Supplementary Information

Unraveling the chemical structures of organic aerosols from diverse biomass sources through year-long offline analysis in Hyytiälä, Finland

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Text S1 Quantification of organic matter by the least squares method

In the case that all quantified fragment ions are used for the least squares method, five ions (m/z 28, 44, 50, 76, and 104) deviate significantly from the regression line for some samples with low concentrations. Because of their high signal intensities, these ions could substantially affect the overall fitting result. To assess the influence of different ion exclusion methods on the quantification of WSOM, WSOC from the AMS analysis (WSOM divided by OM/OC) was compared with that from the TOC analysis with the following four methods: S1, excluding m/z 28 and 44; S2, excluding m/z 50, 76, and 104; S3, excluding all five ions; and S4, with no ions excluded. As shown in Figure S1, the method in which all five ions were excluded (S3) yielded a higher Pearson correlation coefficient between WSOC from AMS and the TOC analyzer (r = 0.99) than any other method (r = 0.97). In addition, compared with the slope of other methods (0.89–0.95), S3 exhibited the slope closest to unity (0.99). For these reasons, the exclusion of all five ions was adopted for the quantification of WSOM in this study.

Text S2 Calculation of particle volume concentration from DMPS-derived size distributions

Particle number size distributions dN/dlogD_p, where N and D_p denote particle number concentration and particle diameter, respectively, in the diameter range of 100–1000 nm were obtained from the differential mobility particle sizer (DMPS) instrument at the Hyytiälä forest station (the data are available at the SmartSMEAR online platform: https://smear.avaa.csc.fi). The dN/dlogD_p (cm^{-3}) for 21 diameters ($D_{p,i}$, i = 1, 2, ..., 21, from small to large diameters) were used to calculate particle volume concentrations. Except for $D_{p,1}$ and $D_{p,21}$, the $D_{p,i}$ were considered as the geometric mean diameters of consecutive size bins, and the lower and upper ends of the bin corresponding to $D_{p,i}$, $D_{p,lower}$ and $D_{p,upper,i}$, respectively, were determined by assuming logarithmically equal spacing between adjacent DMPS diameters:

$$D_{\mathrm{p,lower},i} = \sqrt{D_{\mathrm{p},i-1} D_{\mathrm{p},i}}, \quad D_{\mathrm{p,upper},i} = \sqrt{D_{\mathrm{p},i} D_{\mathrm{p},i+1}} \qquad \text{(S1)}$$

$D_{p,lower,1}$ and $D_{p,upper,21}$ were set to 100 and 1000 (nm), respectively.

The particle volume concentration for the bin corresponding to $D_{p,i}$ (V_i, μm^3 cm^{-3}) was calculated as follows:

$$V_i = \frac{\pi}{6} D_{\mathrm{p},i}^3 \cdot \frac{\mathrm{d}N}{\mathrm{dlog}D_{\mathrm{p},i}} \cdot (\mathrm{log}D_{\mathrm{p,upper},i} - \mathrm{log}D_{\mathrm{p,lower},i}) \qquad \text{(S2)}$$

The total volume concentration was calculated as the sum of V_i over all bins within the selected size range.

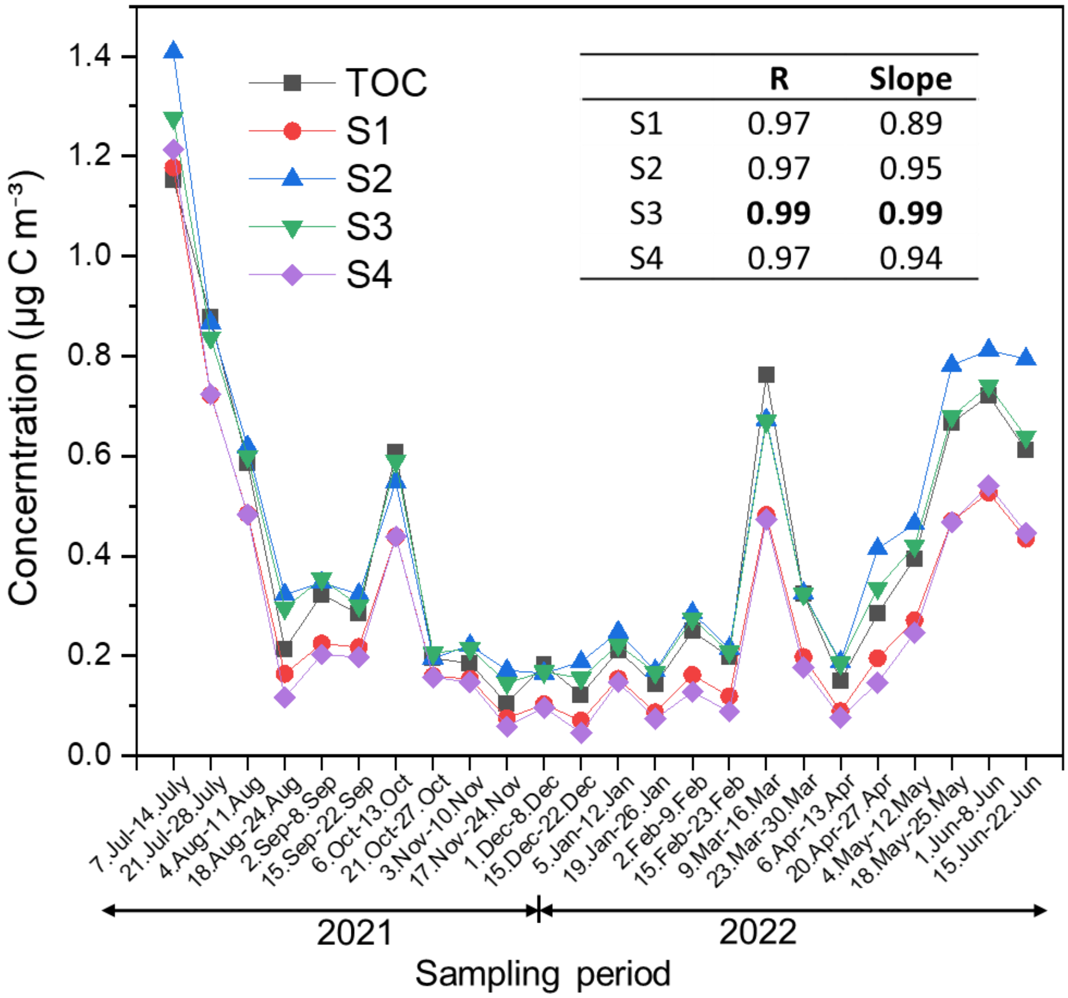

Figure S1. Comparison of WSOC concentrations derived from AMS using different fragment ion screening methods with those from TOC measurements.

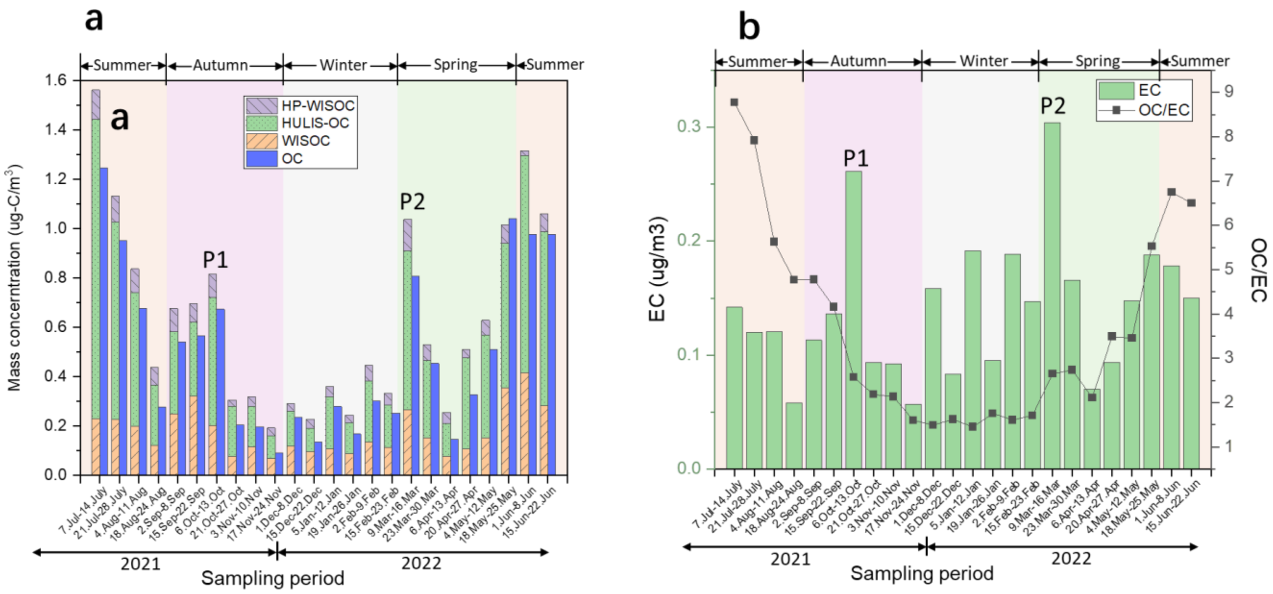

Figure S2. (a) Seasonal variations in the carbon concentrations of the HP-WSOM, HULIS, and WISOM fractions (HP-WISOC, HULIS-OC, and WISOC, respectively), and the concentrations of OC from the thermal/optical carbon analysis.. (b) The variations in the concentrations of EC and the OC/EC ratios.

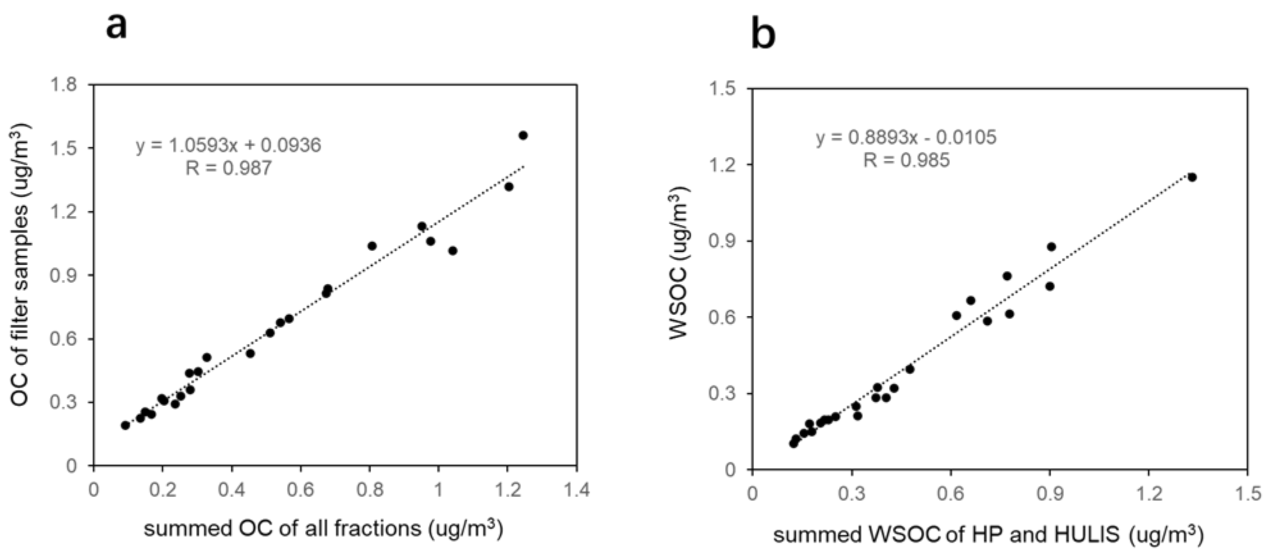

Figure S3. (a) Scatter plot of the summed OC derived from the carbon analyzer and that from AMS. (b) Scatter plot of the WSOC derived from the TOC analyzer and the sum of carbon in HP-WSOM and HULIS from the AMS. The dotted lines represent regression lines, and the equations of the lines and correlation coefficients (*r*) are also presented.

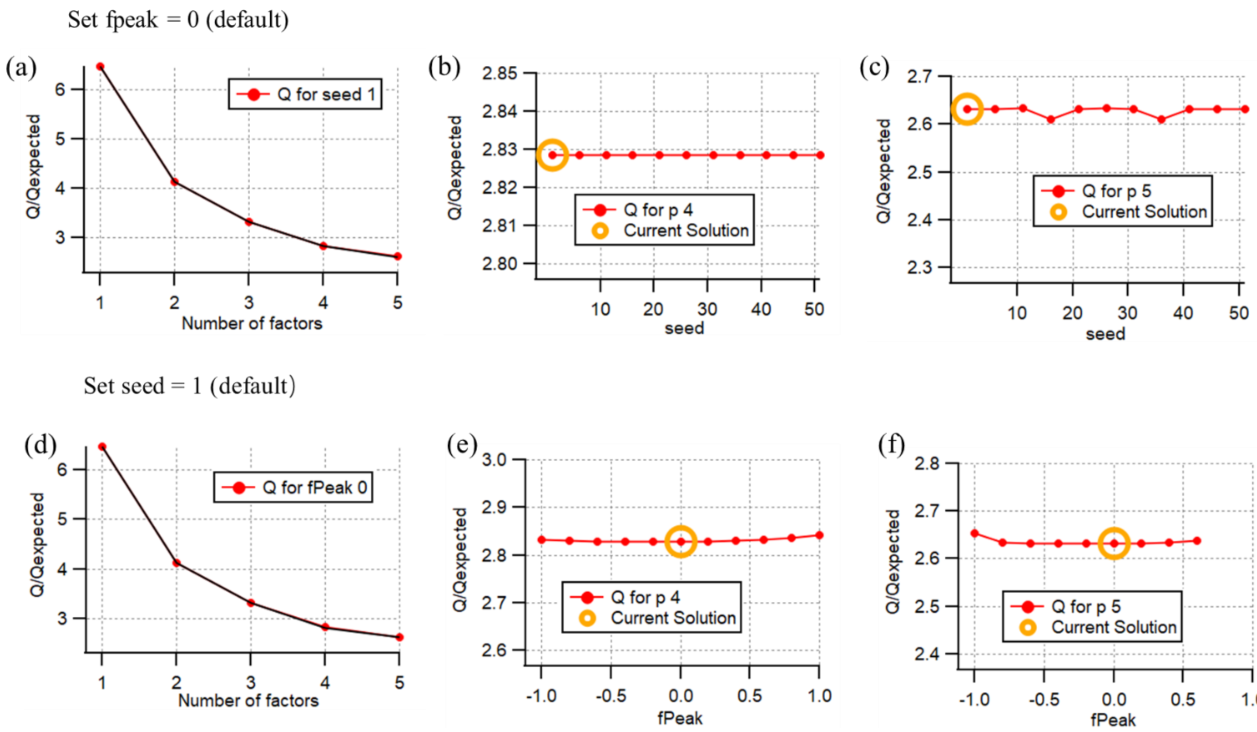

Figure S4. Evaluation of the PMF solutions using $Q/Q_{expected}$ as a function of the number of factors, seed values, and fPeak values: (a) $Q/Q_{expected}$ as a function of the number of factors for seed = 1; (b) $Q/Q_{expected}$ as a function of seed for the 4-factor solution; (c) $Q/Q_{expected}$ as a function of seed for the 5-factor solution; (d) $Q/Q_{expected}$ as a function of the number of factors for fPeak = 0; (e) $Q/Q_{expected}$ as a function of fPeak for the 4-factor solution; (f) $Q/Q_{expected}$ as a function of fPeak for the 5-factor solution.

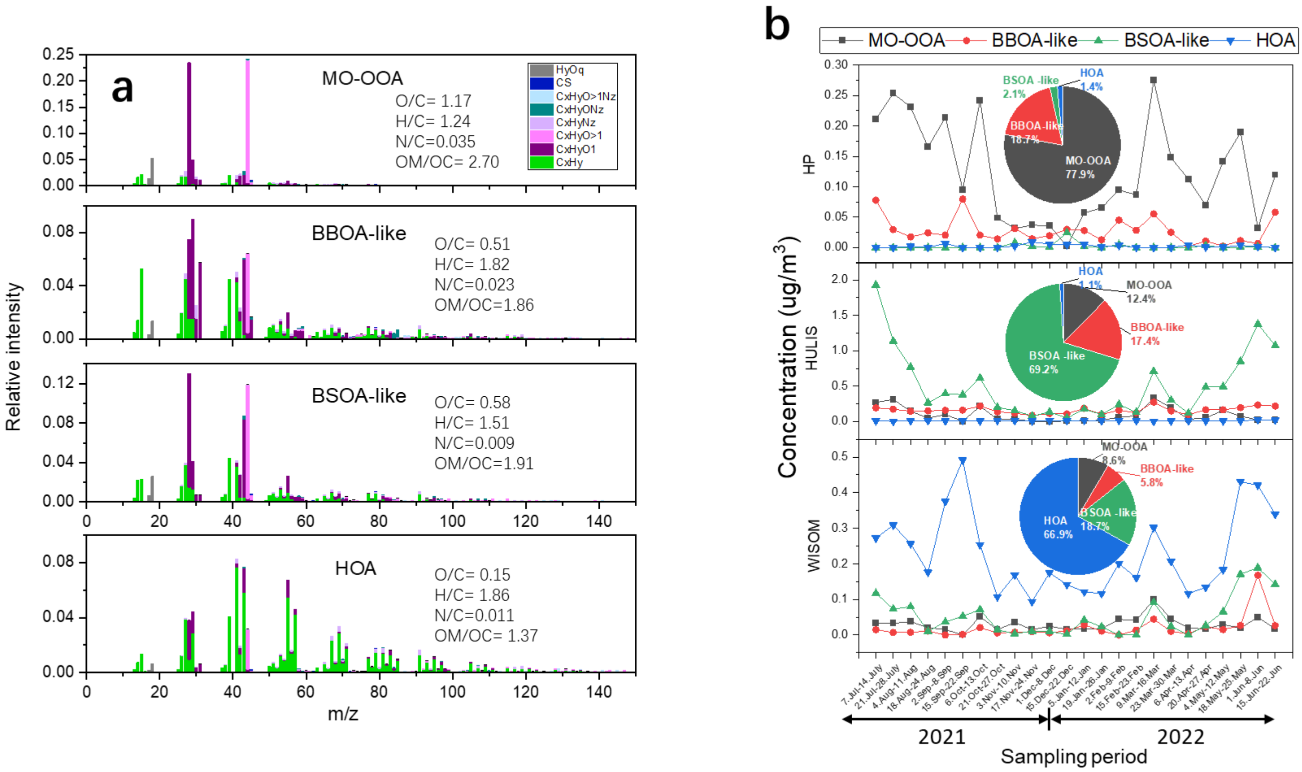

Figure S5. (a) HR–AMS spectra of the PMF factors from the four-factor solution and results from the elemental analysis. (b) Time series and mean contributions of MO-OOA, BBOA-like, BSOA-like, and HOA factors in HP-WSOM, HULIS and WISOM.

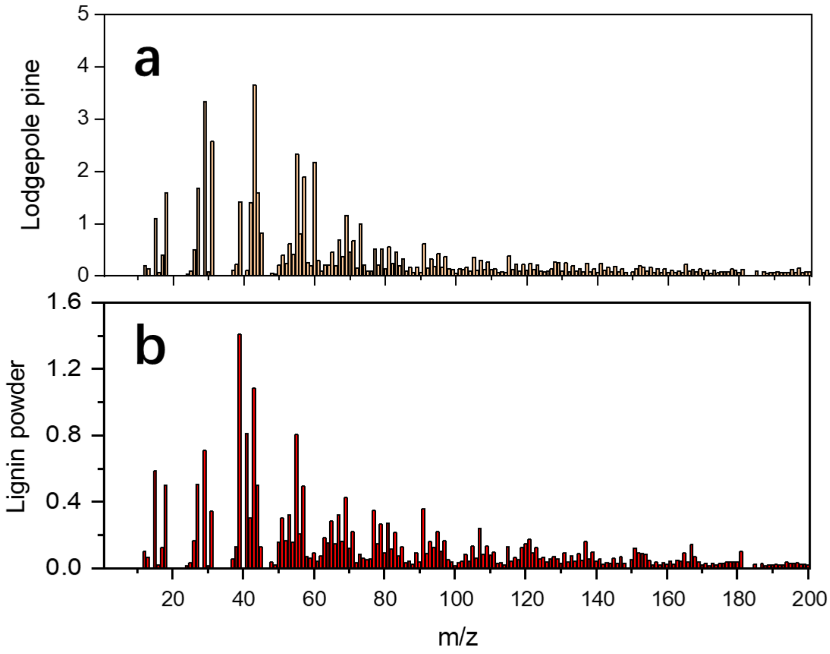

Figure S6. (a) Reference spectra of (a) lodgepole pine and (b) lignin powder, both retrieved from the AMS spectral database (Ulbrich et al., 2009; Ulbrich).

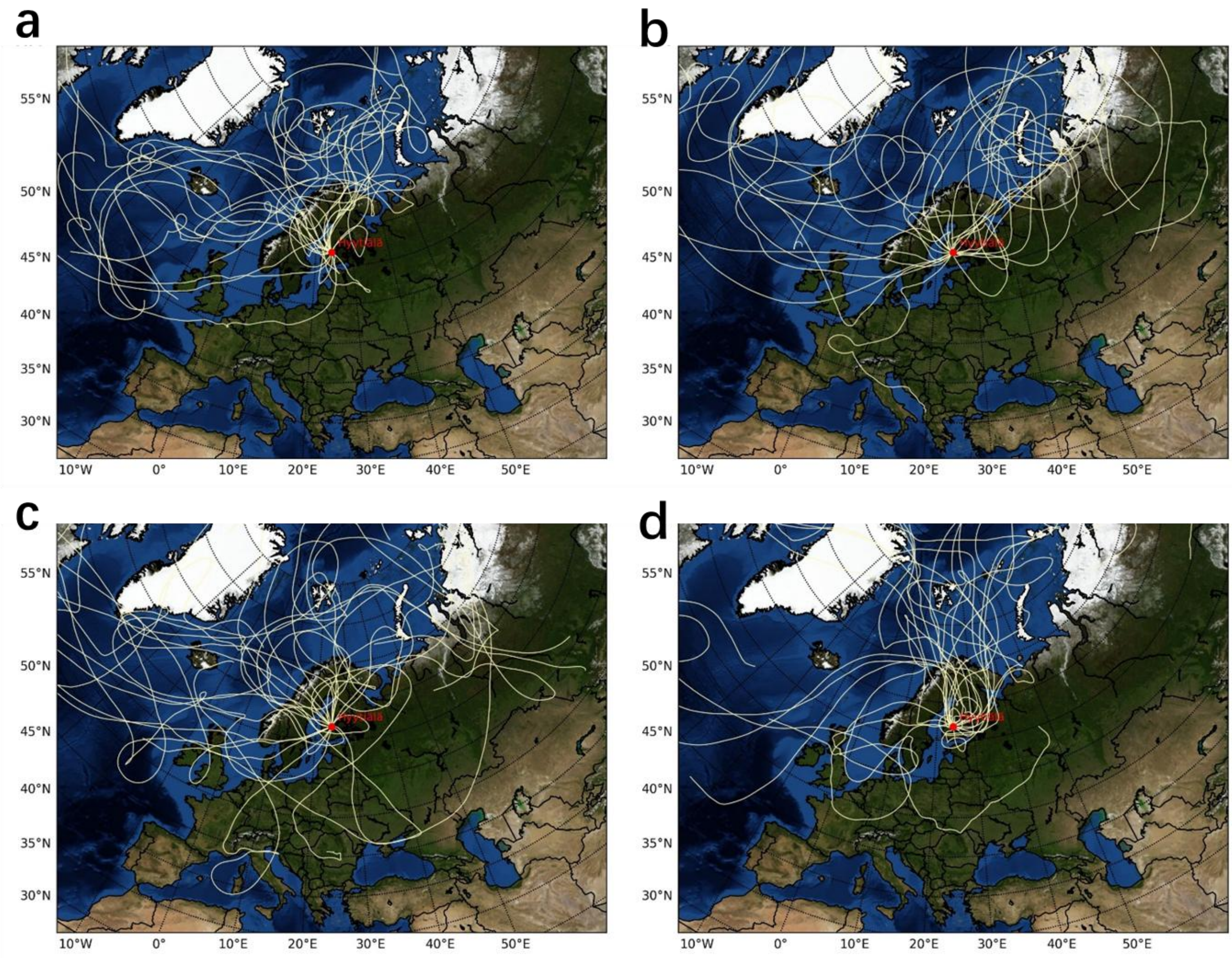

Figure S7. Ten-day backward air mass trajectories for (a) summer, (b) autumn, (c) winter, and (d) spring.

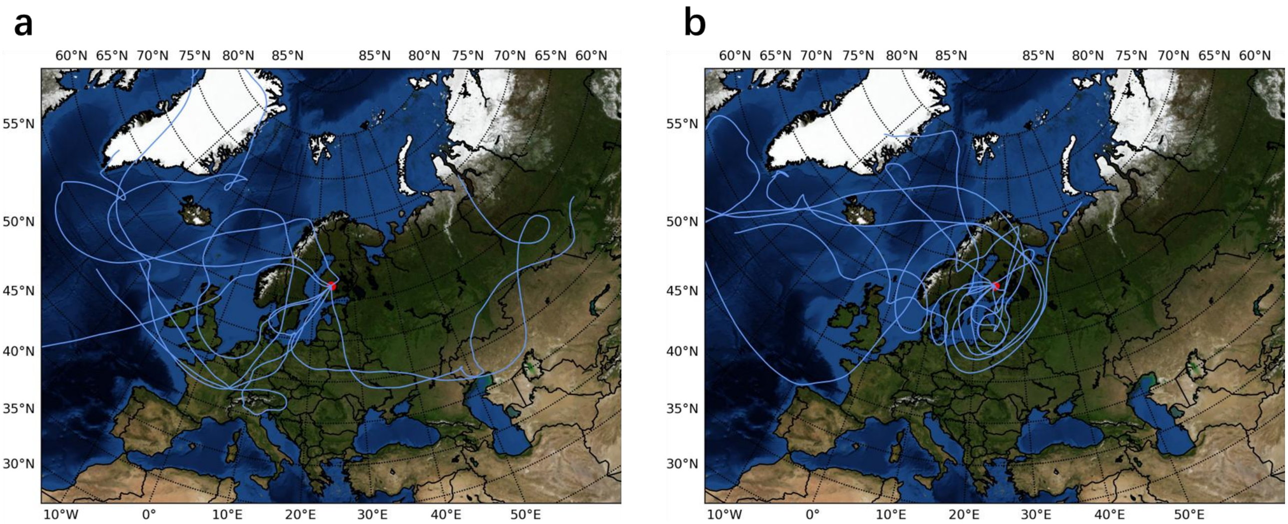

Figure S8. Ten-day backward air mass trajectories during periods P1 (a) and P2 (b).

Table S1. Sample information.

Sample ID	Sampling start time (UTC+2)	Sampling end time (UTC+2)	Duration (h)	Sampled air volume (m^3)
FIN20QFF002	14:33, 7 Jul, 2021	12:16, 14 Jul, 2021	166	11471.3
FIN20QFF004	14:10, 21 Jul, 2021	8:11, 28 Jul, 2021	162	11192.1
FIN20QFF006	8:33, 4 Aug, 2021	6:53, 11 Aug, 2021	166	11464.1
FIN20QFF009	11:40, 18 Aug, 2021	13:14, 24 Aug, 2021	146	9996.2
FIN20QFF011	14:48, 2 Sep, 2021	13:07, 8 Sep, 2021	142	9847.5
FIN20QFF014	11:36, 15 Sep, 2021	12:29, 22 Sep, 2021	169	11659.5
FIN20QFF018	12:58, 6 Oct, 2021	13:25, 13 Oct, 2021	168	11662.5
FIN20QFF021	14:59, 21 Oct, 2021	12:27, 27 Oct, 2021	141	9745.4
FIN20QFF023	14:40, 3 Nov, 2021	13:53, 10 Nov, 2021	167	11509.6
FIN20QFF026	15:01, 17 Nov, 2021	13:35, 24 Nov, 2021	167	11434.1
FIN20QFF028	14:59, 1 Dec, 2021	14:13, 8 Dec, 2021	167	11495.7
FIN20QFF031	15:59, 15 Dec, 2021	14:05, 22 Dec, 2021	166	11440.1
FIN20QFF034	11:04, 5 Jan, 2022	10:03, 12 Jan, 2022	167	11458.9
FIN20QFF037	14:46, 19 Jan, 2022	13:45, 26 Jan, 2022	167	11514.9
FIN20QFF039	15:59, 2 Feb, 2022	13:53, 9 Feb, 2022	166	11431.1
FIN20QFF042	15:56, 15 Feb, 2022	14:34, 23 Feb, 2022	191	13139
FIN20QFF046	10:48, 9 Mar, 2022	14:38, 16 Mar, 2022	172	11883.8
FIN20QFF048	13:22, 23 Mar, 2022	13:21, 30 Mar, 2022	168	11608.8
FIN22QFF002	14:31, 6 Apr, 2022	12:57, 13 Apr, 2022	166	11517.4
FIN22QFF004	14:50, 20 Apr, 2022	13:06, 27 Apr, 2022	166	11465.2
FIN22QFF007	15:43, 4 May, 2022	13:45, 12 May, 2022	190	13123
FIN22QFF009	13:51, 18 May, 2022	12:37, 25 May, 2022	167	11561.1
FIN22QFF012	14:58, 1 Jun, 2022	13:14, 8 Jun, 2022	166	11472.5
FIN22QFF014	7:50, 15 Jun, 2022	13:29, 22 Jun, 2022	174	11994.7

Table S2. Extraction efficiency of samples using the SPE technique.

Sample ID	Organic matter ($\mu g\ m^{-3}$)			SPE extraction efficiency (%)
	WSOM	HULIS	HP-WSOM	
FIN20QFF002	2.52	2.40	0.31	107.2%
FIN20QFF004	1.71	1.63	0.37	116.8%
FIN20QFF006	1.15	1.07	0.30	119.8%
FIN20QFF009	0.58	0.48	0.24	123.6%
FIN20QFF011	0.70	0.66	0.29	136.5%
FIN20QFF014	0.56	0.56	0.18	129.9%
FIN20QFF018	1.17	1.06	0.29	115.1%
FIN20QFF021	0.39	0.39	0.06	114.1%
FIN20QFF023	0.41	0.32	0.09	98.0%
FIN20QFF026	0.27	0.17	0.06	86.3%
FIN20QFF028	0.31	0.26	0.09	112.5%
FIN20QFF031	0.28	0.18	0.06	84.0%
FIN20QFF034	0.41	0.39	0.13	125.9%
FIN20QFF037	0.31	0.23	0.13	115.8%
FIN20QFF039	0.53	0.48	0.21	130.1%
FIN20QFF042	0.42	0.34	0.18	126.1%
FIN20QFF046	1.38	1.32	0.43	126.9%
FIN20QFF048	0.67	0.65	0.25	134.6%
FIN22QFF002	0.36	0.26	0.19	124.9%
FIN22QFF004	0.65	0.71	0.10	125.1%
FIN22QFF007	0.83	0.82	0.18	120.8%
FIN22QFF009	1.31	1.13	0.23	103.7%
FIN22QFF012	1.40	1.66	0.05	122.4%
FIN22QFF014	1.20	1.33	0.23	129.8%

Table S3. Repeatability of the quantification of organic fractions.

	WSOM (μg m⁻³)	WISOM (μg m⁻³)	HP-WSOM (μg m⁻³)	HULIS (μg m⁻³)
FIN20QFF006_1st analysis	1.19	0.31	0.33	1.10
FIN20QFF006_2nd analysis	1.10	0.32	0.28	1.04
Difference	-7.7%	3.9%	-17.0%	-4.9%
FIN20QFF018_1st analysis	1.19	0.34	0.27	1.04
FIN20QFF018_2nd analysis	1.24	0.28	0.28	0.88
Difference	4.6%	-16.5%	1.8%	-15.4%

Table S4. Proportions of the mean mass contributions of the PMF factors of the four-factor solution (ug m^{-3}).

Sample ID	MO-OOA	BBOA	BSOA	HOA
FIN20QFF002	17.0%	9.3%	66.1%	7.6%
FIN20QFF004	28.5%	9.3%	51.1%	11.0%
FIN20QFF006	27.0%	10.3%	49.5%	13.2%
FIN20QFF009	30.5%	21.3%	30.7%	17.6%
FIN20QFF011	28.4%	14.0%	32.6%	25.0%
FIN20QFF014	8.4%	20.4%	35.8%	35.3%
FIN20QFF018	31.4%	15.5%	40.2%	12.9%
FIN20QFF021	16.6%	27.8%	37.6%	18.1%
FIN20QFF023	17.4%	27.6%	28.6%	26.4%
FIN20QFF026	15.5%	30.7%	25.1%	28.7%
FIN20QFF028	13.3%	27.7%	27.5%	31.5%
FIN20QFF031	5.9%	39.7%	19.9%	34.5%
FIN20QFF034	14.6%	36.3%	30.9%	18.2%
FIN20QFF037	28.8%	26.0%	23.5%	21.8%
FIN20QFF039	26.0%	25.2%	28.0%	20.8%
FIN20QFF042	35.5%	25.7%	18.5%	20.3%
FIN20QFF046	35.2%	17.5%	35.8%	11.5%
FIN20QFF048	39.2%	17.1%	28.1%	15.5%
FIN22QFF002	40.5%	18.6%	20.8%	20.1%
FIN22QFF004	14.9%	20.2%	52.6%	12.2%
FIN22QFF007	28.7%	14.7%	43.9%	12.7%
FIN22QFF009	15.9%	12.3%	52.4%	19.4%
FIN22QFF012	4.4%	15.9%	64.1%	15.6%
FIN22QFF014	9.5%	15.9%	59.6%	15.0%
Mean	17.0%	9.3%	66.1%	7.6%

Table S5. Proportions of the mean mass contributions of the PMF factors of the five-factor solution (μg m^{-3}).

Sample ID	MO-OOA	BBOA1	BSOA	BBOA2	HOA
FIN20QFF002	10.3%	9.2%	66.6%	6.7%	7.1%
FIN20QFF004	20.4%	10.4%	57.5%	1.4%	10.4%
FIN20QFF006	21.8%	9.7%	48.3%	7.8%	12.3%
FIN20QFF009	24.3%	19.1%	31.2%	9.0%	16.4%
FIN20QFF011	25.9%	12.4%	24.5%	14.6%	22.5%
FIN20QFF014	7.5%	16.8%	22.0%	23.0%	30.7%
FIN20QFF018	27.6%	13.5%	34.8%	12.3%	11.8%
FIN20QFF021	12.7%	23.4%	28.9%	18.6%	16.4%
FIN20QFF023	13.2%	22.7%	22.6%	17.3%	24.2%
FIN20QFF026	13.5%	25.6%	13.4%	21.4%	26.1%
FIN20QFF028	11.0%	22.6%	12.9%	25.2%	28.3%
FIN20QFF031	4.7%	31.8%	3.3%	29.1%	31.1%
FIN20QFF034	17.0%	29.0%	4.8%	33.1%	16.0%
FIN20QFF037	27.9%	21.9%	9.2%	21.3%	19.7%
FIN20QFF039	24.8%	20.4%	15.4%	20.0%	19.4%
FIN20QFF042	33.1%	24.1%	9.0%	15.0%	18.9%
FIN20QFF046	32.2%	16.3%	26.9%	14.3%	10.4%
FIN20QFF048	34.7%	16.7%	25.2%	9.0%	14.5%
FIN22QFF002	37.5%	16.9%	13.5%	12.9%	19.1%
FIN22QFF004	12.4%	16.8%	40.2%	19.6%	11.0%
FIN22QFF007	27.8%	11.7%	31.3%	17.7%	11.4%
FIN22QFF009	15.4%	9.7%	37.4%	20.5%	17.0%
FIN22QFF012	3.9%	11.9%	47.5%	23.1%	13.7%
FIN22QFF014	7.1%	14.2%	45.5%	20.0%	13.1%
Mean	19.5%	17.8%	28.0%	17.2%	17.6%