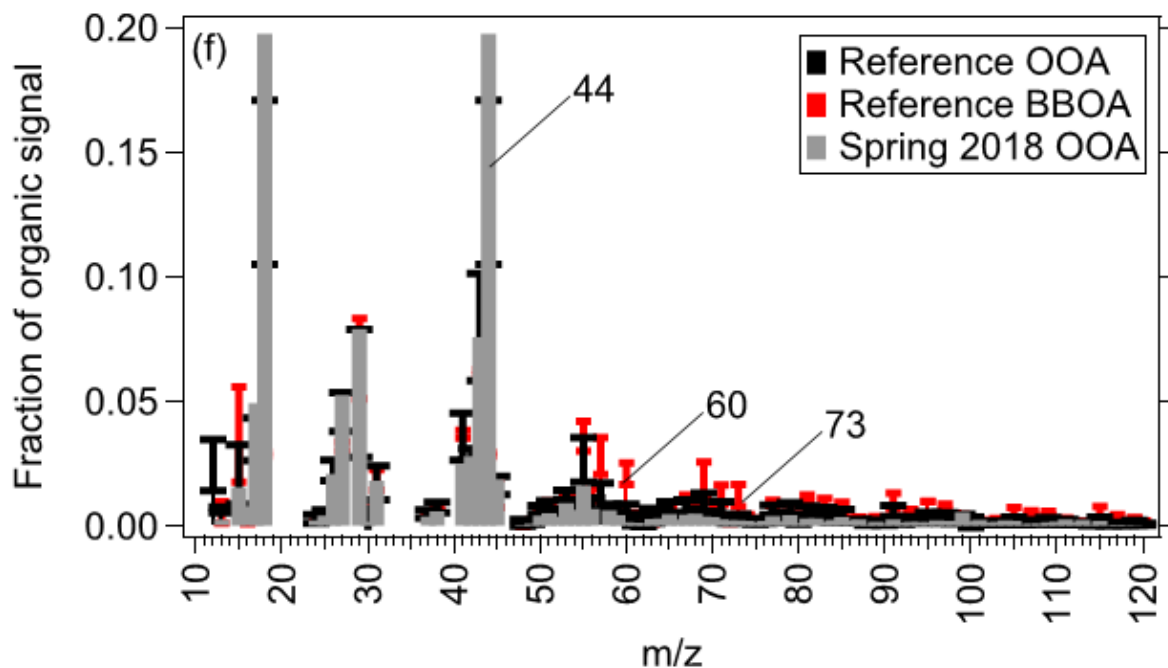



Figure S5 shows the average mass spectrum of organic-only PMF oxidized organic aerosol (OOA) factor in different seasons, which is similar to the reference OOA factor. The whiskers in the graphs represent ±1 standard deviation of the reference spectra. The comparison of PMF factor MS with reference profiles is shown in the order: (a) winter 2017, (b) spring 2017, (c) summer 2017, (d) monsoon 2017, (e) winter 2018, and (f) spring 2018. MS in most seasons are marked by a higher contribution at m/z 44 than the reference OOA profile, pointing to the highly oxidized nature of aerosols.

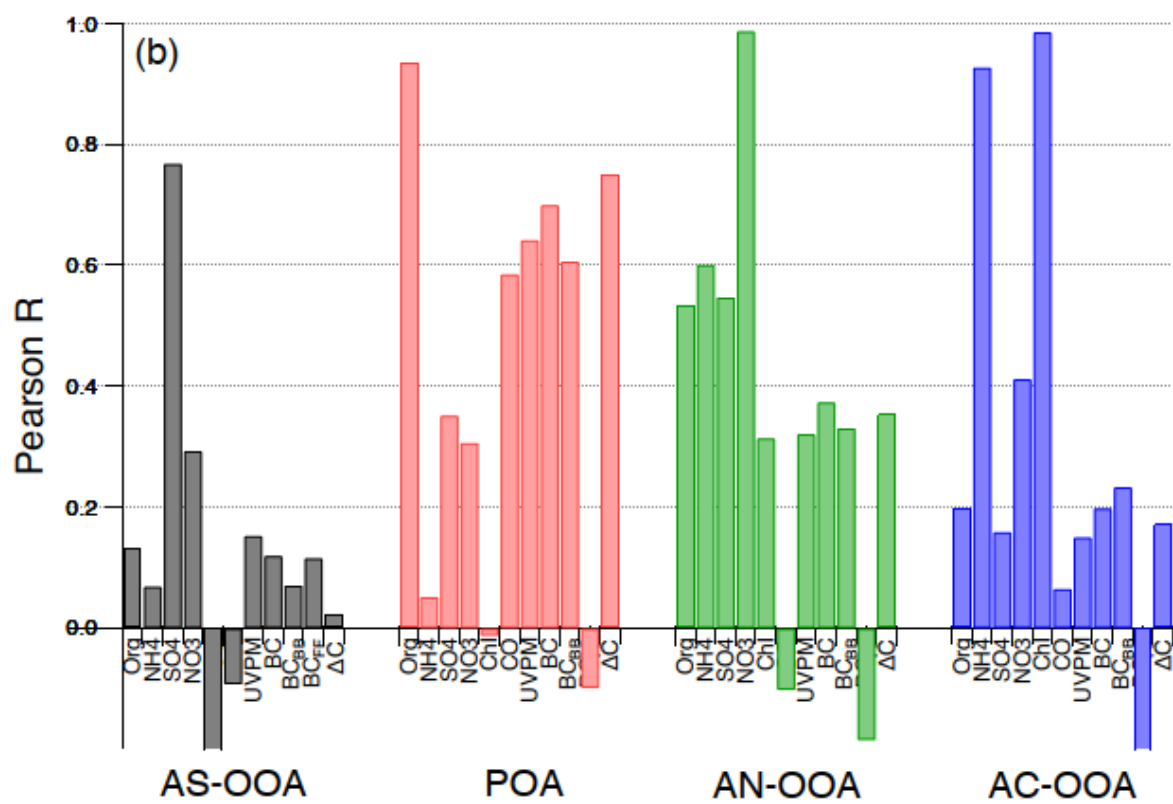
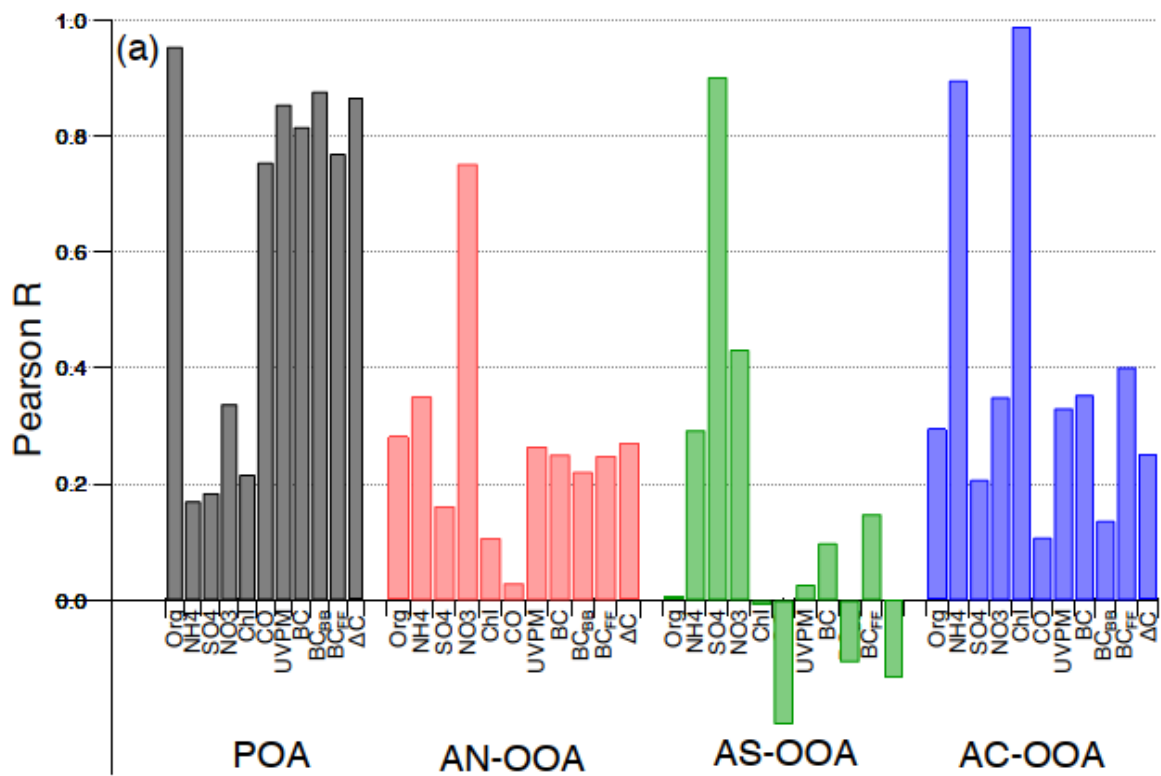
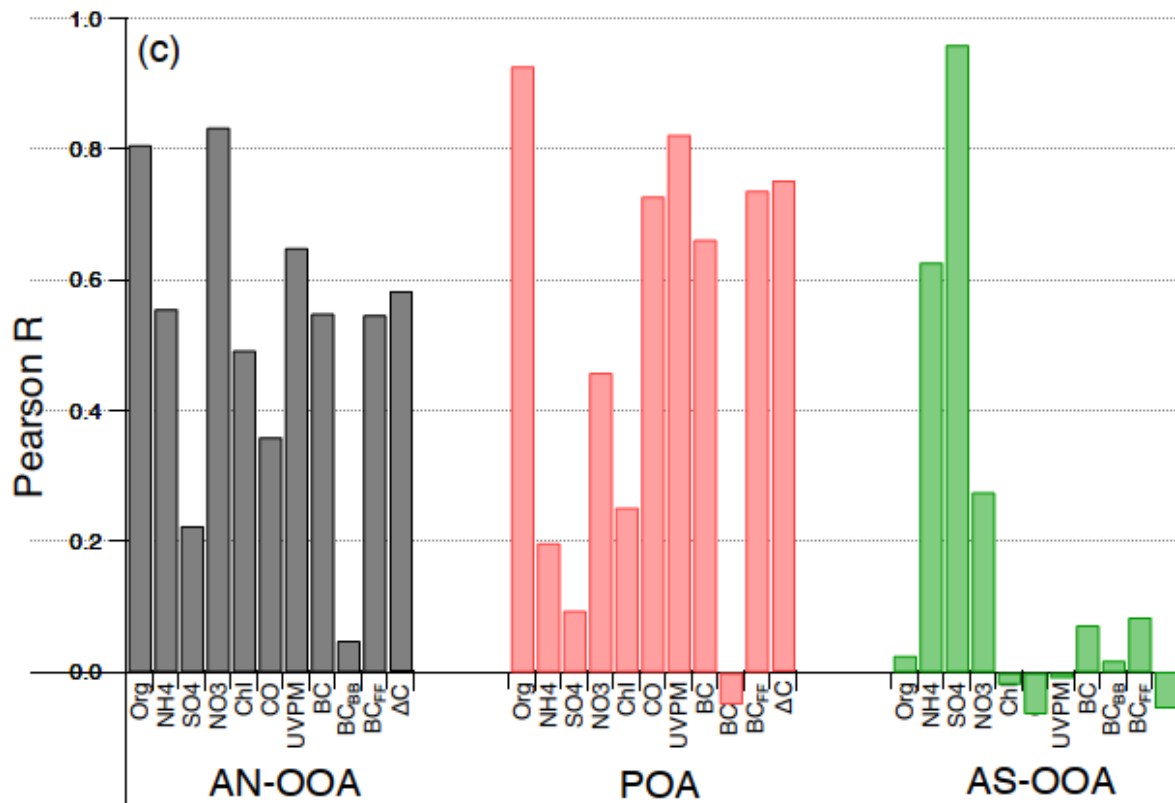
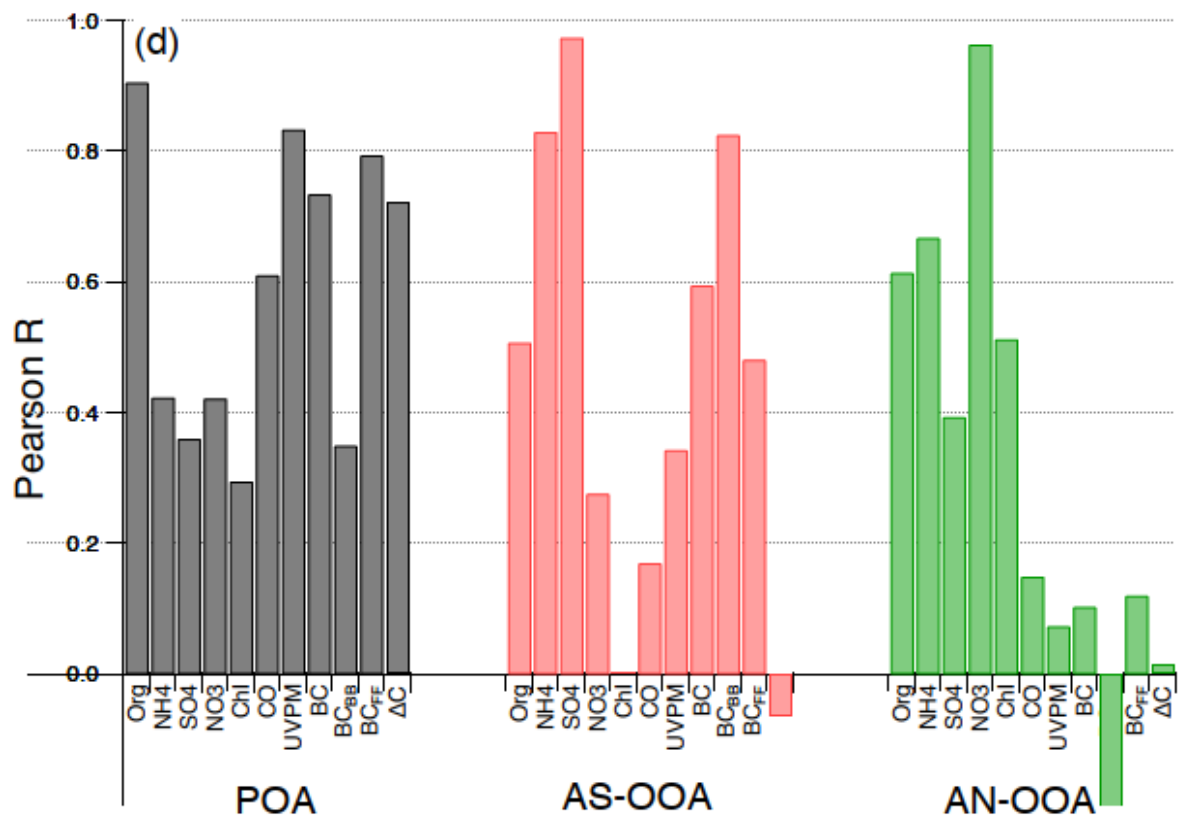
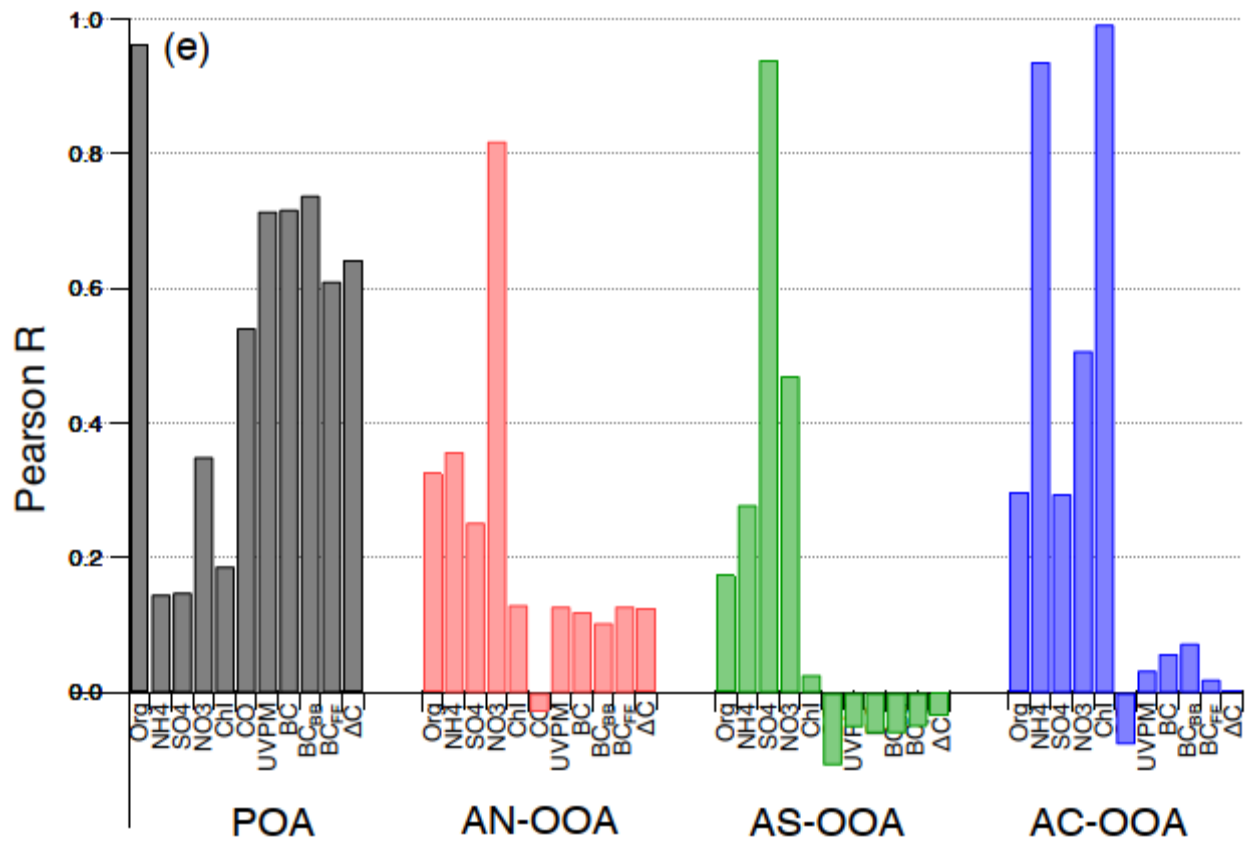
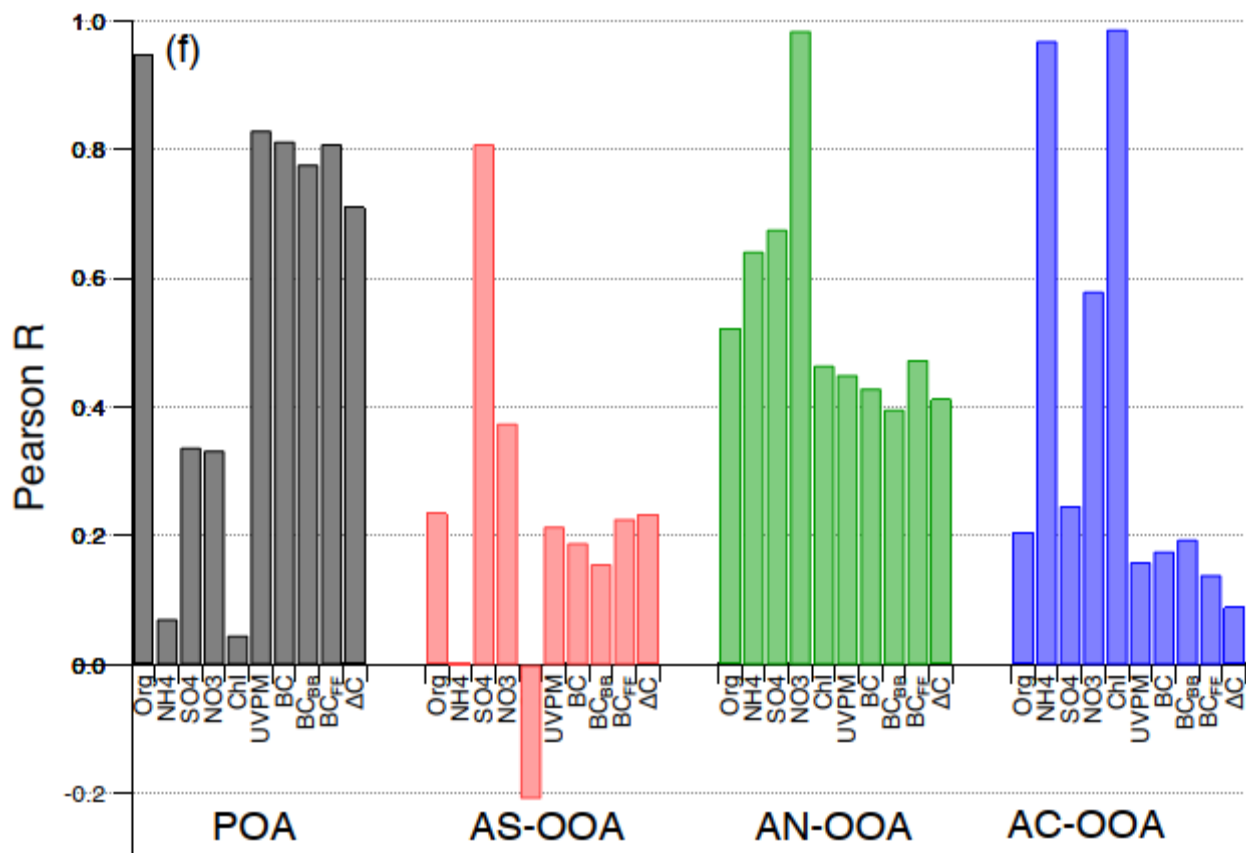



Figure S6 shows the time series correlations of combined organic-inorganic PMF factors with tracer species in different seasons. The comparison of PMF factors with tracers is shown in the order: (a) winter 2017, (b) spring 2017, (c) summer 2017, (d) monsoon 2017, (e) winter 2018, and (f) spring 2018. Clearly, AC-OOA (or, AC) does not correlate with biomass burning tracers BC_{BB} and ΔC.

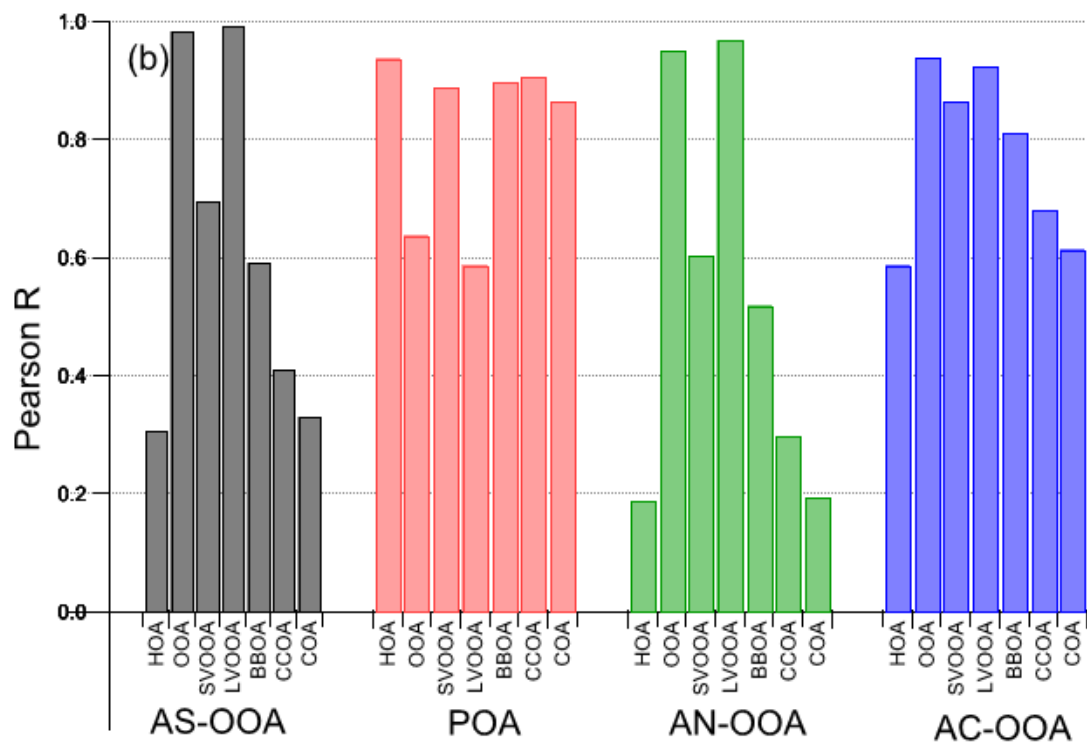
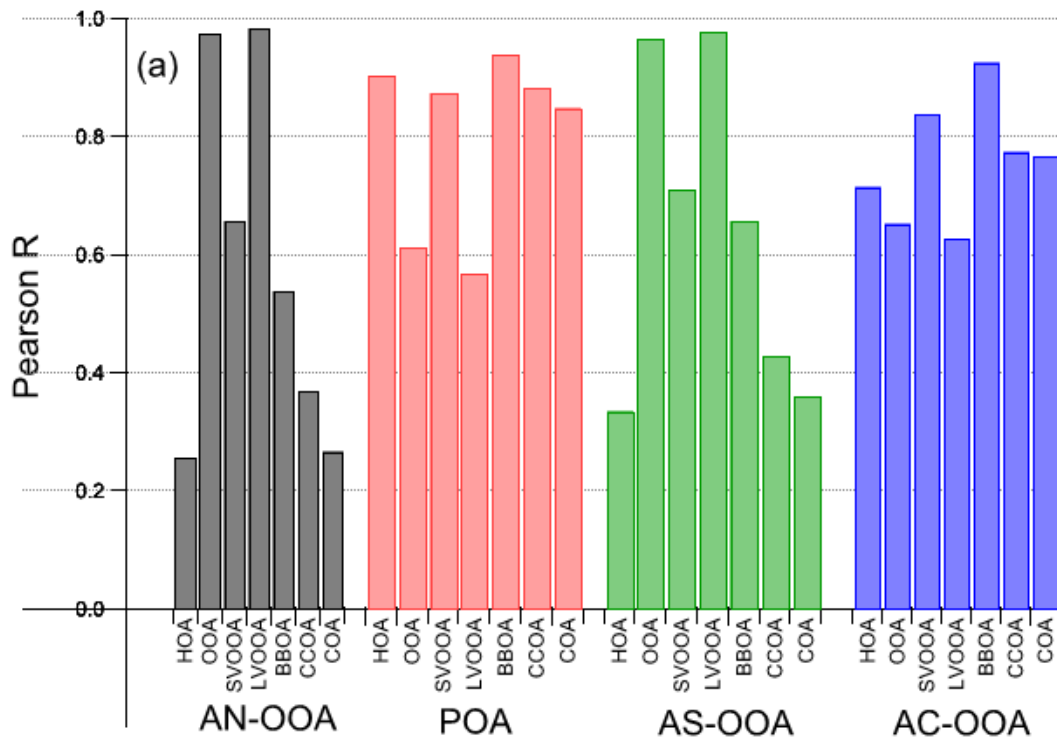
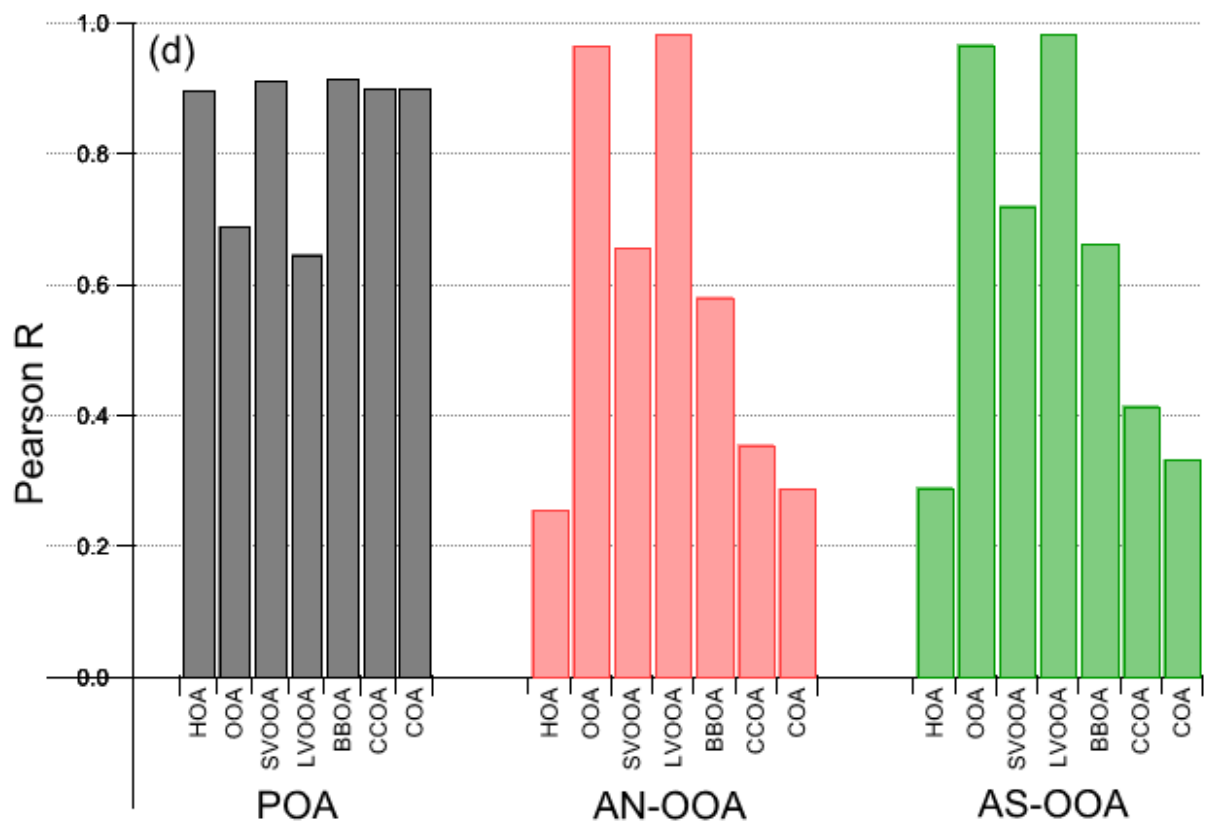
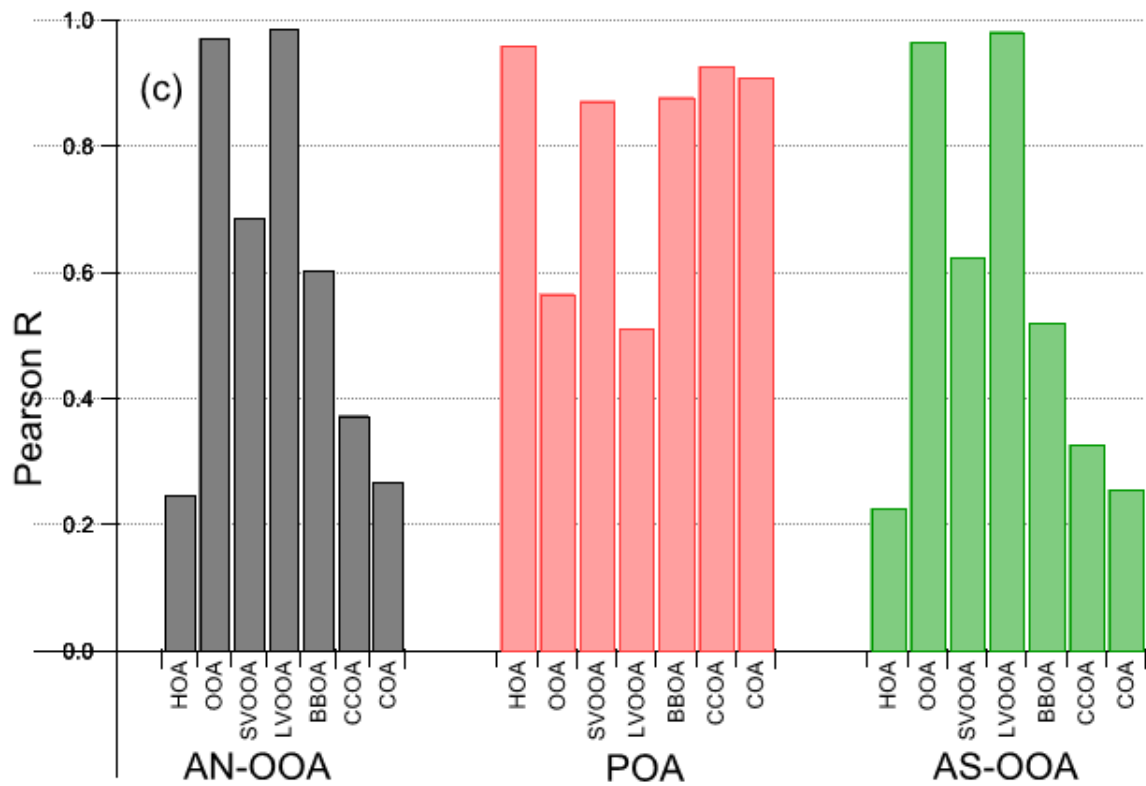
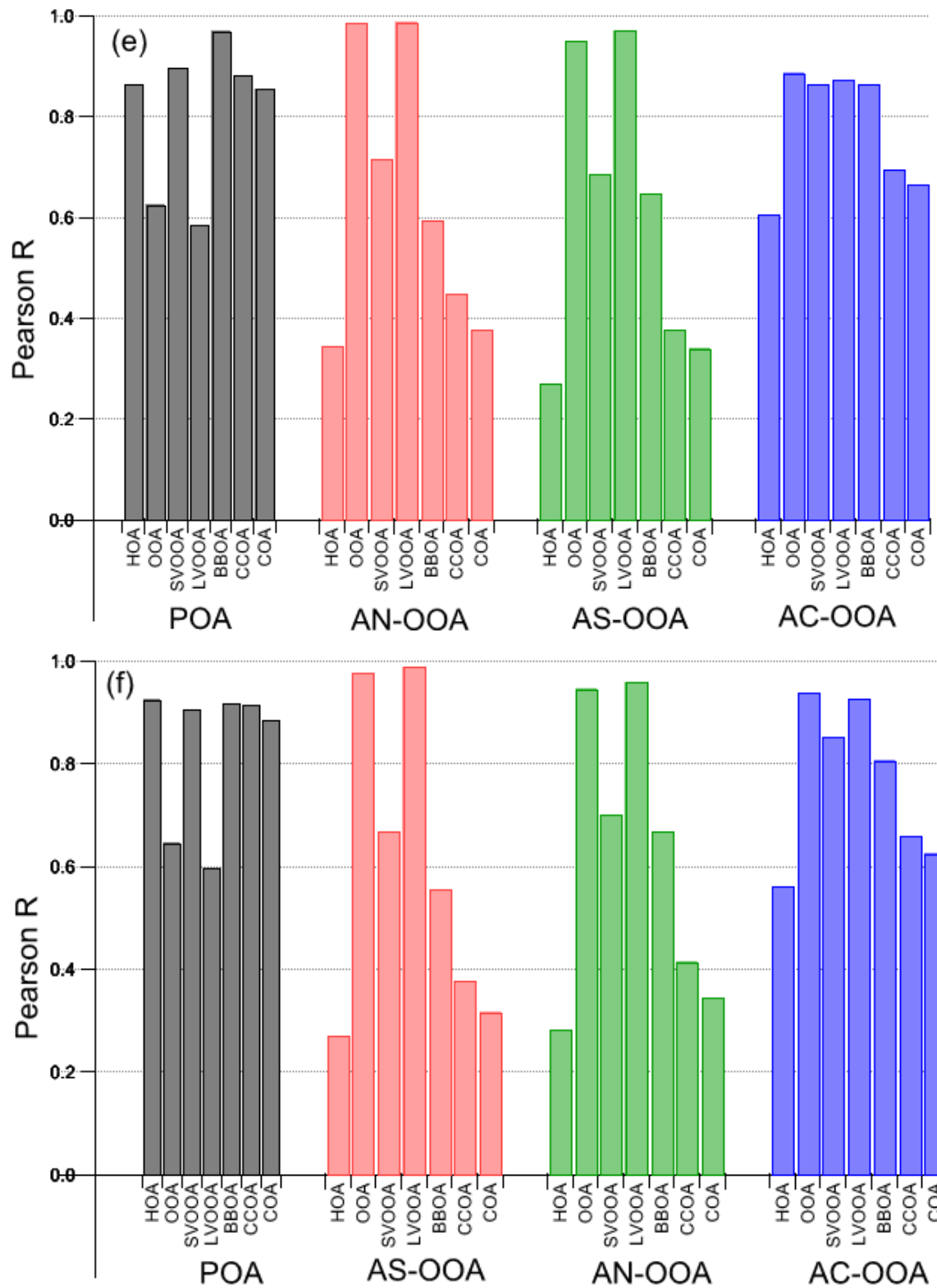



Figure S7 shows the combined organic-inorganic PMF factor MS correlations with reference profiles in the order: (a) winter 2017, (b) spring 2017, (c) summer 2017, (d) monsoon 2017, (e) winter 2018, and (f) spring 2018. Clearly, all PMF factors show strong correlations with at least

one reference profile. Also, AC-OOA correlates with both BBOA and OOA (or, SVOOA/LVOOA) reference profiles.

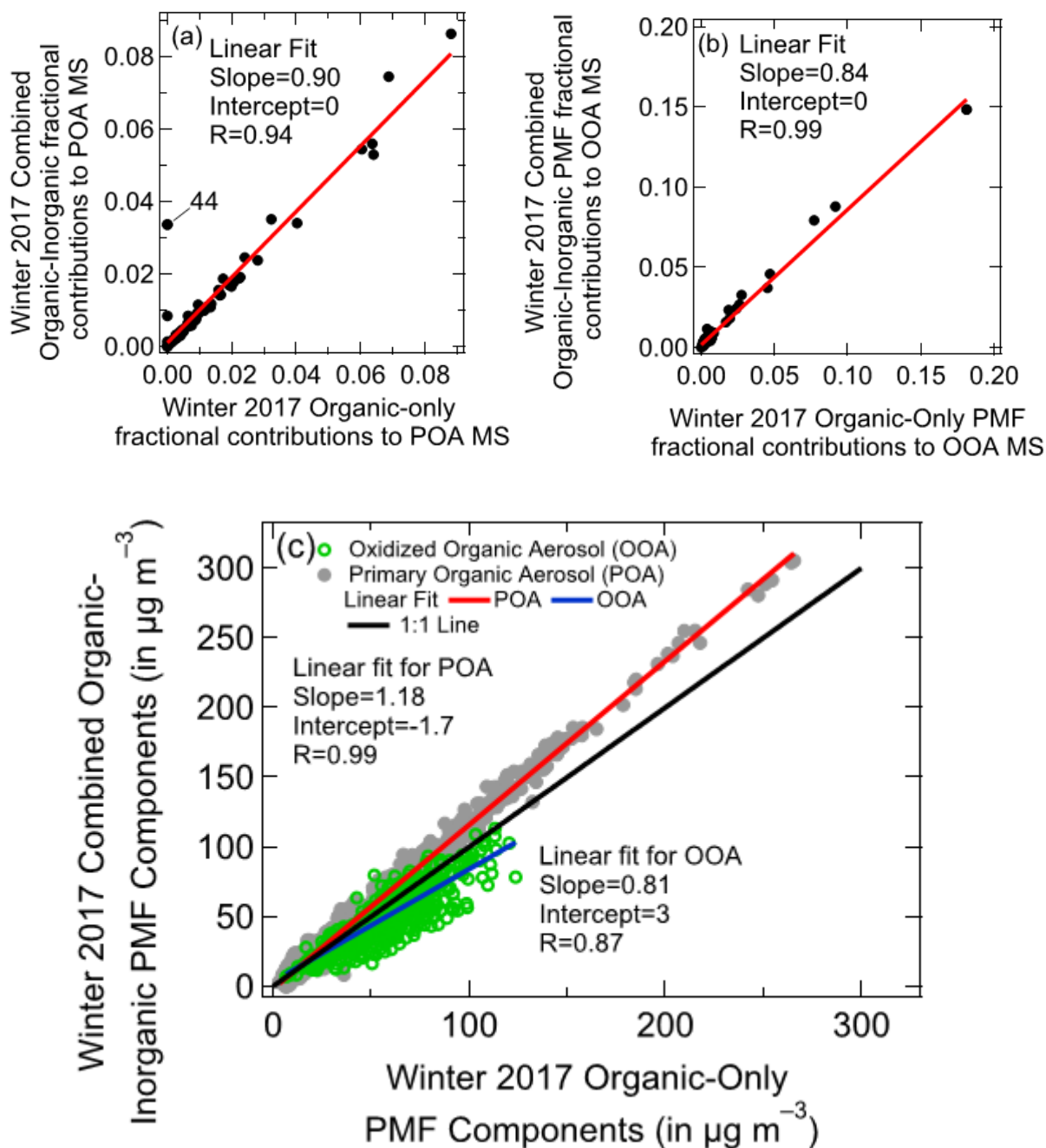



Figure S8 shows the comparison of combined organic-inorganic PMF and organic-only PMF MS for (a) the POA factor and (b) the OOA factor in winter 2017. Subplot (c) shows the comparison of combined organic-inorganic PMF and organic-only PMF-based factor concentrations (µg m⁻³). The Pearson R coefficient indicates excellent linear correlations between the two analyses in all subplots. Based on the slope of the time series correlations, the organic-inorganic combined PMF estimates 18% more POA and about 19% less OOA than organic-only PMF in winter 2017.

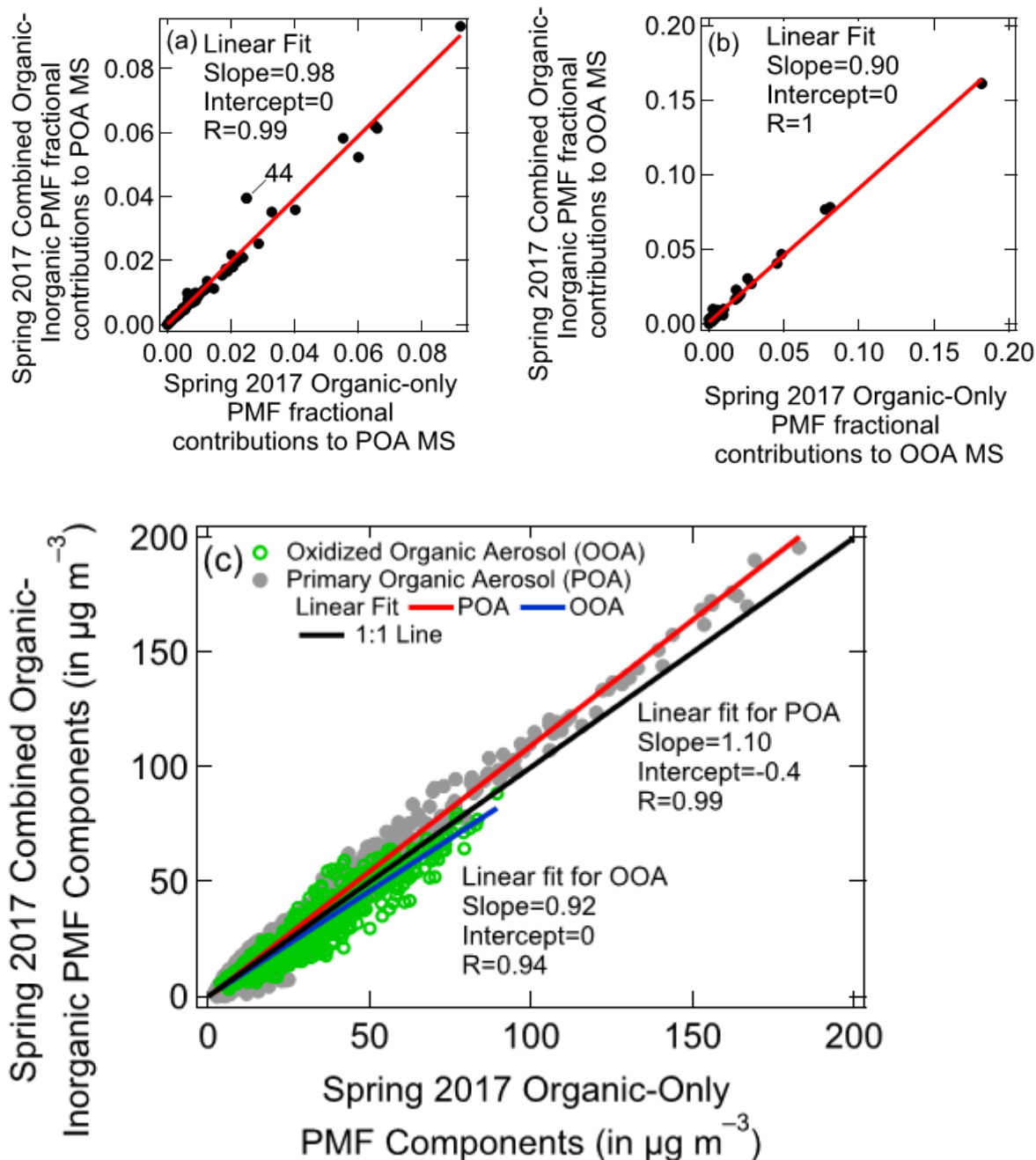



Figure S9 shows the comparison of combined organic-inorganic PMF and organic-only PMF MS for (a) the POA factor and (b) the OOA factor in spring 2017. Subplot (c) shows the comparison of combined organic-inorganic PMF and organic-only PMF-based factor concentrations (µg m⁻³). The Pearson R coefficient indicates excellent linear correlations between the two analyses in all subplots. Based on the slope of the time series correlations, the organic-inorganic combined PMF estimates 10% more POA and about 8% less OOA than organic-only PMF in spring 2017.

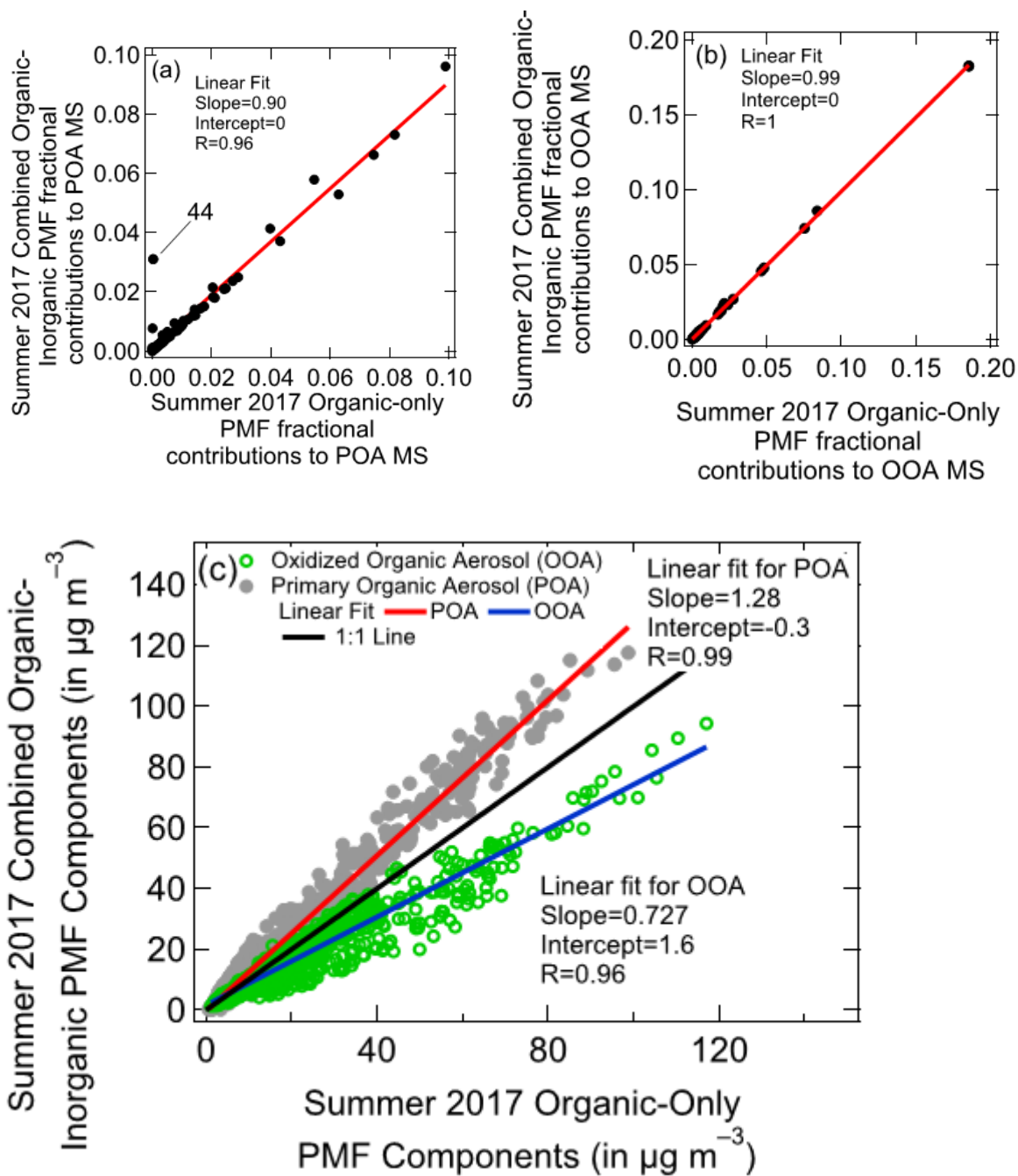



Figure S10 shows the comparison of combined organic-inorganic PMF and organic-only PMF MS for (a) the POA factor and (b) the OOA factor in summer 2017. Subplot (c) shows the comparison of combined organic-inorganic PMF and organic-only PMF-based factor concentrations (µg m^{-3}). The Pearson R coefficient indicates excellent linear correlations between the two analyses in all subplots. Based on the slope of the time series correlations, the organic-inorganic combined PMF estimates 28% more POA and about 27% less OOA than organic-only PMF in summer 2017.

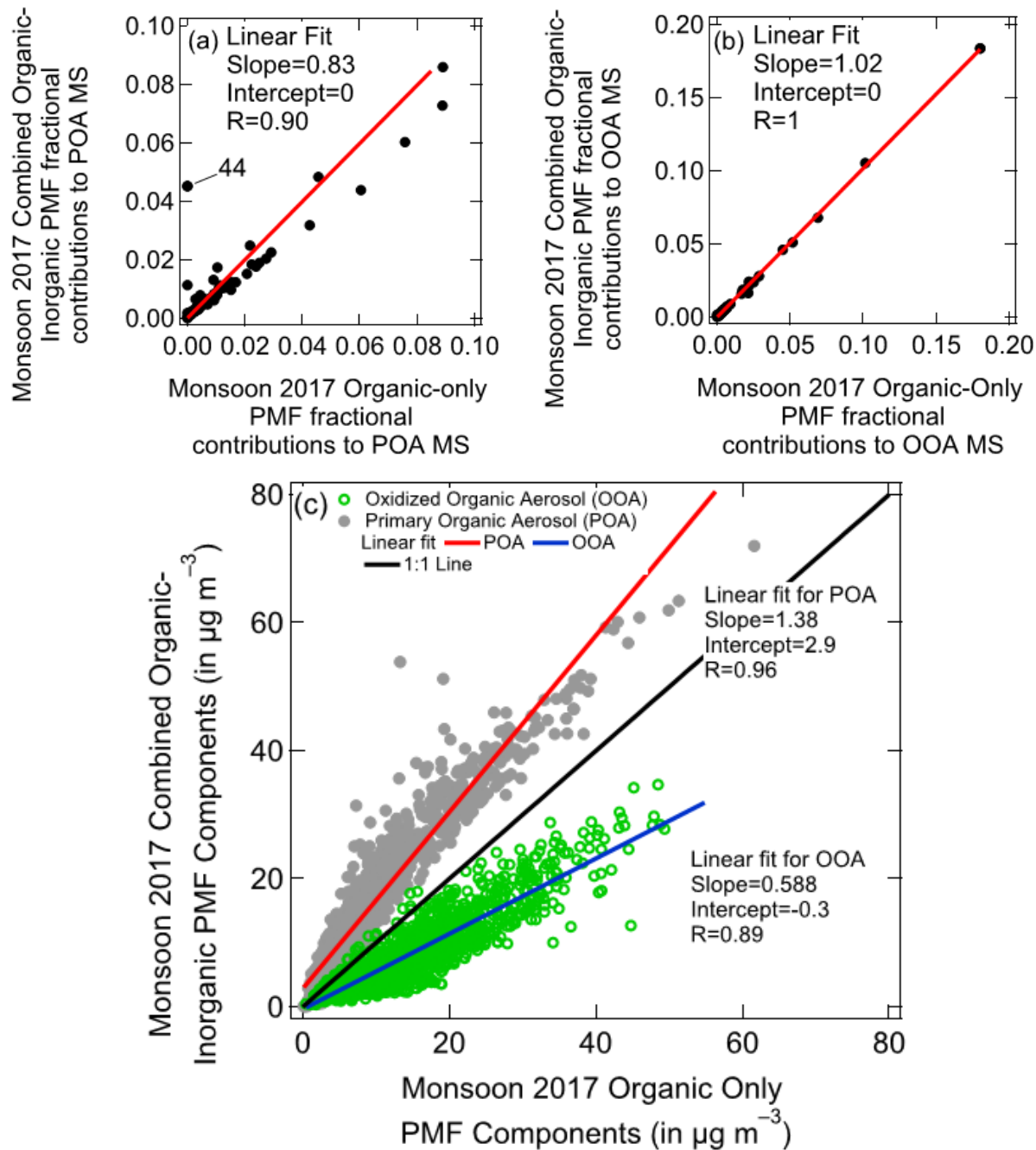



Figure S11 shows the comparison of combined organic-inorganic PMF and organic-only PMF MS for (a) the POA factor and (b) the OOA factor in monsoon 2017. Subplot (c) shows the comparison of combined organic-inorganic PMF and organic-only PMF-based factor concentrations (µg m^{-3}). The Pearson R coefficient indicates excellent linear correlations between the two analyses in all subplots. Based on the slope of the time series correlations, the organic-inorganic combined PMF estimates 38% more POA and about 41% less OOA than organic-only PMF in monsoon 2017.

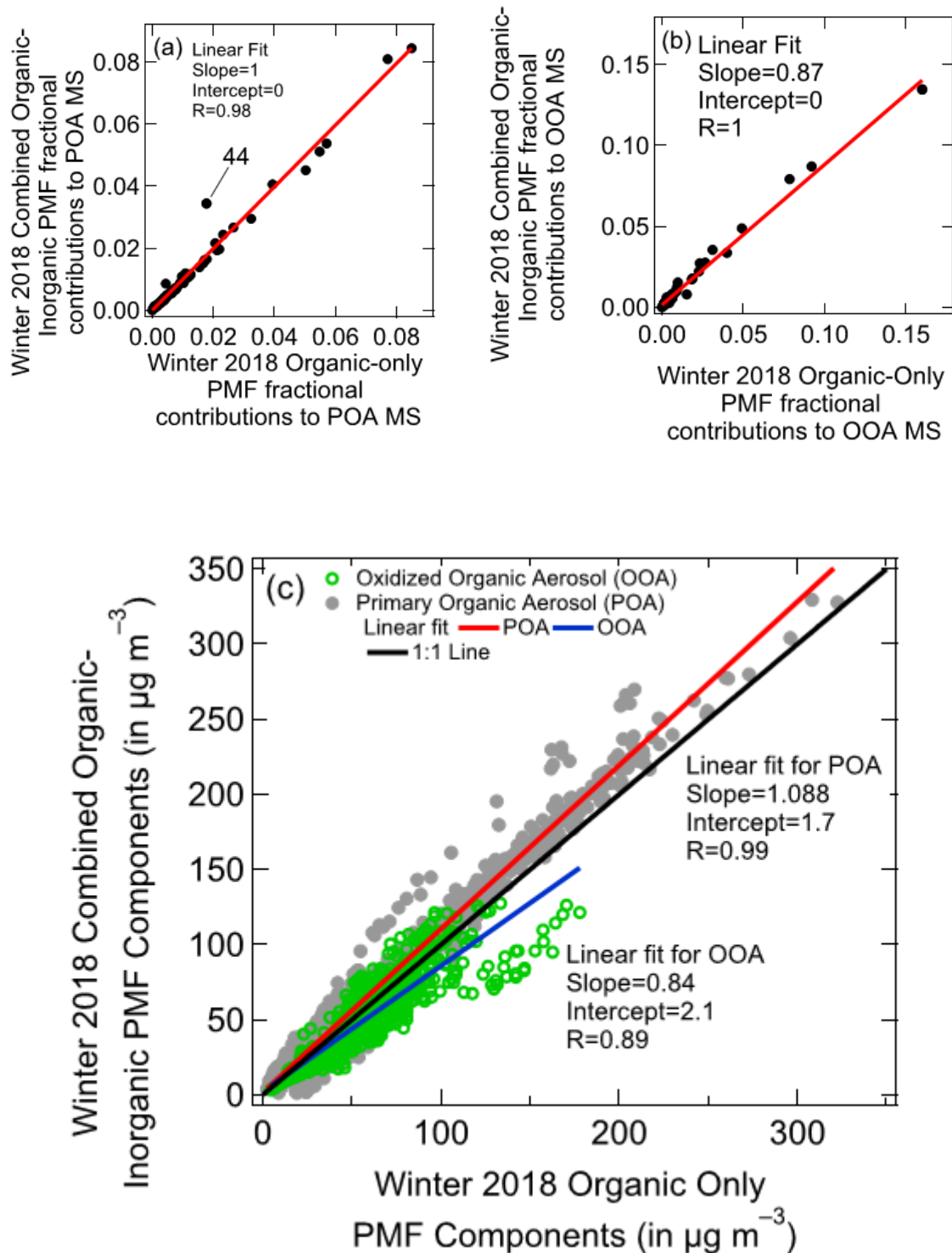



Figure S12 shows the comparison of combined organic-inorganic PMF and organic-only PMF MS for (a) the POA factor and (b) the OOA factor in winter 2018. Subplot (c) shows the comparison of combined organic-inorganic PMF and organic-only PMF-based factor concentrations (µg m⁻³). The Pearson R coefficient indicates excellent linear correlations between the two analyses in all subplots. Based on the slope of the time series correlations, the organic-inorganic combined PMF estimates about 9% more POA and 16% less OOA than organic-only PMF in winter 2018.

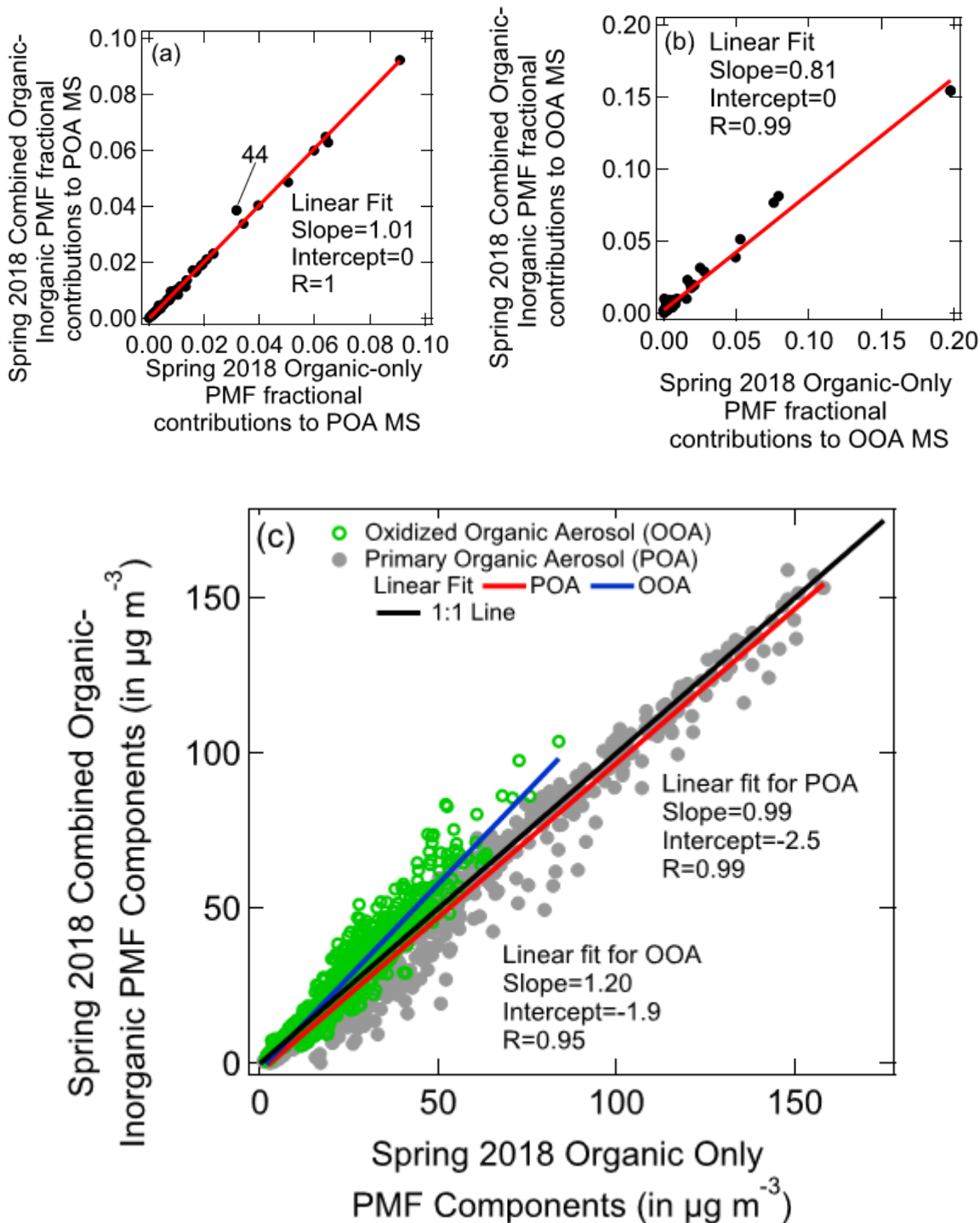



Figure S13 shows the comparison of combined organic-inorganic PMF and organic-only PMF MS for (a) the POA factor and (b) the OOA factor in spring 2018. Subplot (c) shows the comparison of combined organic-inorganic PMF and organic-only PMF-based factor concentrations (µg m^{-3}). The Pearson R coefficient indicates excellent linear correlations between the two analyses in all subplots. Based on the slope of the time series correlations, the organic-inorganic combined PMF estimates about 1% less POA and 20% more OOA than organic-only PMF in spring 2018.

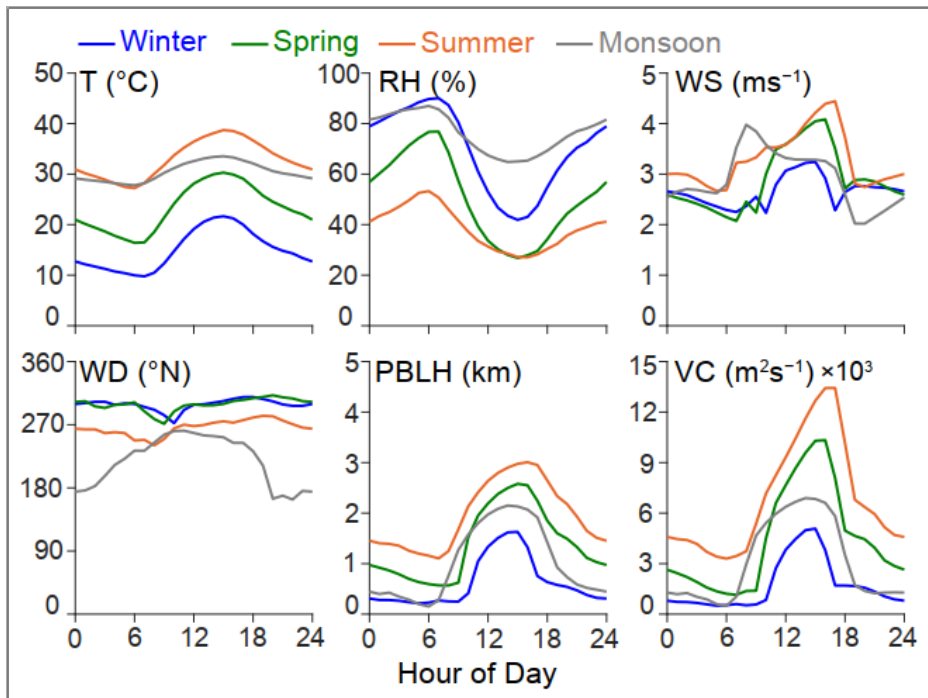



Figure S14 Diurnal profiles of meteorological parameters (temperature, relative humidity, wind speed, wind direction, PBLH, and VC) by season. Average values by season and hour of the day are presented for all parameters except wind direction. The median value is presented for wind direction. Ventilation coefficient (VC) = PBLH × wind speed. Adapted from Gani et al. (2018).

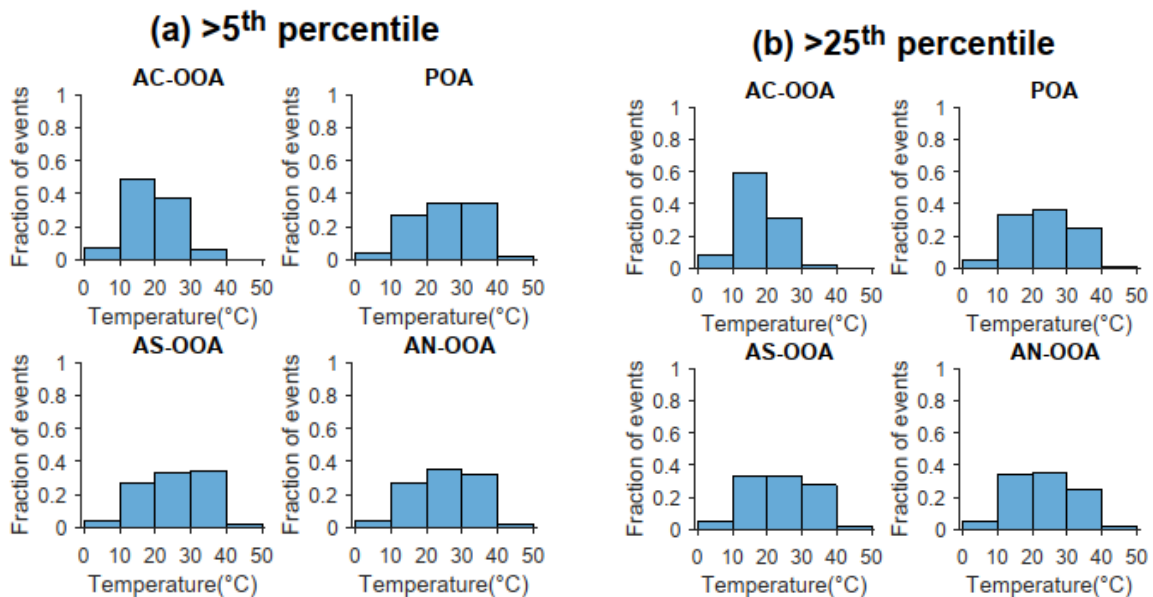
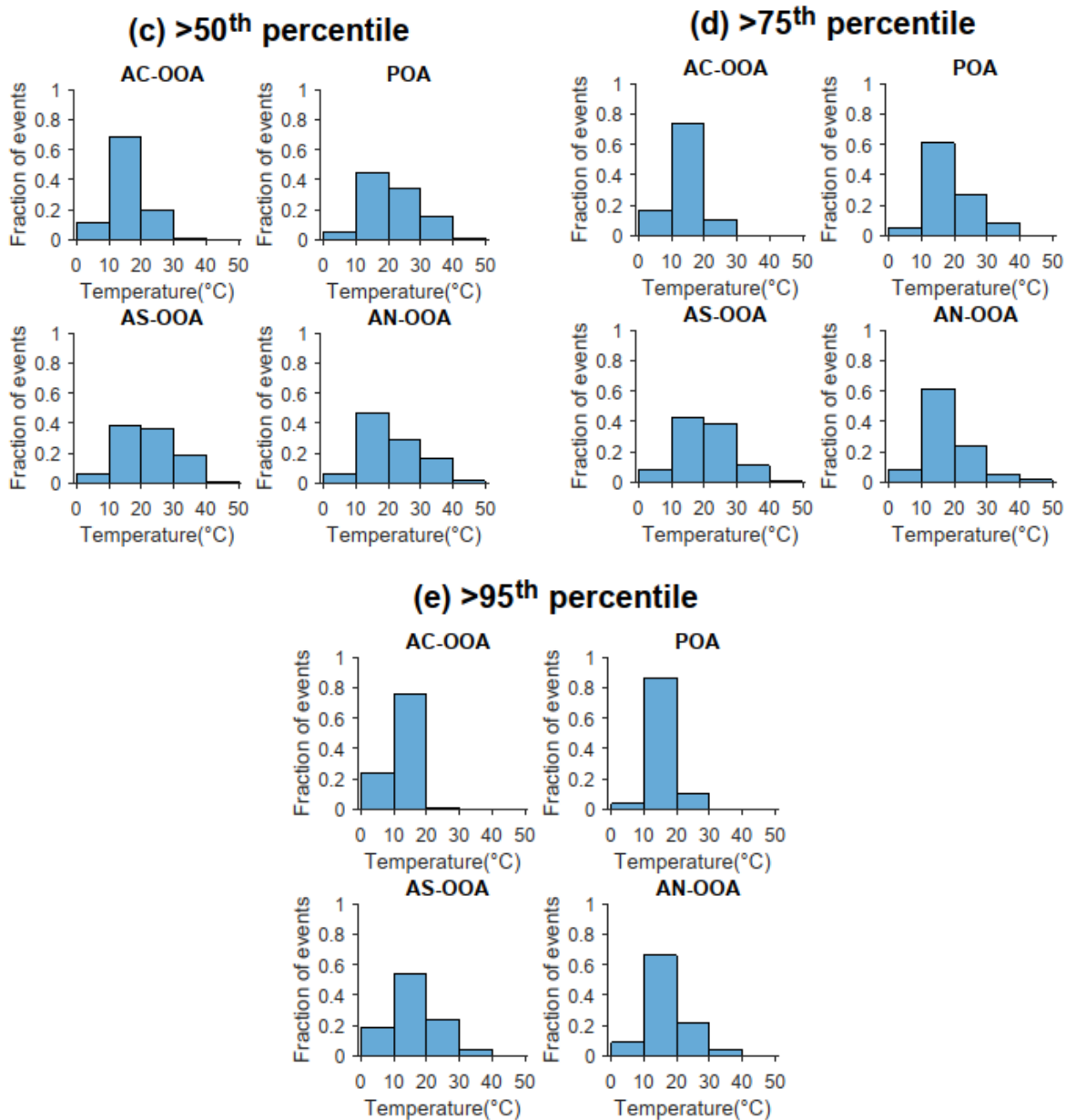



Figure S15 shows histogram plots of the fraction of events corresponding to each combined organic-inorganic PMF factor in different temperature bins (°C). The subplots correspond to a selection of data for each factor based on percentiles greater than (a) 5%, (b) 25%, (c) 50%, (d)75%, and (e) 95%. Based on these plots, POA shows nearly 90% of its high pollution episodes in the 10–20°C bin.

2. Volatility Basis Set (VBS) application

Combining data from laboratory studies and field campaigns in Paris, Greece and Finokalia, Pandis and co-workers have shown that the 1-D volatility basis set (VBS, Donahue et al., 2006) obtained for different source apportionment factors (based on the external mixture assumption) are reasonably representative of the volatility of the actual mixed aerosol system and are similar

once normalized for concentrations (Karnezi et al., 2018). As shown in the main manuscript Table 3, at times, factor concentrations in Delhi exceed 100 µg m^{-3}. In the absence of volatility data for Delhi, we use the Mexico City VBS for different factors due to the availability of data from the volatility bin C_i* (298 K) equal to 100 µg m^{-3} (Cappa and Jimenez, 2010). We assume constant gas plus particle phase fractions corresponding to volatility bins ($\log_{10}C$* (in µg m^{-3})) from 10^{-7} to 10^2 and use PMF-based Delhi data to estimate total concentrations (gas plus particle phase) that, under conditions of equilibrium partitioning, generate measured concentrations in the particle phase. To account for different variables, we run the above procedure on organic-only PMF-based seasonally representative diurnal averages. In the first run, diurnal data for winter and summer of 2017 is input together with actual temperature and RH to generate equilibrium concentrations of gas-phase organics. In the second run, the obtained total concentrations in winter 2017 corrected for VC effects are run with the temperature and RH of summer 2017. We call this run the "winter in summer" scenario. Thus, to estimate maximum PM formation potential relative to the sources in winter 2017, diurnal "source" concentration averages for winter 2017 are applied to summer—the goal being to allow repartitioning for achieving equilibrium. The limitation of this approach is that using linear corrections for ventilation coefficient might be overcompensating its effect.

Both summer and winter result in about the same total HOA-associated concentrations (59 and 62 µg m^{-3} respectively) as well as diurnal variations (Fig. S16a), while total OOA-associated concentrations half from winter to summer (76 µg m^{-3} to 38 µg m^{-3}), along with flattened diurnal variations (Fig. S16b). Additionally, the "winter in summer" scenario gives total concentration associated with HOA as 19 µg m^{-3} and that associated with OOA as 24 µg m^{-3}, and particle phase concentration of HOA as 3 µg m^{-3} and OOA as 12 µg m^{-3}. Compared to summer (PM$_1$ HOA ~ 14 µg m^{-3}, OOA ~ 19 µg m^{-3}), this scenario has both lower totals and lower PM1 estimates. These results indicate the presence of very high concentrations of HOA organic precursors in Delhi even in summer. This simplified analysis points to the striking importance of ventilation coefficient and temperature in controlling the total levels and gas–particle partitioning.

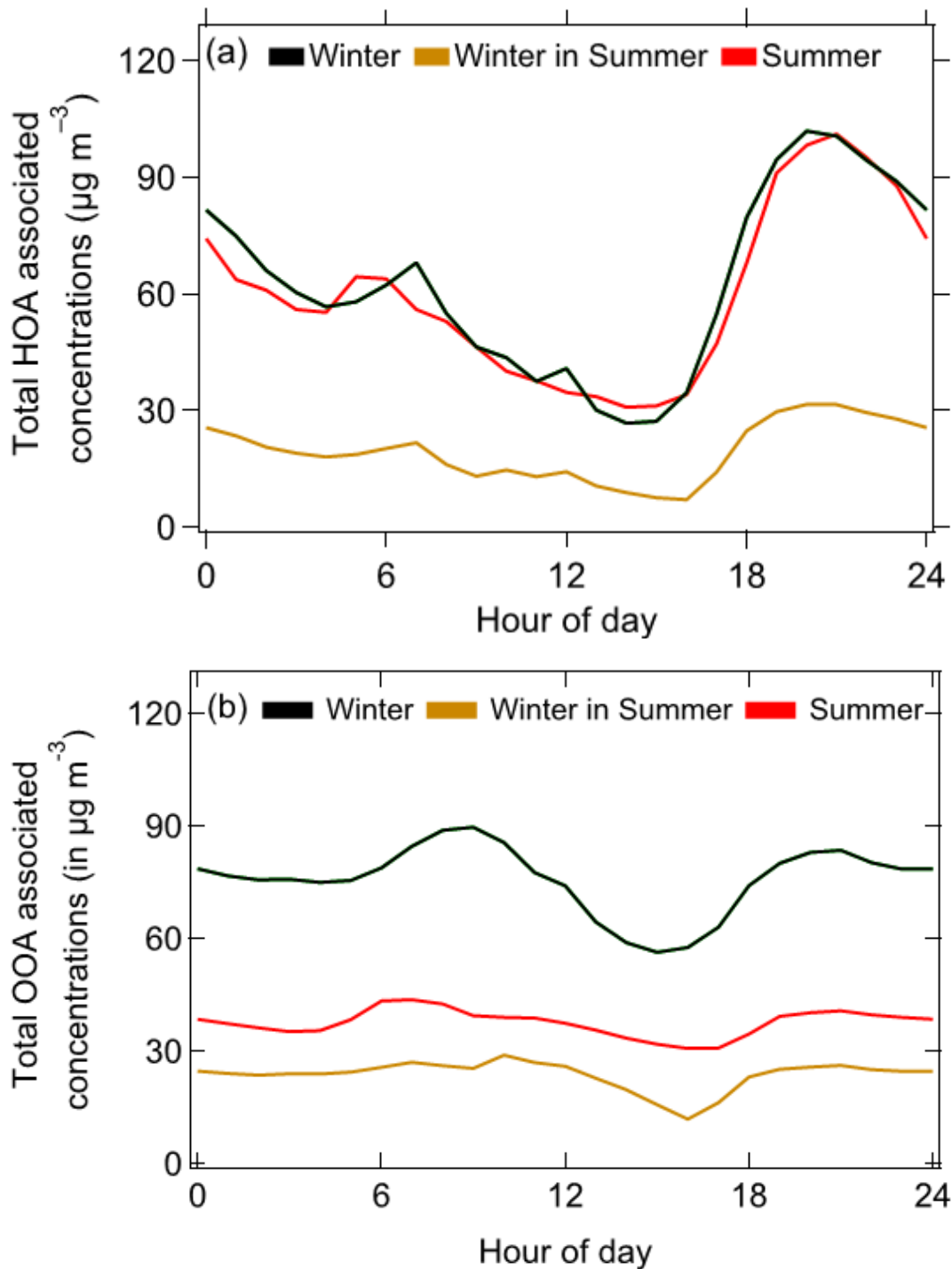



Figure S16 This figure shows the diurnal variations of (a) total HOA-associated concentrations, (b) total OOA-associated concentrations. Application of VBS to winter and summer diurnal averaged data generates very similar diurnal variations in total HOA-associated concentrations. In contrast, total OOA-associated concentrations have halved between winter and summer and have flatter diurnal variations.

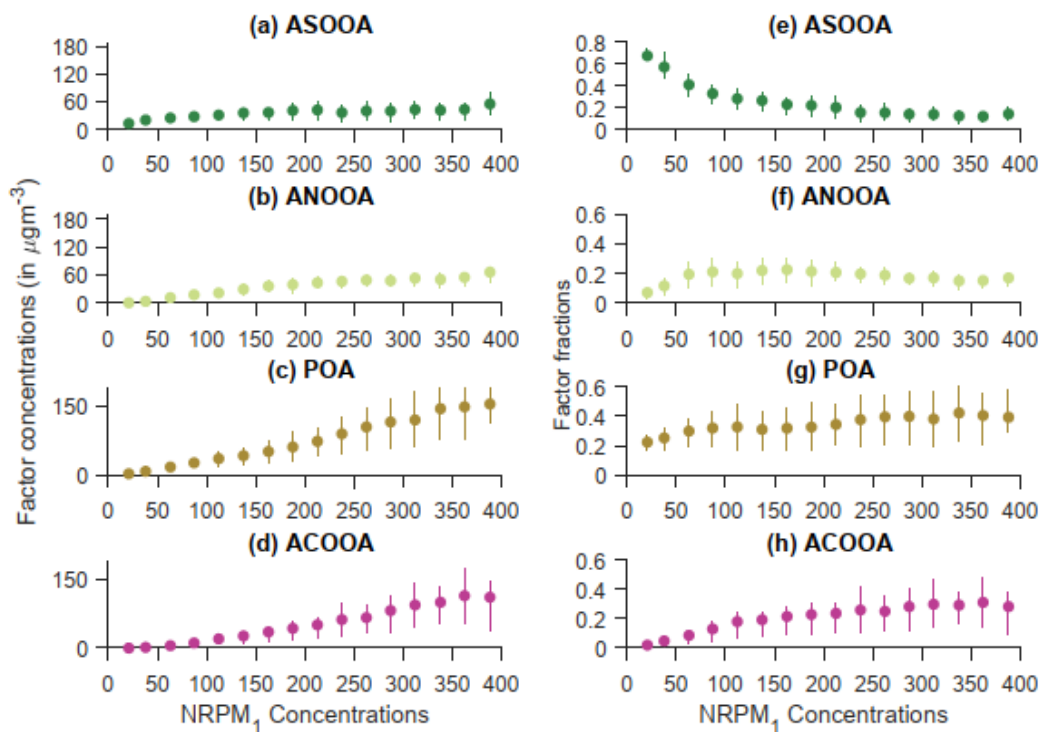



Figure S17 shows combined organic-inorganic PMF (a)–(d) factor concentrations, and (e)–(h) factor fractions versus total $NRPM_1$ concentrations. As $NRPM_1$ concentrations increase, concentrations (fractions) of ANOOA and ASOOA stabilize (decrease). On the other hand, concentrations and fractions of POA and ACOOA, increase continuously. Additionally, POA seems to approach higher concentrations than ACOOA. This figure points to the importance of primary aerosols in high pollution episodes.

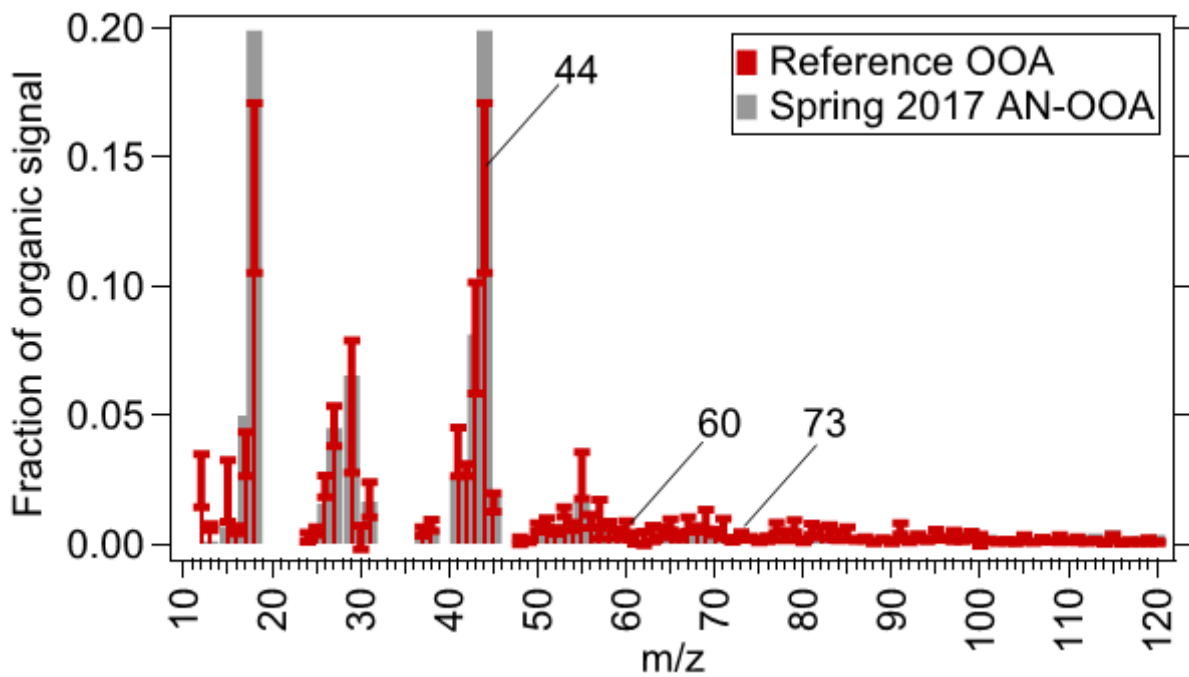
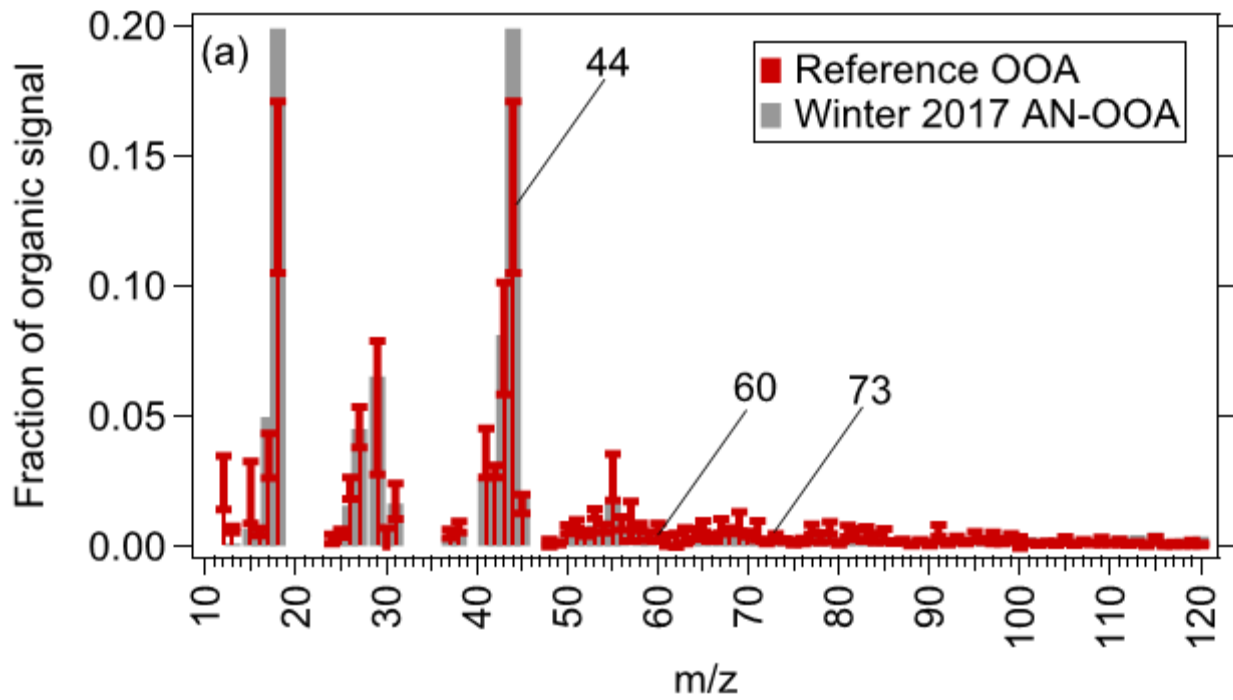
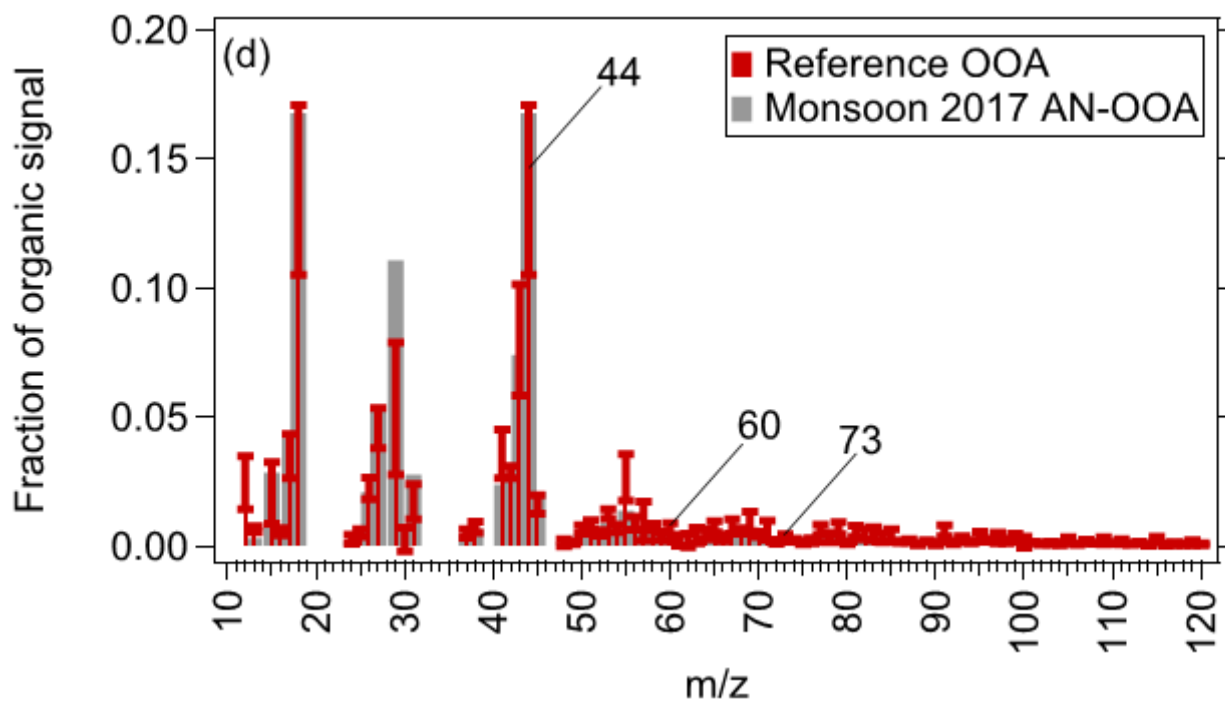
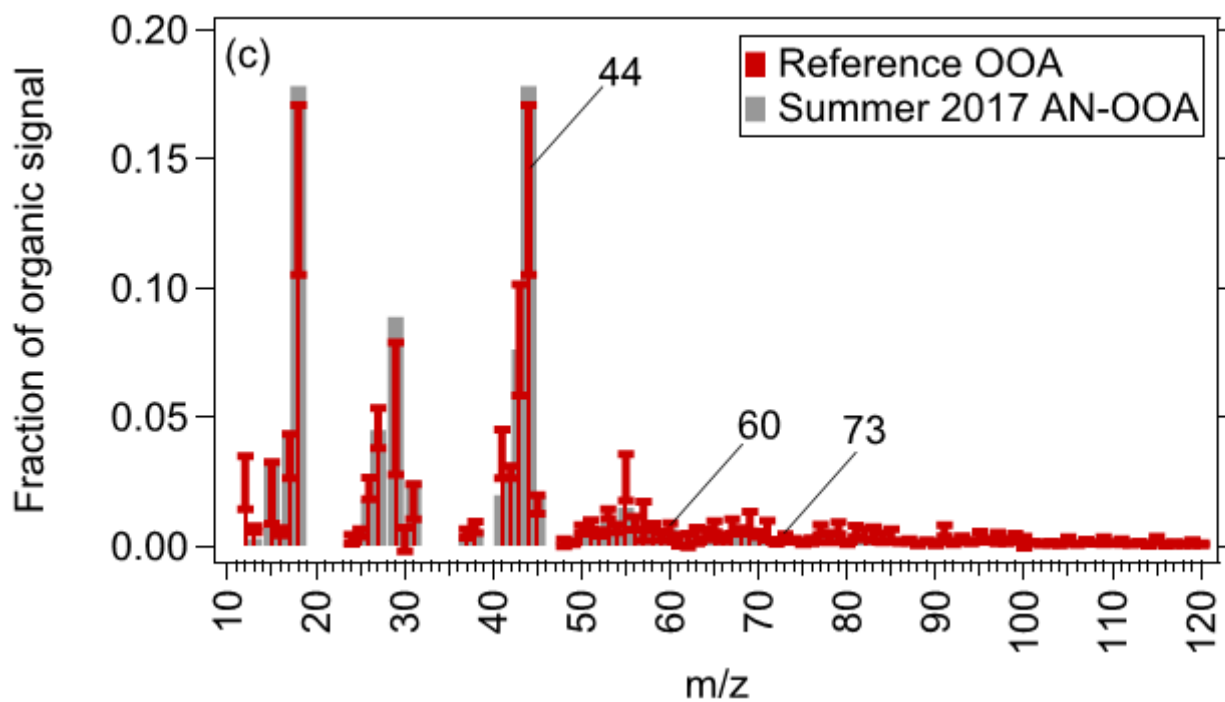
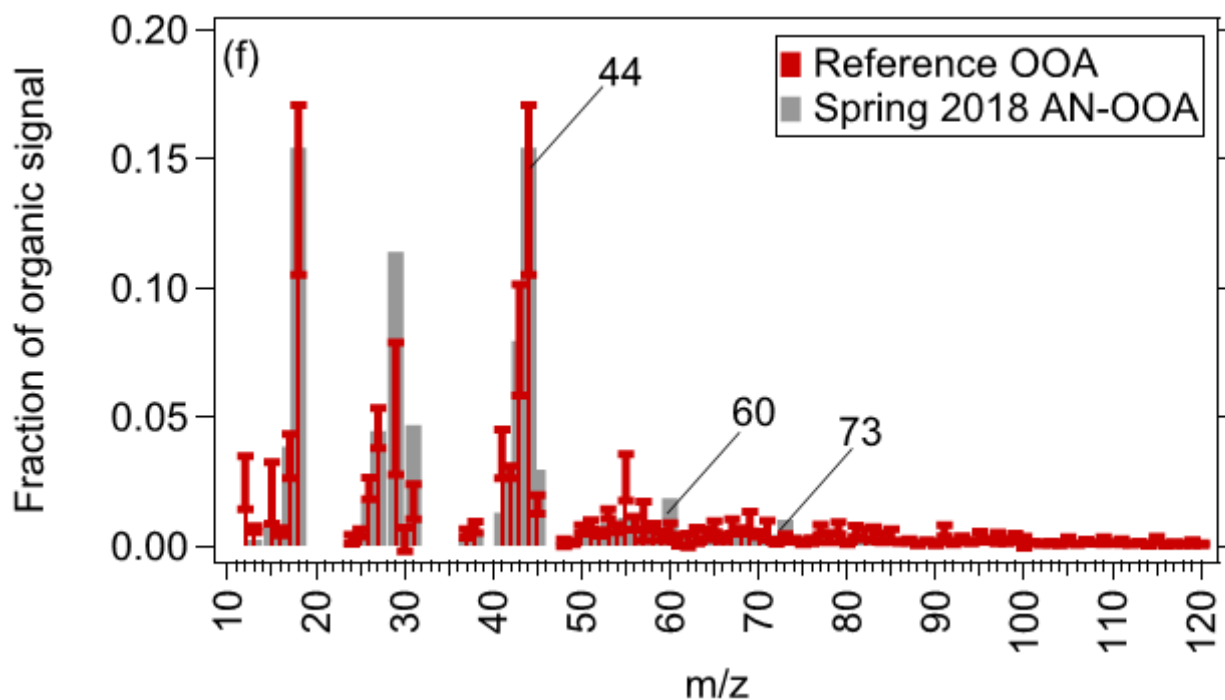
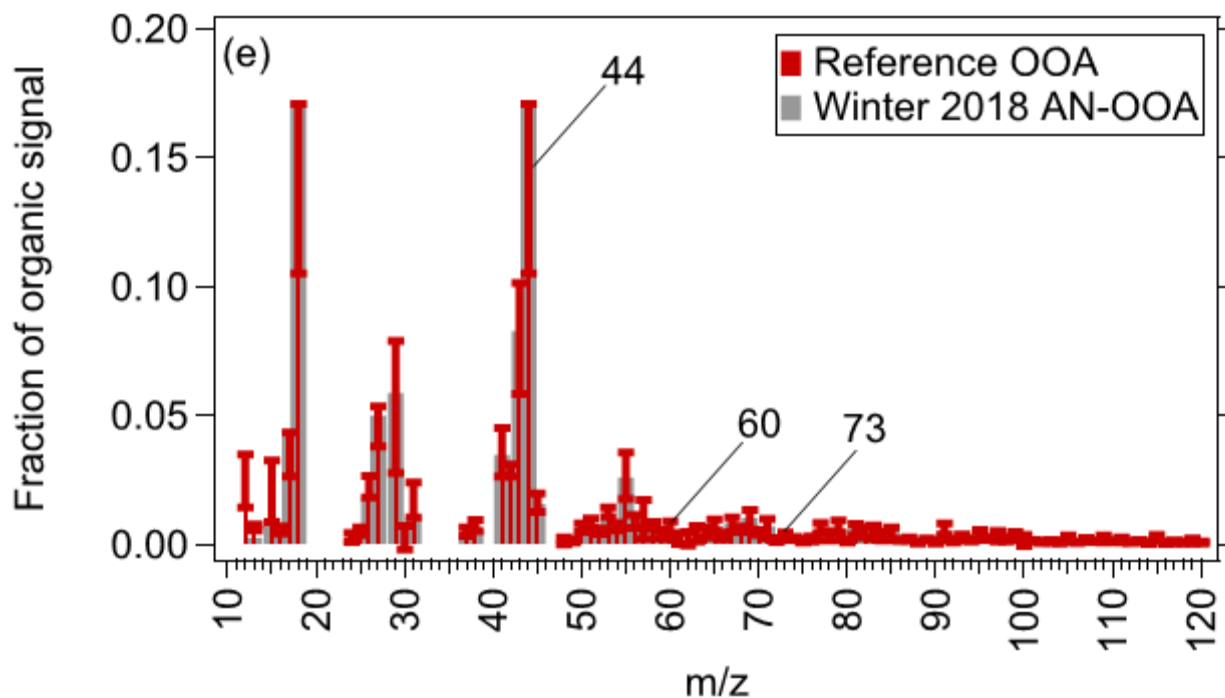



Figure S18 shows the average mass spectrum of the organic component (AN-OOA) of the combined organic-inorganic PMF factor ammonium nitrate mixed with oxidized organic aerosol (ANOOA) in different seasons. The whiskers in the graphs represent ±1 standard deviation of the reference spectra. The comparison of PMF factor MS with reference profiles is shown in the order: (a) winter 2017, (b) spring 2017, (c) summer 2017, (d) monsoon 2017, (e) winter 2018, and (f) spring 2018. Clearly, the AN-OOA mass spectral profile is similar to reference OOA.

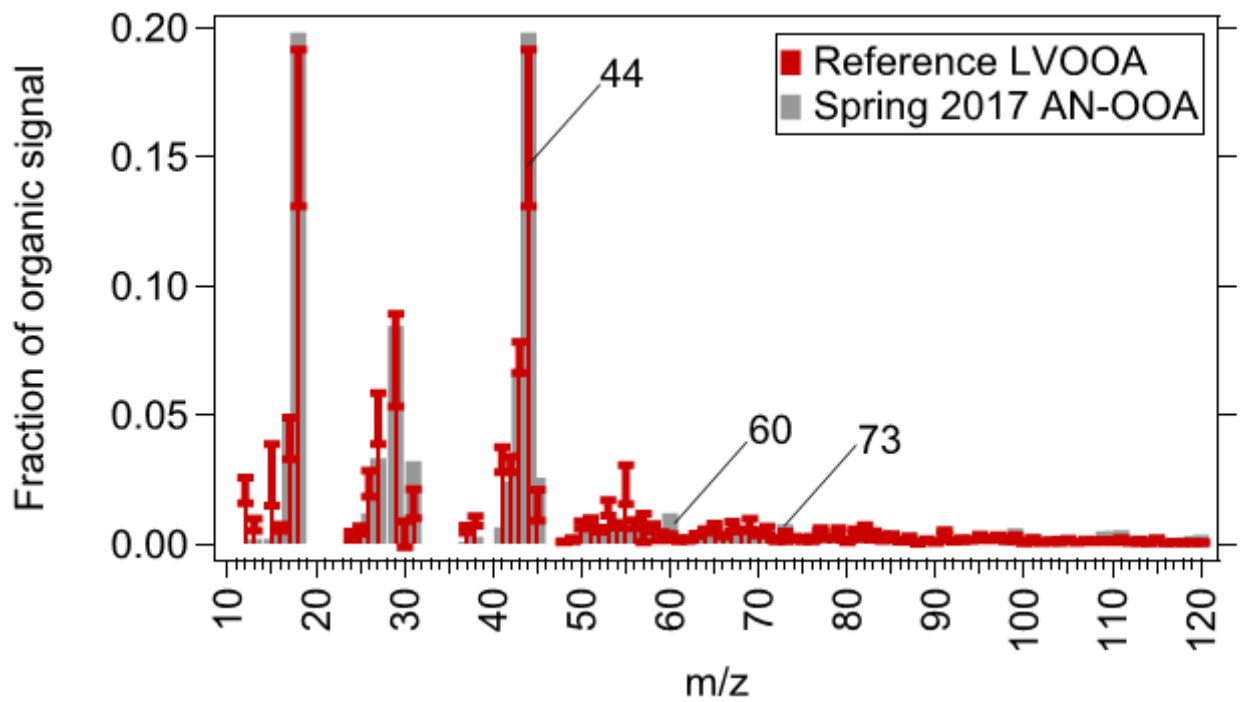
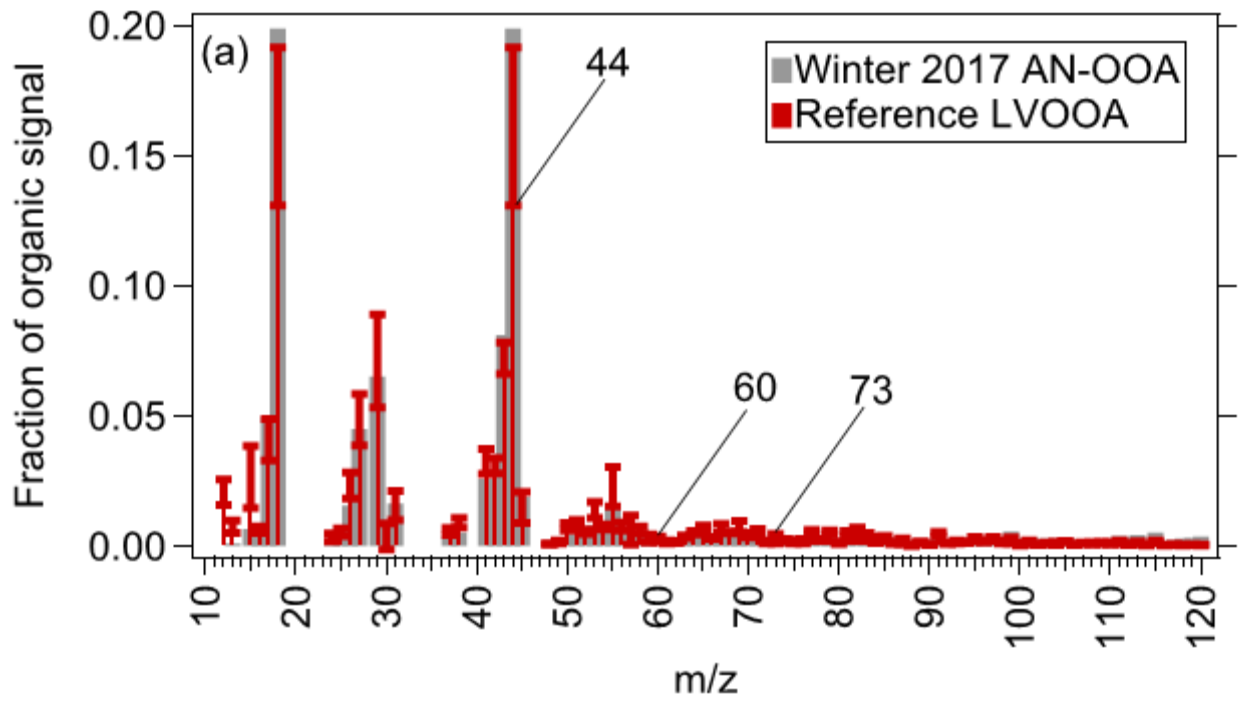
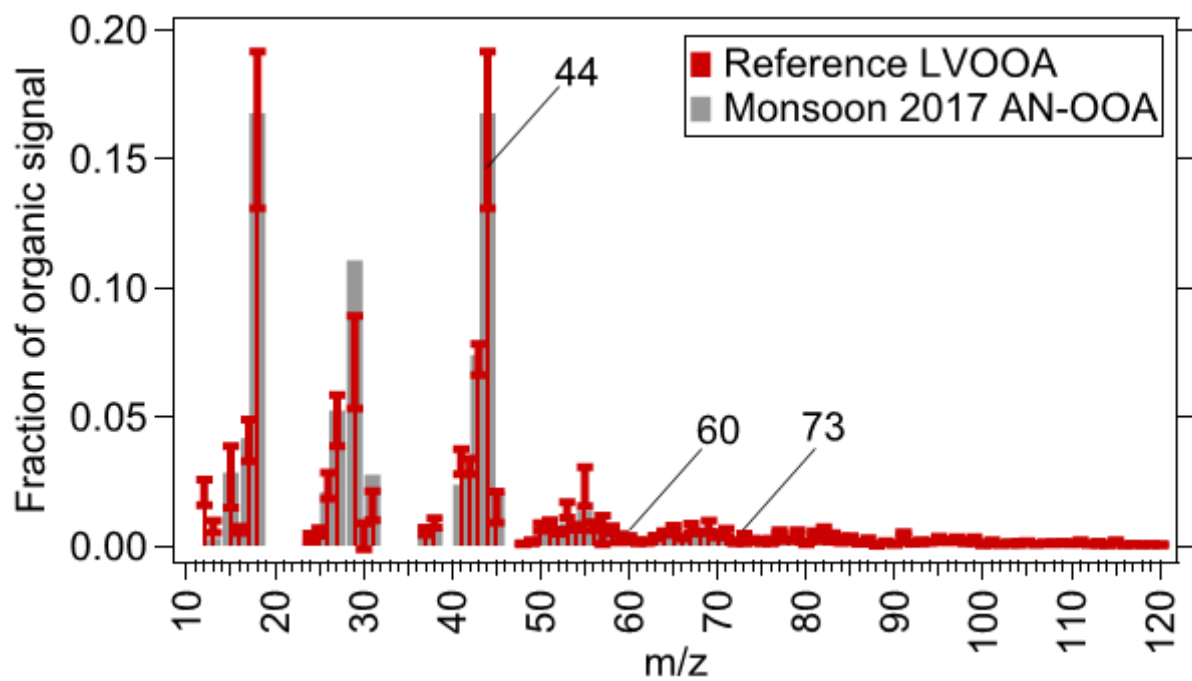
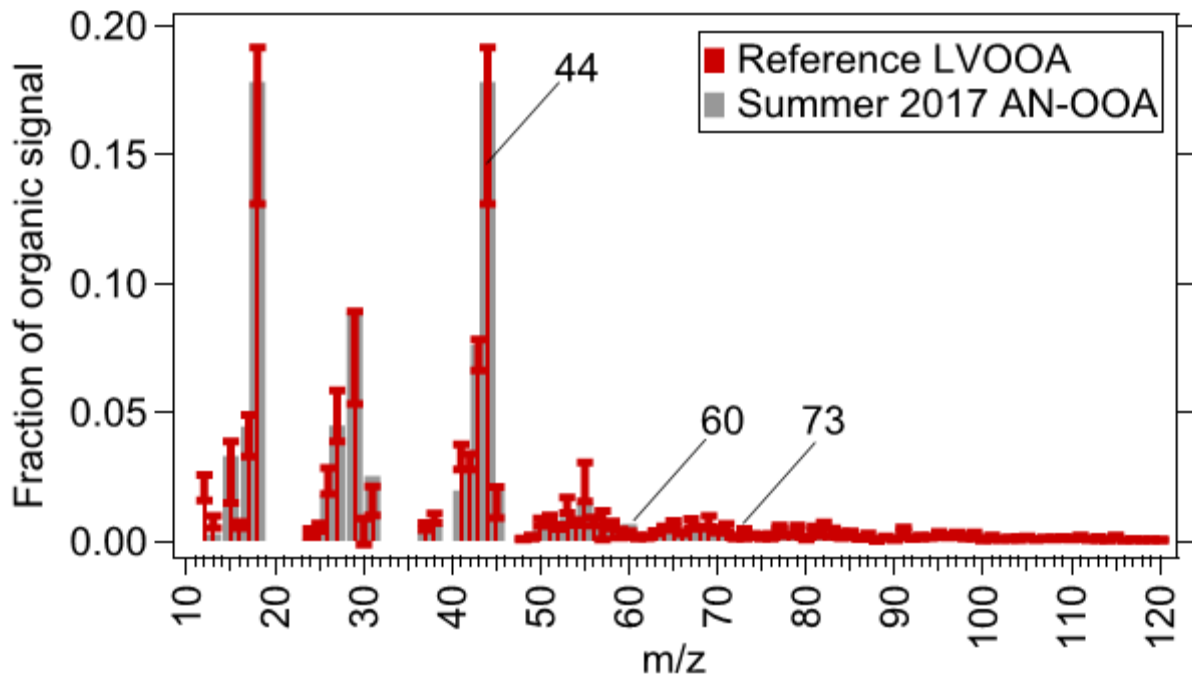
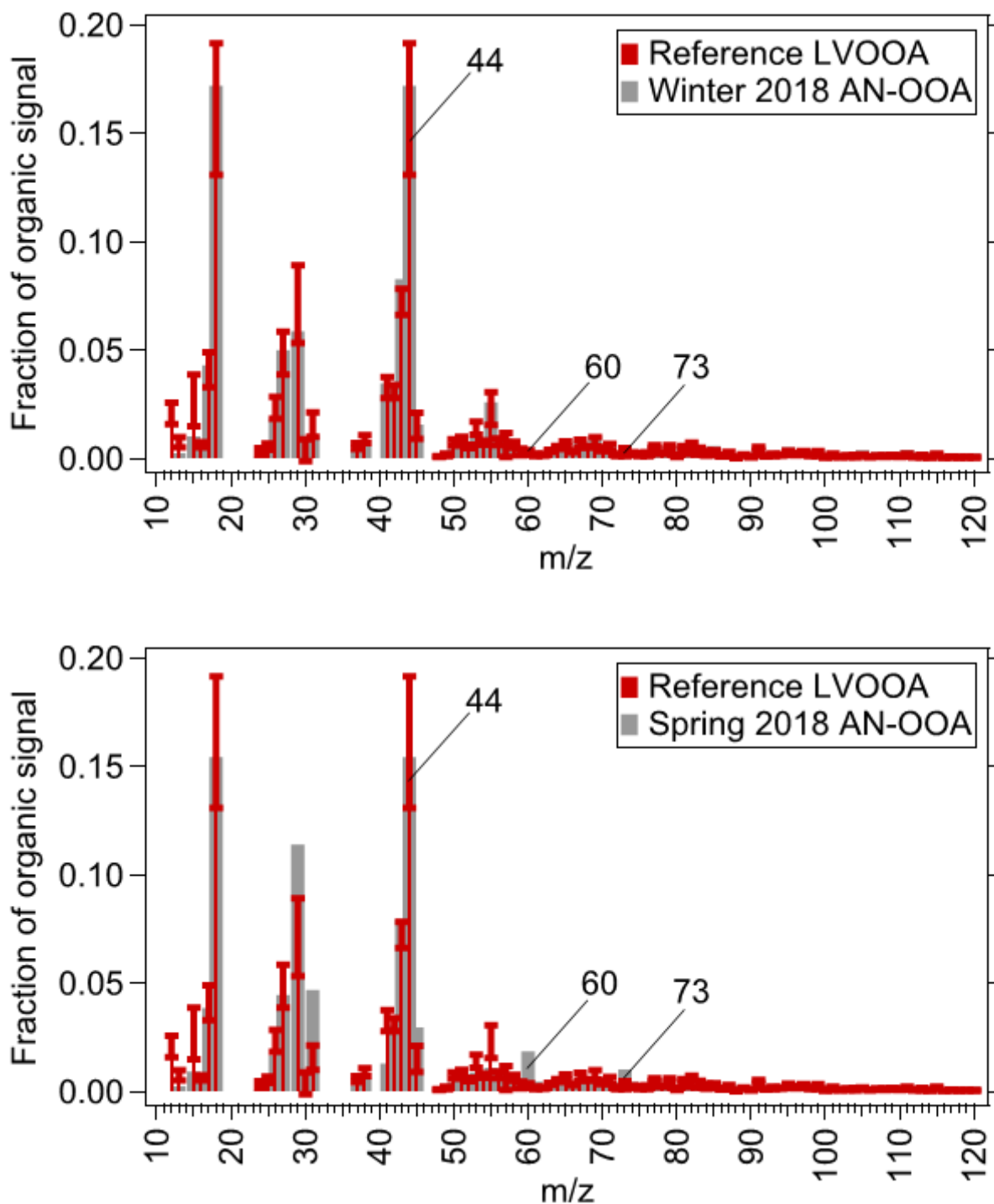



Figure S19 shows the average mass spectrum of the organic component (AN-OOA) of the combined organic-inorganic PMF factor ammonium nitrate mixed with oxidized organic aerosol (ANOOA) in different seasons. The whiskers in the graphs represent ±1 standard deviation of the reference spectra. The comparison of PMF factor MS with reference profiles is shown in the order:

(a) winter 2017, (b) spring 2017, (c) summer 2017, (d) monsoon 2017, (e) winter 2018, and (f) spring 2018. The AN-OOA MS is similar to the reference LVOOA profile.

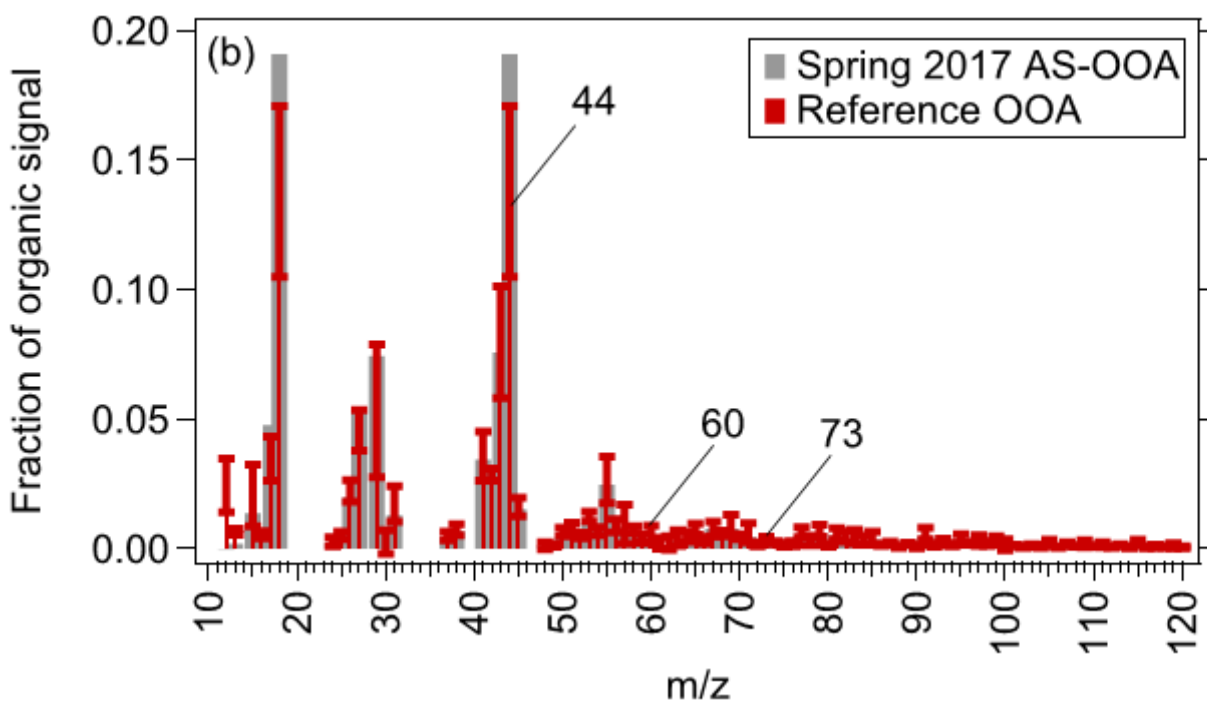
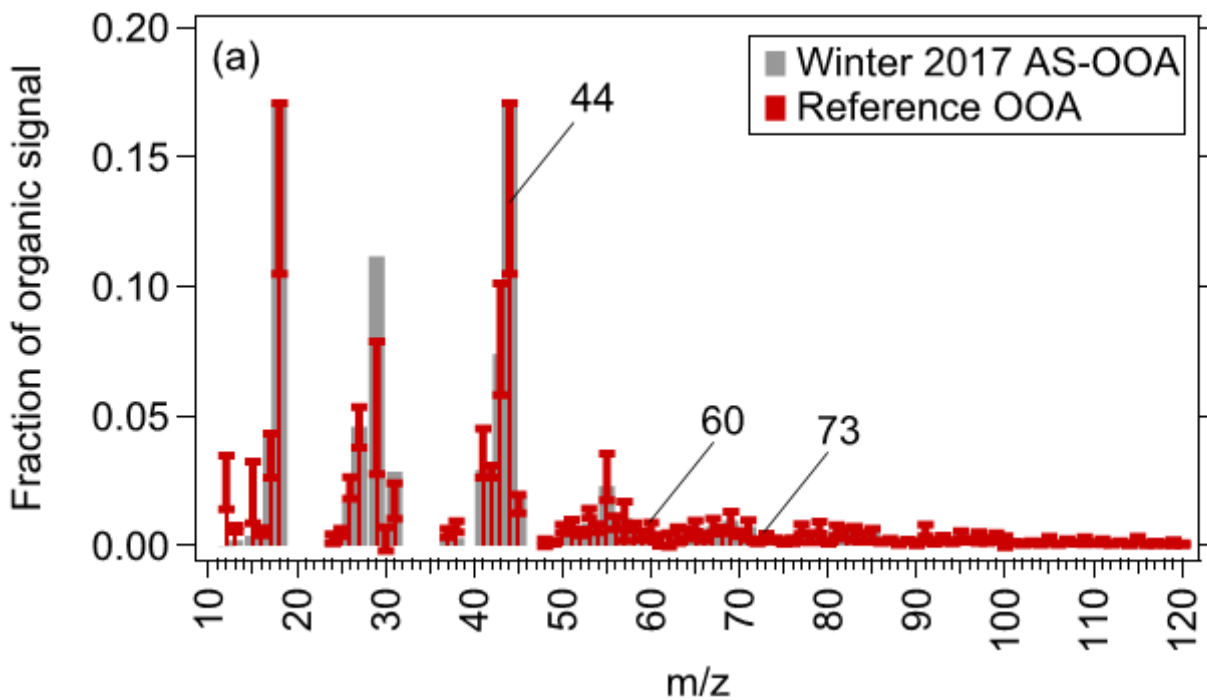
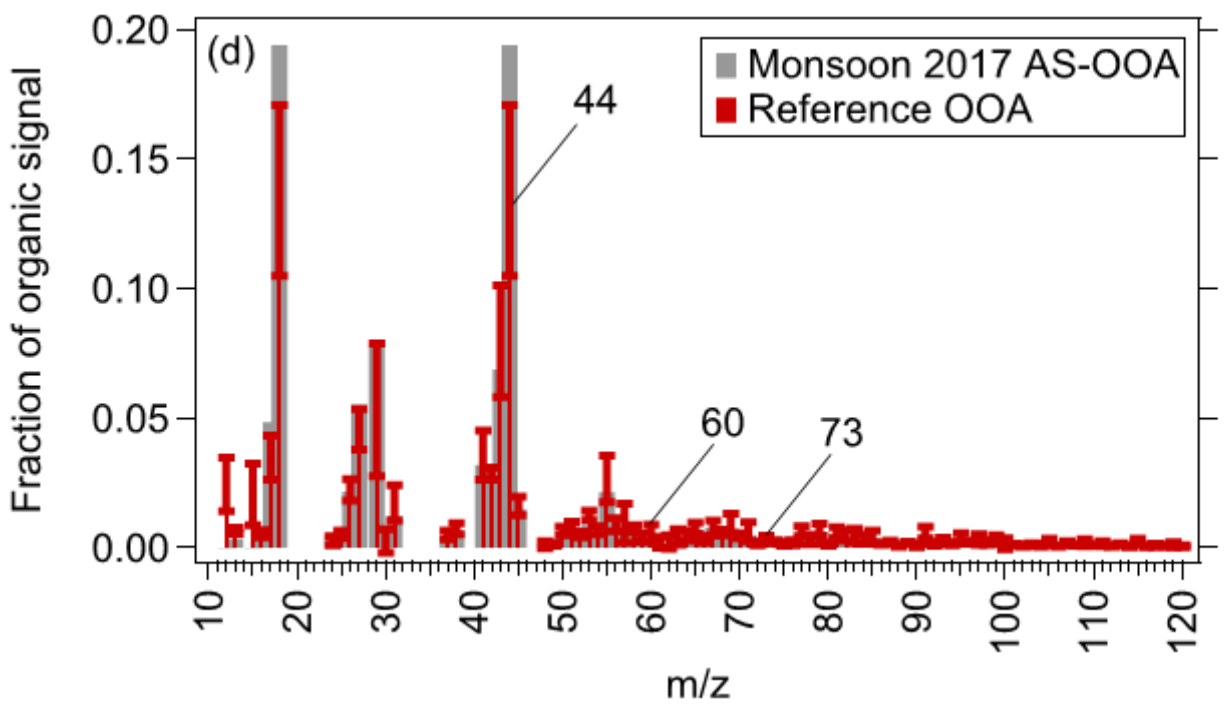
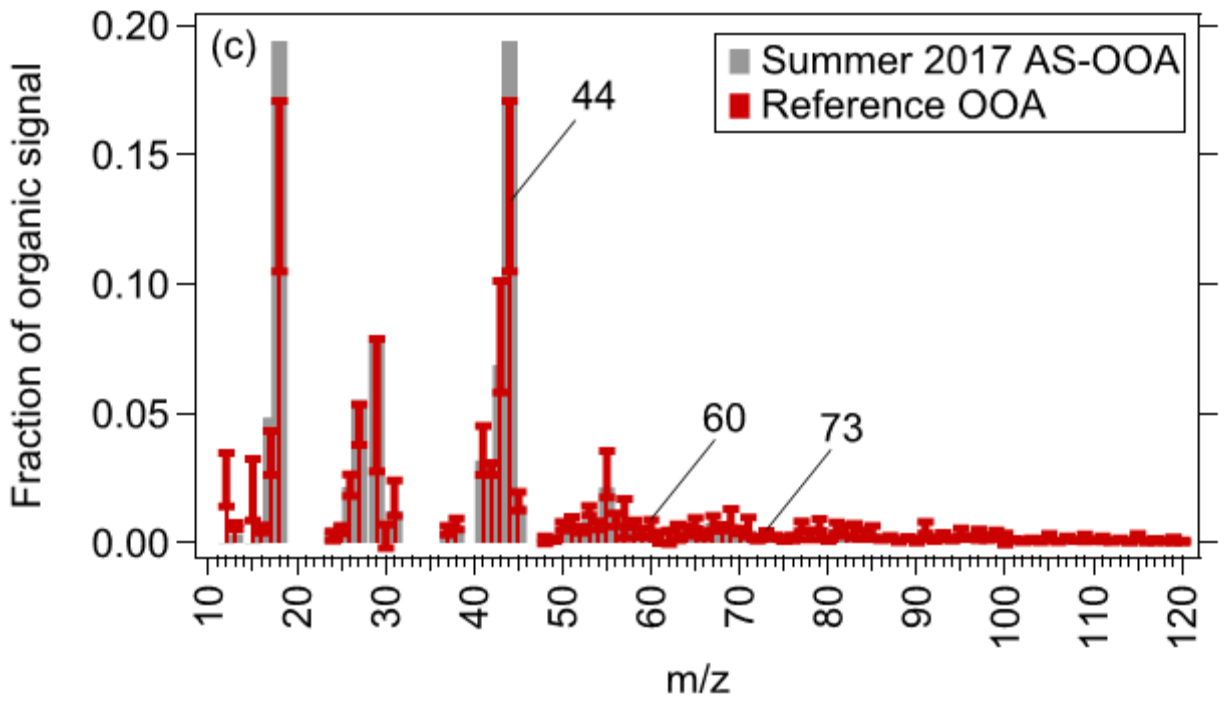
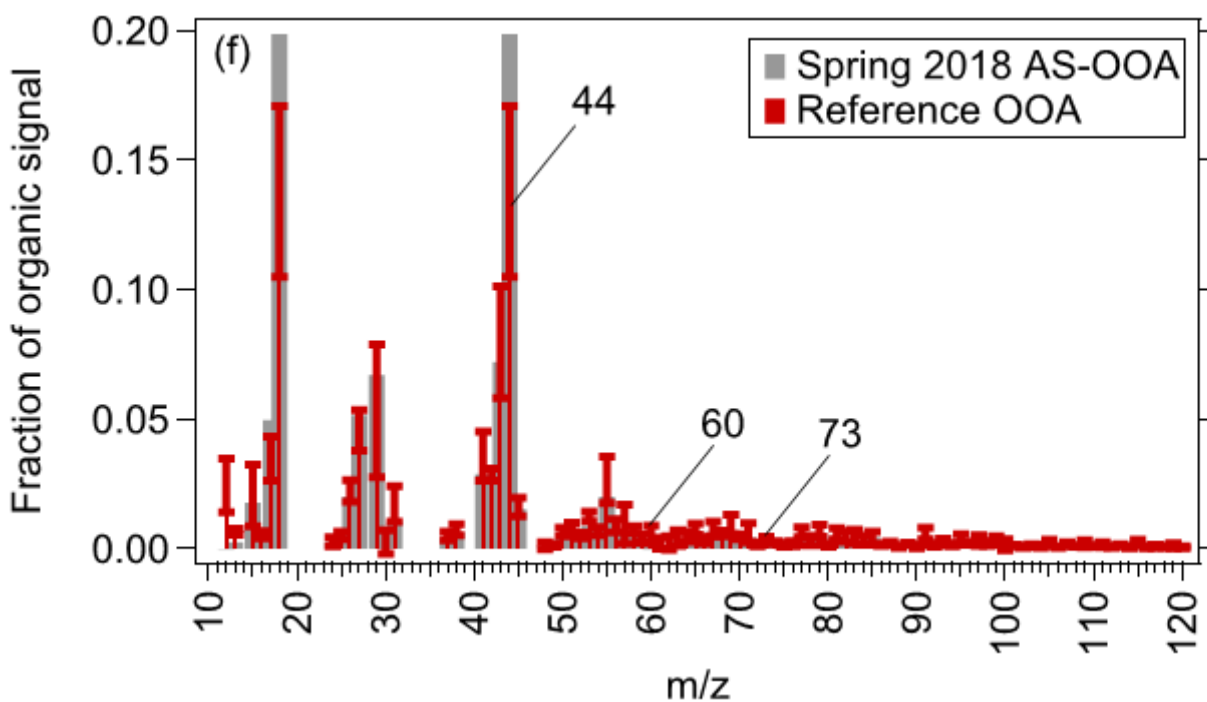
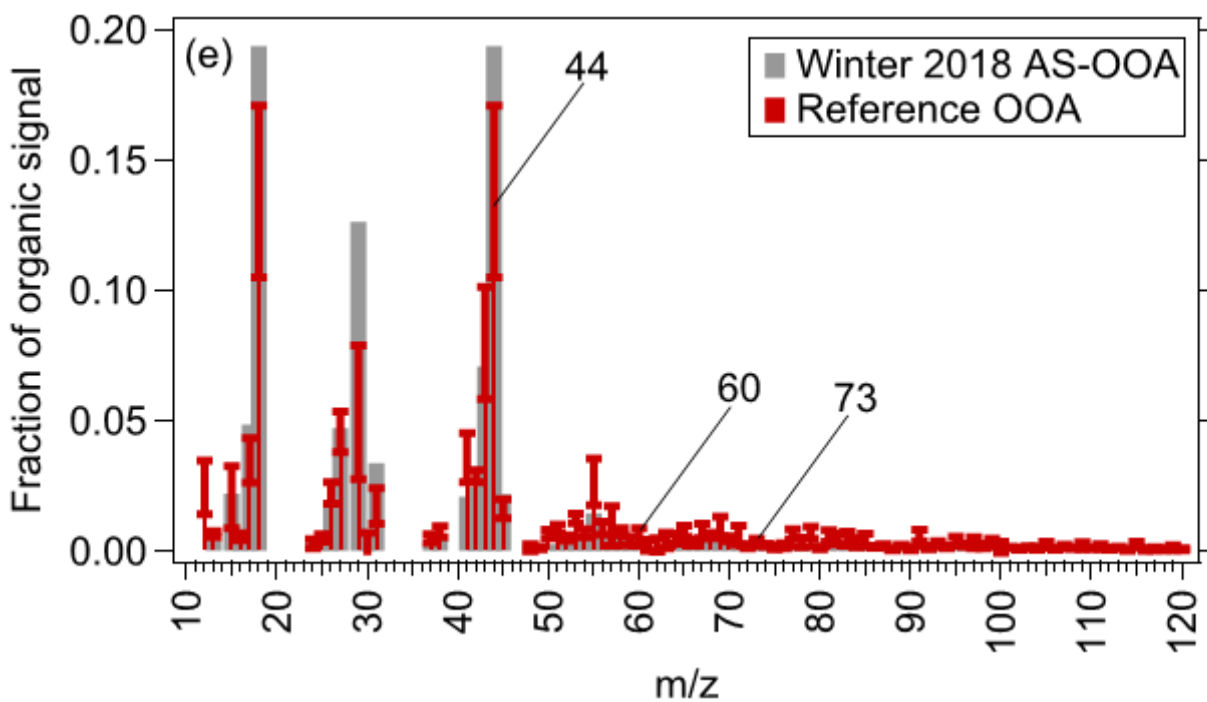



Figure S20 shows the average mass spectrum of the organic component (AS-OOA) of the combined organic-inorganic PMF factor ammonium sulfate mixed with oxidized organic aerosol (ASOOA) in different seasons. The whiskers in the graphs represent ±1 standard deviation of the

reference spectra. The comparison of PMF factor MS with reference OOA MS profile is shown in the order: (a) winter 2017, (b) spring 2017, (c) summer 2017, (d) monsoon 2017, (e) winter 2018, and (f) spring 2018. Clearly, AS-OOA profiles are similar to reference OOA.

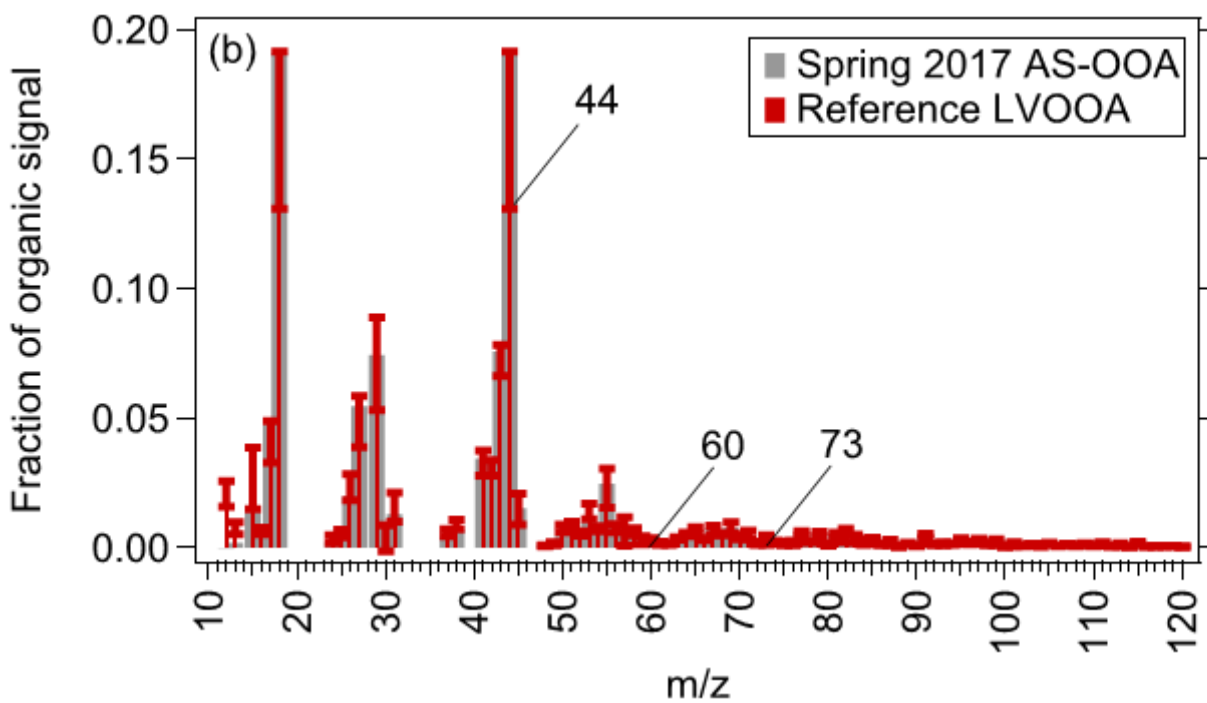
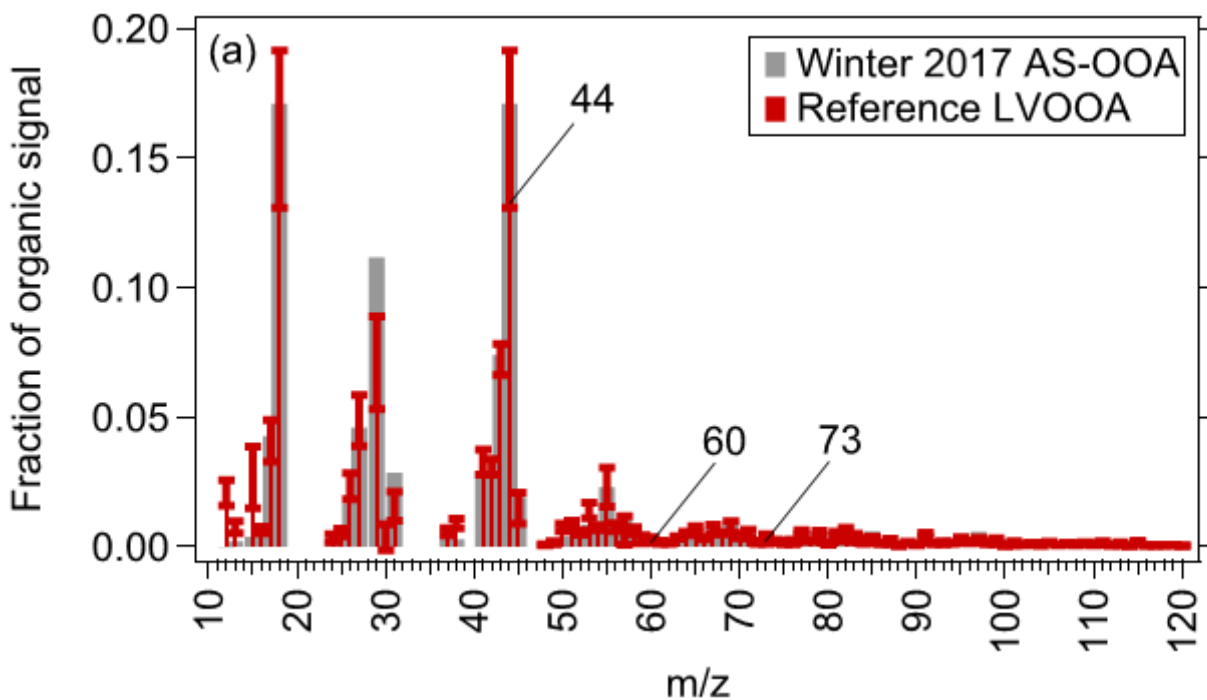
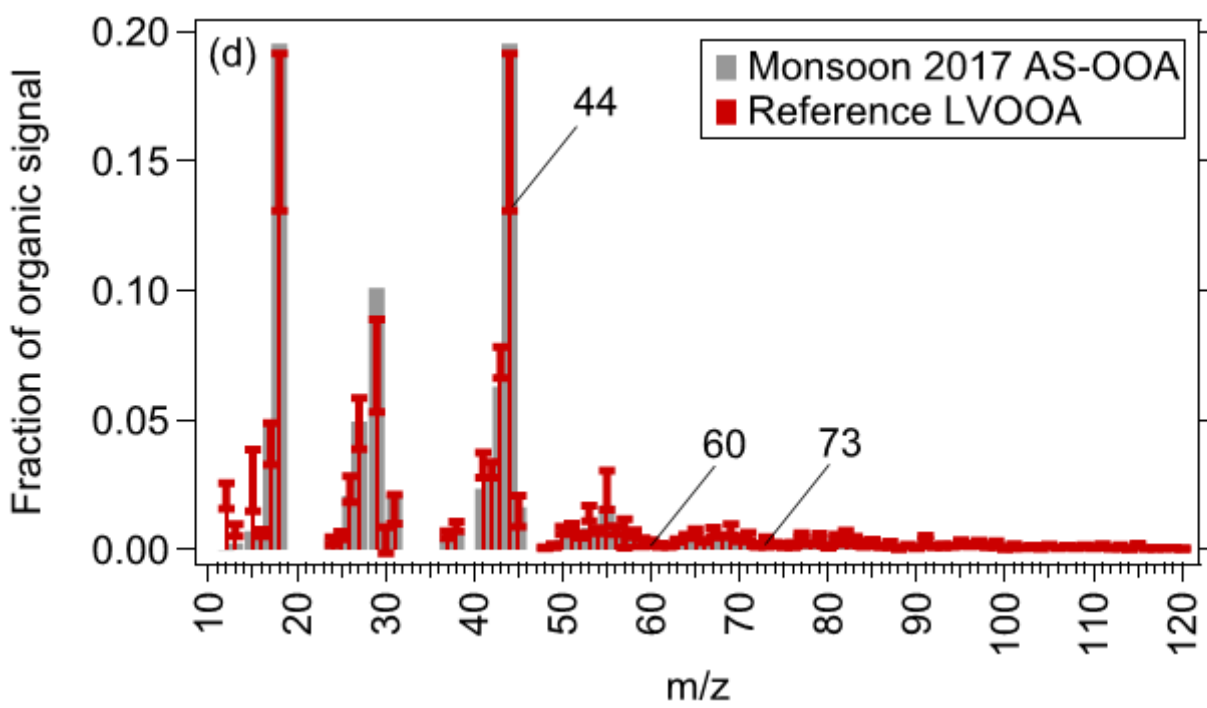
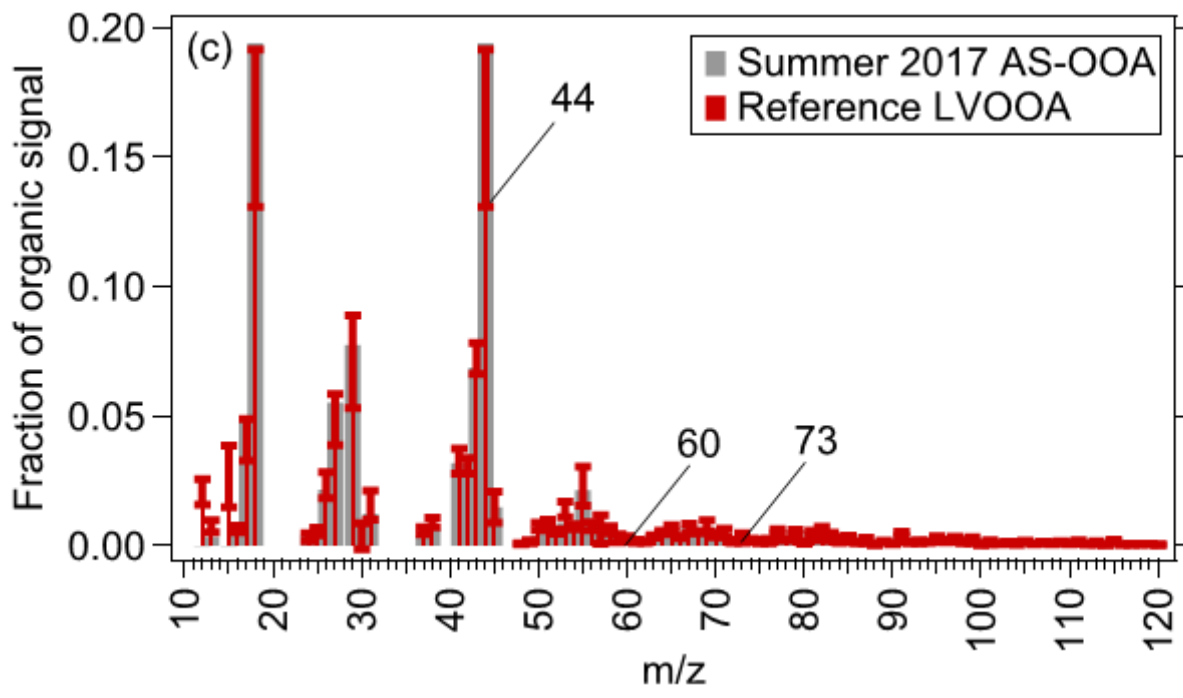
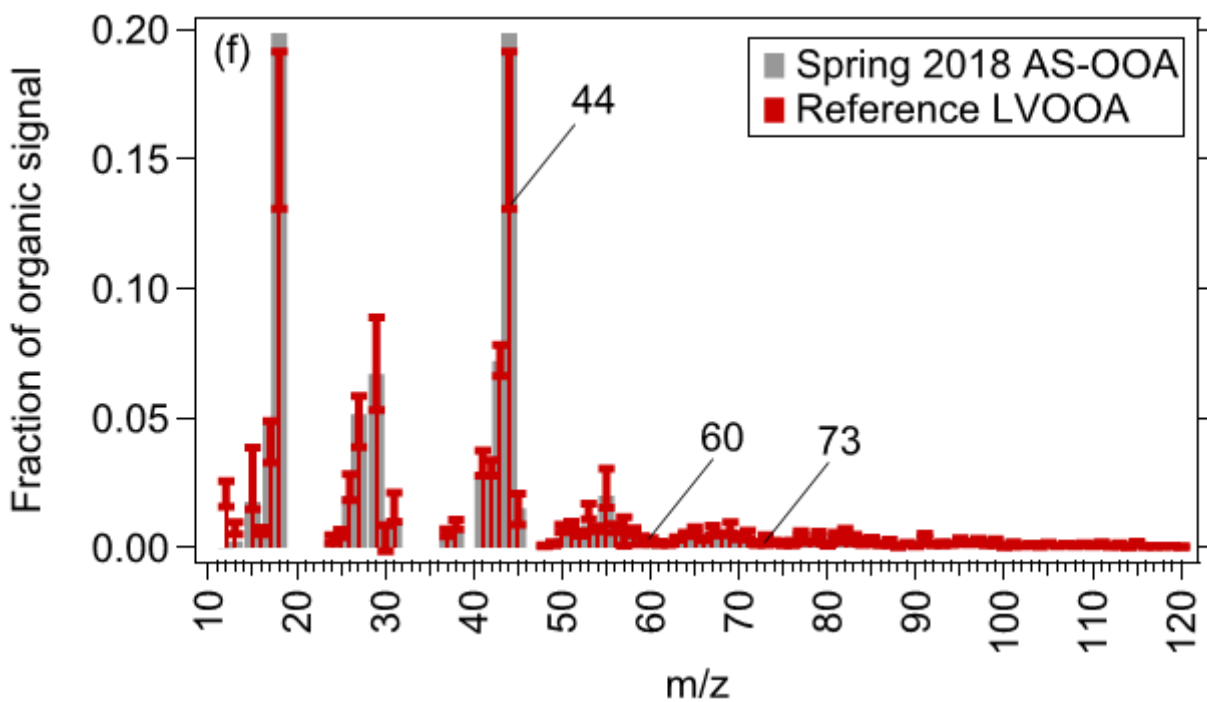
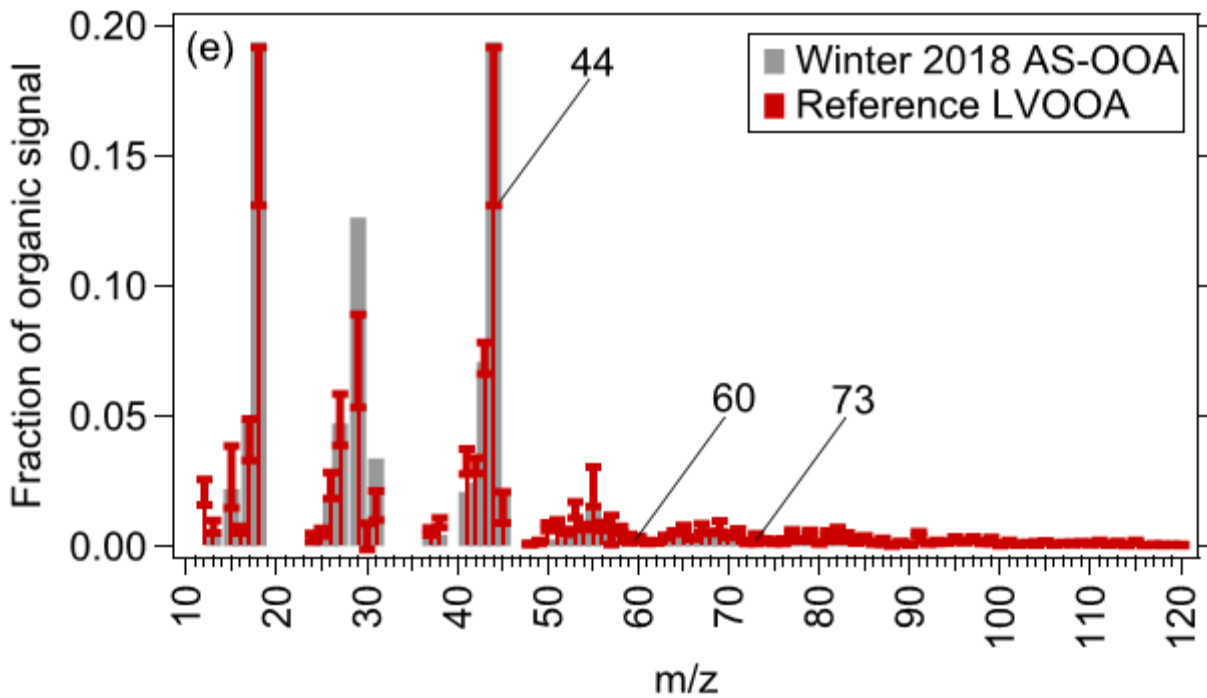



Figure S21 shows the average mass spectrum of the organic component (AS-OOA) of the combined organic-inorganic PMF factor ammonium sulfate mixed with oxidized organic aerosol (ASOOA) in different seasons, which is similar to the reference LVOOA profile. The whiskers in the graphs represent ±1 standard deviation of the reference spectra. The comparison of PMF factor MS with reference profiles is shown in the order: (a) winter 2017, (b) spring 2017, (c) summer 2017, (d) monsoon 2017, (e) winter 2018, and (f) spring 2018.

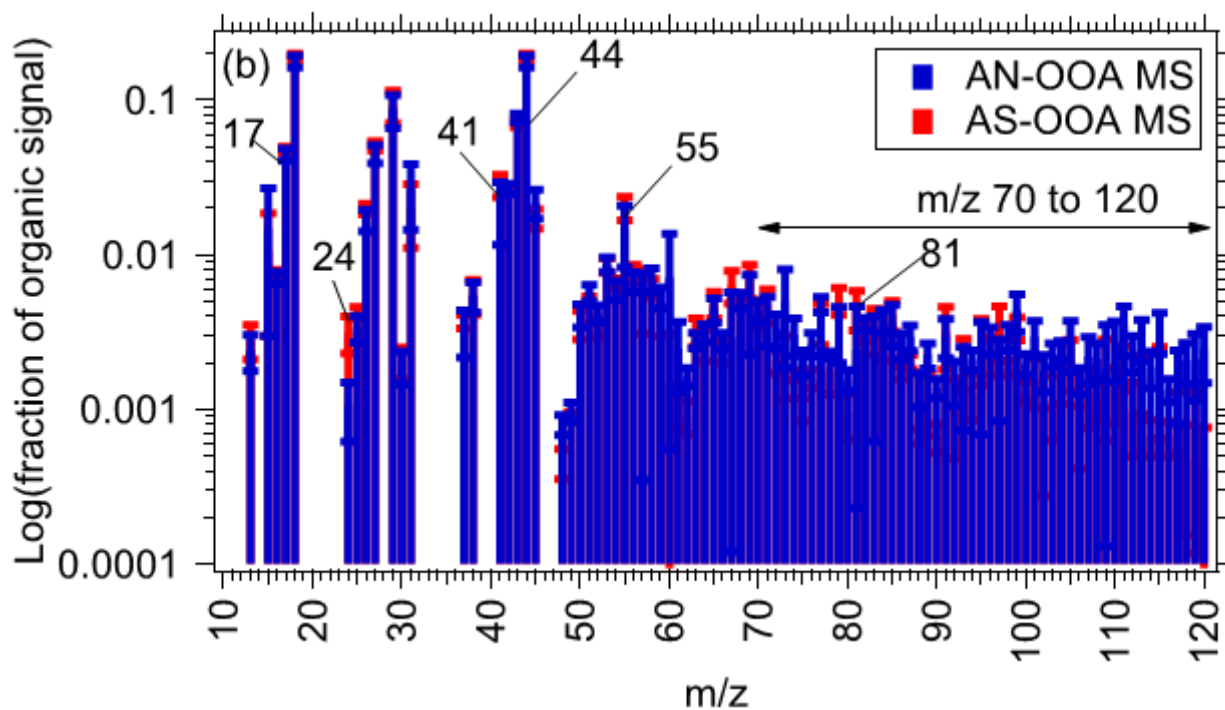
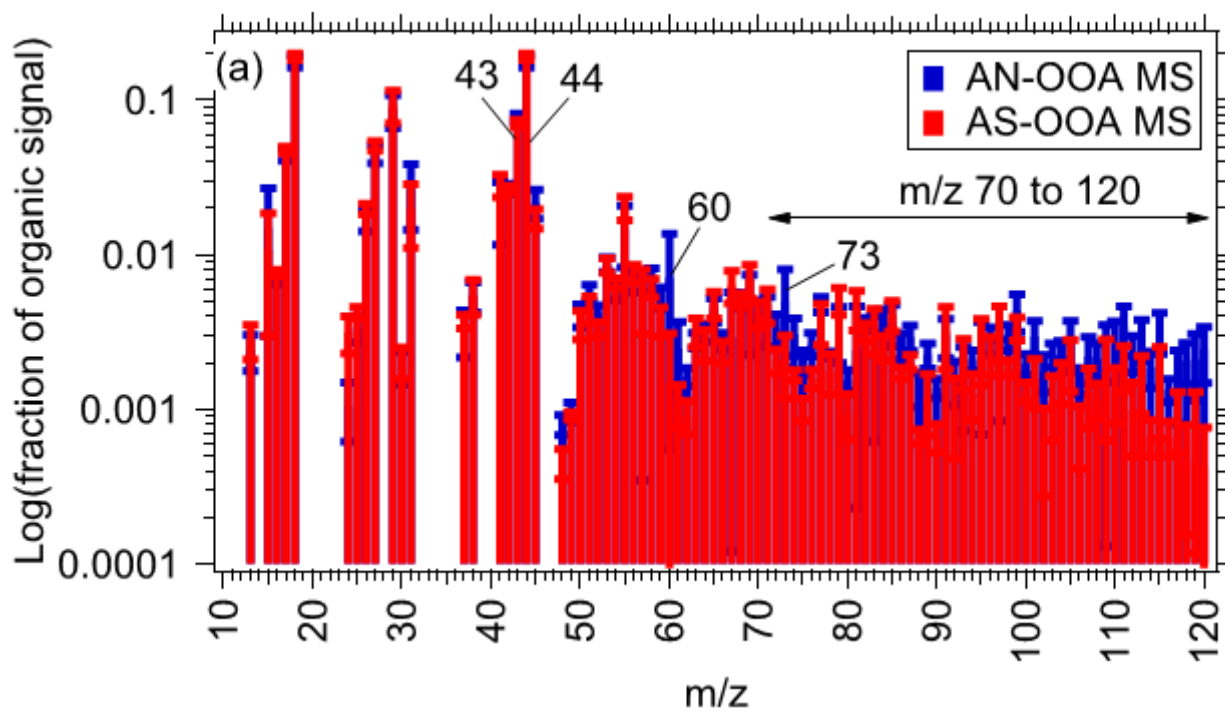



Figure S22 shows the comparison of logarithmic fractional contributions at different m/zs in the organic components AN-OOA and AS-OOA of the combined organic-inorganic PMF factors ANOOA and ASOOA respectively with (a) AS-OOA overlaid on AN-OOA and (b) AN-OOA overlaid on AS-OOA. AS-OOA profiles have a higher contribution at prominent lower m/zs, such

as 17, 24, 41, 44, 55, and 81. AN-OOA has higher mean contributions at m/z 43 and higher m/zs between 70–120.

(e) >95th percentile

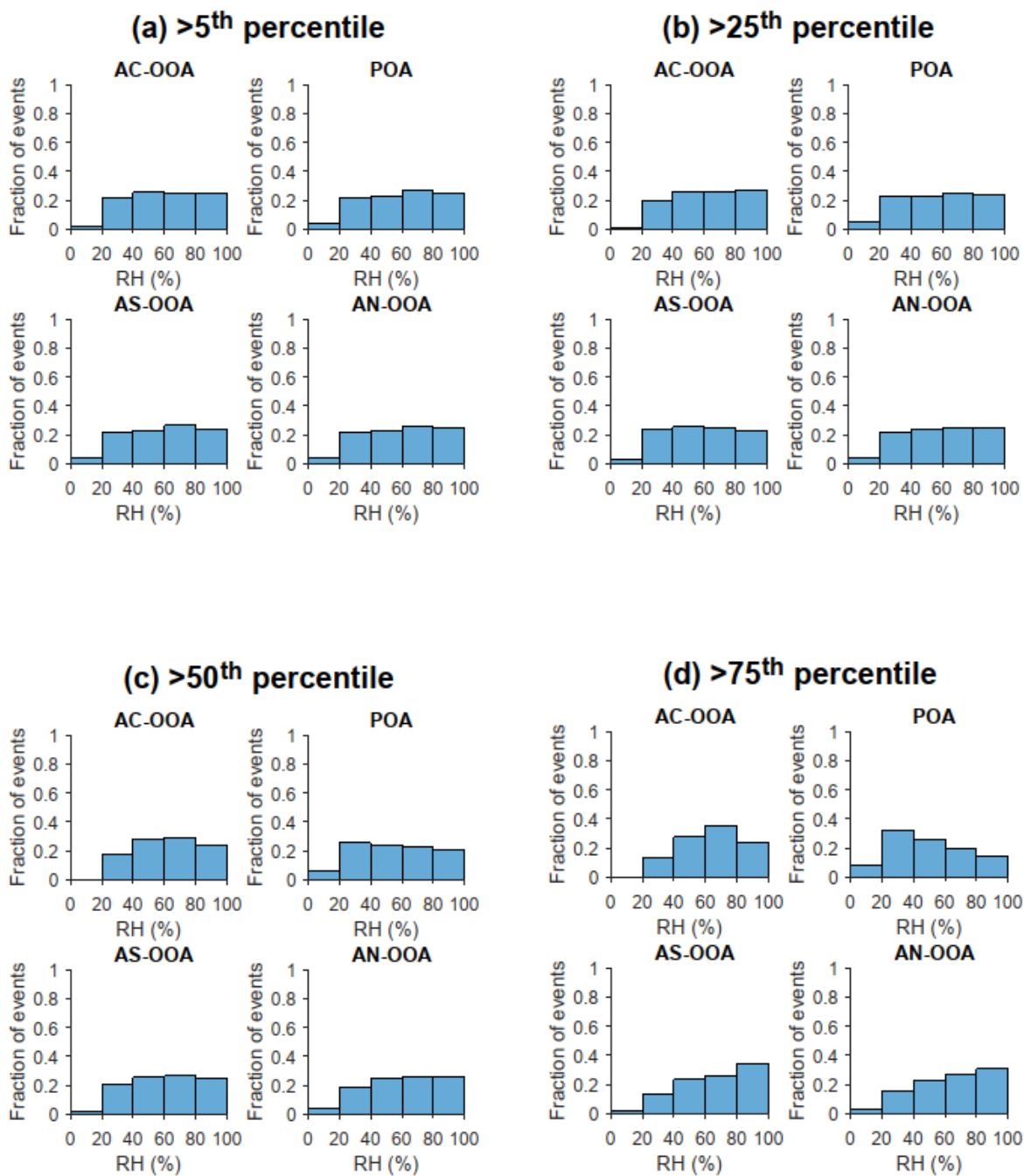
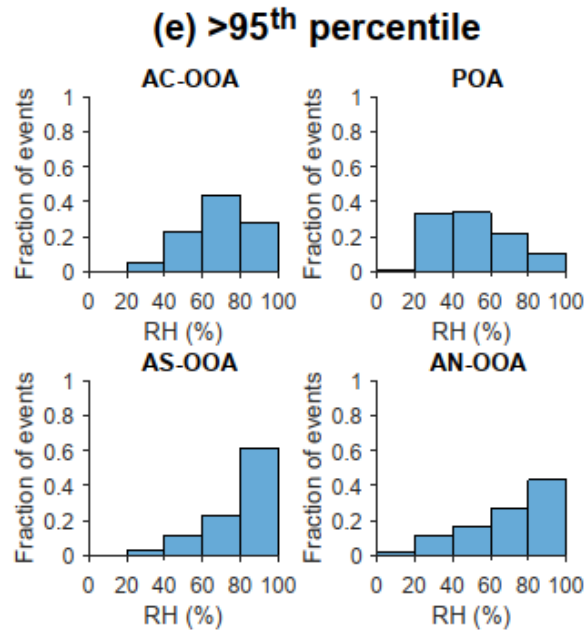



Figure S23 shows histogram plots of the fraction of events corresponding to each combined organic-inorganic PMF factor at different RH bins. The subplots correspond to a selection of data for each factor based on percentiles greater than (a) 5%, (b) 25%, (c) 50%, (d)75%, and (e) 95%. Based on these plots, higher pollution episodes of ASOOA are associated with higher RH, especially at greater than 95 percentiles.

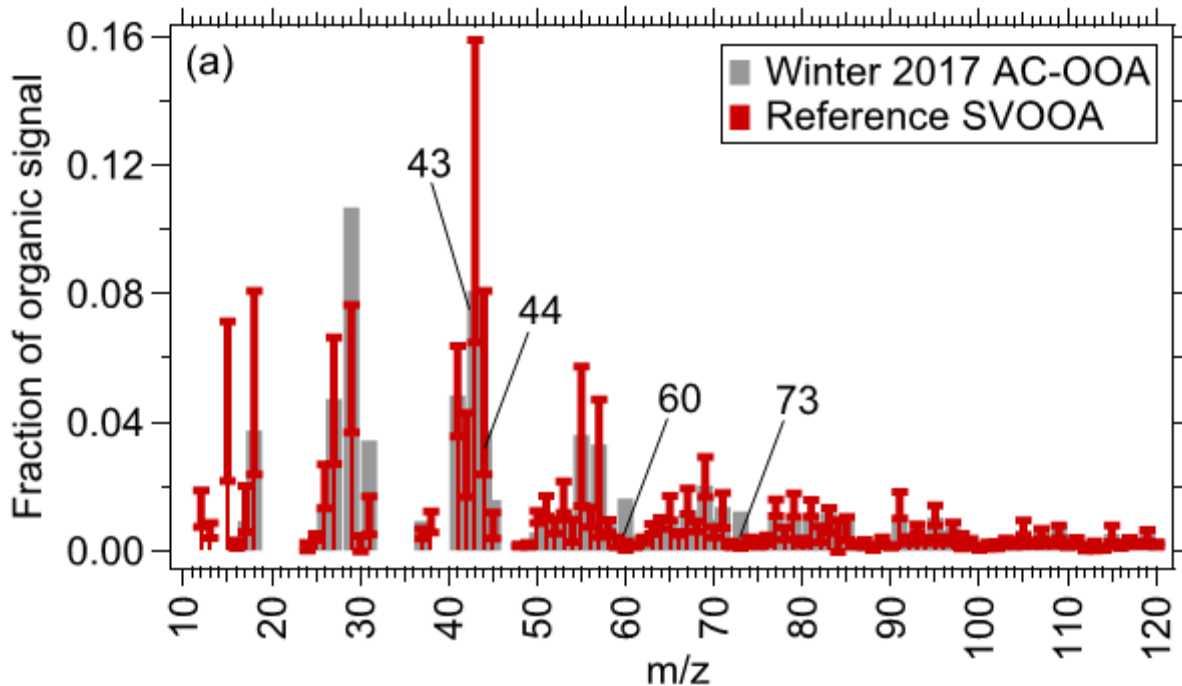
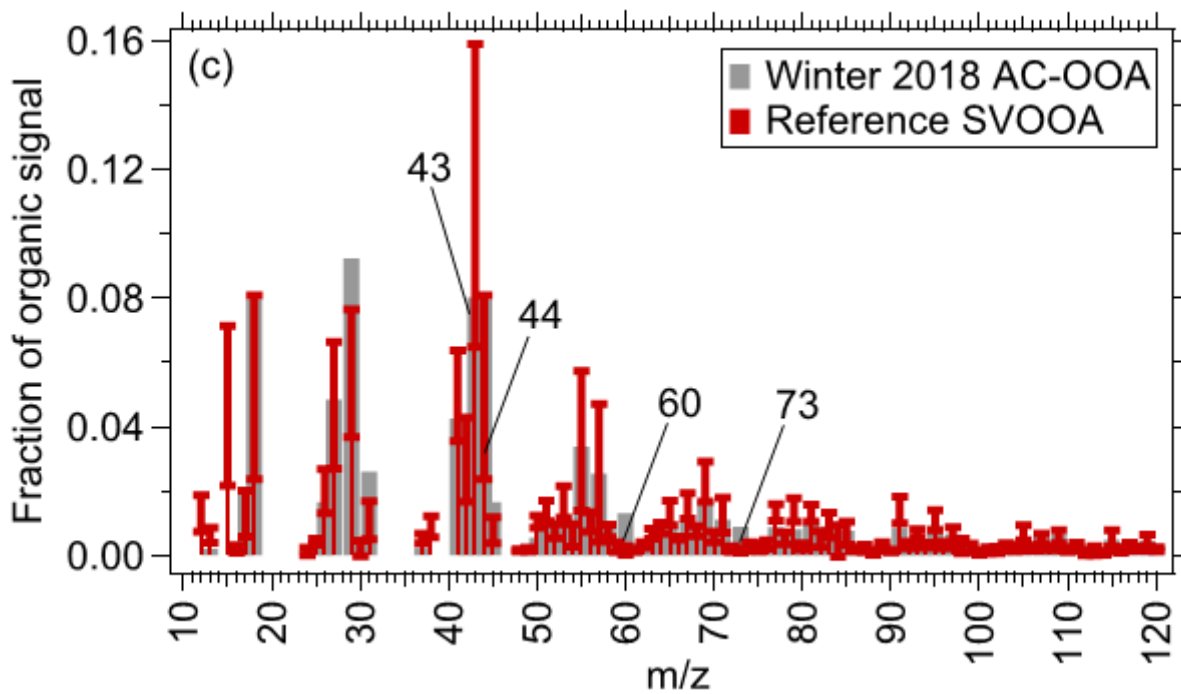
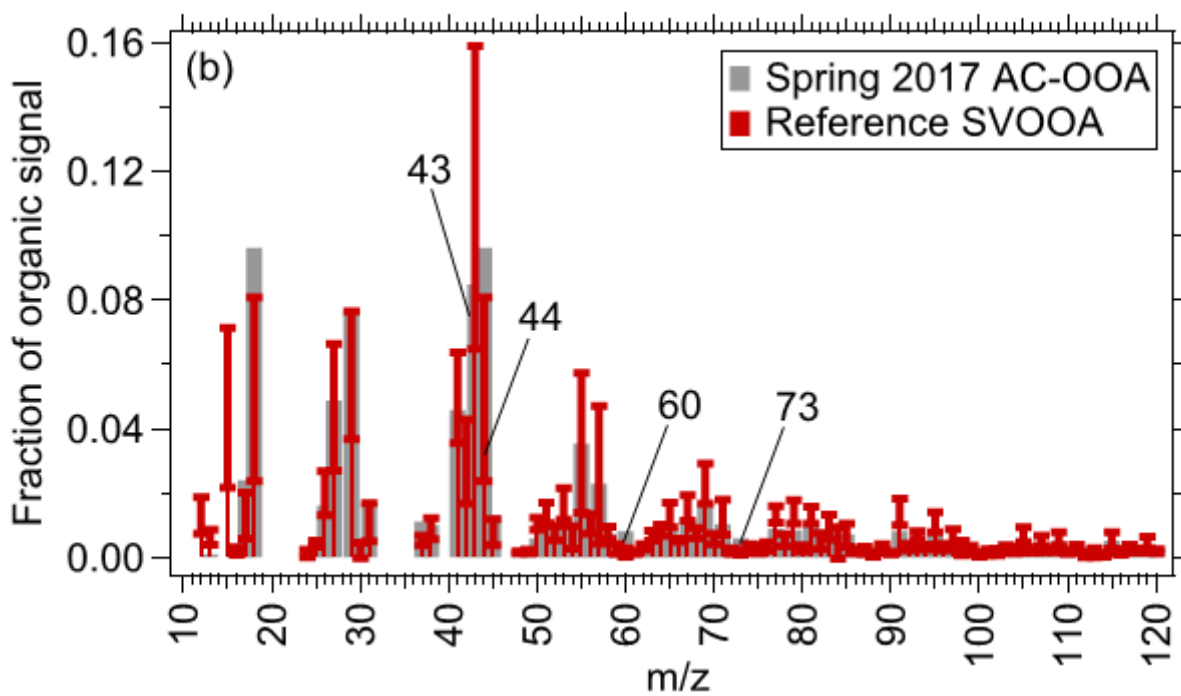
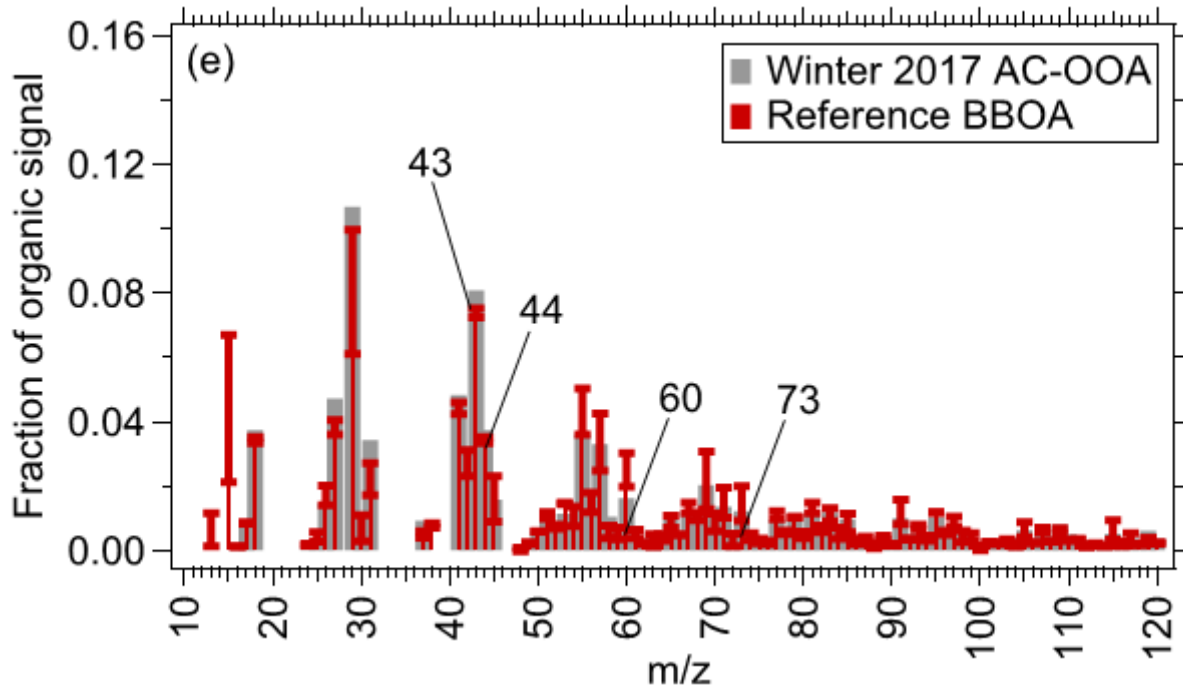
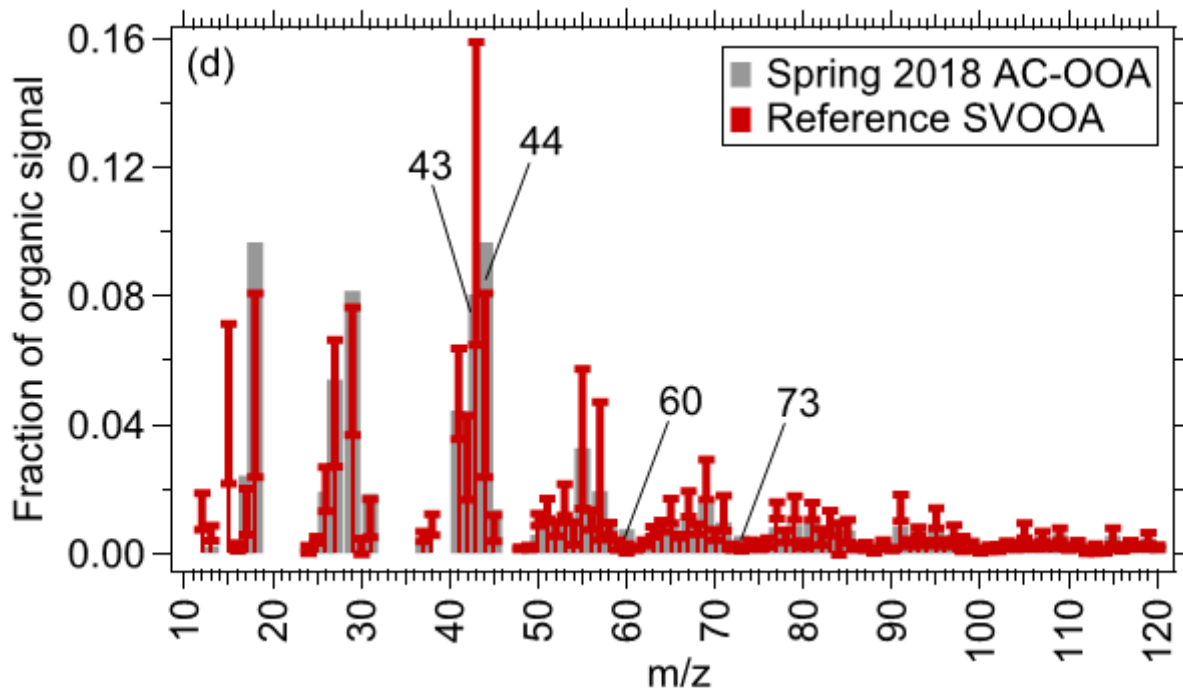
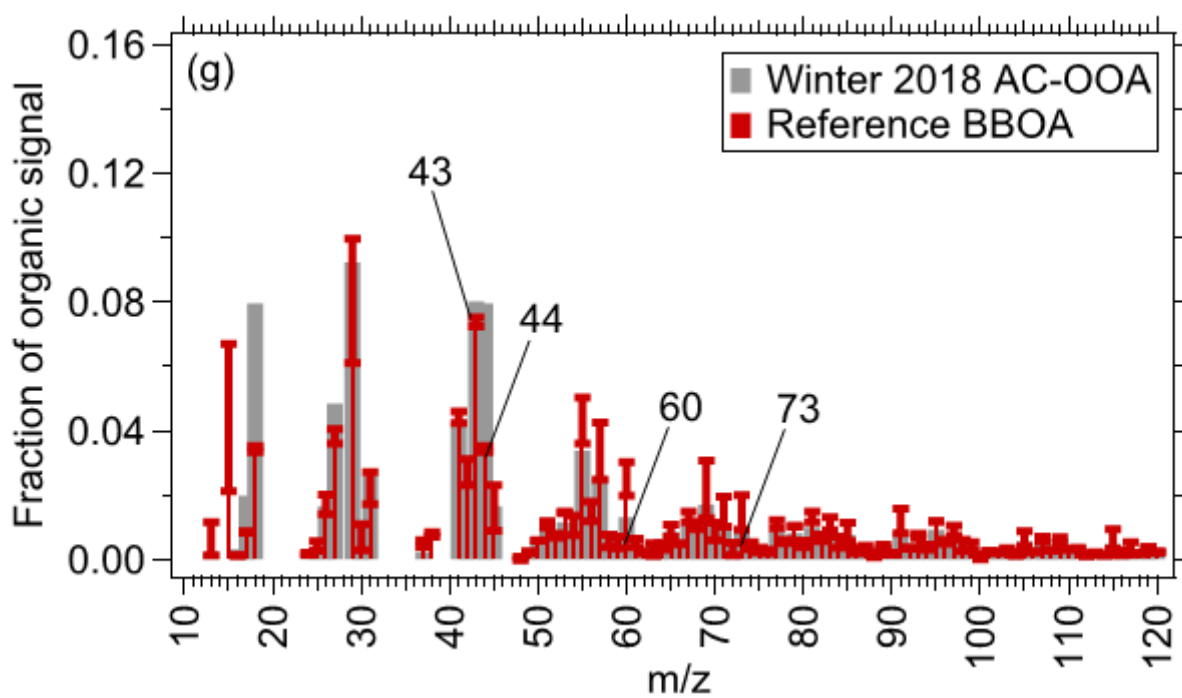
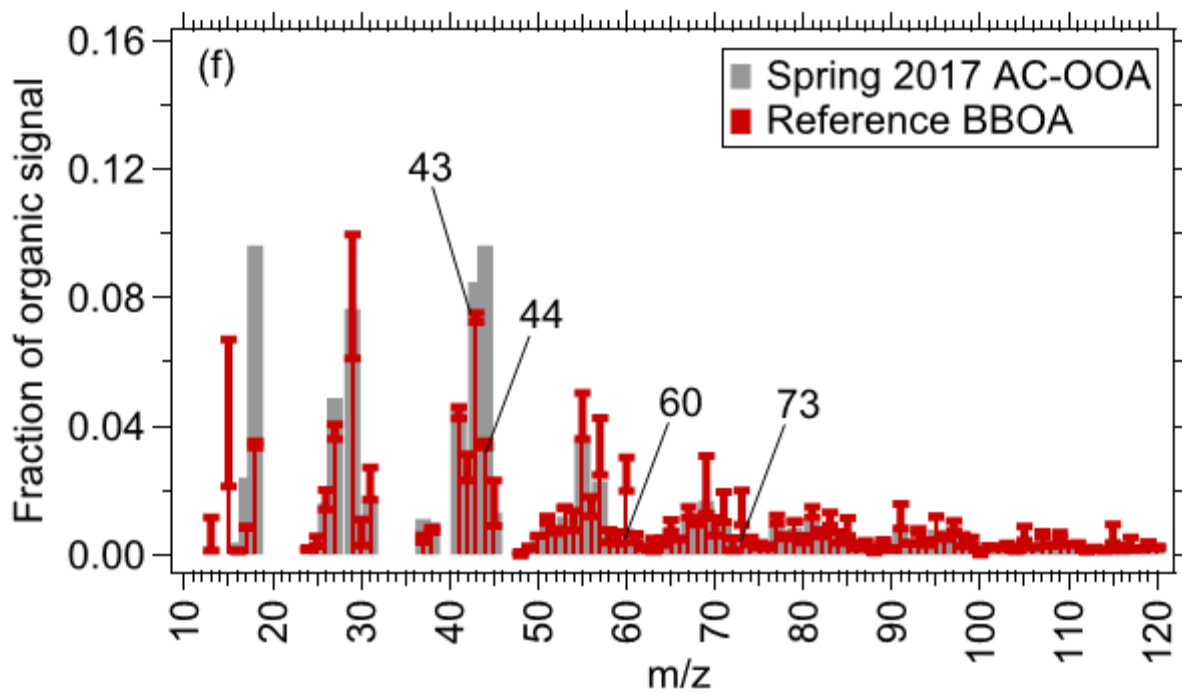
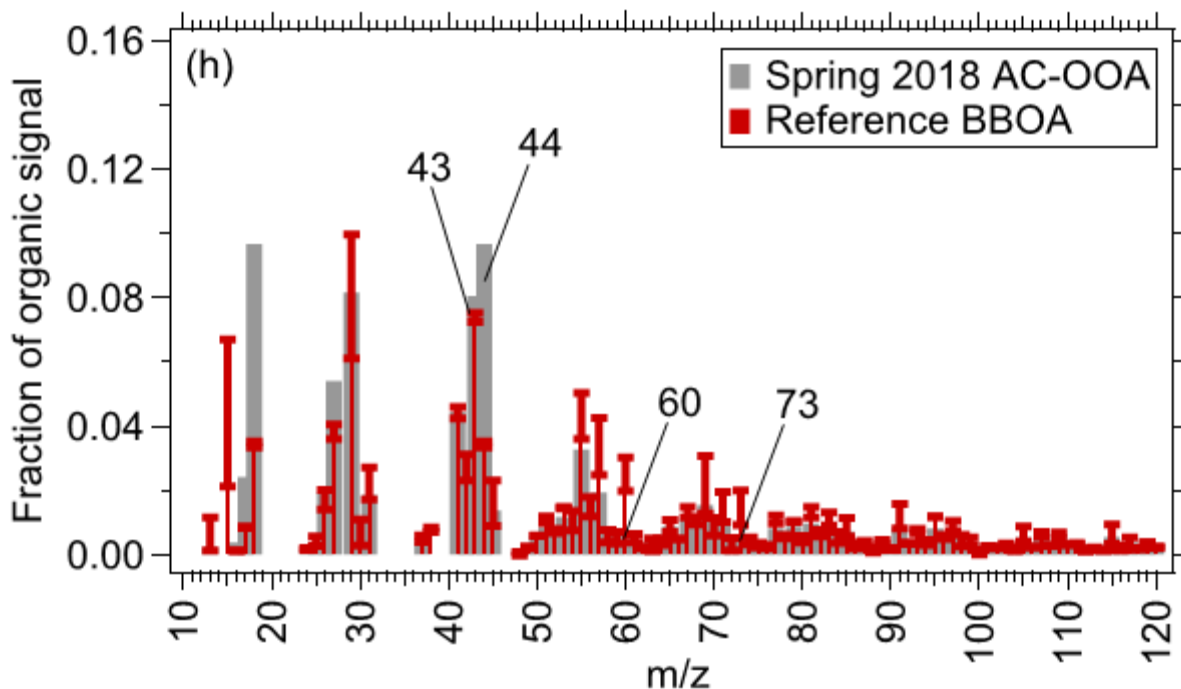



Figure S24 shows the average mass spectrum of the organic component (AC-OOA) of the combined organic-inorganic PMF factor ammonium chloride mixed with oxidized organic aerosol (ACOOA) in different seasons, which shows similarities to the reference SVOOA and BBOA factors. The whiskers in the graphs represent ±1 standard deviation of the reference spectra. The comparison of PMF factor MS with the SVOOA reference profile are in the order: (a) winter 2017, (b) spring 2017, (c) winter 2018, and (d) spring 2018. The comparison of PMF factor MS with the BBOA reference profile are in the order: (e) winter 2017, (f) spring 2017, (g) winter 2018, and (h) spring 2018. These figures show that the factors resemble oxidized biomass burning aerosol (higher fraction of organics at m/z 44 than reference BBOA profile).

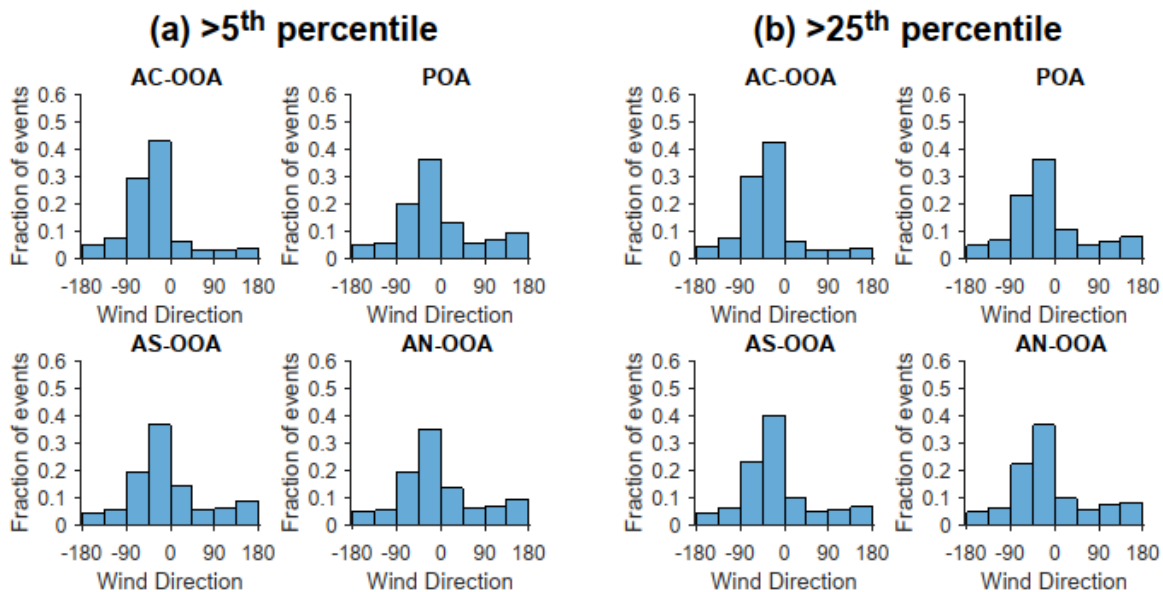
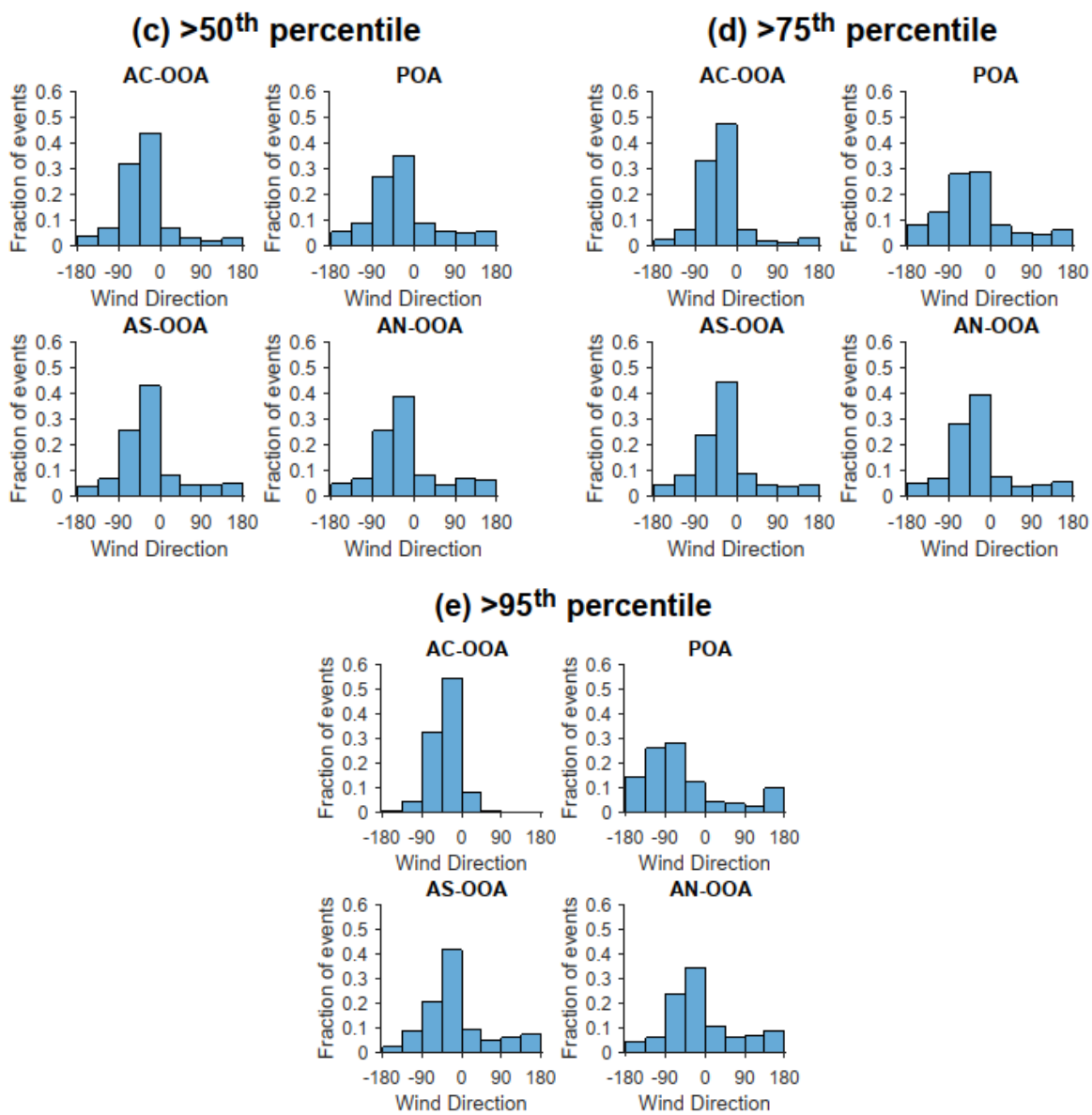



Figure S25 shows histogram plots of the fraction of events corresponding to each combined organic-inorganic PMF factor at different wind directions (°). The subplots correspond to a selection of data for each factor based on percentiles greater than (a) 5%, (b) 25%, (c) 50%, (d)75%, and (e) 95%. Based on these plots, ammonium chloride shows exceptional directionality, pointing to sources in the N-NW direction.

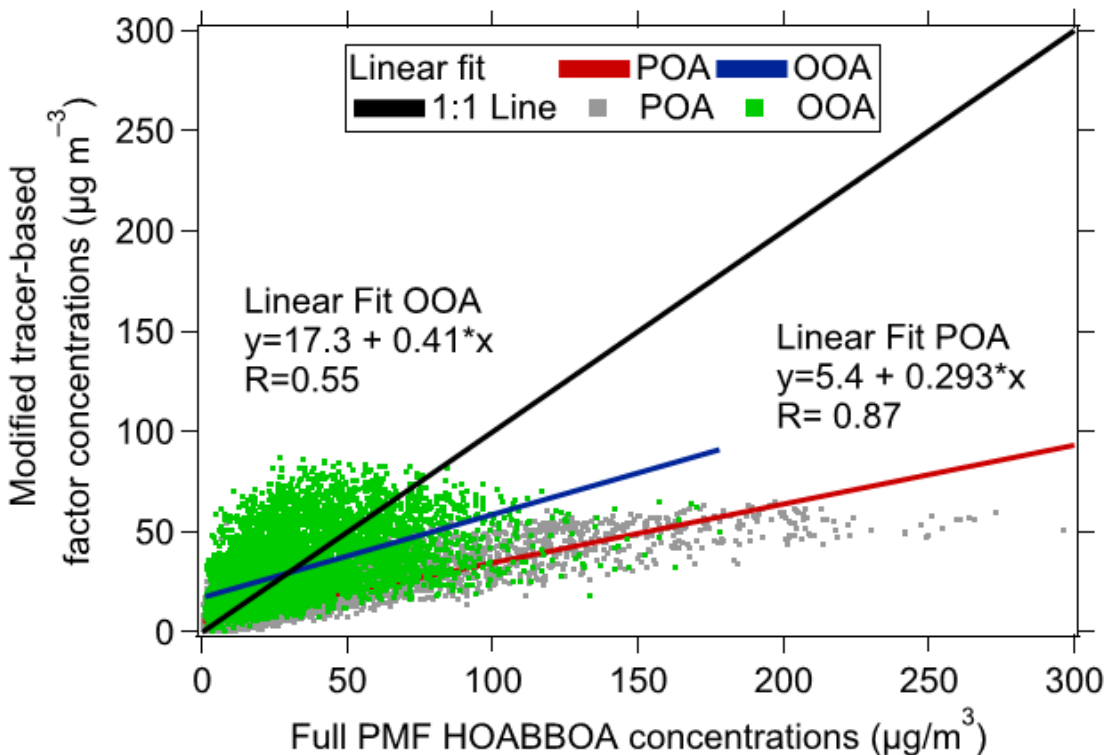



Figure S26 shows the comparison of the tracer-based OOA and POA concentrations with those obtained from organic-only PMF, without the application of mass closure. The linear correlations and slopes are substantially different from 1 and point to the limitation of this tracer approach.

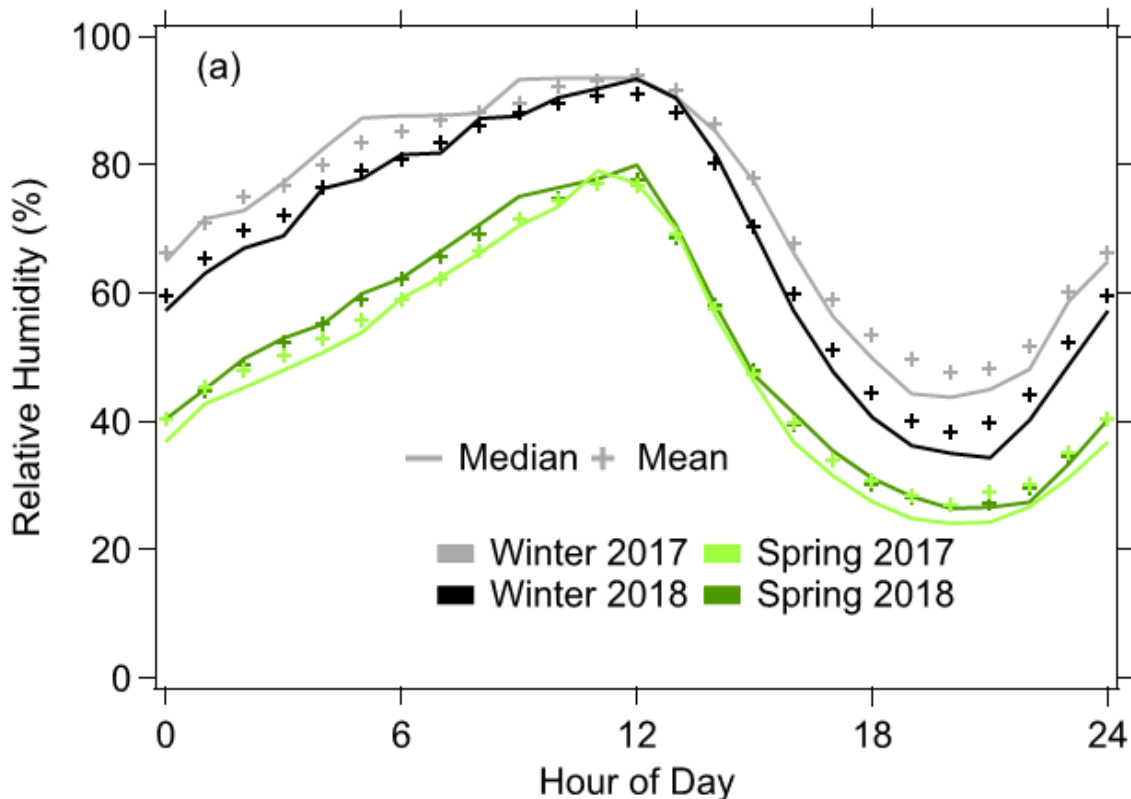
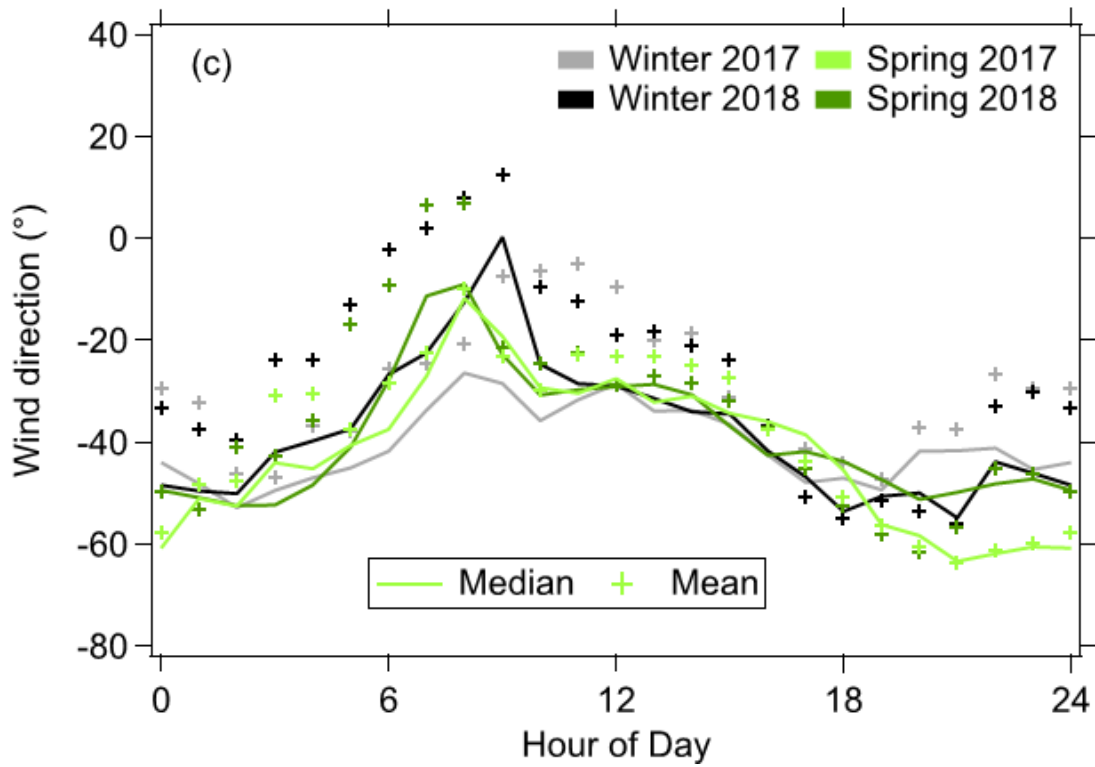
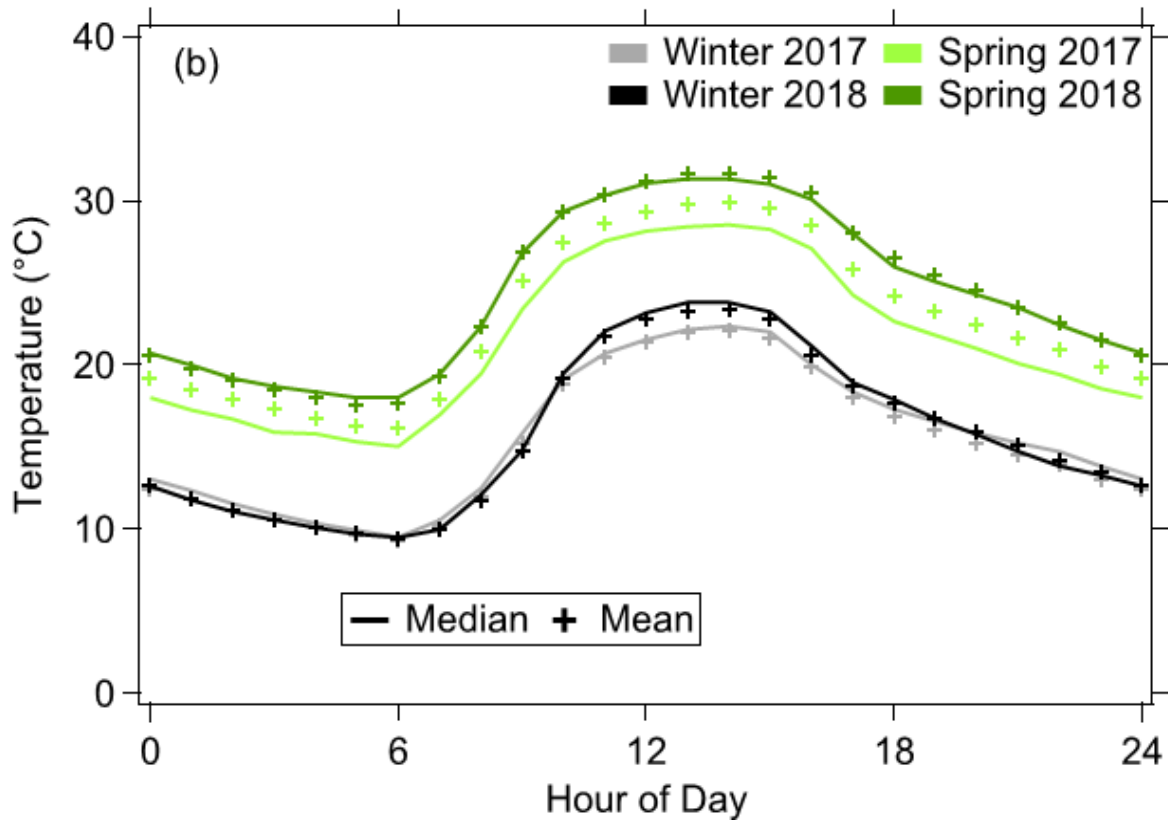
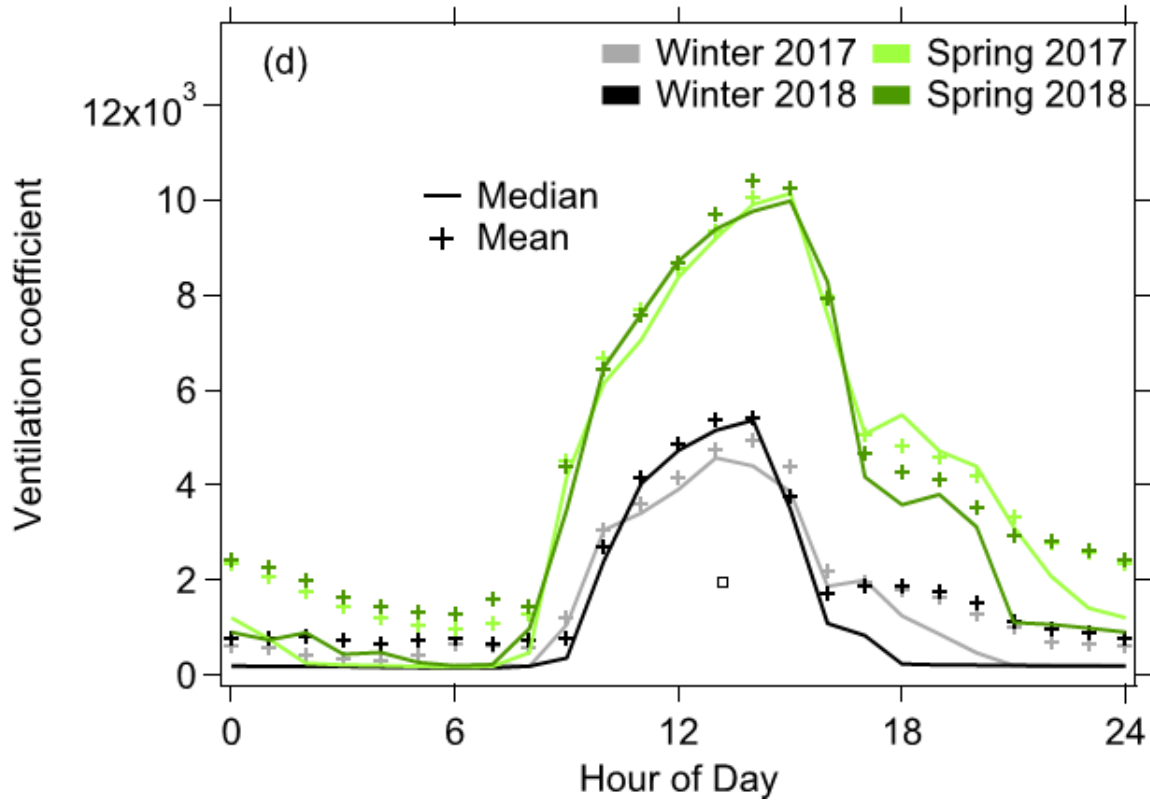
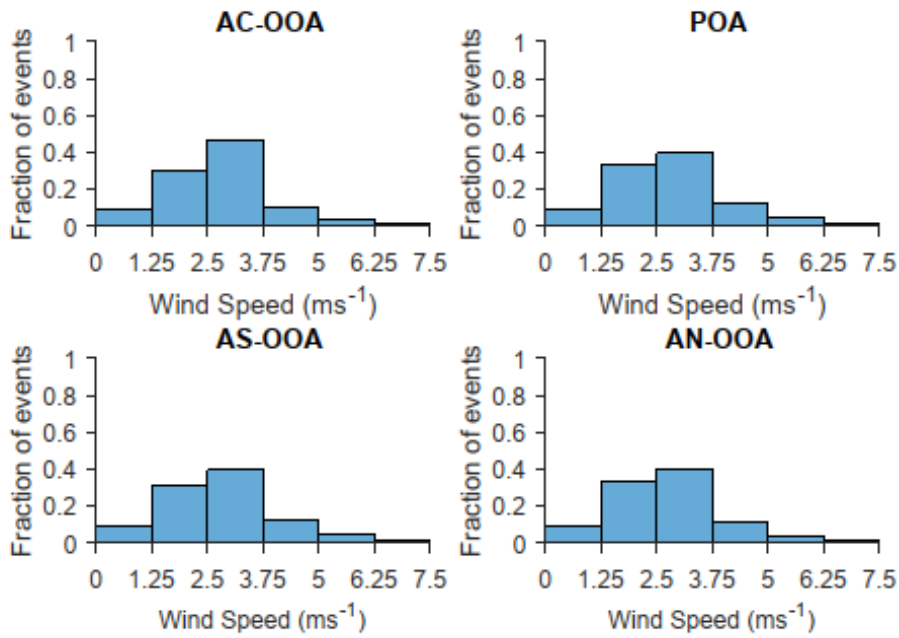
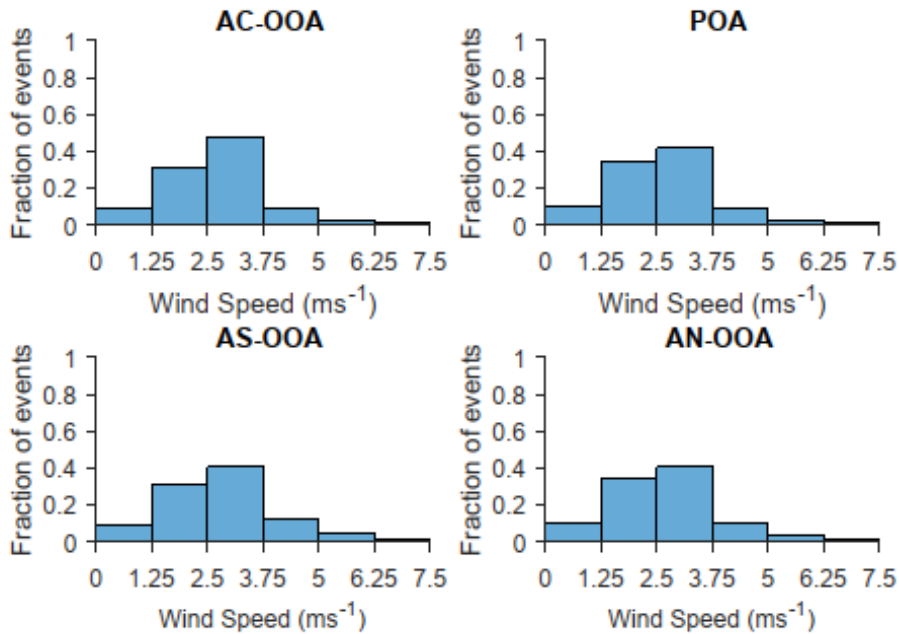
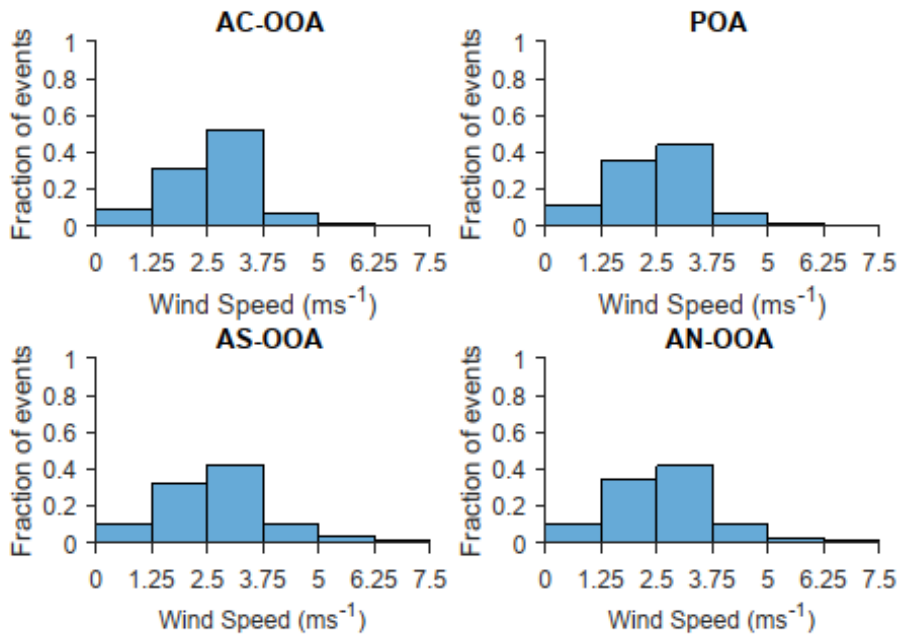
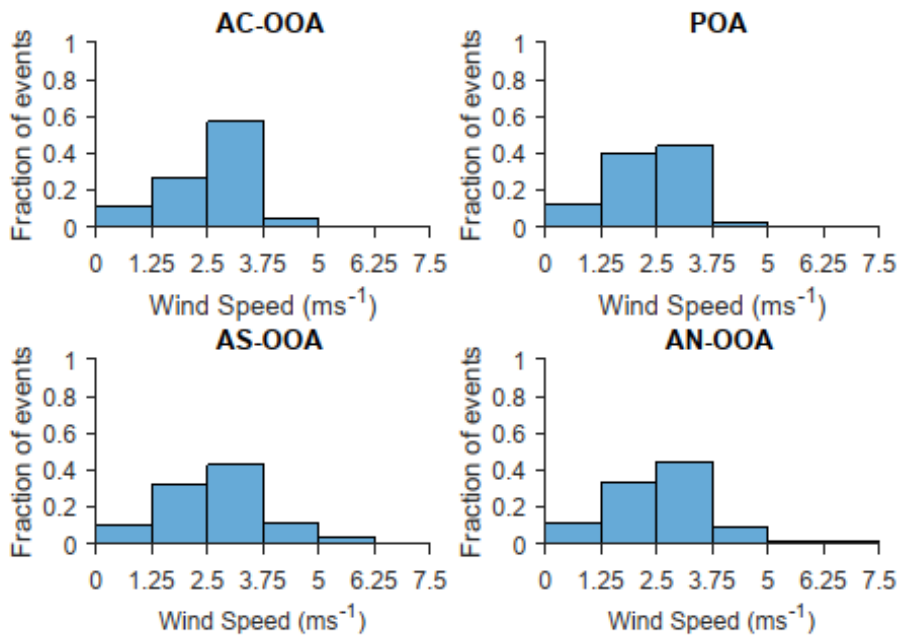



Figure S27 This figure shows the diurnal patterns of mean and median (a) relative humidity (%), (b) temperature (°C), (c) wind direction (°), (d) ventilation coefficient (m^2 s^{-1}) across winters and springs of 2017 and 2018.

(c) >50th percentile

(d) >75th percentile

(e) >95th percentile

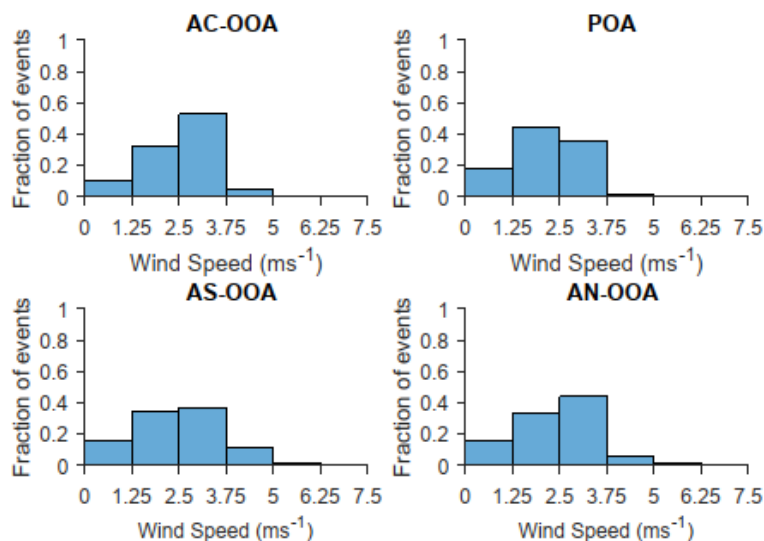
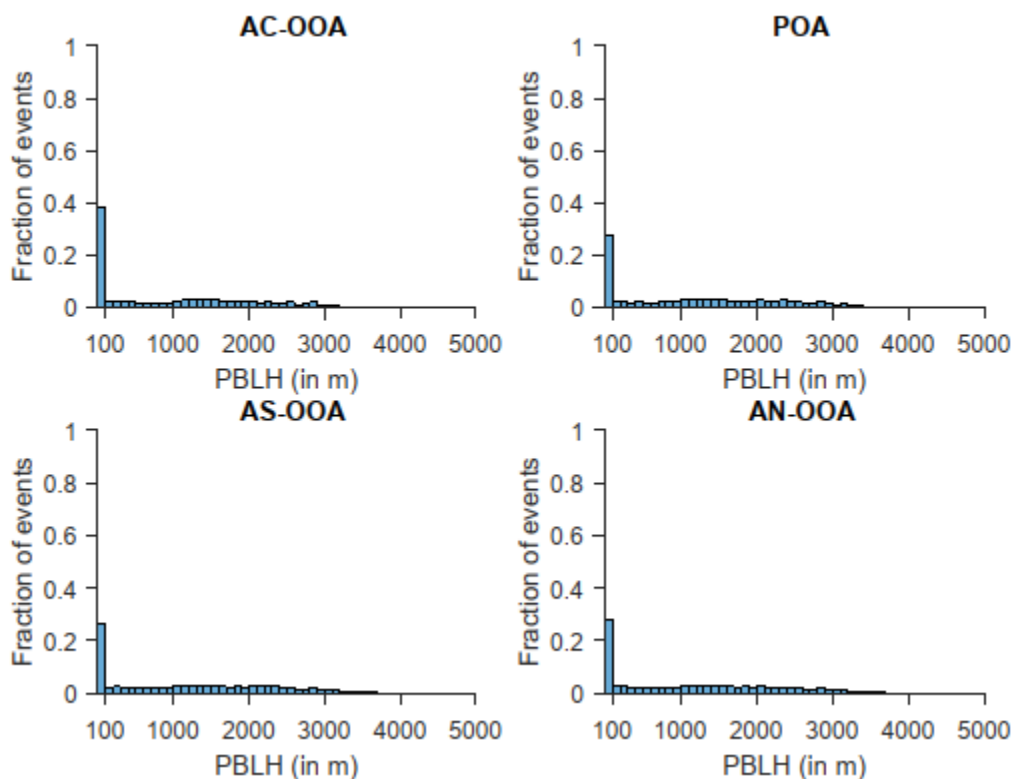
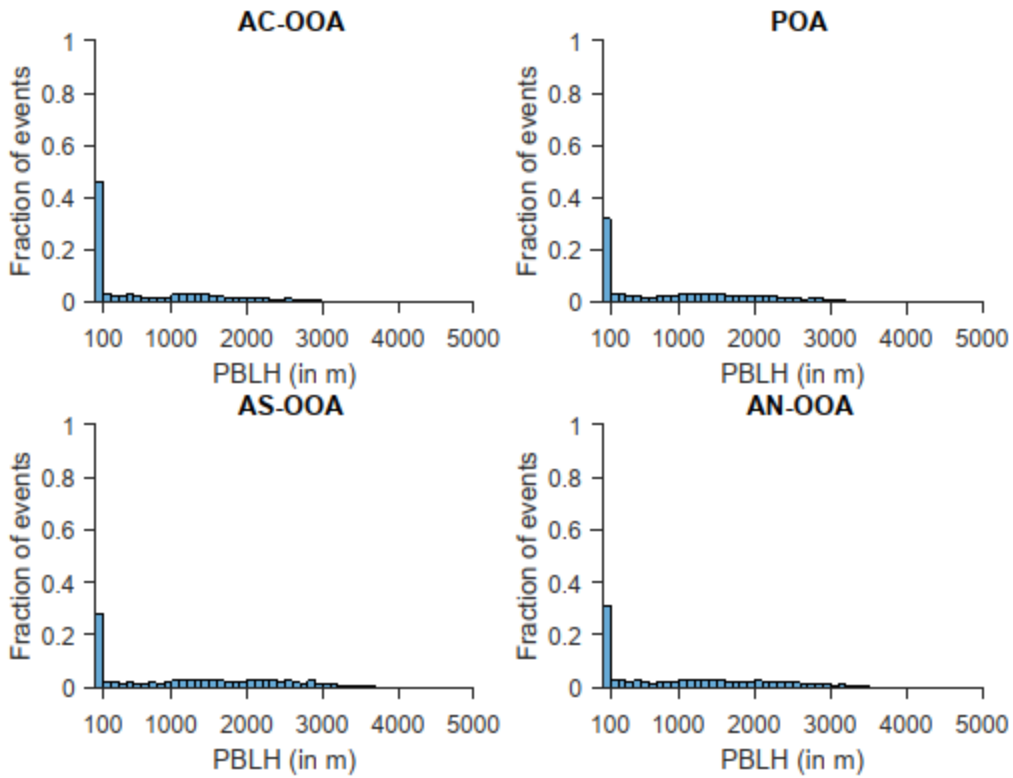



Figure S28 shows histogram plots of the fraction of events corresponding to each combined organic-inorganic PMF factor in different wind speed bins. The subplots correspond to a selection of data for each factor based on percentiles greater than (a) 5%, (b) 25%, (c) 50%, (d)75%, and (e) 95%. Based on these plots, for all factors at nearly all percentiles studied, pollution increases with wind speed, up to 3.75 ms^{-1}.

(a) >5th percentile

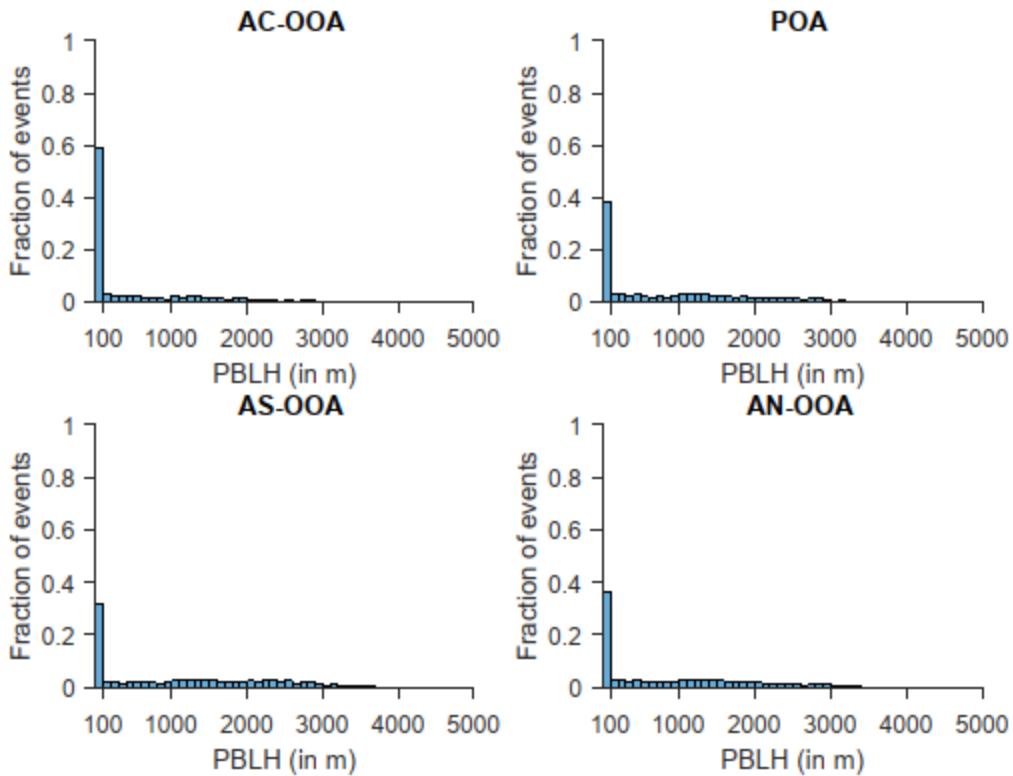
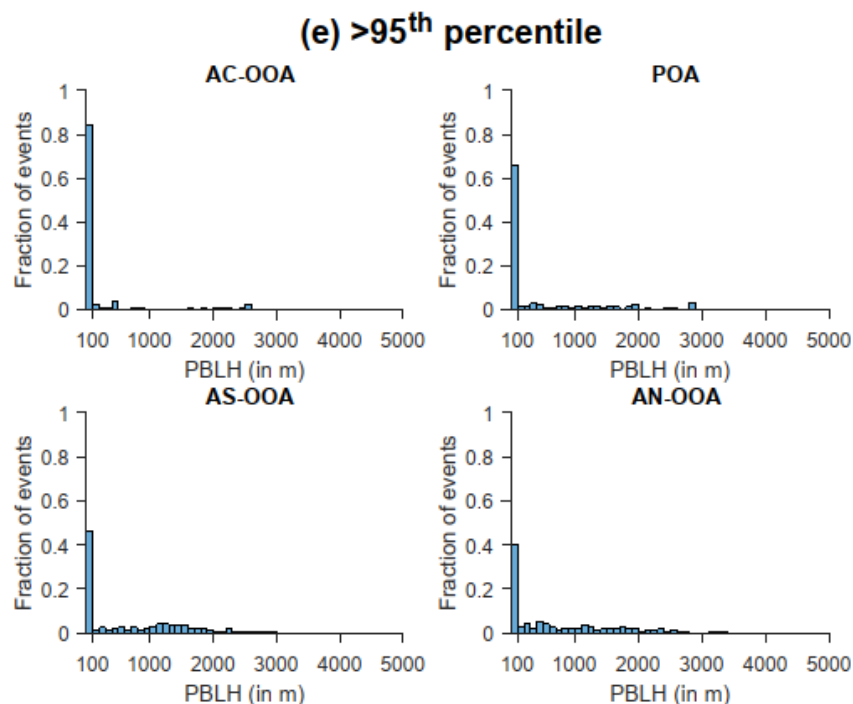
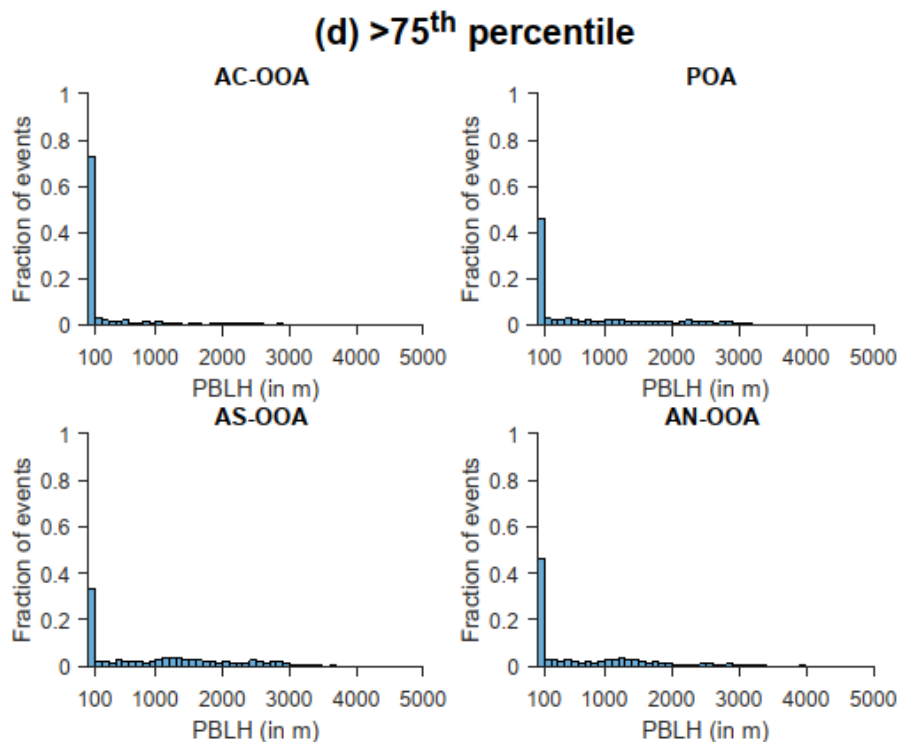



Figure S29 shows histogram plots of the fraction of events corresponding to each combined organic-inorganic PMF factor in different PBLH bins. The subplots correspond to a selection of data for each factor based on percentiles greater than (a) 5%, (b) 25%, (c) 50%, (d)75%, and (e) 95%. Based on these plots, percent of chloride episodes in the lowest bin (PBLH<100 m) increases from 50% to >90%. In comparison, POA episode % increases from about 40% to 75%, whereas AN-OOA and AS-OOA increase from about 40% to 60%. Thus, boundary layer dynamics seem to regulate all components—not just primary or secondary.

Figure S30 This figure shows the histogram plots of the fraction of events corresponding to each combined organic-inorganic PMF factor in different VC bins. The subplots correspond to a selection of data for each factor based on percentiles greater than (a) 5%, (b) 25%, (c) 50%, (d)75%, and (e) 95%. Based on these plots, the lowest ventilation coefficient up to 500 units displays increasing clustering for higher percentiles of episodes as the selection is made from 5th to 95th percentile. The increase is from ~55% to 80% for POA and ~55% to about 80% for AN-OOA and AS-OOA. Clearly, the modulation is similar for primary and secondary components.

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