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Supplementary Material

Summertime Aerosol Over the West of Ireland Dominated by Secondary Aerosol During Long-Range Transport

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OA Source Apportionment:

Free PMF identified two factors: peat and OOA. As shown in Figure S1, there is a large drop in the Q/Qexp value from 1 to 2 factors, and Q/Qexp is 0.81 at 2 factors. However, no strong change in Q/Qexp was observed by further increasing the number of factors. Figure S2 shows that 3-factor or 4-factor solutions led to the splitting of factors and no more meaningful factors could be identified.

In the 2-factor solution, Factor 1 was identified as an OOA-like factor because it correlated well, R = 0.94, with the reference OOA profile from Ng et al, [2] (Table S1). OOA-like factor contains a typically high signal at mass to charge ratio (m/z) 44, arising mainly from CO_2^+ and associated with aerosol aging or secondary formation. Factor 2 was identified as a peat-like factor that correlated well (R = 0.91) with the reference peat profile (Table S1); its correlation with other reference factors was poorer (e.g., r = 0.75–0.77 with HOA) [3]. Figure S3 shows the time series of the OOA-like and peat-like factors. The time series of OOA-like factor correlated well with sulfate (R = 0.83), indicating a secondary nature. Peat-like factor correlated well with the time series of m/z 60 (R = 0.81), a marker of biomass burning emission. The diurnal cycle of OOA shows a flat pattern at a relatively high concentration level (~1.2 μg m^{-3}, Figure S4a), indicating regional transport was the major source. On average, OOA contributed 85% of the total OA mass. In contrast, peat-like factor remained at a very low concentration level (<0.2 μg m^{-3}) during the day, but it rose to ~0.5 μg m^{-3} at ~21:00.

However, the profile of peat-like factor in the free PMF 2-factor solution (Figure S2a) contained no m/z 44 fraction and higher than expected m/z 29 fraction when compared to the reference peat profile [3], compromising their attributions. To evaluate the contribution of peat with different degree of variation (0% to 90%, Figure S5) from the reference peat profile, *a* value approach within ME-2 was applied [3]. Over the range of *a* value (0.0–0.9), the mean value of the relative contribution for peat was 16% ± 0.9% (± standard deviation), ranging from 15% to 18% (Figure S5). OOA factor contributed 84% ± 0.9%, ranging from 82% to 85%. The small variation between solutions with different *a* values suggests a relatively low bilinear model uncertainty. In the main text, the solution with *a* value of 0.1 is presented.

Figure S6 shows the residual of the ME-2 analysis. As expected, m/z 29 has a relatively higher residual. No profile structure nor diurnal patterns that could link to other sources could be identified, indicating the current ME-2 solution represented the data very well.

Table S1. The correlation coefficient between the 2-factor solution factor profiles in free PMF and the reference factor profile from literature [1-3].

R	OOA_avg [1]	OOAII_avg	BBOA_avg	HOA_avg	HOA_Paris [2]	COA_Paris	Wood	Smoky Coal	Peat [3]
Factor1	0.94	0.53	0.42	0.12	0.12	0.23	0.34	0.16	0.26
Factor2	0.33	0.75	0.87	0.75	0.77	0.86	0.77	0.86	0.91

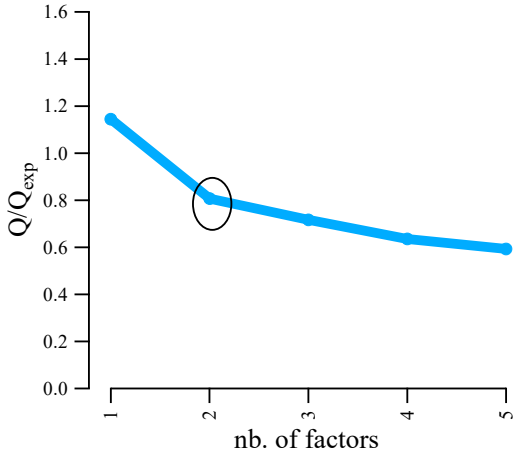

Figure S1. Q/Qexp as a function of number (nb.) of factors.

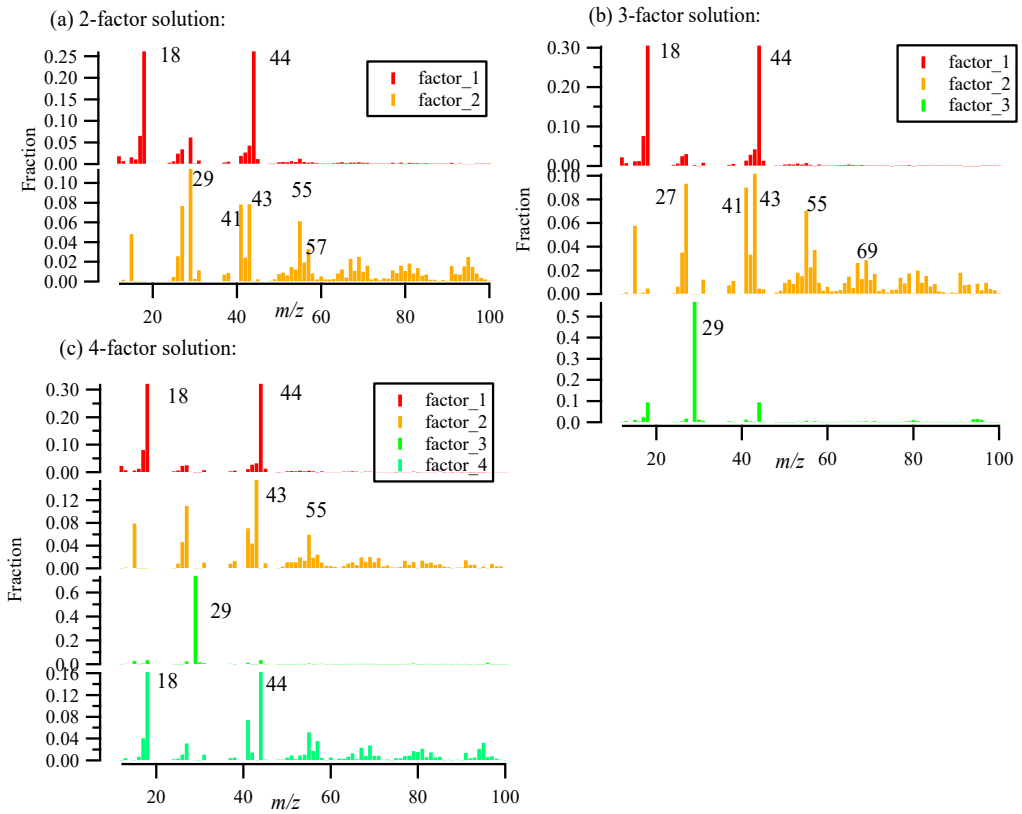

Figure 2. The mass spectra of the (**a**) 2-factor; (**b**) 3-factor; and (**c**) 4-factor solutions from the free PMF analysis.

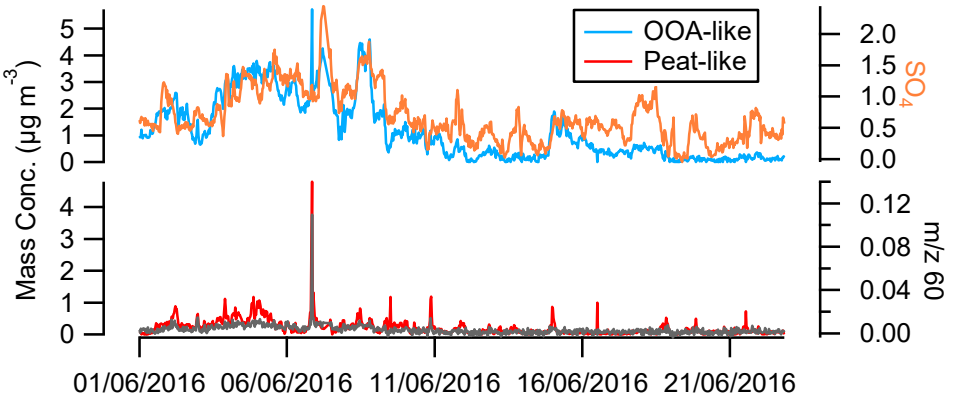

Figure 3. The time series of OOA-like and peat-like factor (left axis) from the free PMF series. Also shown are the time series of sulfate and m/z 60 (right axis).

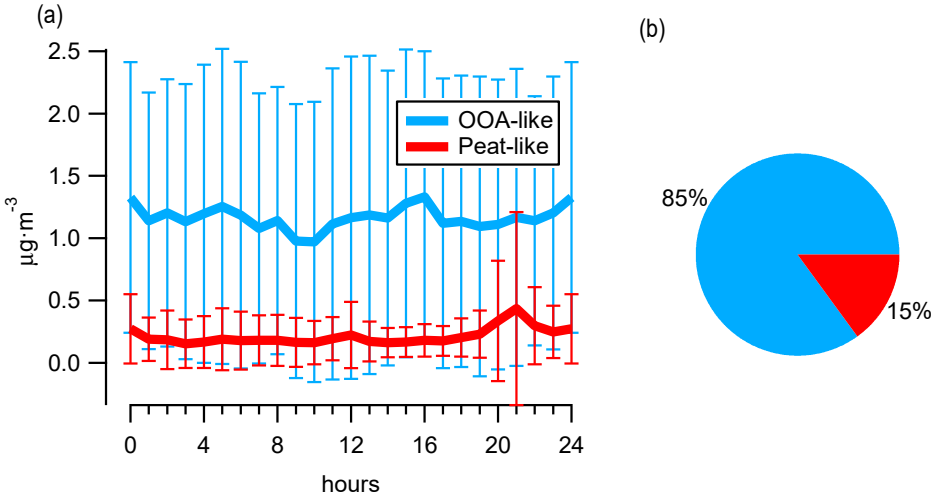

Figure 4. The diurnal cycle (**a**) and the relative contribution of the peat and OOA to the total OA (**b**). The error bar stands for one standard deviation.

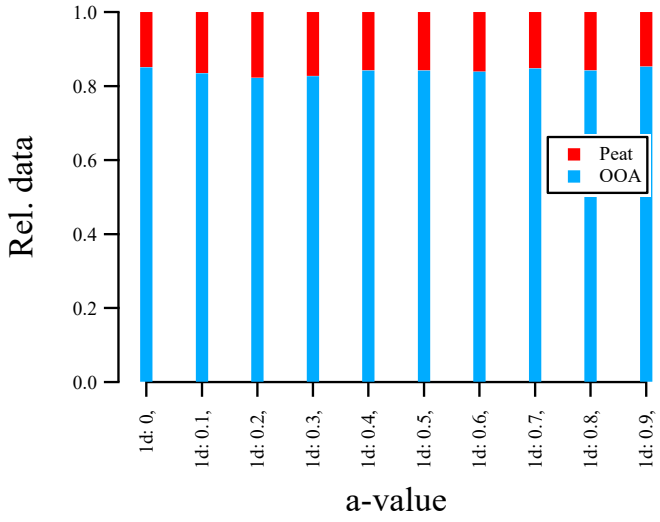

Figure 5. Relative contribution of the resolved peat and OOA as a function of a values from 0 to 0.9 with ME-2.

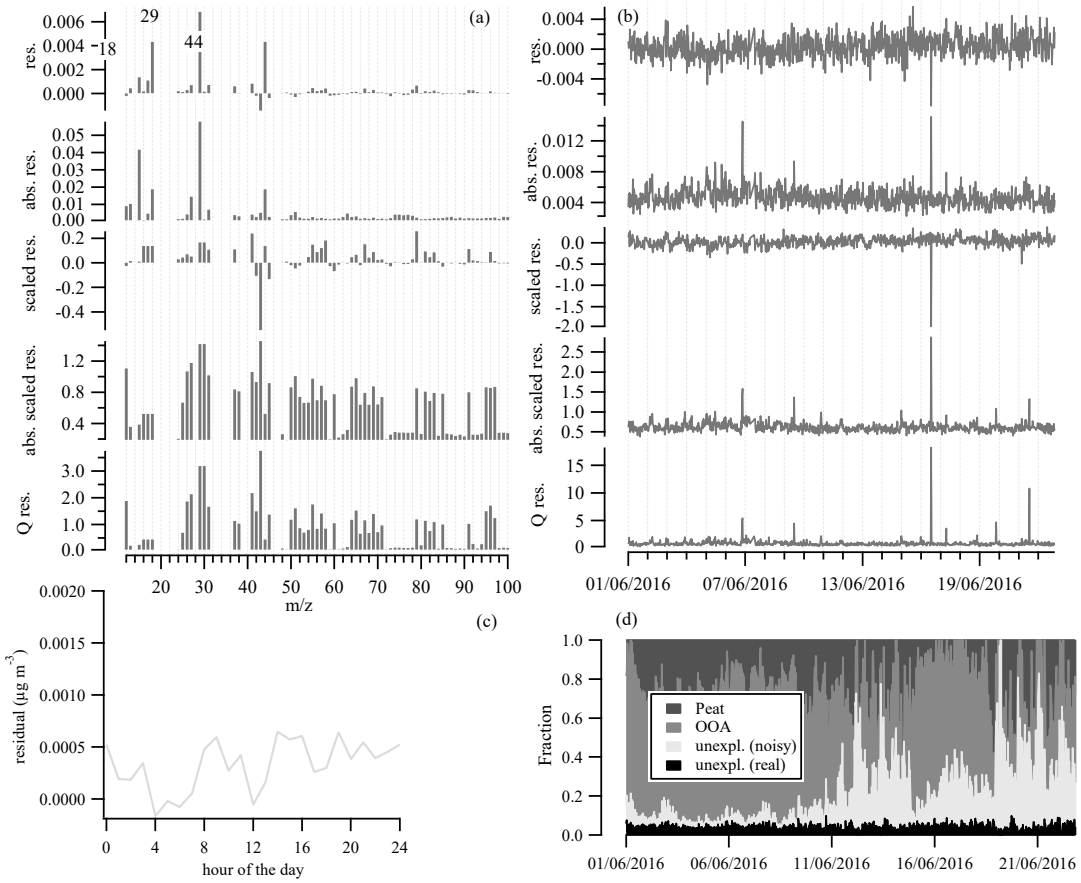

Figure 6. Residual of *m*/*z* (**a**), time series (**b**), diurnal of residual (**c**), and time series of the fraction of peat, OOA, and residue (**d**) of the ME-2 2-factor solution.

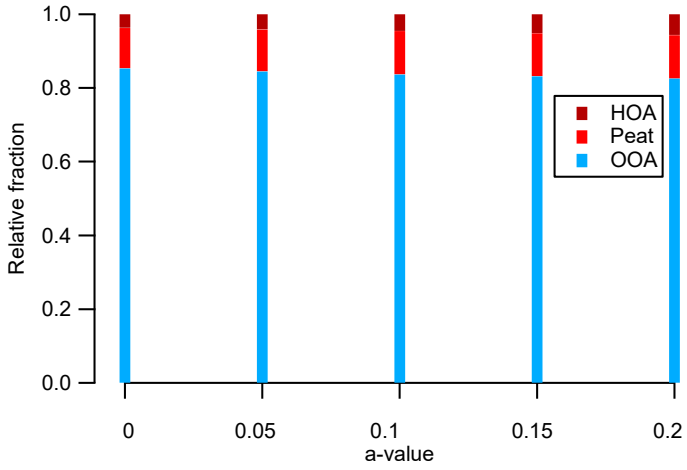

Figure 7. Relative contribution of HOA, peat, and OOA as a function of *a* value from 0 to 0.2. HOA comprised a small fraction of total OA (4–6%) over the range of *a* values (0–0.2). Peat contributed 11%–12% of the total OA, while OOA contributed 82%–85% of the total OA.

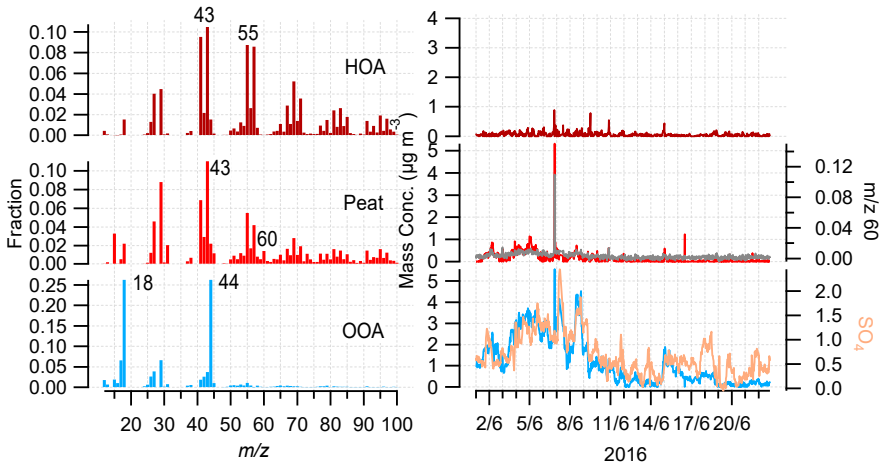

Figure 8. Profile (at *a* value of 0.1) and time series of hydrocarbon-like OA (HOA), peat, and OOA (oxygenated organic aerosol). Also shown are the time series of m/z 60 and sulfate.

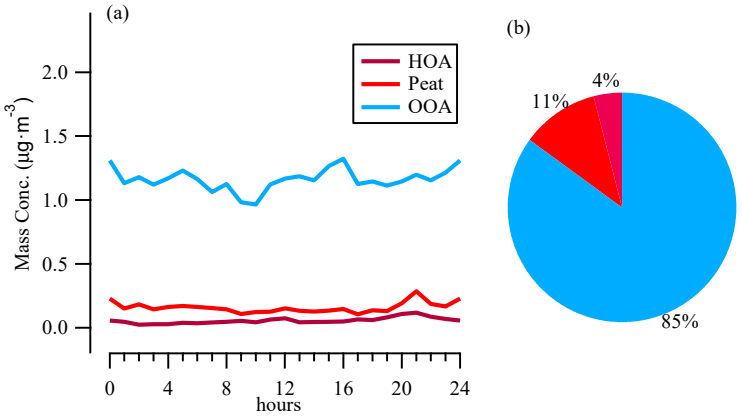

Figure 9. The diurnal cycle (**a**) and the relative contribution of the HOA, peat, and OOA to the total OA (**b**) at *a* value of 0.1.

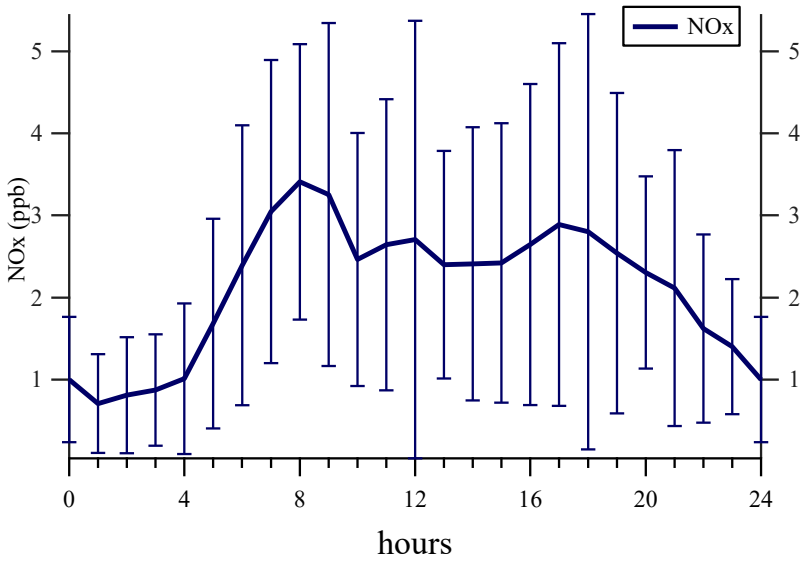

Figure 10. Diurnal cycle of NOx (in ppb). NOx was monitored by a collocated chemiluminescent analyzer (API, model 200A). The error bar is one standard deviation.

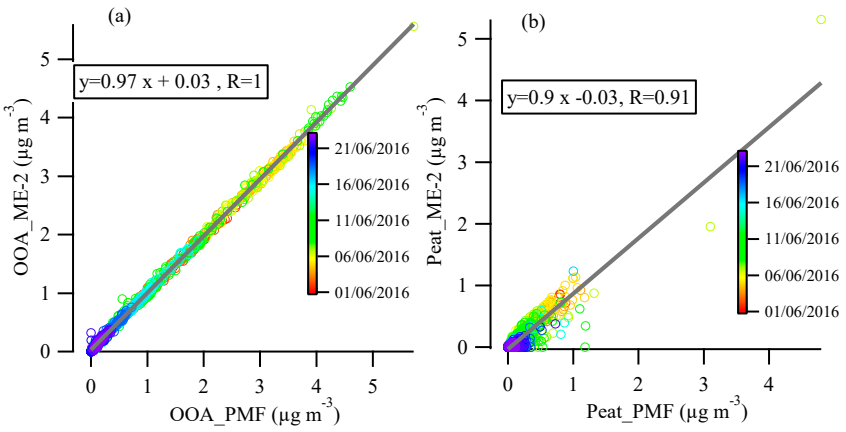

Figure 11. Linear correlation between the time series of (**a**) OOA from the ME-2 3-factor solution (*a* value = 0.1) versus OOA from the free PMF 2-factor solution and (**b**) peat factor from the ME-2 3-factor solution (*a* value = 0.1) versus OOA from the free PMF 2-factor solution, color-coded by date. The inset shows the correlation coefficient and slope.

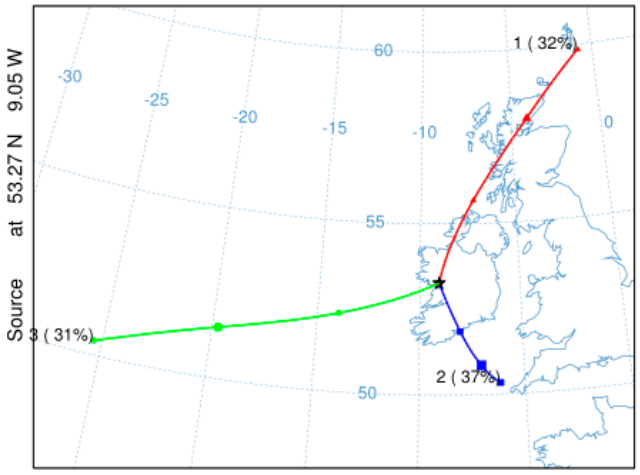

Figure 12. Classification of air mass trajectories with occurrence rates: 37% for southeasterly (SE) continental; 32% for northeasterly (NE) continental; and 31% for marine.

References

1. Ng, N. L.; Canagaratna, M. R.; Jimenez, J. L.; Zhang, Q.; Ulbrich, I. M.; Worsnop, D. R., Real-Time Methods for Estimating Organic Component Mass Concentrations from Aerosol Mass Spectrometer Data. *Environ. Sci. Technol.* **2011**, *45*, 910–916.
2. Crippa, M.; Decarlo, P.F.; Slowik, J.G.; Mohr, C.; Heringa, M.F.; Chirico, R.; Poulain, L.; Freutel, F.; Sciare, J.; Cozic, J.; et al. Wintertime aerosol chemical composition and source apportionment of the organic fraction in the metropolitan area of Paris. *Atmos. Chem. Phys.* **2013**, *13*, 961–981.
3. Lin, C.; Ceburnis, D.; Hellebust, S.; Buckley, P.; Wenger, J.; Canonaco, F.; Prévôt, A. S. H.; Huang, R.-J.; O'Dowd, C.; Ovadnevaite, J., Characterization of Primary Organic Aerosol from Domestic Wood, Peat, and Coal Burning in Ireland. *Environ. Sci. Technol.* **2017**, *51*, 10624–10632.