What chemical species are responsible for new particle formation and growth in the Netherlands? A hybrid positive matrix factorization (PMF) analysis using aerosol composition (ACSM) and size (SMPS)

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Abstract. Aerosol formation acts as a sink for gas-phase atmospheric species that controls their atmospheric lifetime and environmental effects. To investigate aerosol formation and evolution in the Netherlands, a hybrid positive matrix factorization (PMF) analysis has been conducted using observations from May, June, and September 2021 collected in a rural site of Cabauw in Central Netherlands. The hybrid input matrix consists of the full organic mass spectrum acquired from a time-of-flight aerosol chemical speciation monitor (ToF-ACSM), ACSM inorganic species concentrations, and binned particle size distribution concentrations from a scanning mobility particle sizer (SMPS). These hybrid PMF analyses discerned ~~six~~four factors that describe aerosol composition variations: ~~four~~two size-driven factors that are related to new particle formation (NPF) and growth (~~F6, F5,~~ F4, and F3), and two bulk factors driven by composition, not size (F2~~,~~ and F1). The distribution of chemical species across these factors shows different compounds responsible for nucleation and growth of new particles. The smallest-diameter size factor (~~F6~~F4) contains ammonium sulfate and organics, and typically ~~occurs~~peaks during the daytime. Newly formed particles, represented by ~~F6~~F4, are correlated mainly with wind from the southwesterly-westerly~~, northerly,~~ and easterly sectors that transport sulfur oxides (SO_x), ammonia (NH_3), and organic precursors to Cabauw. As the particles grow from ~~F6~~F4 to F3 and bulk factors, nitrate and organics plays an increasing role, and the particle loading diurnal cycle shifts from daytime to a nighttime maximum. ~~The inorganic ion balance and organics composition in the bulk atmosphere affects the chemical composition variation across factors and seasons. Changing ammonium sulfate-nitrate equilibrium shifts inorganic species among factors, and greater~~Greater organics availability makes secondary organic aerosol (SOA) more influential in summertime aerosol growth, principally due to volatility differences produced by seasonal variation in photooxidation and temperature.

Keywords: new particle formation (NPF), positive matrix factorization (PMF), particle size distribution, sulfate aerosol, nitrate aerosol, organic aerosol

1. Introduction

Atmospheric aerosols are solid or liquid particles suspended in the air that are formed from natural or anthropogenic sources (Haywood, 2016). To describe the aerosol particle size distribution, four modes are generally distinguished according to the particle geometric diameter (D_p): nucleation mode ($D_p < 20$ nm), Aitken mode (20 nm $< D_p < 100$ nm), accumulation mode ($\text{100}90$ nm $< D_p < 1000$ nm), and coarse mode ($D_p > 1$ μm) (Hussein et al., 2004; Wu et al., 2008). New particle formation (NPF) is identified by a rapid buildup of high atmospheric concentrations of aerosol particles in the nucleation mode. These particles subsequently grow into Aitken mode particles and further (Maso et al., 2005; Spracklen et al., 2010; Salimi et al., 2015; Kerminen et al., 2018; Lee et al., 2019).

Aerosols impact the Earth by absorbing and scattering solar and terrestrial radiation (Andreae and Crutzen, 1997; Grantz et al., 2003; Wong et al., 2017; Marrero-Ortiz et al., 2019), and indirectly by producing or modifying clouds (Lohmann and Feichter, 2005; Mahowald et al., 2011; Fan et al., 2018). NPF plays a prominent role in cloud formation by contributing to over 50% of cloud condensation nuclei formation, which affects the lifetime and radiative properties of clouds (Bianchi et al., 2016; Gordon et al., 2016; Haywood, 2016; Dall'Osto et al., 2018; Lee et al., 2019). These phenomena affect the ecosystem physically by modifying radiation diffusion, temperature, and precipitation (Grantz et al., 2003; Haywood, 2016; Lee et al., 2019). Aerosols also influence the ecosystem chemically through influencing the spatial patterns of nitrogen deposition (van der Swaluw et al., 2011; Wamelink et al., 2013) and oxidative processes (Xing et al., 2017), leading to ecological harm such as soil pollution, water acidification, eutrophication, and loss of biodiversity (Erisman et al., 2011; Wamelink et al., 2013). In terms of public health, aerosols exhibit adverse effects on human health due to their size and chemical composition. NPF events are typically followed by air quality degradation, which is consistently associated with elevated pulmonary and cardiovascular morbidity and mortality worldwide (Ayala et al., 2012; Pope et al., 2020).

Sulfuric acid (H_2SO_4) is typically understood to be the most prevalent nucleation-inducing agent in NPF events, together with other airborne chemical species, including nitrate nitric acid (HNO_3), bases (e.g., amines), and organic acids (Zhang et al., 2012; Kulmala et al., 2013; Zhang et al., 2015; Wagner et al., 2017; Lehtipalo et al., 2018; Kürten, 2019; Lee et al., 2019; Brean et al., 2021; Olin et al., 2022). Numerous studies also report low-volatility organic species, such as terpene oxidation products and organic nitrates, participating in the formation of new particles (Berkemeier et al., 2016; Bianchi et al., 2016; Tröstl et al., 2016; Barsanti et al., 2017; Dall'Osto et al., 2018; Kerminen et al., 2018; Lee et al., 2019; Heinritzi et al., 2020).

In this work, we show that co-located measurements of aerosols' atmospheric composition and particle size distribution can be used to characterize the chemical composition of new particle and aerosol components that facilitate their growth. A time-of-flight aerosol chemical speciation monitor (ToF-ACSM, Aerodyne Inc.) allows the continuous and real-time quantification of non-refractory chemical species in ambient air (Ng et al., 2011; Fröhlich et al., 2013). For particle size distributions, the scanning mobility particle sizer (SMPS) provides real-time measurement of submicron particle number concentrations of different sizes (Amaral et al., 2015; Wiedensohler et al., 2018 2012).

Aerosol mass spectrometry measurements have been used extensively with positive matrix factorization (PMF) as a strategy for aerosol source apportionment, especially regarding the organic components (Lanz et al., 2007; Jimenez et al., 2009; Ulbrich et al., 2009; Ng et al., 2010; Zhang et al., 2011). This paper combines the full organic mass spectrum and chemical species concentrations from ToF-ACSM with particle size distribution from SMPS into a hybrid PMF input matrix, to study the association between chemical composition and particle size distribution. A similar approach for hybrid ACSM-SMPS PMF analysis was used for a European aerosol dataset comparison (Dall'Osto et al., 2018). Previous studies on aerosol source apportionment in the Netherlands have focused on organic aerosol composition (Mooibroek et al., 2011; Mensah et al., 2012; Schlag et al., 2016). Here, we analyze ACSM-SMPS datasets from Cabauw, the Netherlands, collected as part of the Ruisdael Observatory Land-Atmosphere Interactions Intensive Trace-gas and Aerosol (RITA) campaign in May to September 2021 (https://ruisdael-observatory.nl), using PMF to characterize the chemical species responsible for new particle formation and growth across several seasons. Several studies have shown NPF events dependent on air mass origin transporting different pollutants (Hamed et al., 2007; Modini et al., 2009; Castro et al., 2010; Asmi et al., 2011; Németh and Salma, 2014; Nieminen et al., 2014; Qi et al., 2015; Mordas et al., 2016; Kolesar et al., 2017; Peng et al., 2017; Kerminen et al., 2018; Pushpawela et al., 2019), and therefore we also explore relationships between wind direction, wind speed, and factor timeseries time series to interpret source apportionment.

2. Methods and Instrumentation

2.1. Cabauw site and meteorological conditions

Measurements were performed at the CESAR tower (51.970° N, 4.926° E), managed and operated by the Royal Netherlands Meteorological Institute (KNMI, the Netherlands) (see Fig. 1 1a). The tower is located near Cabauw, in the province of Utrecht, the Netherlands, approximately 18 km southwest of Utrecht city center, 31 km east of the city and (largest in Europe) port of Rotterdam, 45 km south of Amsterdam, and about 45 km southeast of the Dutch North Sea coast. To the east and south of the site are the provinces of Gelderland and Noord-Brabant, which consist mainly of forests, agricultural lands with clay and sand soil types for crops, and animal farms, specifically chicken and pig farms in the south and cattle in the east (CBS, 2022). The Cabauw site itself is rural and surrounded by agricultural lands. The dataset used in this analysis contains overlapping ACSM

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95 and SMPS data split into periods from 11–31 May 2021, 1–22 June 2021, and 1–30 September 2021, providing some seasonal
variation. To simplify, we will refer to these periods as May, June, and September, respectively, in this paper.
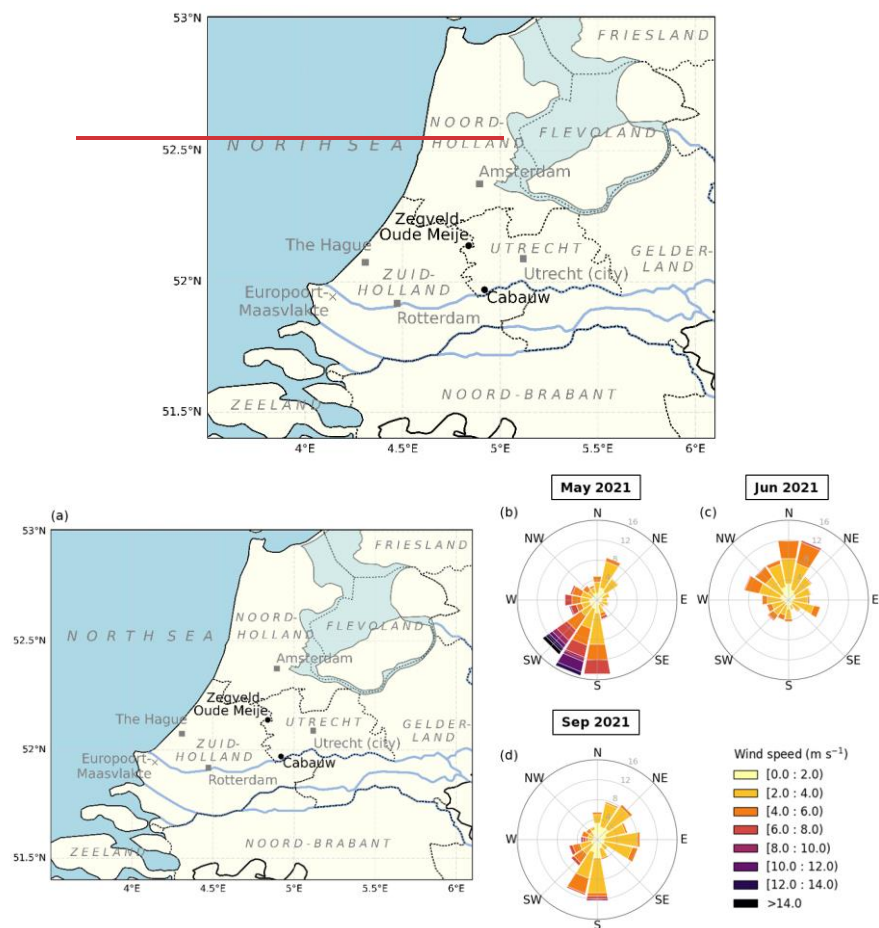
Figure 1. (a) Map of a part of the Netherlands showing the locations of the measurement stations Cabauw (main site) and Zegveld-Oude
100 Meije (auxiliary NH$_3$ measurements). The province, sea, and ~~neighbouring~~neighboring country names are indicated in italic and light grey.
The big cities of Amsterdam, The Hague, Rotterdam, and Utrecht in the area collectively known as "Randstad" are situated in Noord-
Holland, Zuid-Holland, and Utrecht provinces. The urban and harbor area of Rotterdam extends as Europoort-Maasvlakte to the mouth of

the Maas River. **(b-d)** Wind rose plots for May, June, and September 2021. Winds from S up to SW sector were dominant in May. In June, the prevailing winds were from WNW up to the NNE sector. In September, two major wind directions were from the E and S sectors.

Weather data were retrieved from the Royal Netherlands Meteorological Institute (KNMI, https://www.knmi.nl). In general, May 2021 was characterized by moderate spring temperatures (11.8 ℃ on average) with scattered precipitation transitioning into the warmer summer period. June 2021 had the highest temperatures (18.7 ℃ on average) and was the sunniest of the three periods, reflecting summer weather. September 2021 showed warm temperatures, (16.2 ℃ on average), with less radiation and precipitation compared to May 2021. Winds from south to southwest sector (180° to 225°) dominated in spring (May), bringing plumes from the agriculture-heavy province of Noord-Brabant. In summer (June), the prevailing air masses were coming from west-northwest to north-northeast (292.5° to 22.5°), bringing air from the North Sea and some major cities along the coast and/or in the Randstad, such as Rotterdam, The Hague, Amsterdam, and Utrecht. More diverse wind plumes were observed in September, ranging from easterly (22.5° to 112.5°), coming from the forested nature and agricultural areas in the province of Gelderland, and southerly (180° to 202.5°), coming from the province of Noord-Brabant. The meteorological variables for each period are summarized in Table 1 and the wind variables are visualized as wind roses in Fig. 21b-d.

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Table 1. Meteorological conditions on three periods analyzed (May, June, and September 2021). The periods represent spring, summer, and autumn weather, respectively.

Period	Temperature (ºC)	Downward shortwave radiation (W m^{-2})	Precipitation (mm)
11–31 May 2021	11.8 (mean) 3.5 (low), 23.0 (high)	211.7 (mean) 1032.2 (max)	96.6 (total)
1–22 Jun 2021	18.7 (mean) 8.1 (low), 29.6 (high)	264.9 (mean) 957.2 (max)	31.2 (total)
1–30 Sep 2021	16.2 (mean) 5.7 (low), 26.7 (high)	142.0 (mean) 818.9 (max)	24.4 (total)
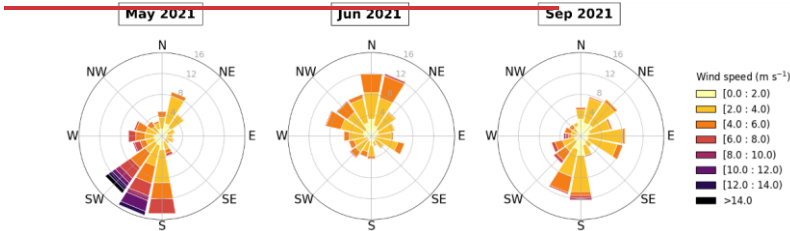
2.2. Measurement setup

2.2.1. Chemical species measurements

~~Figure 2. Wind rose plots for May, June, and September 2021. Winds from S up to SW sector were dominant in May. In June, the prevailing winds were from WNW up to the NNE sector. In September, two major wind directions were from the E and S sectors.~~

2.3. Measurements

The ToF-ACSM was the main instrument employed ~~for this analysis. . The instrument has been detailed in other work (Fröhlich et al., 2013). The ACSM was installed with an inlet at 5-meter height, a cyclone with size cut of 2.5 µm (PM$_{2.5}$), and an aerodynamic lens in the inlet system~~ allowing the analysis of non-refractory organics, ammonium, nitrate, sulfate, and chloride~~, and potassium~~ in the aerosol phase. The instrument has been detailed in other work (Fröhlich et al., 2013). The Ambient air was drawn into the instrument ~~is~~ through a stainless-steel tubing inlet system equipped with a PM$_{2.5}$ size-cut cyclone (URG-2000-30ED) and a Nafion dryer, sampling at 4.5-meter height with flow rate of 2 L min^{-1}. An intermediate pressure lens (IPL) is used as aerodynamic lens allowing transmission of particles in the PM$_{2.5}$ fraction (Xu et al., 2017). The instrument uses a capture vaporizer (CV) ~~instead of the standard vaporizer (SV), which is designed~~ to increase the particle collection efficiency ~~(Middlebrook et al., 2012; CE)~~ compared to standard vaporizer (SV) (Jayne and Worsnop, 2016). By having a narrow entrance, the CV increases the particle collision events and thus increases the contact with the hot vaporizer surface, minimizing particles that bounce without evaporation (Hu et al., 2017~~).~~) and resulting in higher CE. Consequently, however, the fragmentation patterns are shifted towards smaller ion masses due to ~~the~~ additional thermal decomposition (Hu et al., 2017; Xu et al., 2017;

Zheng et al., 2020). The average flow rate in the sample line of the instrument is 1.22 cm^3 s^{-1} (0.07 L min^{-1}). Combining the PM$_{2.5}$ cut cyclone, PM$_{2.5}$ aerodynamic lens, and CV allows the ToF-ACSM to be a PM$_{2.5}$ measurement (Xu et al., 2017).

The ToF-ACSM provides unit mass resolution (UMR) mass spectra with 10-minute time resolution which are analyzed using Tofware v3.2 in Igor Pro 8. The fractions of measured UMR signals were assigned to individual aerosol species using the fragmentation table. (Allan et al., 2004). On-site calibrations are performed to determine the ionization efficiencies of the chemical species. The calibration with The calibrations of ionization efficiency (IE) and relative IE (RIE) were performed following the procedures described in previous studies by using 300–350 nm pure ammonium nitrate (NH$_4$NO$_3$) and ammonium sulfate ((NH$_4$)$_2$SO$_4$) dissolved in aqueous solution. The calibration with gives ionization efficiency (IE) IE value of 250.0 ions pg^{-1} for nitrate (NO$_3$), and relative ionization efficiency (RIE) RIE values of 1.40, 1.67, 1.30, and 3.35, and 1.00 for organics, (Org), sulfate (SO$_4$), chloride (Cl), and ammonium (NH$_4$), and potassium (K), respectively. The detection limit values for the ToF-ACSM are expected to be similar to other studies using the same instrument setup (Fröhlich et al., 2013; Zheng et al., 2020), where the values are 198–351.8 ng m^{-3} for Org, 182–470.3 ng m^{-3} for NH$_4$, 21–41.8 for NO$_3$, 18–33.6 ng m^{-3} for SO$_4$, and 11–31.4 ng m^{-3} for Cl.

In addition to the aerosol measurements by the ToF-ACSM, ambient sulfur dioxide (SO$_2$) concentrations were obtained from the open-source data of Landelijk Meetnet Luchtkwaliteit (LML, https://www.luchtmeetnet.nl).), measured at the same location. Ammonia (NH$_3$) concentrations were obtained from measurements in Zegveld-Oude Meije station, 20 km to the north of Cabauw station (see Fig. 1), also acquired from LML. The particle size distribution concentration measurements were conducted using a TROPOS-SMPS with 8 nm to 800 nm size range and 5-minute time resolution from a 5-meter height inlet. The co-located weather data were retrieved from the Royal Netherlands Meteorological Institute (KNMI, https://www.knmi.nl).1a), also acquired from LML.

2.2.2. Particle size distribution measurements

The particle size distribution measurements were conducted using a TROPOS-SMPS. The instrument has been detailed in other work (Wiedensohler et al., 2012). Ambient air was sampled using a stainless-steel inlet equipped with PM$_{10}$ size-cut cyclone and Nafion dryer at 4.5-meter height sampling with a flow rate of 16.7 L min^{-1}. The SMPS inlet was placed approximately 3 m lateral distance from the ACSM instrument inlet. The instrument consists of a Vienna-type differential mobility analyzer (DMA) and a butanol-based TSI condensation particle counter (CPC) 3750. The flow rate in the instrument is 1.0 L min^{-1}. The TSI CPC 3750 has the collection efficiency of 100% at the first selected and reported size of 10 nm.

The raw dataset was processed using a linear multiple charge inversion algorithm to derive the particle number size distribution (PNSD or dN/dlog(D$_p$)) (Wiedensohler et al., 2012; Pfeifer et al., 2014). The MPSS inversion algorithm version 2.13 was utilized to obtain final PNSD from the raw dataset. The final PNSD has 5-minute time resolution and covers 71 geometric

mean diameters (D_p) from 8 nm to 853 nm. The particle number concentrations (dN) for individual D_p were then calculated by multiplying PNSD with dlog(D_p) values.

~~2.4.~~2.3. Positive matrix factorization (PMF)

The 10-minute average matrices of <u>UMR</u> organic fragment mass spectra <u>with mass-to-charge ratio (m/z) 12 to 120</u> were combined with the <u>inorganic</u> species average mass concentrations (i.e., ~~organics (Org),~~ ammonium (NH$_4$), nitrate (NO$_3$), sulfate (SO$_4$), <u>and</u> chloride (Cl~~), and potassium (K))~~)), and the 10-minute average particle number concentrations (dN) in 18 particle diameter ~~(D_p)~~ size bins <u>from 71 geometric mean diameters (D_p)</u> to generate hybrid input data matrices for PMF analysis. Each organic fragment ~~mass-to-ratio (m/z),~~ <u>(m/z),</u> species concentration, and size-binned particle concentration is treated as an individual variable in the PMF.

The <u>values and errors of organic fragment mass spectra and inorganic</u> mass concentration ~~variable values and errors~~ <u>variables, and the minimum error (minErr) of all species</u> were generated by Tofware v3.2~~.~~ <u>in Igor Pro 8.</u> The <u>10-minute resolution</u> particle size dataset <u>was obtained</u> from the ~~SMPS instrument as~~ <u>5-minute resolution particle number concentration described in the Sect. 2.2.2. The particle number concentrations are</u> categorized into 18 size bin variables (8–10 nm; 10–13 nm; 13–16 nm; 16–20 nm; 20-25 nm; 25–32 nm; 32–40 nm; 40–51 nm; 51–65 nm; 65–83 nm; 83–107 nm; 107–140 nm; 140–185 nm; 185–249 nm; 249–342 nm; 342–481 nm; 481–691 nm; and 691–853 nm). Each size bin contains the sum of four concentration points~~,~~ <u>(except for the last bin containing only three concentration points), then</u> averaged to 10 minutes. We use larger bin sizes for the larger diameters because larger particles occur less frequently. The errors for each size bin are taken to be the ~~population standard deviation of the raw data. The variable values of species mass concentrations and particle number concentrations were weighted prior to analysis to ensure that individual peaks have similar magnitude as the organic mass spectrum. This weighting was done to give all variables the same importance in the PMF analysis.~~ <u>standard deviation of the raw data.</u>

We performed the analysis using the PMF Evaluation Tool (PET) v3.08 <u>(</u>Ulbrich et al., 2009) in Igor Pro 8. The details of applying positive matrix factorization (PMF) to aerosol mass spectrometry datasets have been discussed elsewhere ~~in detail~~ (Paatero and Tapper, 1994; Paatero, 1999; Ulbrich et al., 2009). ~~The first step of the factor analysis was identifying the optimum number of factors by running unconstrained experiments using 2 to 10 factors. The optimum number of factors is selected by considering the lowest residuals of the PMF solutions, and whether all the factors are environmentally reasonable and unique based on their chemical composition. For all three-month datasets, this analysis converges to an optimum of 6 factors. The ordering of the factors is not identical across months and for ease of presentation, we reorder them so that factors of similar identity have the same factor number across months. The percent of signal explained by each factor is presented alongside plots of the factor profiles, to enable the reader to deduce the original factor ordering. The resulting hybrid PMF solution matrix is split back up into organic mass spectrum, species mass concentrations, and particle number concentration bin matrices, and the value of each variable is readjusted (undoing the previously described re-weighting) so that the ACSM species mass~~

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~~concentrations can still be interpreted quantitatively~~Prior to analysis before the PMF input matrix preparation, the variable values and errors of species mass concentrations and particle number concentrations were downweighted in reference to the highest average peak of the original organic mass spectrum, m/z 44 (f_{44}). During PMF input matrix preparation in PETv3.08, the m/z 44, 28, 18, 17, and 16 signals in the organic mass spectrum are also downweighted as provided by the procedure to account for duplicated information of m/z 44 in the organic mass spectrum (Ulbrich et al., 2009). The details of PMF variable downweighting can be found in Sect. S3.

The first step of the factor analysis was identifying the optimum number of factors (p) by running unconstrained experiments using 2 to 8 factors and varying the seed value (min = 0; max = 20; delta = 1) to pick different initial values for the PMF algorithm. The optimum p is selected by considering the lowest residuals and local minima (Q/Q_{exp}) of the PMF solutions. Alongside the local minima, we considered whether all the factors are environmentally reasonable and unique mainly based on their particle size distribution and chemical composition. After the optimum p and seed value are chosen, the rotationality of the best PMF solution is explored by varying the rotation (f_{peak}) value (min = -1, max = +1, delta = 0.2). Bootstrapping runs with 100 iterations on the chosen PMF solution were performed to estimate the uncertainty in the factor profile variables and time series, ensuring the robustness of the solution.

To determine the organic and inorganic composition in each PMF factor, the particle size distributions are removed from the factor profile. The total organic mass fraction is considered as the sum of organic fragments fraction from m/z 12 to 120, while the inorganic mass fractions are upweighted back and taken as NH_4, NO_3, SO_4, and Cl mass fractions. The final fraction of each species is determined by dividing the species mass fraction with the total organic and readjusted inorganic mass fraction.

2.5.2.4. Wind analysis

To analyze the factors using wind variables, we investigate the prevailing wind for several pollution episodes observed in the dataset. Bivariate polar plots are generated for ~~selected~~ factor reconstructed mass concentration derived from PMF analyses and mass concentration for each ACSM species in each period using the "Openair" package in the "R" environment (Carslaw and Ropkins, 2012). The wind parameters are obtained from co-located measurement of 10-meter wind direction data acquired from KNMI.

3. Results and Discussion

3.1. Mean bulk atmospheric chemical composition across periods

We hypothesize that the mean bulk atmospheric chemical composition influences how the chemical species are distributed across the PMF factors. Therefore, we discuss this topic before the PMF solutions. To compare the mean bulk composition among periods, we choose the springtime period (May) as reference. The mean concentrations of atmospheric species and the

species percentages in the bulk atmosphere are summarized in Table S1. In summer (June), we observe roughly a doubling in aerosol concentration for all IA and an increase with a factor 2.6 in OA compared to spring (May). In autumn (September), the particle concentrations decrease again, with a relatively larger decrease for sulfate.

Table 2. Mean bulk atmospheric chemical composition in the three periods, summarized as the values of total aerosol mass loading in µg m^{-3}, ion balance ratio (NH_{4_bal}) from linear regression, and mean organic-to-inorganic ratio (m_{Org}/m_{IA}). A more detailed information about each chemical species can be seen in Table S1.

Mean value	May 2021 (spring)	Jun 2021 (summer)	Sep 2021 (autumn)
Bulk aerosol composition[a] ■ Org ■ SO$_4$ ■ NH$_4$ ■ Cl ■ NO$_3$	37.7% 1.6% 17.5% 15.3% 27.9%	45.1% 1.0% (Cl) 16.2% 13.4% 24.2%	42.4% 0.9% (Cl) 10.9% 14.6% 31.2%
Aerosol mass loading[c]	6.60 µg m^{-3}	14.12 µg m^{-3}	5.15 µg m^{-3}
NH_{4_bal}[b]	0.997 ± 0.001	0.986 ± 0.001	1.066 ± 0.001
m_{Org}/m_{IA}[a]	0.61	0.82	0.74

[a] mass concentration, [b] molar concentration, [c] total mass of aerosol detected by ToF-ACSM (m$_{Org}$+m$_{NO_3}$+m$_{NH_4}$+m$_{SO_4}$+m$_{Cl}$)

The ion balance ratio, or also called ammonium balance ($NH_{4\_bal} = n_{NH_4}/(n_{NO_3}+2\times n_{SO_4}+n_{Cl})$), is the ratio between the measured ammonium (n_{NH_4}) and the total ammonium required to neutralize the major anions ($n_{NO_3}+2\times n_{SO_4}+n_{Cl}$). The ratio illustrates the excess of atmospheric ammonium (cation), or nitrate (anion), and other possibilities based on aerosol chemistry (see Sect. S2 for details). Ambient aerosol is normally charge-balanced, meaning that the major cation (NH_4^+) and major anion species (NO_3^-, SO_4^{2-}, and Cl^-) should have roughly one-to-one molar ratio ($NH_{4\_bal} \approx 1$). Among three periods analyzed, the ion balance ratio was found to be close to unity for all periods. This infers that the bulk aerosol charge is fully neutralized.

We introduce mean organic-to-inorganic mass ratio (m_{Org}/m_{IA}) to quantitatively compare bulk OA and IA composition across seasons. Based on this ratio, in summertime (June), we have composition richer in organics compared to spring and autumn. This difference is likely due to increasing biogenic emissions of VOC in summertime, and higher temperature-induced increases in anthropogenic VOC concentrations.

3.2. Identification of PMF factors

3.1.1.1. Identification of PMF factors

260 #### 3.1.1.1.1.1. Factor particle size distributions and composition

From the unconstrained experiments using the combined ACSM-SMPS matrix, the best PMF solution was found with six factors for the combined ACSM-SMPS matrix in each of the datasetsto have 4 factors for May 2021 (Fig. 32), June 2021 (Fig. S1), and September 2021 (Fig. S2), with similarities observed across monthsS2). The determination of PMF solution is detailed in Sect. S3. The resulting hybrid PMF solution matrix is split into organic mass spectrum, species mass concentrations, and 265 particle number concentration bin matrices for the ease of presentation. The fragments of m/z below 20 are included in the PMF analysis but are not shown in the figures as they do not convey information for the spectrum interpretation. The signal factor axes for inorganic composition and particle size distribution are rescaled and fixed to allow comparison across factors. As each period encompasses around one month of time series data, the factors discerned by the hybrid PMF analyses show typical average aerosol composition during each period, rather than individual pollution episode profiles that may vary over 270 time. Similarities and differences of factors across months will be discussed further below.
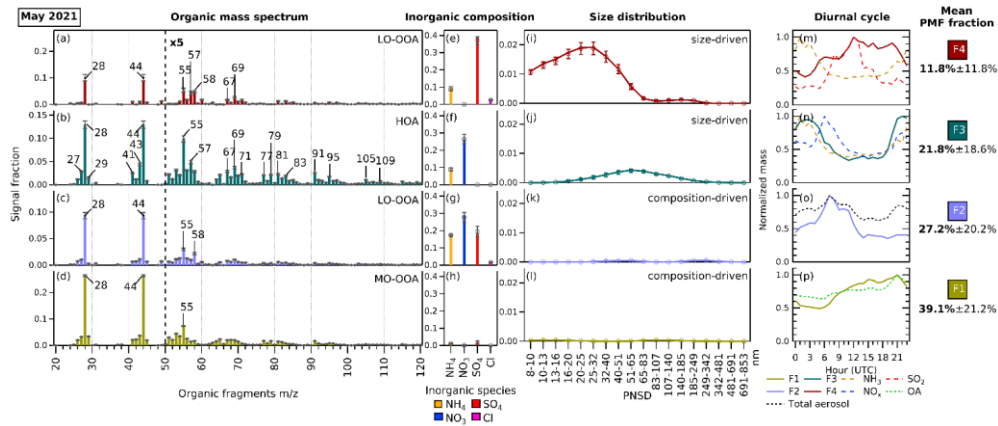
Figure 2. The profiles of 4-factor PMF solution from the combined ACSM-SMPS dataset in May 2021. Each factor is split into three matrices with their own rescaled signal fraction axes. The error bars in each variable represents standard deviation generated by performing 275 bootstrapped run of the solution. The panel **a-d** shows the organic fragment mass spectrum from m/z 20 to 120 from ACSM (m/z < 20 not included). The panel **e-h** shows the ACSM standard inorganic aerosol species concentrations (ammonium (NH_4), nitrate (NO_3), sulfate (SO_4), and chloride (Cl)). The panel **i-l** shows the particle size distribution profiles from the SMPS. On the panel **m-p**, the diurnal cycles of the factors and related species are depicted. The mean PMF fractions and their standard deviations are shown indicating the mean contribution of each hybrid PMF factor to the "total variable reconstruction" by PMF throughout the period. Note that the standard deviations shown here 280 indicate real variability in contribution of each factor, and not uncertainty. The factors in May 2021 are assigned as: (F1) MO-OOA, (F2)

NH$_4$+NO$_3$+SO$_4$+LO-OOA, (F3) size-driven NH$_4$+NO$_3$+HOA, and (F4) size-driven NH$_4$+SO$_4$+LO-OOA. Similar figures for June and September 2021 can be found in Fig. S1 and Fig. S2.

3.2.1. Factor particle size distributions and composition

FourTwo factors have particle size profiles distributed inassociated with specific diameter subranges, which we interpret as

285 related to new particle formationNPF and growth. We therefore call these factors "size-driven". The size-driven factors resolved from the analysis possess some similarities in composition across months, from ammonium sulfate-rich aerosol (F6) to varying mixture of organic aerosol (OA) and inorganic aerosol (IA) (F5, F4, and F3) (see Fig. 4). We interpret the where the factor associated with the smallest diameter size-driven factor as a nucleation-mode factor (F6), which then grows with different composition, on average progressing from F6 to F3. The two particle sizes has bulk composition driven factors are

290 distributed across particle sizes of ammonium sulfate aerosol (F4) while the larger sizes is linked to the bulk composition of ammonium nitrate aerosol (F3). The other two factors are unrelated to specific particle size and therefore called "composition-driven" factors, consisting of: (F2), an OA and IA mixed factor with a variable composition, and (F1), an organic aerosol factor with occasional traces of ammonium sulfate aerosolOA-dominant factor.

3.1.2.3.2.2.   Factor organic profiles

295 The organic mass spectrum of each factor profile can be used to obtain information regarding the degree of oxidation level of the factor. Oxidized, which can be related to atmospheric aging of each factor profile. In general, OA can be categorized into two types: primary organic aerosols (POA), and secondary organic aerosols (SOA). Oxygenated organic aerosols (OOA) are often considered to be SOA, while other OA profiles are generally considered POA (Chen et al., 2022).compounds

300 OOA are characterized by a relatively high m/z 28 (f$_{28}$) and m/z 44 (f$_{44}$) signalfragment signals, originating primarily from CO$^+$ and CO$_2^+$ fragments of carboxyliccarboxylate groups in organic compounds. produced by thermal decomposition inside the ACSM vaporizer (Alfarra et al., 2004). ThisThe f$_{44}$ fragment is often related to a high degree of oxidation and photochemical ageing (Alfarra et al., 2004; Ng et al., 2010). It is also important to note that the ACSM used in this paper has

305 a CV instead of an SV inlet (see Sect. 2.2.1), which is known to produce higher f$_{44}$ values due to enhanced thermal decomposition (Hu et al., 2017; Zheng et al., 2020). The m/z 43 (f$_{43}$) fragment is characteristic for both oxidizedoxygenated organic compounds (CH$_3$CO$^+$) and saturated hydrocarbon compounds (C$_3$H$_7^+$). Thus, factors with higher f$_{44}$ and lower f$_{43}$ values are understood to be more oxidized and are often classified as an oxygenated organic aerosol (OOA). Meanwhile,while lower f$_{44}$ and higher f$_{43}$ values implies that the factor is less oxidized. OOA may appear in more than one factor in a PMF solution and thus it is common to distinguish less oxidized-OOA (LO-OOA) and is often labelled hydrocarbon-like organic

310 aerosol (HOA). In this paper, we use these values only to compare more oxidized-OOA (MO-OOA). To assess the variation in OOA oxidation level between aerosol, the triangle plot (Ng et al., 2010) is normally used to compare f$_{44}$/f$_{43}$ values among resolved OOA factors. It is also important to note that the ACSM used in this paper has a CV instead of a SV inlet in the PMF

solution (see ~~Sect. 2.2), which~~Fig. S6). OOA generally increase throughout the afternoon as its formation is ~~known to produce higher f_{44} values due to enhanced thermal decomposition~~photochemically driven (Hu et al., ~~2017), and therefore cannot be directly compared to PMF organic profiles in other works.~~2016; Sun et al., 2016) and accumulate in the evening due to the shallow nocturnal boundary layer. In the morning, the concentration decreases as clean airmasses introduced into the rising boundary layer diluting existing aerosol concentrations (Stull, 1988).

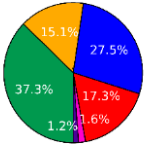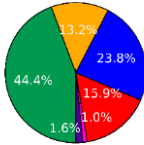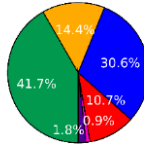~~**3.2.** Bulk atmospheric chemical composition across periods~~

13

We hypothesize that the bulk atmospheric chemical composition influences how the chemical species are distributed across the PMF factors. The three periods have different average chemical composition as detected by the ToF-ACSM measurements. The mean concentrations of atmospheric species and the species percentages in the bulk atmosphere are summarized in Table S1. For this assessment, we are using three mean concentration ratios summarized in Table 2 to characterize average composition. Ion balance ratio ($n_{NH_4}/(n_{NO_3}+2\times n_{SO_4}+n_{Cl})$) is the ratio between the measured ammonium (n_{NH_4}) and the total ammonium required to neutralize the major anions ($n_{NO_3}+2\times n_{SO_4}+n_{Cl}$). It illustrates the excess of atmospheric ammonium (cation), or nitrate (anion), and other possibilities based on aerosol chemistry (see Sect. S2 for details). This ion balance ratio was found to be unity in May (suggesting charge-balanced condition), less than unity in June (suggesting nitrate excess), and more than unity in September (suggesting ammonium excess). We also examine the mean sulfate to nitrate molar concentration ratio (n_{SO_4}/n_{NO_3}), determining a sulfate-rich or sulfate-poor condition relatively. The mean organic to ammonium mass ratio (m_{Org}/m_{NH_4}) is used to show whether a period is organic-rich relative to other periods.

We have three different composition regimes measured during the three periods based on these ratios. In springtime (May), we can see a sulfate-rich and nitrate-excess regime. In summertime (June), we have an organic-rich, sulfate-rich with nitrate-excess regime. Lastly, a sulfate-poor and ammonium-excess regime is observed in autumn (September). Below, we will discuss how these regimes influence the chemical composition of factors that were obtained from PMF analyses. POA consists of various sources which can be identified from the appearance of certain fragmentation patterns in the organic mass spectrum, diurnal cycle, as well as correlation with other measurements. Some of the most common POA from PMF analysis are hydrocarbon-like organic aerosols (HOA), biomass burning organic aerosol (BBOA), cooking organic aerosols (COA), and coal combustion organic aerosol (CCOA) (Chen et al., 2022). POA have similar characteristics of alkyl and alkenyl fragments ($C_nH_{2n+1}^+$: m/z 29, 43, 57, 71, … and $C_nH_{2n-1}^+$: m/z 27, 41, 55, 69, …). HOA as a type of POA is often correlated with anthropogenic combustion pollutants, such as NO_x and black carbon from vehicular emission (Alfarra et al., 2004; Mohr et al., 2009; Zheng et al., 2020). Other POA profiles are distinguished by looking at certain fragments (e.g. m/z 60 and 73 for BBOA (Schneider et al., 2006; Weimer et al., 2008; He et al., 2010), m/z 55 for COA (He et al., 2010; Mohr et al., 2012), m/z of larger fragments related to polycyclic aromatic hydrocarbons (PAHs) for CCOA (Hu et al., 2013)). While CV increases the f_{44} values and smaller organic fragments due to enhanced thermal decomposition, larger fragments become underestimated (Hu et al., 2017; Zheng et al., 2020) and therefore the differences between POA factors becomes more subtle.

The PMF analyses in this study resolved one POA factor (as HOA factor) and three SOA factors (one LO-OOA factor and two MO-OOA factors) across periods, where each organic profile has its corresponding IA composition and size distribution. Among size-driven factors, the factor related to the smallest particle sizes (F4) has OA assigned as LO-OOA, while the OA associated with the second size-driven factor (F3) is assigned as HOA. In the composition-driven factors, the OA+IA mixture factor (F2) resolves an LO-OOA profile while the OA factor (F1) resolves an MO-OOA profile.

Table 2. Mean bulk atmospheric chemical composition in the three periods, summarized as the values of ion balance ratio ($n_{NH_4}/(n_{NO_3}+2\times n_{SO_4}+n_{Cl})$) from linear regression, mean sulfate-to-nitrate ratio (n_{SO_4}/n_{NO_3}), and mean organic-to-ammonium ratio (m_{Org}/m_{NH_4}). The concentrations were detected by the ToF-ACSM in Cabauw. A more detailed information can be seen in Table S1.

Mean ratio	May 2021 (spring)	Jun 2021 (summer)	Sep 2021 (autumn)
Bulk aerosol composition* ■ Org ■ SO$_4$ ■ NH$_4$ ■ Cl ■ NO$_3$ ■ K	15.1% 27.5% 37.3% 17.3% 1.2% 1.6%	13.2% 23.8% 44.4% 15.9% 1.0% 1.6%	14.4% 30.6% 41.7% 10.7% 0.9% 1.8%
$n_{NH_4}/(n_{NO_3}+2\times n_{SO_4}+n_{Cl})$**	0.99	0.98	1.08
n_{SO_4}/n_{NO_3}**	0.41	0.43	0.23
m_{Org}/m_{NH_4}*	2.47	3.36	2.90
Composition regime	sulfate-rich	nitrate excess, organic- and sulfate-rich	ammonium excess, sulfate-poor

*mass concentration, **molar concentration

3.40.3.3. Size-driven factors (F7, F6, F5, and F4 and F3)

Using the hybrid ACSM-SMPS datasets, ~~four~~two size-driven factors emerge from the PMF analyses as ~~F6, F5,~~ F4, and F3 (see Fig. 3, ~~Fig. S1, and Fig. S2~~). These factors are considered "size-driven" due to the approximately normally distributed particle concentrations in a specific sub-range of diameter. The ~~four~~two factors display different particle size clusters increasing in diameter from ~~F6~~F4 to F3. ~~The size-driven factors have diverse composition characterized by a variety of OA and IA mixtures, as can be seen in Fig. 4, discussed in more detail below.~~
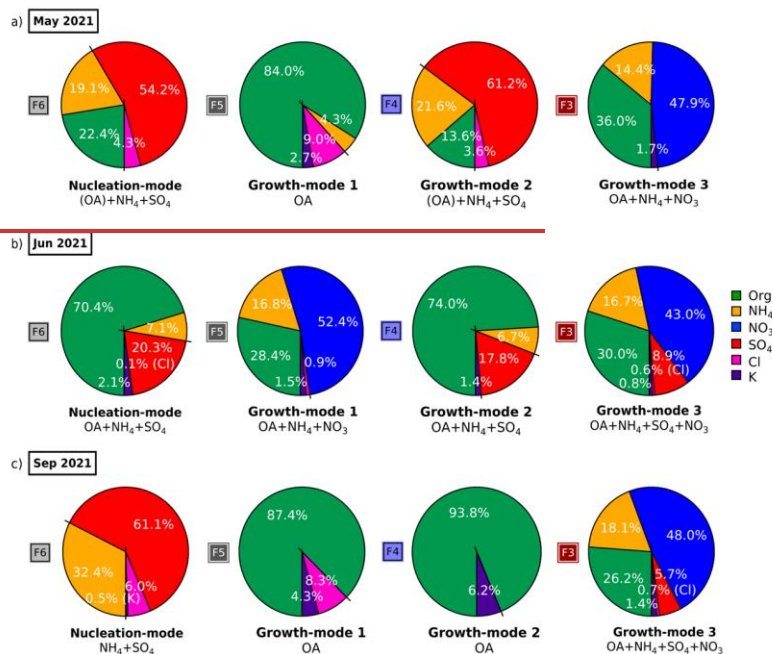
New particle formation (NPF) events are characterized by the rapidly increasing particle number concentration below 20 nm followed by particle growth, creating nearly vertical aligned peaks in particle number concentration plotted against time (Heintzenberg et al., 2007; Kerminen et al., 2018). In Fig. 5By comparing the time series of particle size distribution (dN/dlogD$_p$), total mass loading, and PMF mass fraction (see Fig. 4 (May) and Fig. S3, we (June and September)), we can observe that the episodes during which the smallest size-driven factor (F6)factors' fraction increasesincrease occur when the total aerosol mass concentration is relatively low. This is to be expected, as during these periods, the condensational sink, which would compete by scavenging low-volatility gases or small particles, is reduced. If we zoom into the timeseriestime series, the NPF growth shapes appear during episodes that are dominated by the smallest size factor, F6F4 and/or F3 (see Fig. S4). The trace inorganic ions (chloride and potassium) in the factors are found to be correlated with the existence of sulfate

and organic species, respectively, hinting at possible correlations with sea spray and biomass burning aerosol, respectively (see details in Sect. S4).

The reconstructed PMF masses show the influence of sunlight and temperature on NPF events. The average PMF mass fraction of the size-driven F4 is higher in summertime (June) compared to other periods (see Fig. 3) due to higher mean radiation and temperatures (see Table 1). In summer (June), F4 accounts in average 14.9% of total reconstructed PMF mass while in spring (May) and autumn (September), it only represents 11.8% and 7.8%, respectively. The more frequent appearance of NPF growth events during summer can be seen in Fig. S3a-c. Other studies have likewise found the occurrence of NPF events is generally favored in high radiation (Modini et al., 2009; Peltola et al., 2022) and warmer temperatures (Jokinen et al., 2022; Peltola et al., 2022). This is because solar radiation provides the UV radiation that promotes photochemical reactions and turbulent motions needed to form new particles (Wehner et al., 2015; Dada et al., 2017; Kerminen et al., 2018; Sellegri et al., 2019).
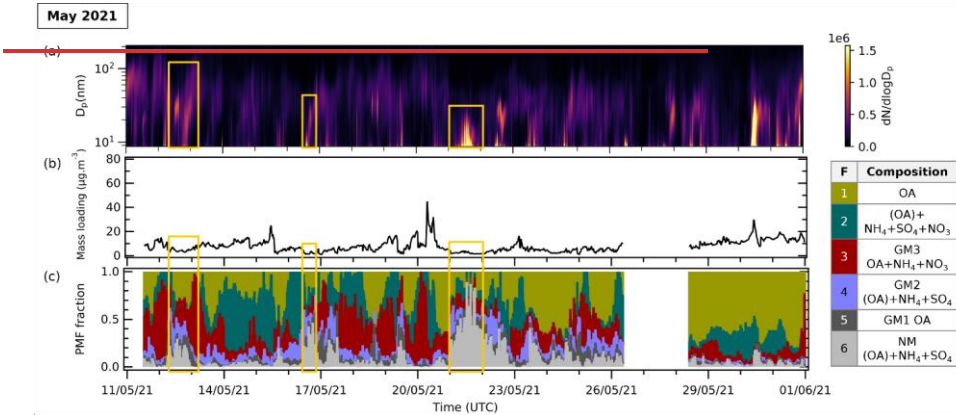
Figure 3. (a-b) Normalized average particle size distribution of two size-driven factors of F4 (maroon) and F3 (turquoise) across periods. The line plot shows particle number concentration (dN) fract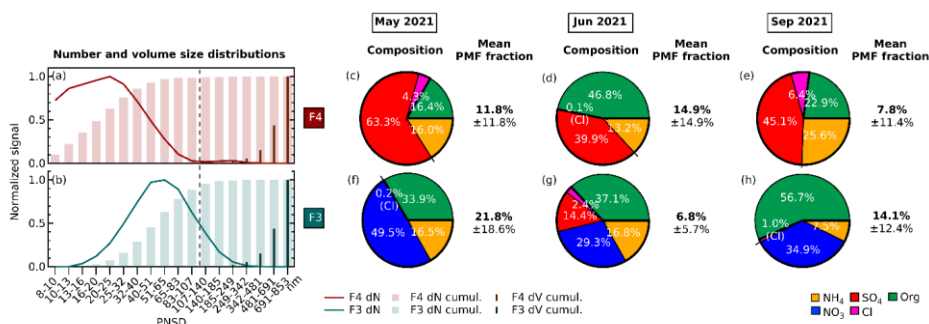ion on each size bin. The thick histogram represents cumulative particle number concentration (dN) fraction as the particle size increases, while the thin histogram represents cumulative particle volume (dV = dN×(4/3)×π×(D$_p$/2)^3) fraction. The vertical dashed dark grey line divides the particle diameters where particles are transmitted with <50% efficiency on the left (diameter less than ~100 nm) and with at least 50% efficiency by PM$_{2.5}$ lens of ToF-ACSM on the right (diameter more than ~100 nm). **(c-h)** Pie charts showing mass percentage of each aerosol species contributing to each size-driven factor in May 2021, June 2021, and September 2021. Green represents organics (Org), orange represents ammonium (NH$_4$), dark blue represents nitrate (NO$_3$), dark red represents sulfate (SO$_4$), and pink represents chloride (Cl). F4 are dominated by ammonium sulfate while F3 are dominated by ammonium nitrate. The mean PMF fractions and their standard deviations are shown indicating the mean contribution of the factor to the total reconstructed PMF mass.
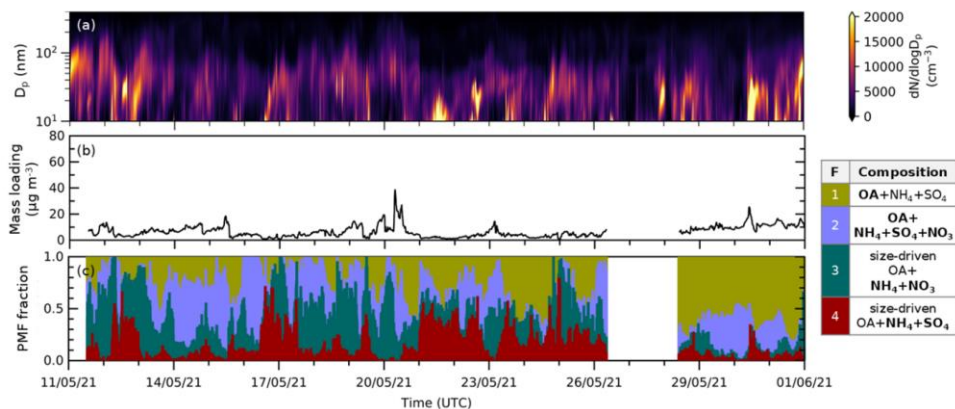
Figure 4. Time series of (a) particle size distribution (dN/dlogD$_p$) in cm^{-3} with logarithmic scale in particle size obtained from SMPS measurements, (b) total mass loading calculated from ACSM species concentration (using Tofware) in μg m^{-3}, and (c) reconstructed PMF fraction (stacked) from analysis in May 2021. ~~Orange outlined sections indicate periods during which high episodes of size-driven factors are observed. These episodes~~Episodes of F4 and F3 coincide with relatively low total aerosol mass conditions and high fine particle concentrations. Similar figures for June and September 2021 can be found in Fig. S3.

3.3.1. ~~F6 correspond~~ Particle size distributions

F4 corresponds to the bulk composition when the particles in the nucleation mode ~~is~~ growing into Aitken mode size range ~~(8 < D_P <~~, with modal size of 20-25 nm (see Fig. 3(a)). F3 is characterized by clustered particle sizes in the Aitken and accumulation mode region, with modal size of 51-65 nm~~)~~. (see Fig. 3(b)). The F4 and F3 mass loading shows a good correlation with particle number concentration in the size bin of 20-25 nm and 51-65 nm, respectively, across periods (see Fig. S5). The size range differs slightly across months but ~~is~~F4 always appears as the smallest particle size range among factors, which we therefore designate as ~~nucleation mode.~~ "nucleation-mode" factor, while F3 with larger particle size range is designated as "growth-mode" factor.

Some concerns may arise because the ACSM and SMPS measure different particle size ranges, especially the smaller sizes which are the major interest of this study. According to a study conducted using a ToF-ACSM in the same configuration as this study, the $PM_{2.5}$ lens in the ToF-ACSM transmits particles with vacuum aerodynamic diameter (D_{va}) between 100 nm and 3 μm with efficiency above 50%, decreasing to around 20% for D_{va} ~ 55–60 nm (Xu et al., 2017). Meanwhile, the SMPS instrument samples particles with diameters ranging from 10 to 800 nm. As we are mainly interested in elucidating the composition of NPF and growth in sizes finer than 100 nm, we address here the influence of this mismatch on interpretation of our PMF results.

In Fig. 3a, we observe that F4 mainly related to aerosol with sizes that have transmission efficiency <50% in $PM_{2.5}$ ToF-ACSM, while in Fig. 3b, only the size bins of 107–140 nm in F3 have transmission efficiency ≥50%. The small-sized particles will make a negligible contribution to the $PM_{2.5}$ mass and the larger particles will always dominate the particle volume size distribution, regardless of whether the finer particles are efficiently sampled or not by ACSM. Nevertheless, although the ACSM does not directly measure the finest particle composition, the factor still illustrates the bulk chemical composition that occurs during and favors the formation and growth of new particles. Moreover, the PMF tool does not recognize that the diameter bins are sequential, so the factors whose particle diameters cluster in certain range confirm that F4 and F3 composition indeed happen during NPF and growth when the fine particle loading is the greatest.

3.3.2. Chemical composition

In all periods, ~~F6~~ the nucleation-mode F4 has ammonium sulfate as ~~a~~the major component~~.~~ (see Fig. 3c-e). The factor further consists of ammonium (~~7.1~~13% to ~~32.4~~26%), sulfate (~~20.3~~40% to ~~61.6~~63%), organic compounds (~~0.0~~16% to ~~70.4~~47%), and traces of chloride (0.1% to 6.~~0%) and potassium (0.0% to 2.1%).~~

455 ~~The~~4%). Organics are known to participate in particle formation and growth (Riipinen et al., 2012; Hodshire et al., 2016), while in this study, the mass percentage share between ammonium, sulfate, and organics of ~~F6 depend~~F4 depends on the mean bulk organic composition ~~regime~~ in each period (see Fig. 4~~3~~c-e). The ~~sulfate-rich regime with~~ low mean bulk ~~organics~~organic composition in springtime and autumn (May and September) leads to ~~F6~~F4 being largely ammonium (16% and 26%) and sulfate (~~19.1~~63% and ~~54.2%, respectively),~~45%), followed by OA (~~22.4~~16% and 23%) and chloride (4.~~8~~3% and 6.4%). The

460 organic-~~rich and sulfate~~-rich regime in summer (June, see Table 2) results in ~~F6 being dominated by~~the increase of OA (~~70.4%)~~ ~~rather than~~in F4 (47%) and less ammonium ~~and,~~ sulfate ~~(7.1,~~ and chloride (13%, 40% and ~~20.3~~0.1%, respectively~~), with traces~~ ~~of chloride (0.1%) and potassium (2.1%). In autumn (September), the ammonium-excess and sulfate-poor regime with low~~ ~~bulk organics results in the F6 composition being exclusively ammonium and sulfate (32.4% and 61.1%, respectively), with~~ ~~traces of chloride (6.0%) and potassium (0.5%). We~~). F4 represents from 9.5% up to 14.3% of total reconstructed PMF mass

465 in the solution with the highest being during summer when there is more contribution from organic masses. On the other hand, the growth-mode F3 is composed of mainly ammonium nitrate aerosol (see Fig. 3f-h). The factor further composed of ammonium (8% to 17%), nitrate (29% to 50%), organic compounds (34% to 57%), and traces of chloride (0.2% to 2.4%). In contrast to other months, the PMF analysis also resolves variations in F3 containing sulfate (14%) during summertime (June).

470 Overall, we interpret these results to ~~mean~~indicate that sulfate is a key component of ~~condensation nuclei~~nucleating particles during NPF events~~, regardless of the bulk atmospheric composition.~~. When the mean bulk organic concentration is high~~,~~ and more oxidized (e.g., summertime), it participates more abundantly in particle nucleation. ~~With excess ambient~~While sulfate is key to nucleation, nitrate plays a more important role in particle growth (see Sect. S2).

3.3.3. Organic profiles

475 The organic mass spectrum profile from each size-driven factors and their diurnal cycles in each period are shown in Fig. 5. Across seasons, LO-OOA is part of the nucleation-mode particles composition. The factors are assigned as LO-OOA due to their f_{44}/f_{43} values compared to other OOA factors (see the triangle plot in Fig. S6). The LO-OOA F4 profile resolved in this study is comparable to LO-OOA resolved in other aerosol mass spectrometry studies using CV (Zheng et al., 2020; Joo et al., 2021), although fragments with m/z > 50 are observed less. From this trend, we infer that only lower volatility, oxygenated

480 organic compounds can condense on freshly nucleated particles. In terms of diurnal cycle, the F4 mass loading does not follow the typical LO-OOA pattern, but rather together with the formation of, ammonium~~, however, particle condensation can occur~~ ~~without organic compounds.~~

~~Oxidation levels further explain the OA contribution difference in nucleation-mode particles. We can observe this variation~~

485 ~~by looking at the organic fragment spectrum of F6. High f_{44} value is observed in F6 where OA participates in new particle~~ ~~condensation during spring (May, f_{44} = 0.32) and summer (June, f_{44} = 0.33). In these months, higher mean radiation promotes~~ ~~photooxidation of organic vapors and~~ sulfate is responsible for the increase in new particle loading during the day, as seen in

the diurnal cycles (Fig. 5g,i,k). The organic-rich regime in summer (see Table 2) combined with higher mean temperature also favors the abundant production of semi-volatile oxidized organic compoundsOA which can condense rapidly onto newly

490   formed particles, resulting in higher OA contribution to nucleation-mode particles. In September, when mean radiation is lower, OA does not appear in F6. The organic mass spectra are consistent with this lower degree of oxidation, with lower f_{44} and high f_{43} valueleading to the increase of OA to 47%, compared to 16% in spring and 23% in autumn (September, $f_{44} =$ 5.8×10^{-6} and $f_{43} = 0.16$).

495   We infer that only lower volatility, oxidized organic compounds can condense on freshly nucleated particles. The organic-rich regime combined with higher mean temperature favors the abundant condensation of available semi-volatile OA onto newly formed particles.see Fig. 3). Consistent with these results, several aerosol chamber experiments have reported that highly oxygenated- organic molecules (HOM) from biogenic and anthropogenic organic precursors play a dominant role in new particle formation and growth (Schobesberger et al., 2013; Ehn et al., 2014; Riccobono et al., 2014; Tröstl et al., 2016; Mohr

500   et al., 2019; Pospisilova et al., 2020; Zhao et al., 2021).

F5 to F3: growth-mode factors

F5, F4, and F3 are characterized by clustered particle sizes in the Aitken and accumulation mode region ($20 < D_P < 691$ nm). The size range differs across period but has particle size progressively growing from F5 to F3, which we thus designate the

505   "growth-mode" factors. The growth-mode factors contain different composition across seasons, depending on the available semivolatile species for condensation.

In springtime (May), less-volatile and less-oxidized organic compounds ($f_{44} = 8.2 \times 10^{-6}$ and $f_{43} = 0.13$) condense onto newly formed particles, increasing the organic contribution in F5. The increase of OA in F5 is also observed for autumn (September),

510   although in the case more highly oxidized organic compounds ($f_{44} = 0.21$ and $f_{43} = 0.07$) condense onto new particles. We suggest that although oxidized organic compounds are not involved in early particle condensation when the mean radiation is lower, they are incorporated in later growth. For spring and autumn, F5 consists of largely OA composition (84.0% to 87.4%), ammonium (4.3% only in May), chloride (8.3% to 9.0%), and potassium (2.7% to 4.3%).

515   In summertime (June), there is a substantial amount of nitrate (52.4%) in F5 alongside less oxygenated OA (28.4%, $f_{44} =$ 2.8×10^{-8} and $f_{43} = 0.17$), ammonium (16.8%), chloride (0.9%), and potassium (1.5%). The ion balance ratio in June was less than unity, which can be due to excess nitrate aerosol (see Sect. S2). We propose that it indicates the promotion of semi-volatile organic nitrate formation in the summertime, condensing onto the newly formed particles as the temperature lowers. Organic nitrate comes from reaction between NO_x with less oxygenated organic compounds and condensing into aerosol phase more

520   easily in this period. Further, we infer the possibility of biogenic source of the organic compounds involved in this organic

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nitrate source, due to the fact that we observe this composition only in the hottest and sunniest month of June and less oxygenated.

As particles grow into the larger size ranges F4 and F3, they incorporate more OA and ammonium salts. F4 resembles the composition of either the two smallest size-driven factors (F6 or F5), which may be due to continuation of smaller particle growth with the same composition. F3, the largest particle size range among size-driven factors, contains nitrate as the main component (43.0% to 48.0%) followed by OA (26.2% to 36.0%), and ammonium (14.4% to 18.1%). The dominant contribution of nitrate is observed across periods regardless of the nitrate composition regime. Overall, the composition of these size-driven factors suggests that, while sulfate is key to nucleation, nitrate plays a more important role in particle growth, which is related to the ammonium-sulfate-nitrate aerosol chemistry (see Sect. S2).

Relationships with mean radiation and temperatures

The reconstructed PMF masses show the influence of mean downward shortwave radiation and temperature on NPF events. The average PMF mass fraction of nucleation-mode particles (F6) is higher in summertime (June) compared to other periods (see Fig. S1) due to higher mean radiation and temperatures (see Table 1). In summer (June), F6 accounts in average 22.3% of total reconstructed PMF mass while in spring (May) and summer (September), they only represent 6.2% and 4.1%, respectively. The more frequent appearance of NPF growth events during summer can be seen in Fig. S3a. The occurrence of NPF events is generally favored in high radiation (Modini et al., 2009; Peltola et al., 2022) and warmer temperatures (Jokinen et al., 2022; Peltola et al., 2022). Solar radiation provides the UV radiation that promotes photochemical reactions and turbulent motions needed to form new particles (Wehner et al., 2015; Dada et al., 2017; Kerminen et al., 2018; Sellegri et al., 2019).
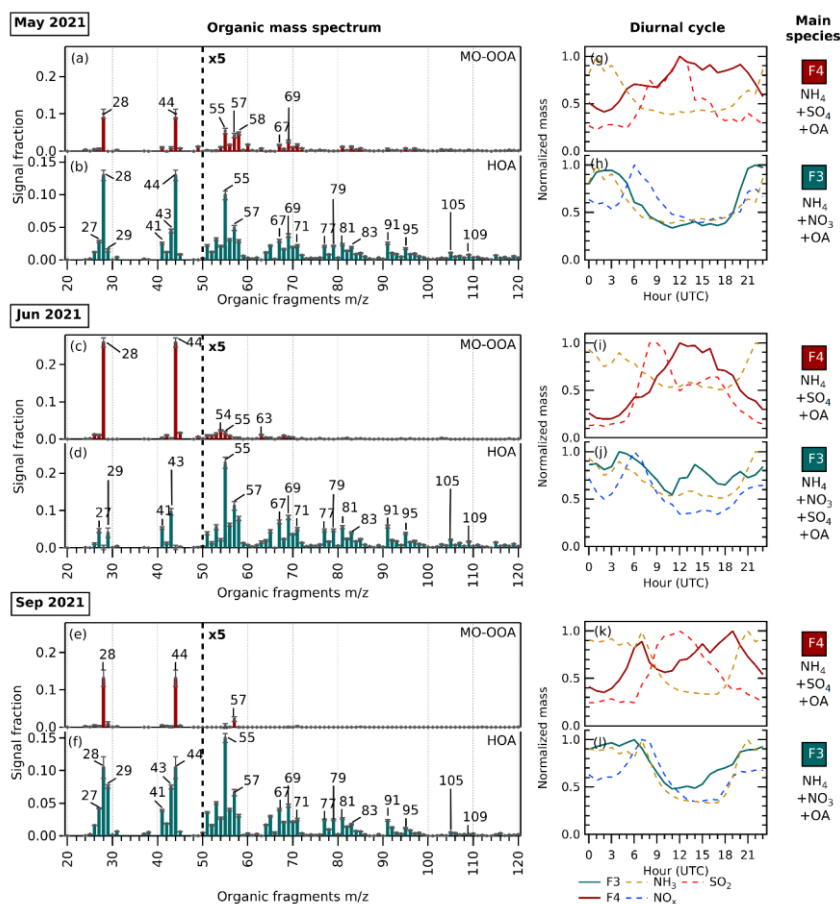
Figure 5. (a-f) Organic mass spectrum from m/z 20 to 120 (m/z < 20 not included) of F4 (maroon) showing MO-OOA factor profiles and F3 (turquoise) showing HOA factor profiles in May 2021, June 2021, and September 2021. The error bars in each m/z were generated from bootstrap run. **(g-l)** Diurnal cycles of corresponding factors and potential precursor gases. The diurnal cycles of F4, mainly composed of ammonium sulfate, are shown together with its precursors, NH_3 and SO_2. The diurnal cycles of F3, mainly composed of ammonium nitrate, are shown together with its precursor, NH_3 and NO_x.

F3, seen as the growth-mode factor related mainly to ammonium nitrate, is associated with an HOA-like organic profile. The factor is assigned as HOA due to the alkyl and alkenyl fragments that are abundant (m/z 27, 29, 41, 43, 55, 57, 69, and 71).

The diurnal cycle of F3 in this study shows similarity with general non-urban HOA diurnal patterns, with increase of loading at nighttime (see Fig. 5h,j,l), contrary to typical diurnal pattern of HOA in urban site with peaks during morning and evening rush hour (Chen et al., 2022). It suggests that the growth-mode F3 may be related to transported vehicular emissions from urban areas and/or local primary organic emissions. Organic nitrates can also be formed from reaction between NO_x with less oxygenated volatile organic compounds (VOCs) through NO_3 or alkyl peroxy radicals (Berkemeier et al., 2016). The diurnal pattern of F3 is consistent with this organic nitrate formation, followed by condensation onto the newly formed particles as the temperature lowers at night. During the summer, a small increase in F3 mass loading during the daytime also can be observed, hinting at enhancement of daytime organic nitrate formation in the hottest and sunniest period.

During the summer, the values of f_{28} and f_{44}/f_{43} as oxygenated organic markers in F4 are higher compared to other seasons, while they are almost absent in F3. In the chemical composition discussed in Sect. 3.3.2, sulfate also makes appearance in F3 unlike other seasons. We hypothesize that the PMF solution did not resolve the two size-driven factors in summer (Jun) similarly to other seasons, and therefore the aerosol composition is more mixed between NPF and growth particles. Mathematically, this is reflected in the local minima of the chosen PMF solution. Despite being the lowest minima in the PMF solution space, Q/Q_{exp} in June scores the lowest compared to May and September (see Table S3).

3.3.4. New particle formation (NPF) and growth pathway

The NPF events shown by the time series of particle number size distribution and size-driven factor loading reveal that particle formation and growth takes around 6 to 12 hours (see Fig. S4). The high occurrence of ammonium sulfate and oxidized organic molecules in the aerosol phase observed during nucleation-mode F4 episodes marks the beginning of NPF. This is related to ammonium sulfate formation from the reaction between ammonia and sulfuric acid, and uptake of oxygenated organic compounds. We can consider F3 as a "sequential" pathway of F4 growing in size; this sequential nature is observed in some NPF events shown in Fig. S4, when F3 peaks after F4. F4 grows into F3 when nitric acid and/or organic nitrates and hydrocarbon-like semi-volatile organic compounds are dominant in the aerosol composition.

One might argue that F3 cannot be considered as the successor of F4 as it does not contain any sulfate (for May and September), which should remain from initial nucleation. Another possible explanation is that F3 emerges directly from ammonium nitrate as a "parallel" nucleation pathway. Other studies have observed this nucleation mode to occur very rarely and only in the free troposphere, at lower temperature and very clean air conditions, through reaction between nitric acid and NH_3 (Höpfner et al., 2019; Wang et al., 2020). In a "combined" hypothesis, F3 emerges from F4, but the particles rapidly favor the pathway of growing mainly by ammonium nitrate condensation to the particle phase. The simultaneous pathway of F4 and F3 growth can be observed in some NPF events in Fig. S4.

The diurnal cycles of the size-driven factors shown in Fig. 6 (May) and Fig. S5 (June and September) also shows the influence of shortwave radiation and temperature on particle formation. Going from F6 to F3, we observe that the factors' diurnal pattern

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tends to shift from a daytime peak (F6 peaks in the middle of the day) to higher nighttime concentration as the particle size grows. Regional scale NPF normally takes place during the daytime between sunrise and sunset, where it can carry on for several hours (Hamed et al., 2007; Hussein et al., 2009; Németh and Salma, 2014; Qi et al., 2015; Dai et al., 2017; Kerminen et al., 2018; Kalkavouras et al., 2020), although there are also instances of NPF happening during the night in various locations (Hirsikko et al., 2012; Vehkamäki and Riipinen, 2012; Rose et al., 2018; Kammer et al., 2018) or quiet NPF during non-event days (Kulmala et al., 2012; Dada et al., 2018; Kulmala et al., 2022). Daytime peaks in F6 can be seen in spring (see Fig. 6) and summer (see Fig. S5) when the mean radiation is higher. This peak is less visible during autumn when mean radiation is lower (see Fig. S5). The sulfate-rich new particle factor F6 also appears around the same time as the precursor gas SO_2, with the most obvious match between SO_2 and the F6 diurnal cycle observed in spring (May, see Fig. 6).

Unlike the nucleation-mode F6, the growth-mode F5 and F4 have different diurnal patterns across periods, corresponding to their diverse compositions. F5 and F4 also exhibit consistently less diurnal variation, except for F5 during summer (see Fig. S5), when it tracks with the highest mean radiation across periods. In summertime (June), when there was more daylight and radiation available to promote NPF and growth, F5 has a pronounced peak in the afternoon, later than the F6 peak.

F3 shows more elevated nighttime concentrations across seasons (see Fig. 6 and Fig. S5). Lower nocturnal temperatures foster the condensation of semivolatile chemical species into the aerosol phase, increasing the nighttime particle concentration. The increase in the particle concentration during the night can also be facilitated by a shallower nocturnal boundary layer.
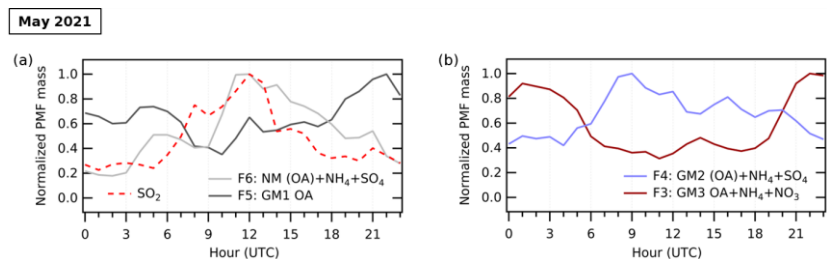
This process leads to the negligible amount of sulfate and abundance of ammonium nitrate during particle growth, hence sulfate mass being unresolved in the F3 composition (for May and September). Chamber experiments and theoretical studies support this interpretation of NPF occurring with only minor involvement of sulfate (Liu et al., 2018; Wang et al., 2020, 2022). The chemistry of ammonium sulfate and nitrate aerosol formation is discussed in more detail in Sect. S2.

Figure 6. Normalized diurnal cycles in May 2021 of (a) the size-driven factors of F6 and F5, and SO_2 as the sulfate precursor, and (b) the size-driven factors of F4 and F3. Notice that from F4 to F3, the factors' diurnal pattern shifted from high daytime to high nighttime concentration. Similar figures for June and September 2021 can be found in Fig. S5.

Commented [NF3]: 7) Fig 6 and associated figures in SI, it i[s] surprising how the normalized mass spans what appears to be a la[rge] time frame than the NPF event. E.g., Fig. S4 shows that the event[s] are ~ 4 - 6 hours; however, looking at Fig. 6 (and associated figur[es]) it seems that it takes a full 12 hrs to go from F6 --> F3. Clairifica[tion] in how this figure/results are related to NPF needs to be further detailed.

3.40.6.3.3.5. Relationship of new particle formation with wind variables

To study the relationship between wind variables and new particle formation in the rural site of Cabauw, we compare timeseries of wind variablesanalyses were done using bivariate polar plots of size-driven F4 and the reconstructed PMF fraction of the nucleation-mode (F6)F3 by wind speed and first growth-mode (F5) in Fig. 7 (May) and Fig. S6 (June and September).wind direction (see Fig. 6). We observe that new particle formation episodesnucleation-mode F4 are correlated mainly with air masses transported from southwesterly-westerly sector or northerly, and sometimes from the easterly sector. These wind sectors are the suppliers of organics,supply sulfate, ammonium, and organics (Fig. S8), and their precursor gasgases that determine the main composition of F6F4 (see Fig. S7 and Fig. S8S9). Westerlies represent a source of sulfate, which mainly comes from sulfur oxides (SO_x) emission along the waterway of Rotterdam's harbor, the busiest port in Europe. The sulfate in air transported to Cabauw from the northern to eastern sector may arise from SO_x precursor from other urban, shipping, industry centers (e.g., Amsterdam city and port, Utrecht city), and power plants to the site (see Fig. 1) (Henschel et al., 2013; Fioletov et al., 2016; Ledoux et al., 2018). The supply of ammonium for new particle condensation through NH_3 emission comes from the agricultural practices that take place around the Cabauw site, with tendency of higher NH_3 and ammonium from the southern sector. The easterlies extending to north are also sources of VOCs coming from the forested nature areas in the provinces Utrecht and Gelderland, which are subsequently transformed into SOA.
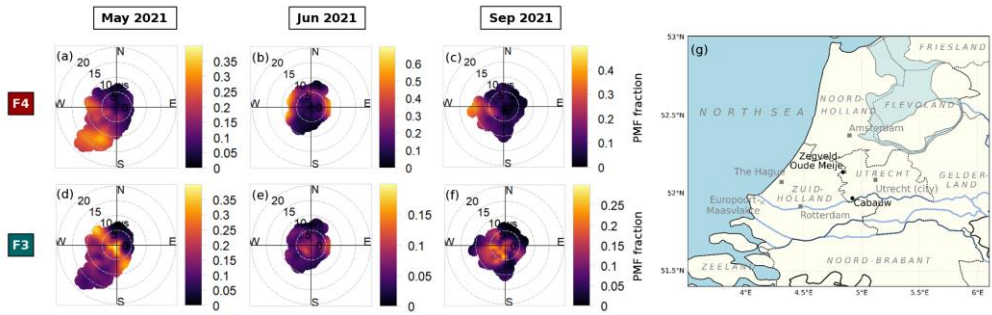
Figure 6. **(a-f)** Bivariate polar plots of size-driven factor mass fraction (F4 and F3) by wind speed and wind direction measured in Cabauw in May, June, and September 2021. We can observe that nucleation-mode particles (F4, **a-c**) fraction is largely correlated with air masses from the southwesterly-westerly sector where the urban and harbor areas of Rotterdam located. The growth-mode particles (F3, **d-f**) fraction is distributed around the site and from southwesterly sector. Similar figures for composition-driven factors can be found in Fig. S7.

The different prevailing wind also affects the F6F4 composition and frequency. In spring (May) and autumn (September), new particle formation mainly correlates with winds from southerly and westerly directions (see Fig. 26a,c), and thus has less organic composition. In summer (June), winds coming from the north oreast contribute to NPF events (see Fig. 26b), supplying more organics to the site. As previously discussed in Sect. 3.3.3, theThe abundant organics combined withdue to higher

radiation and temperatures allow semi-volatile ~~oxidized organics~~SOA to directly condense onto newly formed particles, increasing NPF events and ~~F6~~F4 mass fraction during summer (see Fig. ~~S6~~3d).

~~3.44.~~3.4. ~~Bulk composition~~ Composition-driven factors (F2 and F1)

The two ~~bulk~~ composition-driven factors yielded by the PMF analyses are F2 and F1 (see Fig. ~~3,~~ 2 (May), Fig. S1 (June), and Fig. ~~S1, and Fig.~~ S2~~).~~ (September)). We call these factors ~~bulk~~composition-driven because they are ~~composition-driven and~~ found across the size distribution, rather than in a specific size range. They collectively account for a large fraction of total ~~aerosol mass loading (31.1% to 64.4%).~~reconstructed PMF mass (66% to 78%) and can be considered as the result of size-driven factors further growth into the bulk aerosol. F2 and F1 are both representative of mean atmospheric bulk aerosol composition that are split into two different factors by PMF.

F2 is characterized by the presence of a mixture of OA and IA. ~~In~~ (see Fig. ~~S9, we can see that~~S10m-r). Based on the organic spectrum, the aerosol mixture can be characterized as LO-OOA, comparable to the LO-OOA profile found in other aerosol mass spectrometry studies using CV (Hu et al., 2018; Zheng et al., 2020; Joo et al., 2021). It has similar f_{44}/f_{43} to LO-OOA profile in F4 in average (see triangle plot in Fig. S6). In terms of diurnal cycle ~~of~~. the F2 ~~is~~mass loading does not follow the typical LO-OOA pattern. Normally, LO-OOA would have a higher nighttime concentration and slight decrease during the day (Chen et al., 2022), but we found the diurnal cycle of F2 to be similar to the diurnal pattern of total aerosol mass loading in ~~spring (May). It is less similar in summer (June) and autumn (September) due to scarcity of OA mass, which is mainly found in the size-driven factors.~~this study (see Fig. S10g,i,k). This ~~pattern~~finding suggests that F2 is the result of condensation of available semi-volatile chemical constituents over the course of the day~~.~~ as the continuation of NPF and growth, governed by the availability of both bulk IA and OA composition.

While F2 contains both OA and IA, F1 is dominated by OA (see Fig. S10m-r). It represents the continuation of NPF and growth enriched by organic compounds. F1 is composed mainly of ~~OA with~~organics (82% to 94%) and a trace amount of ~~IA, containing the majority of OA in every month.~~ammonium (2% to 6%) and sulfate (2% to 12%). A trace of nitrate aerosol (2%) can also be found in F1 in the summer (June). The abundance of m/z 44 fragments and high f_{44}/f_{43} values (see Fig. S6) indicates that factor F1 represents aged ~~organic aerosol~~SOA, resembling ~~OA~~OOA profiles observed at the same site in previous studies (Mensah et al., 2012; Paglione et al., 2014; Schlag et al., 2016) and MO-OOA profiles observed in aerosol mass spectrometry with CV (Hu et al., 2018; Zheng et al., 2020; Joo et al., 2021). F1 exhibits a diurnal pattern consistent with MO-OOA, with concentration rising slightly across the day. It has a relatively stable concentration throughout the day because the factor is driven largely by long-range transport of aerosol (Kodros et al., 2020; Chen et al., 2022), but with slightly increasing concentration from morning to afternoon due to photochemical oxidation. Wind analysis suggests that the bulk SOA in F1 is related to airmasses arriving from the easterly sector that spans from north (~0º) to south (~180º) (see Fig. S7). To the east, the province of Gelderland is mostly covered by agricultural grass land and forested nature areas that emit VOCs, therefore increasing the amount of OA produced. Easterly wind directions may also contain the accumulated pollutants or VOCs from continental Europe, and therefore may contain a variety of OA from either biogenic or anthropogenic sources.~~2016). The factor is related to airmasses arriving from the easterly to southerly sector (see Fig. S10 in Sect. S3 for details).~~ Considering the organic profile, the high mass loading percentage, and the source regions across periods, we attribute F1 to background regional and continental OA.

4. Conclusions

In this work, we have shown that hybrid ACSM-SMPS PMF analysis can be used to determine the bulk chemical ~~constituents~~composition associated with new particle formation and growth. The analyses of three selected periods enable us to use the seasonality of the factor profiles, representing conditions of spring (sunny and warm) for May, summer (very sunny and hot) for June, and autumn (less sunny and warm) for September, as well as different prevailing winds, to attribute factor sources. ~~Different chemical composition regimes were observed across these seasons, which manifested as differences in the species controlling aerosol growth.~~

New particle formation episodes appeared when the total aerosol concentration was low, with key contributions from ammonium sulfate,~~ regardless of bulk aerosol composition regime.~~ and oxygenated organic compounds across seasons, despite the high nitrogen emission in the Netherlands. This new particle formation and growth exhibits a diurnal pattern dominated by daytime formation that shifts to nighttime growth as the particle size increases. While sulfate ~~promote~~promotes new particle formation, nitrate ~~is~~and semi-volatile organics are more influential in ~~condensational~~ growth. ~~Organics participate in either new particle formation or growth.~~

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The ~~abundance of organics, sulfate, and~~ substantial contribution of nitrate and less oxidized organic aerosols to F3, and its shift to a nighttime peak in concentration, indicate that ammonium ~~aerosol, as well as the mean radiation and temperature, govern the chemical species distribution across the factors. As a result, different modes of new particle formation and growth exist. The sulfate-rich regime in spring results in the nucleation mode containing a mixture ammonium sulfate and organics.~~ and organic nitrate condensing during the particle growth when the temperature is lower. The organic-rich regime, higher mean radiation, and higher mean temperature in summer results in larger contribution of ~~oxidized~~oxygenated organic vapors in new particle formation. ~~The ammonium excess condition in autumn promotes nucleation without the presence of organic compounds.~~

~~A particle growth mode that arises from condensation of semi-volatile organics from the bulk atmospheric composition is observed in F5. In particular, the substantial contribution of nitrate in F5 during summer could be seen as the possible promotion of organic nitrate formation in nitrate excess condition in higher radiation, condensing during the particle growth when the temperature is lower. F4 is seen as the continuation of previous growth modes with similar composition but larger particle size range. The factor with the largest particle diameter sub-range, F3, has a nitrate-rich composition across the seasons, illustrating the ubiquitous importance of nitrate.~~

New particle formation is most pronounced with winds from the southwest-west, ~~or north~~ and ~~east~~sometimes northeast. These directions supply precursors gases, with the westerlies bringing SO_x from the port of Rotterdam, southwesterlies bringing NH_3 from agricultural emissions, and ~~northerlies and~~ easterlies bring organic vapors from the forest and nature areas. ~~There is also an indication of SO_x sources from other urban centers to the north and east.~~. The influence of the wind direction can be clearly seen during the summer, where instead of southern and western winds, the prevailing winds were from the north and east and brought abundant organics, resulting in the rapid growth of large amounts of OA.

In sum, this ~~novel~~ combination of composition and size information into the statistical ~~PMF tool, combined with~~method of PMF, augmented by meteorological and gas-phase auxiliary data, provides a powerful tool to assess the factors that control aerosol production in a complex region, heavily influenced by agricultural and industrial activities, alongside biogenic emissions of VOCs.

Code availability

The analysis and graphics are mainly generated using Igor Pro 8. The code utilized in the PMF analysis is part of the PMF Evaluation Tool (PET) v3.08 written as Igor procedures, available at https://cires1.colorado.edu/jimenez-group/wiki/index.php/PMF-AMS_Analysis_Guide#PMF_Evaluation_Tool_Software, (Ulbrich et al., 2009). The map, pollution roses, and particle size distribution time series are generated using Python 3.9 packages. The map is generated using

"SciTools/cartopy v0.21.1" Python package, available at https://doi.org/10.5281/zenodo.7430317, (Elson et al., 2022). The pollution roses are generated using "windrose v1.8.1" Python package, available at https://doi.org/10.5281/zenodo.7465610, (Celles et al., 2022). The particle size distribution time series are plotted using open-source Python code written by Lee Tiszenkel, available at https://github.com/ltisz/Banana-Plot. The bivariate polar plots of concentrations are generated using "Openair" package in the "R" environment, available at https://davidcarslaw.github.io/openair/, (Carslaw and Ropkins, 2012).

Data availability

The ACSM-SMPS datasets were collected as part of the Ruisdael Observatory Land-Atmosphere Interactions Intensive Trace-gas and Aerosol (RITA) campaign in May to September 2021 (https://ruisdael-observatory.nl) and available upon request. The gaseous phase species concentration can be retrieved from open-source data provided by Landelijk Meetnet Luchtkwaliteit (LML, https://www.luchtmeetnet.nl). The meteorological variables during the period are provided by the Royal Netherlands Meteorological Institute (KNMI, https://www.knmi.nl) and available upon request.

Author contributions

JLF and FRN designed the research; RM, RH, BH, and XL collected the data; FRN and JLF analyzed the data; FRN and JLF wrote the manuscript draft; MCK, RH, and UD reviewed and edited the manuscript.

Competing interests

The authors declare that they have no conflict of interest.

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Supplementary Information – What chemical species are responsible for new particle formation and growth in the Netherlands? A hybrid positive matrix factorization (PMF) analysis using aerosol composition (ACSM) and size (SMPS)

S1. Figures and tables

Table of Figures

Figure S1. The profiles of 4-factor PMF solution from the combined ACSM-SMPS dataset in June 2021. Each factor is split into three matrices with their own rescaled signal fraction axes. The error bars in each variable represents standard deviation generated by performing bootstrapped run of the solution. The panel **a-d** shows the organic fragment mass spectrum from m/z 20 to 120 from ACSM (m/z < 20 not included). The panel **e-h** shows the ACSM standard inorganic aerosol species concentrations (ammonium (NH_4), nitrate (NO_3), sulfate (SO_4), and chloride (Cl)). The panel **i-l** shows the particle size distribution profiles from the SMPS. On the panel **m-p**, the diurnal cycles of the factors and related species are depicted. The mean PMF fractions and their standard deviations are shown indicating the mean contribution of each hybrid PMF factor to the "total variable reconstruction" by PMF throughout the period. The factors in May 2021 are assigned as: (F1) MO-OOA, (F2) $NH_4+NO_3+SO_4+$LO-OOA, (F3) size-driven $NH_4+NO_3+SO_4+$HOA, and (F4) size-driven NH_4+SO_4+LO-OOA.

Figure S2. The profiles of 4-factor PMF solution from the combined ACSM-SMPS dataset in September 2021. Each factor is split into three matrices with their own rescaled signal fraction axes. The error bars in each variable represents standard deviation generated by performing bootstrapped run of the solution. The panel **a-d** shows the organic fragment mass spectrum from m/z 20 to 120 from ACSM (m/z < 20 not included). The panel **e-h** shows the ACSM standard inorganic aerosol species concentrations (ammonium (NH_4), nitrate (NO_3), sulfate (SO_4), and chloride (Cl)). The panel **i-l** shows the particle size distribution profiles from the SMPS. On the panel **m-p**, the diurnal cycle of the factors and related species are depicted. The mean PMF fractions and its standard deviation are shown indicating the mean contribution of each hybrid PMF factor to the "total variable reconstruction" by PMF throughout the period. The factors in May 2021 are assigned as: (F1) MO-OOA, (F2) NH_4+NO_3+ LO-OOA, (F3) size-driven NH_4+NO_3+HOA, and (F4) size-driven NH_4+SO_4+LO-OOA.
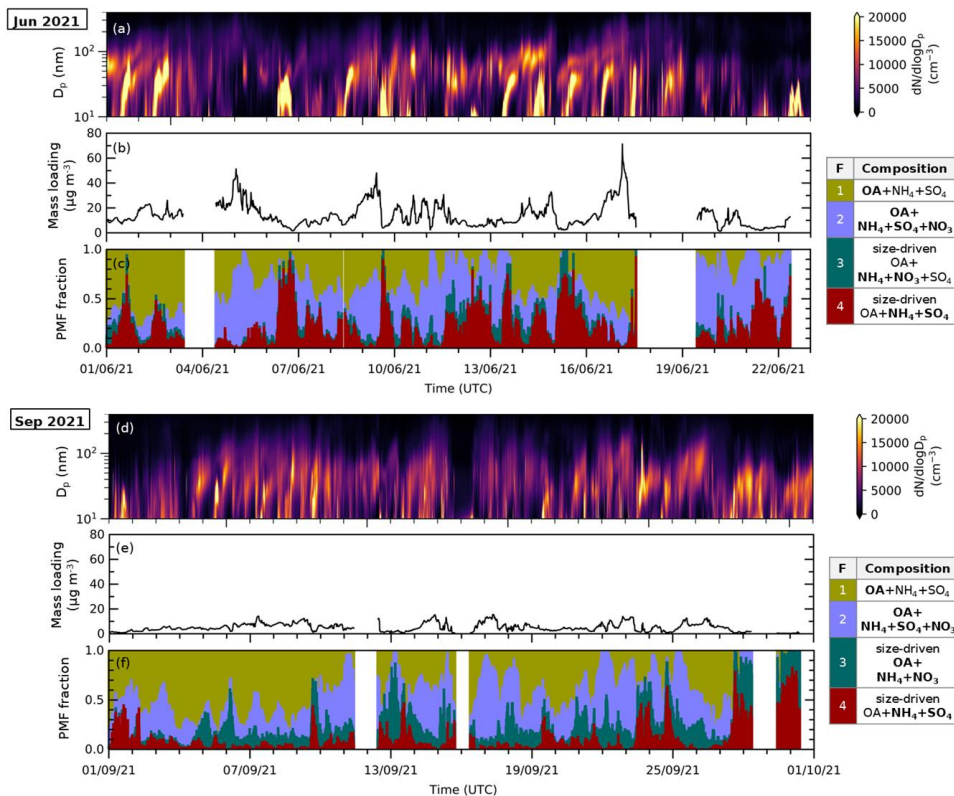
Figure S3. Time series of (**a,d**) particle size distribution ($dN/dlogD_p$) in cm^{-3} with logarithmic scale in particle size obtained from SMPS measurements, (**b,e**) total mass loading calculated from ACSM species concentration (using Tofware) in µg.m^{-3}, and (**c,f**) reconstructed PMF fraction (stacked) from analyses in June and September 2021. 4 Episodes of F4 and F3 coincide with relatively low total aerosol mass conditions and high fine particle concentrations.

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Figure S4. Selected ~~timeseries~~ time series windows during which new particle formation (NPF) events were detected by the scanning mobility particle sizer (SMPS) resembling 'banana' shapes in May 2021 **(a-f)**, June 2021 **(g-k)** and September 2021 **(m-r)**. Rapid increases of fine new particles were observed. ~~at (a) 30/05/2021 00:00 to 31/05/2021 00:00, (b) 13/06/2021 00:00 to 14/06/2021 00:00, and (c) 27/09/2021 12:00 to 28/09/2021 12:00.   5~~During these events, the increase in size-driven factors F4 and F3 can be seen equally in the reconstructed PMF fraction time series. The results suggest the events occur with either simultaneous episodes of F4 and F3 (growth-mode) **(d-f, g-i, j-l, p-r)**, or sequential episodes of both F4 and F3 **(a-c, m-o)**.

Figure S5. (a-c) The bootstrapped time series of F4 and number concentration of particles in the size bin of 20-25 nm and **(d-f)** the bootstrapped time series of F3 and number concentration of particles in the size bin of 51-65 nm in May 2021, June 2021, and September 2021. Both size bins are the median size of the size-driven factors' particle size distribution. The uncentered R Pearson coefficient shown on the right top of each graph shows the correlation between the time series of the factor and the particle number concentration.
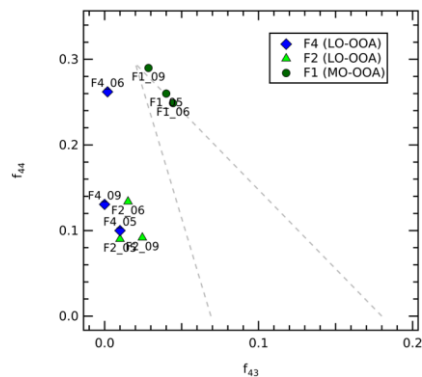
Figure S6. The triangle plot showing f_{44} vs f_{43} signal for resolved LO-OOA in F4 (dark blue, diamond), LO-OOA in F2 (light green, triangle), and MO-OOA in F1 (dark green, dots). The number indicated after the factor's number corresponds to the period (05 for May, 06 for June, and 09 for September). We note that the June F4 signature is closer to the MO-OOA ratios (see Sect. 3.3.3 for discussion). Moving to the top of the triangle means a more oxidized OA. As the measurements were carried on using capture vaporizer (CV) and the triangle plot was first developed for mass spectrometry with standard vaporizer (SV), some of the f_{44}/f_{43} values are outside the triangle.
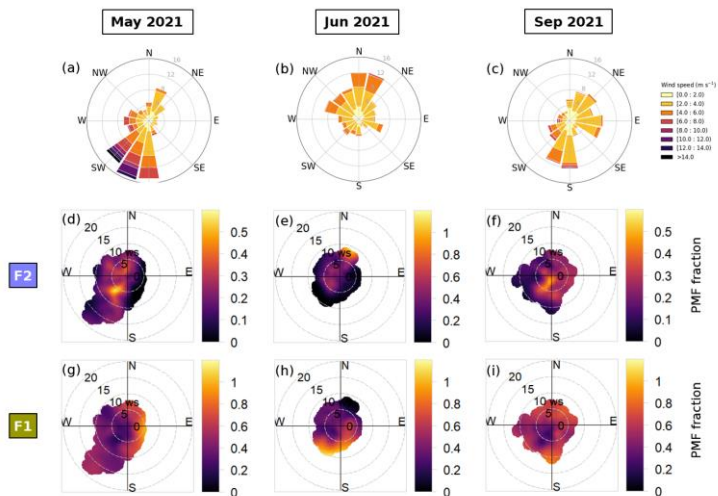
Figure S7. (a-c) Wind roses and (d-i) bivariate polar plots of nucleation-mode particle precursor concentrations composition-driven factor mass fraction (F2 and F1) by wind speed and wind direction measured in Cabauw in May, June, and September 2021. The bulk OA+IA factor (F2, d-f) is shown to be originated from different directions, while the bulk OA factor (F1, g-i) is mainly coming from the easterly and southerly sector.
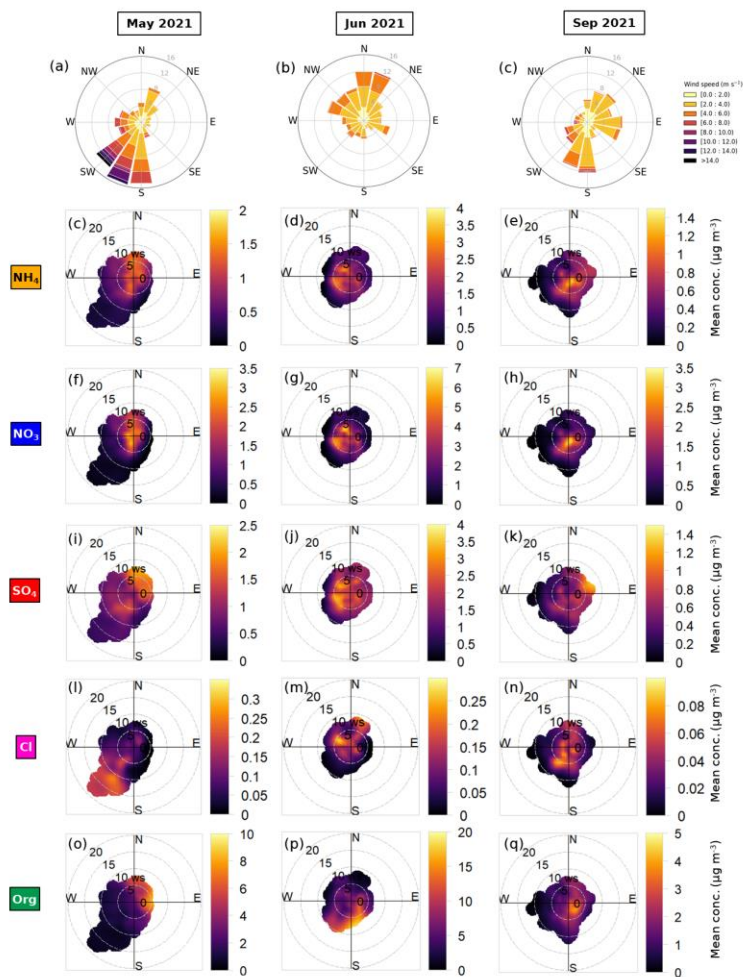
Figure S8. (a-c) Wind roses and (d-q) bivariate polar plots of ACSM-generated chemical species by wind speed and wind direction measured in Cabauw in May, June, and September 2021. 8 The species include ammonium (NH₄, c-e), nitrate (NO₃, f-h), sulfate (SO₄, i-k), chloride (Cl, l-n), and organics (Org, o-q) in 10-minute resolution. NO₃ and SO₄ are found to be correlated to NH₃ source direction (see Fig. S9) across seasons due to formation of ammonium nitrate and sulfate. NO₃ are correlated with the southern and western sector of the site. SO₄ is correlated to westerlies and north-easterlies, influenced by both NH₃ and SO₂ source direction since they react forming ammonium sulfate (Fig. S9).

Figure S9. ~~Diurnal cycles of F2 and total aerosol mass loading measured by the ACSM (top) with associated composition (bottom) across periods.~~

~~Table~~ of Tables

Figure S1. ~~The profiles of 6-factor solution from the combined ACSM-SMPS dataset in June 2021. Each factor is split into three matrices with their own signal fraction axes. The lefthand panel shows the organic fragment mass spectrum profiles from ACSM. The values of f₄₄ (CO₂⁺ fragment) representing higher oxidation level and f₄₃ (CH₃CO⁺ and C₃H₇⁺) representing lower oxidation level are given. The middle~~ panel shows the ACSM standard aerosol species concentrations ~~(organics (Org), ammonium (NH₄), nitrate (NO₃), sulfate (SO₄), chloride (Cl), and potassium (K)). The righthand panel shows the particle size distribution profiles from the SMPS. The mean PMF fractions are shown~~related to ~~the right, indicating the mean contribution of each hybrid PMF factor to the "total variable reconstruction" by PMF throughout the period (note we have reordered factors to be consistent across the 3 months). The factors in May 2021 are assigned as: (F1) OA, (F2) (OA)+NH₄+SO₄+NO₃, (F3) growth-mode 3 OA+NH₄+SO₄+NO₃, (F4) growth-mode 2 OA+NH₄+SO₄, (F5) growth-mode 1 OA+NH₄+NO₃, and (F6) nucleation-mode OA+NH₄+SO₄. Factors with OA listed inside parentheses indicates OA below 25% of the total mass.~~

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Figure S2. The profiles of 6-factor solution from the combined ACSM-SMPS dataset in September 2021. Each factor is split into three matrices with their own signal fraction axes. The lefthand panel shows the organic fragment mass spectrum profiles from ACSM. The values of f_{44} (CO_2^+ fragment) representing higher oxidation level and f_{43} (CH_2CO^+ and $C_3H_7^+$) representing lower oxidation level are given. The middle panel shows the ACSM standard aerosol species concentrations (organics (Org), ammonium (NH_4), nitrate (NO_3), sulfate (SO_4), chloride (Cl), and potassium (K)). The righthand panel shows the particle size distribution profiles from the SMPS. The mean PMF fractions are shown to the right, indicating the mean contribution of each hybrid PMF factor to the "total variable reconstruction" by PMF throughout the period (note we have reordered factors to be consistent across the 3 months). The factors in May 2021 are assigned as: (F1) OA, (F2) $NH_4+SO_4+NO_3$, (F3) growth-mode 3 $OA+NH_4+NO_3$, (F4) growth-mode 2 (OA)+NH_4+SO_4, (F5) growth-mode 1 OA, and (F6) nucleation-mode (OA)+NH_4+SO_4. Factors with OA listed inside parentheses indicates OA below 25% of the total mass. Some factor profiles may have organic fragments mass spectrum despite negligible or no ACSM organic composition (Org) variable contribution. We interpret these fragments showing the profile of trace OA that is insufficient to result in a significant contribution of the Org variable.
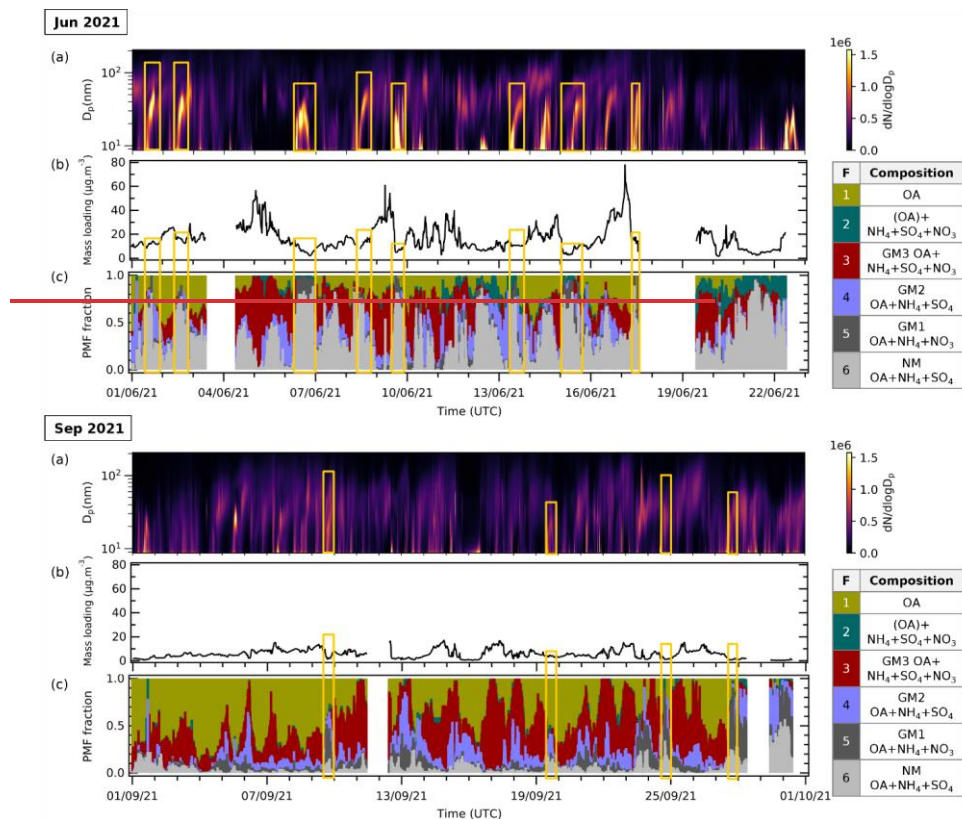
Figure S3. Time series of (a) particle size distribution (dN/dlogD_p) in cm^{-3} with logarithmic scale in particle size obtained from SMPS measurements, (b) total mass loading calculated from ACSM species concentration (using Tofware) in μg.m^{-3}, and (c) reconstructed PMF fraction (stacked) from analyses in June and September 2021. Orange outlined sections indicate periods during which high episodes of size-driven factors are observed. These episodes coincide with relatively low total aerosol mass conditions and high fine particle concentrations.

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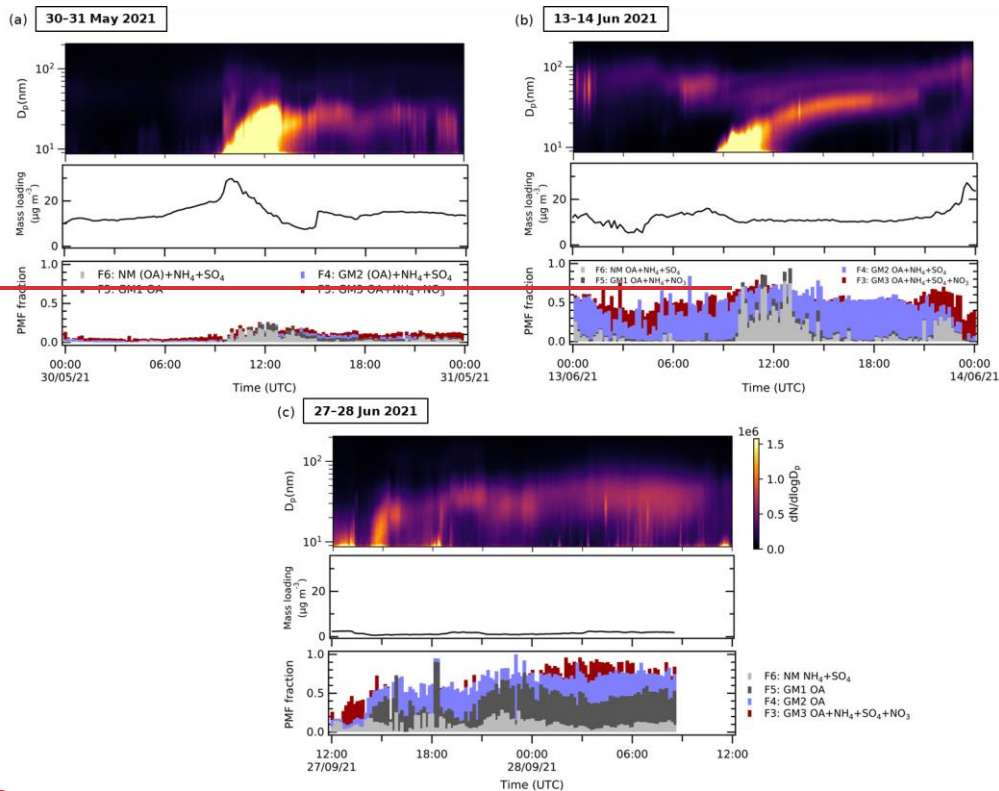
Figure S4. Selected timeseries windows during which new particle formation (NPF) events were detected by the scanning mobility particle sizer (SMPS) resembling 'banana' shapes at (a) 30 May 2021 00:00 to 31 May 2021 00:00 UTC, (b) 13 Jun 2021 00:00 to 14 Jun 2021 00:00 UTC, and (c) 27 Sep 2021 12:00 to 28 Sep 2021 12:00 UTC. Rapid increases of fine new particles were observed. During these events, the increase in size-driven factors F7 and F6 can be seen equally in the reconstructed PMF fraction time series.
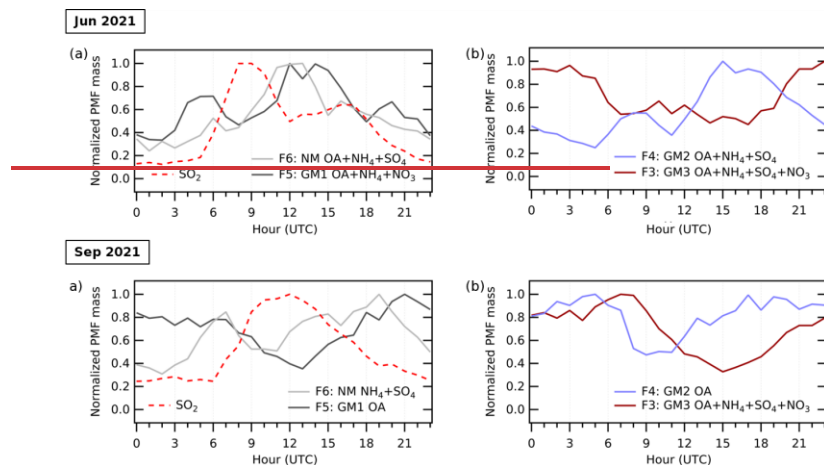
Figure S5. Normalized diurnal cycles in June and September 2021 of (a) the size-driven factors of F6 and F5, and SO₂ as the sulfate precursor, and (b) the size-driven factors of F4 and F3. Notice that from F6 to F3, the factors' diurnal pattern shifted from high daytime to high nighttime concentration.

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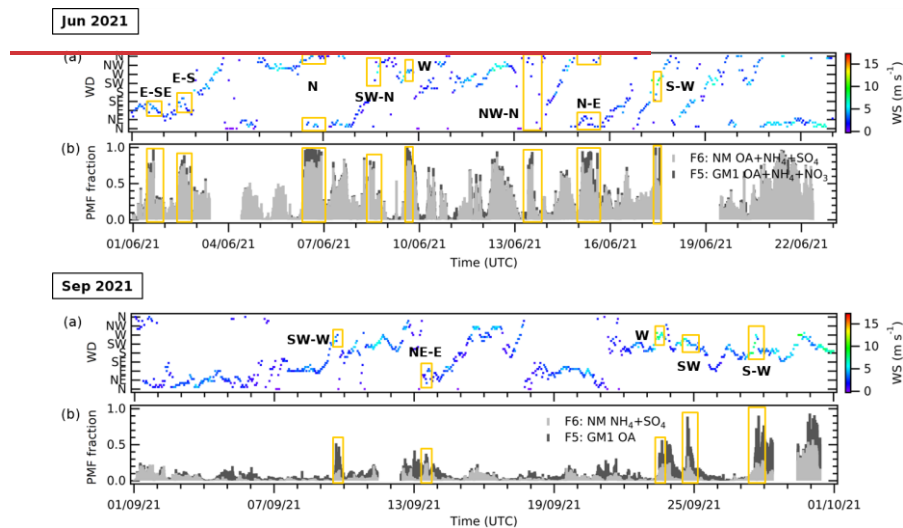
Figure S6. Timeseries of (a) wind direction (WD) color-coded with wind speed (WS), and (b) reconstructed PMF fractions F6 and F5 (stacked) corresponding to nucleation-mode and first growth-mode particles in June and September 2021. Orange outlined sections indicate high F6 and F5 episodes. We can observe that new particle formation is correlated with air masses from the southwesterly-westerly sector or northerly-easterly sector.
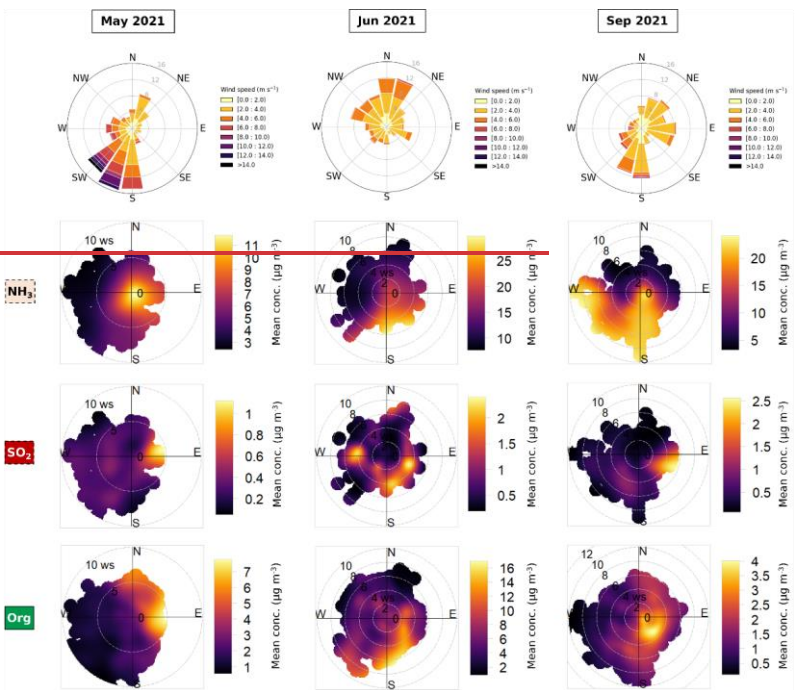
Figure S7. ~~Wind roses and bivariate polar plots of nucleation-mode particle precursor concentrations~~ by wind speed and wind direction measured in Cabauw in May, June, and September 2021. The species include ammonia (NH$_3$, **d-f**) and sulfur dioxide (SO$_2$, **g-i**) in the gaseous phase in hourly resolution, and organics (Org, **j-l**) in the aerosol phase in 10-minute resolution. NH$_3$ is predominant around the site, particularly from the southern sector. SO$_2$ is prevalent from the east and west of the site. Org species are predominantly coming from the eastern sector explaining the correlation of nucleation-mode factor (~~F6~~F4) episodes with easterlies in May and June 2021 when OA participates in early NPF.
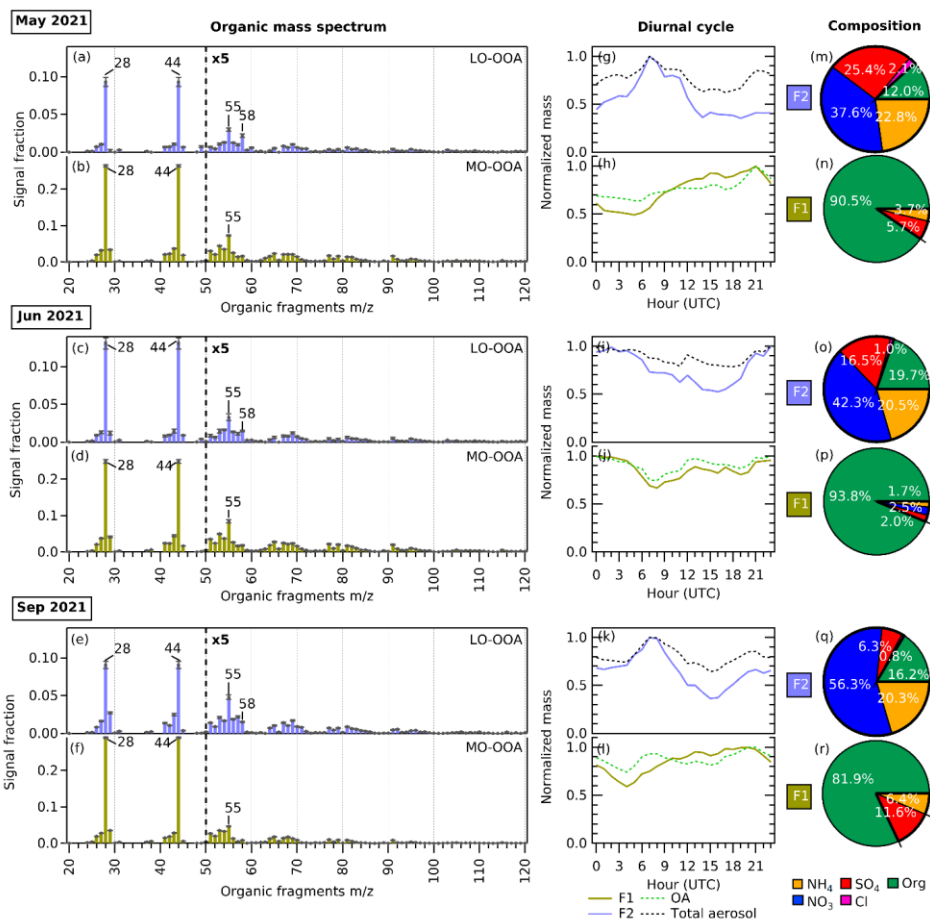
Figure S10. (a-f) Organic mass spectrum from m/z 20 to 120 (m/z < 20 not included) of F2 (purple) showing LO-OOA factor profiles and F1 (lime green) showing MO-OOA factor profiles in May 2021, June 2021, and September 2021. The error bars in each m/z were generated from bootstrap run. (g-l) The diurnal cycles of F2, consisting of OA and IA mixture, follows the diurnal pattern of total bulk aerosol pattern, while F1, mainly consisting of OA, follows the diurnal pattern of bulk OA measured by ToF-ACSM (Org). The MO-OOA F1 concentration increase slightly during the day due to photochemical activity and then concentrated in the boundary layer after sunset. It decreases around the midnight until morning due to

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<u>absence of photochemistry.</u>
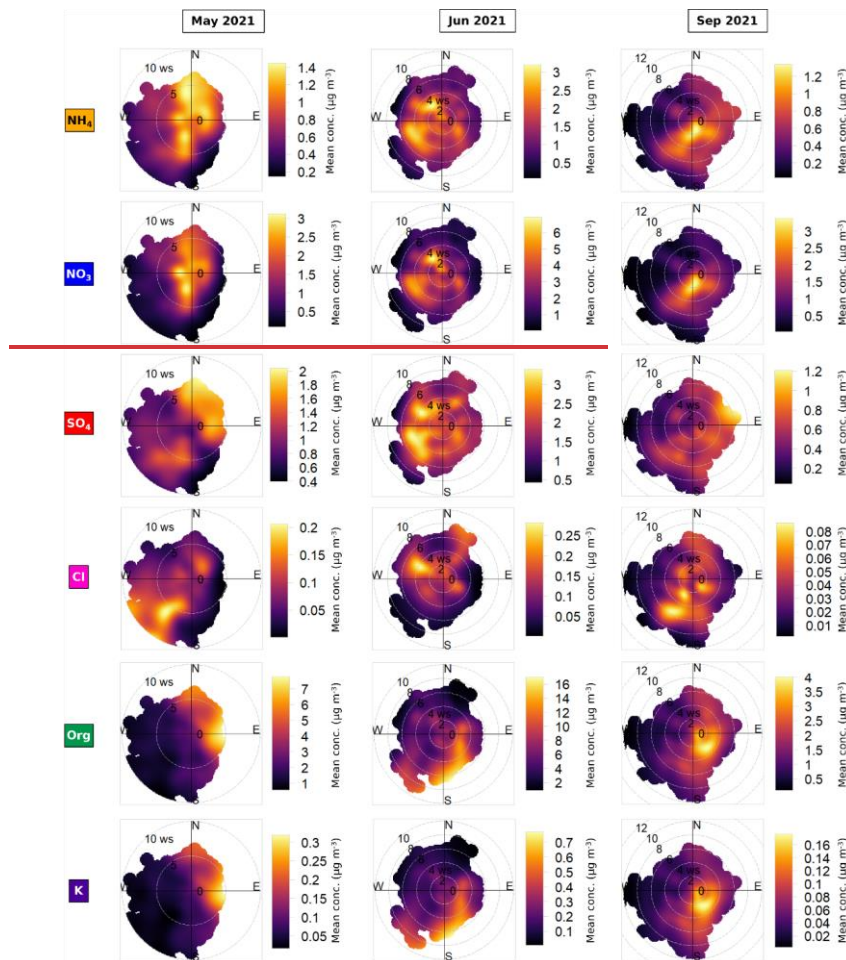
Figure S8. ~~Wind roses~~<u>MO-OOA in F1 shows a more stable diurnal cycle pattern with some increase from the morning to afternoon due to photochemistry. The concentration is accumulated in the evening due to shallow boundary layer</u> and ~~bivariate polar plots~~<u>then diminishes in the early morning due to absence</u> of ~~ACSM-generated chemical~~ <u>photochemistry. **(m-n)** Pie charts showing mass percentage of each aerosol</u> species ~~by wind speed and wind direction measured in Cabauw~~<u>contributing to each composition-driven factor</u> in May <u>2021</u>, June <u>2021</u>, and September 2021. ~~The species include~~<u>Green represents organics (Org), orange represents</u> ammonium (NH₄), <u>dark blue represents</u> nitrate (NO₃), <u>dark red represents</u> sulfate (SO₄), <u>and pink represents</u> chloride (Cl)~~, organics (Org), and potassium (K) in 10-minute resolution. NO₃ and SO₄).~~ F4<u> are </u>~~found to be correlated to NH₃ source direction (see Fig. S7).~~<u> across seasons due to formation of </u>dominated by ammonium sulfate while F3 are dominated by <u>ammonium nitrate </u>~~and sulfate. NO₃ are correlated with the southern and western sector of the site. SO₄ is~~

correlated to westerlies and north-easterlies, influenced by both NH_3 and SO_2 source direction since they react forming ammonium sulfate (see Fig. S7). As trace ions, Cl is correlated with SO_4, while K is correlated with Org.
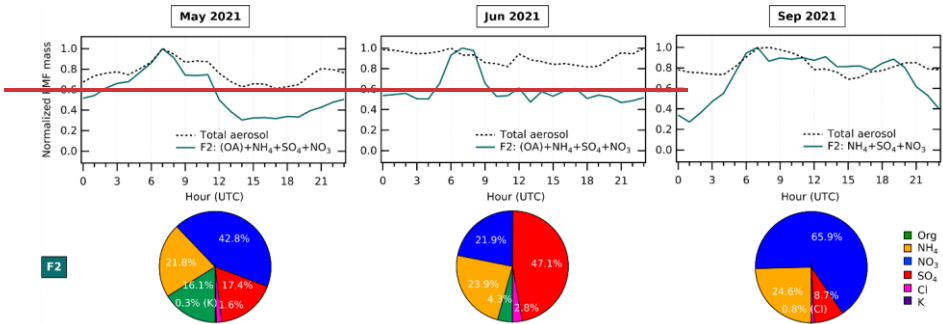
Figure S9. Diurnal cycles of F2 and total aerosol mass loading measured by the ACSM (top) with associated composition (bottom) across periods. F2 has a higher daytime value that resembles the diurnal cycle of total aerosol concentration except in summer (June).

S2. ~~Determining~~Atmospheric **composition** ~~regimes from bulk atmospheric composition~~ and aerosol formation

Ion balance ratio/ammonium balance

The ion balance ratio ~~(n_{NH_4},~~ or also called ammonium balance ($NH_{4\_bal} = n_{NH_4}/(n_{NO_3}+2\times n_{SO_4}+n_{Cl})))$, is used to assess the ion-pairing between cations and anions forming inorganic aerosol (IA). ~~Ambient aerosol is normally charge-balanced, meaning that the major cation (NH_4^+) and anion species (NO_3^-, SO_4^{2-}, and Cl^-) should have one-to-one molar ratio. To calculate the ion balance ratio, we compare the measured ammonium molar concentration (n_{NH_4}) to the total ammonium needed to neutralize the measured major anion concentration ($n_{NO_3}+2\times n_{SO_4}+n_{Cl}$). In spring (May), the ion balance is 0.99 which can be regarded as unity, meaning that the ion charge is fully neutralized. In summer (June), the ion balance ratio is less than unity (0.98). This may be caused by aerosol acidity~~ When the $NH_{4\_bal} < 1$ ~~(Farmer et al., 2010; Docherty et al., 2011)~~ with excess in H^+ aerosol ~~being undetected by the instrument. Alternatively,~~ nitrate or sulfate may be present in compounds other than ammonium salts. ~~They.~~ The anions can form ~~salts~~refractory compounds with ~~undetected~~other cations (e.g., $NaNO_3$, Na_2SO_4, $Ca(NO_3)_2$~~,~~) and thus be less efficiently detected by the spectrometer, or exist in form of organic nitrates and ~~organic~~ sulfates, yielding an additional amount of nominal nitrate and sulfate measured by ACSM (Farmer et al., 2010; Docherty et al., 2011 ~~detected by ACSM~~). ~~It also may be caused by excess aerosol acidity~~ (Farmer et al., 2010; Docherty et al., 2011 ~~). The ion balance ratio in autumn (September) is larger than unity (1.08). This can arise from~~) although the clear relationship between NH_{4_bal} and high aerosol acidity (pH < 0) is observed for mass spectrometry measurements only when $NH_{4\_bal} < 0.65$ (Schueneman et al., 2021). On the other hand, when the $NH_{4\_bal} > 1$, uncharged amines may be detected as ammonium by the ACSM (Farmer et al., 2010; Docherty et al., 2011), or ~~from the presence of~~ unmeasured anions such as carboxylates.

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175 may be present. The aerosol species excess for each period can be deduced from the aerosol formation chemistry in a HNO$_3$-NH$_3$-H$_2$SO$_4$-H$_2$O system (Ansari and Pandis, 1998; Seinfeld and Pandis, 2016; Tsai et al., 2016). When the molar ion balance ratio of free ammonia-to-sulfate total is larger than two, NH$_3$ prefers to react homogeneously with H$_2$SO$_4$ to form ammonium sulfate ((NH$_4$)$_2$SO$_4$). The rest of NH$_3$ will react with HNO$_3$ to form ammonium nitrate (NH$_4$NO$_3$) (Ansari and Pandis, 1998). The surplus is calculated based on the assumption that all available sulfate reacts with ammonia first to form (NH$_4$)$_2$SO$_4$. The

180 remaining NH$_3$ forms NH$_4$NO$_3$ with nitrate and can result in either ammonium or an overabundance of nitrate.

In in spring (May), summer (June), and autumn (September) are 0.997, 0.986, and 1.066 respectively, which can be regarded as close to unity. Therefore, we observe roughly a doubling in can infer that the bulk aerosol concentration charge is fully neutralized for all IA and an increase with a factor 2.6 in OA compared to May. This increase is mainly due to increasing

185 anthropogenic activities, photosynthesis, and evapotranspiration of plants in summer. However, a mean nitrate excess is still observed (n$_{NH_4}$/(n$_{NO_3}$+2×n$_{SO_4}$+n$_{Cl}$) < 1). In autumn (September), the particle concentrations decrease again, with a relatively larger decrease for sulfate. The discrepancy between the decrease of sulfate and other IA species concentrations in September leads to a change in ion balance ratio, generating the ammonium excess discussed previously (n$_{NH_4}$/(n$_{NO_3}$+2×n$_{SO_4}$+n$_{Cl}$) > 1). In addition, to illustrate how the concentration of sulfate relates to nitrate, we introduce the mean sulfate-to-nitrate molar

190 concentration ratio (n$_{SO_4}$/n$_{NO_3}$). The values of n$_{SO_4}$/n$_{NO_3}$ in May, June, and September were 0.41, 0.43, and 0.23 respectively (see summary in Table S1). A lower n$_{SO_4}$/n$_{NO_3}$ as found in autumn (September) suggests a more sulfate-poor regime, while a higher n$_{SO_4}$/n$_{NO_3}$ in spring (May) and summer (June) indicates a more sulfate-rich composition. periods.

Besides the two previous ratios, the mean organic-to-ammonium mass ratio (m$_{Org}$/m$_{NH_4}$) is used to indirectly compare the

195 composition of IA and OA of factors across periods. Ammonium is a good representation of IA, as ammonium salts are the dominant inorganic species in the atmosphere. A mass ratio (m$_{Org}$/m$_{NH_4}$) is used instead of molar ratio because organic species are measured as a mixture of various organic compounds by ToF-ACSM. The m$_{Org}$/m$_{NH_4}$ values in May, June, and September were 2.47, 3.36, and 2.90, respectively (see summary in Table S1). The higher value observed in June implies an organic-rich regime, while the other months are in a more inorganic regime.

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Table S1. Mean bulk atmospheric chemical composition in the three period as detected by the ToF-ACSM and collocated co-located gas measurements in Cabauw. The ion balance ratio (n$_{NH_4}$/(n$_{NO_3}$+2×n$_{SO_4}$+n$_{Cl}$)) was unity in May, less than unity in June, and more than unity in September. An overabundance of nitrate was found in May and June, while ammonium excess is found in September.

Species/ratio	Mean concentration in May 2021 (spring)		Mean concentration in Jun 2021 (summer)		Mean concentration in Sep 2021 (autumn)	
	Mass (µg m^{-3})	Molar (10^{-4} mol m^{-3})	Mass (µg m^{-3})	Molar (10^{-4} mol m^{-3})	Mass (µg m^{-3})	Molar (10^{-4} mol m^{-3})
NH$_3$[*(a)]	7.03	41.37	15.25	89.56	12.67	74.37

NO$_x$ = NO+NO$_2$	9.55	21.79	10.90	24.90	14.78	34.08
SO$_2$	0.34	0.54	0.85	1.33	0.59	0.91
Total aerosol[b]	6.60	-	14.12	-	5.15	-
Org	2.49	-	6.3736	-	2.1418	-
NO$_3^-$	1.84	2.97	3.42	5.52**	1.5760	2.5358
NH$_4^+$	1.01	5.61	1.90	10.54	0.7475	4.10**17
SO$_4^{2-}$	1.15	1.20 (×2 = 2.40)	2.29	2.39 (×2 = 4.78)	0.5556	0.5758 (×2 = 1.1416)
~~K$^+$~~ $NH_{4\ bal}$ [c]	0.08	0.21997 ± 0.001	0.23	0.58986 ± 0.001	0.09	1.066 ± 0.23001
n_{NH_4}/(n_{NO_3}+2×n_{SO_4}) ***	-	0.99	-	0.98	-	1.08
~~n_{SO_4}/n_{NO_3}~~ m_{Org}/m_{IA} [d]	-0.61	0.41	-0.82	0.43	-0.74	0.23
~~m_{Org}/m_{SO_4}~~	2.47	-	3.36	-	2.90	-
Composition regime	sulfate-rich		nitrate excess, organic- and sulfate-rich		ammonium excess, sulfate-poor	

~~*[a]~~ Data taken from Zegveld-Oude Meije measurement station

~~**Aerosol species that are found having excess quantity~~

~~***~~[b] Total mass of aerosol detected by ToF-ACSM (m_{Org}+m_{NO_3}+m_{NH_4}+m_{SO_4}+m_{Cl})

[c] Ion balance ratio/ammonium ratio is the ratio between the measured ammonium (n_{NH_4}) and the total ammonium needed to neutralize the major anions (n_{NO_3}+2×n_{SO_4}+n_{Cl}). The value is obtained from linear regression.

[d] Organic-to-inorganic mass ratio is the ratio between the measured organic aerosol mass (m_{Org}) and the measured inorganic aerosol mass (m_{NO_3}+m_{NH_4}+m_{SO_4}+m_{Cl}). The concentration is obtained from ToF-ACSM measurements.

Ammonium sulfate and nitrate aerosol formation

The ammonium sulfate and nitrate aerosol formation can be explained from the chemistry of a HNO$_3$-NH$_3$-H$_2$SO$_4$-H$_2$O system (Ansari and Pandis, 1998; Seinfeld and Pandis, 2016; Weber et al., 2016; Pye et al., 2020). The formation of ammonium sulfate and nitrate aerosols involves the buffering capacity of semi-volatile NH$_3$ partitioning between the gas and particle phase, reacting with H$_2$SO$_4$ and HNO$_3$ and forming aerosols. Coming from SO$_x$ emission, H$_2$SO$_4$ reacts with NH$_3$ forming a mixture of ammonium bisulfate (NH$_4$HSO$_4$), ammonium sulfate ((NH$_4$)$_2$SO$_4$), and leaving some free gas-phase NH$_3$ in the equilibrium. As sulfate has an extremely low vapor pressure and ammonium are semi-volatile, NH$_4^+$/NH$_3$ acts as a mobile species between gas and aerosol phase, establishing equilibrium between the two phases. With the decrease of SO$_x$ emissions and steady NH$_3$ emissions, NH$_4^+$ will be converted back to gas-phase NH$_3$ favoring the formation of NH$_4$HSO$_4$ and the release H$^+$, keeping the aerosol pH stable (0–3) (Weber et al., 2016). The buffering effect of NH$_4^+$/NH$_3$ is also reflected in the stable ion balance ratio around unity as observed across seasons in this study (see Table S1). The equilibrium mechanism to keep the aerosol pH from rising is expected to occur despite SO$_x$ emission reduction, unless the atmospheric sulfate concentration goes below 0.3 µg m^{-3}, where sulfate starts to be associated with non-volatile cations (Weber et al., 2016). With the addition of HNO$_3$ in the system coming from NO$_x$ emission, ammonium nitrate (NH$_4$NO$_3$) is also formed by either the association of free gas-phase NH$_3$ or NH$_4^+$ in the aerosol phase moving to the gas-phase. Since HNO$_3$ is more volatile than H$_2$SO$_4$, ammonium nitrate is moves more freely between the gas and aerosol phase to buffer the aerosol acidity and reach equilibrium. As the buffering system

relies on chemical species volatility, meteorological conditions like temperature and relative humidity also play role in the formation of ammonium sulfate and nitrate aerosol.

230   In summary, from the chemistry perspective, ammonium sulfate is more likely to become condensation nuclei due to low volatility nature of sulfuric acid favouring the aerosol phase, whereas ammonia or amines (as bases) stabilize it. In consequence, they are more likely to occur in smaller particles. Nitric acid plays role in particle growth as it condenses to the particle phase at smaller rate, and serve more as bridge to facilitate the association ammonium sulfate particle clusters in early NPF (Liu et al., 2018). The association of semi-volatile organic vapors to the condensation nuclei occurs through acid-base

235 chemistry and accretion of organic molecules (Zhang et al., 2004; Hodshire et al., 2016), building up the particle mass throughout aerosol formation and growth.

S3.   PMF analysis

PMF variables downweighting

Downweighting is an important step in hybrid PMF input matrix preparation to ensure the variables have similar magnitude
240 over others, or to remove duplicated variables in the matrix. Downweighting is done first to the species mass concentrations and particle number concentrations. The values and errors of species mass concentrations and particle number concentrations in the matrix ($X_{ij,input}$) were downweighted by dividing the dataset with a downweighting constant (DWC) to get the final values and errors ($X_{ij,DW}$).

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$$X_{ij,DW} = \frac{X_{ij,input}}{DWC}$$

The goal of downweighting is to normalize the magnitude of newly introduced variables in comparison to the organic mass spectrum, by decreasing their magnitude in reference to the spectrum. The dataset from September 2021 is used for the calculation as it represents the lowest concentration of all chemical species among analyzed periods. The 95% percentile
250 concentration is selected for the calculation to avoid using outlier peak in the dataset. The concentration of m/z 44 fragment (C_{f44}) is chosen to represent the organic mass spectrum dataset for the calculation of DWC as it generally has the highest average peak among organic fragments. For the inorganic mass concentration, nitrate concentration (C_{NO_3}) is selected as the reference for the inorganic chemical species since it generally has the highest concentration among measured inorganics. The PNSD in the 51-65 nm size bin (C_{p51-65}) is chosen for the particle size distribution, also for the same reason.

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The PNSD has different unit compared to other variables (cm^{-3} instead of µg m^{-3}). However, we disregard the unit as we are only interested in seeing the particle size concentration variation over time, and how the sizes are being distributed in the

profiles in the PMF solution. In this study, the DWC for PNSD variables was multiplied by 100 to tune down the number distribution values relative to the inorganic species. This empirically tuned multiplier factor is chosen because it gives convergent PMF solutions.

S3. Table F1: Background OA factor

There are two distinct profiles of F1, affected by seasonality of organic rich regime and meteorological variables. In the organic-rich regime during summer (June), this factor consists almost solely of organics (94.1%) with trace potassium (5.8%). In spring (May) and autumn (September), there is less organic (81.2% to 83.5%), again traces of potassium (2.6% to 3.3%), and more significant contributions of ammonium (3.3% to 5.1%) and sulfate (10.0% to 11.1%).

In spring (May) and autumn (September), F1 exhibits a diurnal pattern consistent with a more oxidized oxygenated organic aerosol (MO-OOA) factor, with concentration rising slightly across the day (see Fig. S10). The f_{44} values are 0.28 and 0.32 in spring (May) and autumn (September), respectively. MO-OOA has a relatively stable concentration throughout the day because the factor is typically part of a long-range transported aerosol (Kodros et al., 2020; Chen et al., 2022). The concentration slightly increases from morning to afternoon due to photochemical oxidation. The factor then shows a slight decrease in the late night until sunrise, as its production slows in the absence of radiation. This profile was found in airmasses arriving from the easterly sector that extends from northerly (0°) to southerly-southeasterly (157.5°) (see Fig. S10), making up 42.1% to 49.3% of total reconstructed PMF mass. To the east, the province of Gelderland is mostly covered by agricultural grass land and forested protected nature areas that emit VOCs, therefore increasing the amount of OA produced. Easterly wind directions may also contain the accumulated pollutants or VOCs from continental Europe, and therefore may contain a variety of OA from either biogenic or anthropogenic sources.

Meanwhile, in summer (June), F1 resembles more the description of less oxidized oxygenated organic aerosol (LO-OOA) factor (see Fig. S10). The f_{43} and f_{44} values are 0.09 and 0.17, respectively. LO-OOA has higher nighttime concentration with a slight decrease during the day, suggesting more regional source and higher partitioning of organic vapors into the aerosol phase in the shallow nocturnal boundary layer (Chen et al., 2022). The source region of the organic aerosol is more correlated to wind from the southern sector, extending from northeasterly to southwesterly (45° to 225°) (see Fig. S10). By comparing to other factors in the same month and F1 across season, we suggest that due to organic-rich regime, high mean radiation, and high temperatures, highly oxidized organic compounds participate substantially in the size-driven factors forming new particles. This results in less aged OA (lower f_{44} value) in F1 and F2, and a reduction in the overall PMF fraction of F1 (accounting only 23.7% of total reconstructed PMF mass).

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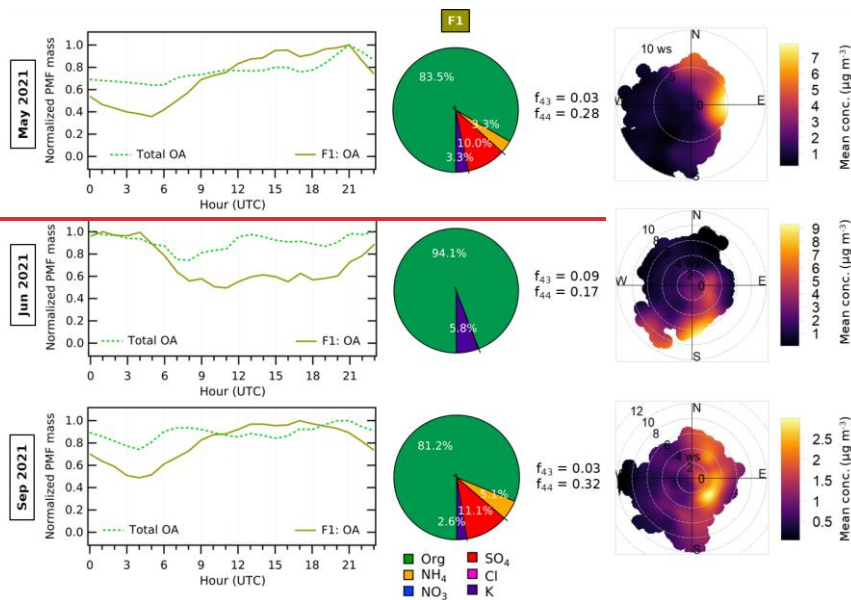
Figure S10. ~~Diurnal cycles of F1 and total OA measured by ACSM in May, June, and September 2021 are shown (left), with associated composition (middle) and bivariate polar plots of F1 concentration by wind speed and direction (right) in 10-minute resolution. The concentrations~~S2. The determination of downweighting constant (DWC) for inorganic species mass species and particle number size distribution (PNSD) in the PMF input matrix prior to analysis. The values are obtained from September 2021 dataset and applied for all analyzed periods.

Variable	Value
$C_{f44;95\%}$ (μg m^{-3})	1.43
$C_{NO3;95\%}$ (μg m^{-3})	4.95
$C_{p51-65;95\%}$ (cm^{-3})	1198.34
$DWC\ inorganic = \dfrac{C_{NO3;95\%}}{C_{f44;95\%}}$	3.45
$DWC\ PNSD = 100 \times \dfrac{C_{p51-65;95\%}}{C_{f44;95\%}}$	83527.07

The information in m/z 44 is duplicated among different organic fragments in the default fragmentation table (Allan et al., 2004) and therefore also need to be downweighted. The downweighting procedure is applied for m/z 44, 28, 18, 17, and 16 signals in the organic mass spectrum as provided by PETv3.08 during PMF input matrix preparation (Ulbrich et al., 2009). A correction calculation for capture vaporizer (CV) is also opted at the end of the PMF analysis to account the additional thermal decomposition in smaller fragments.
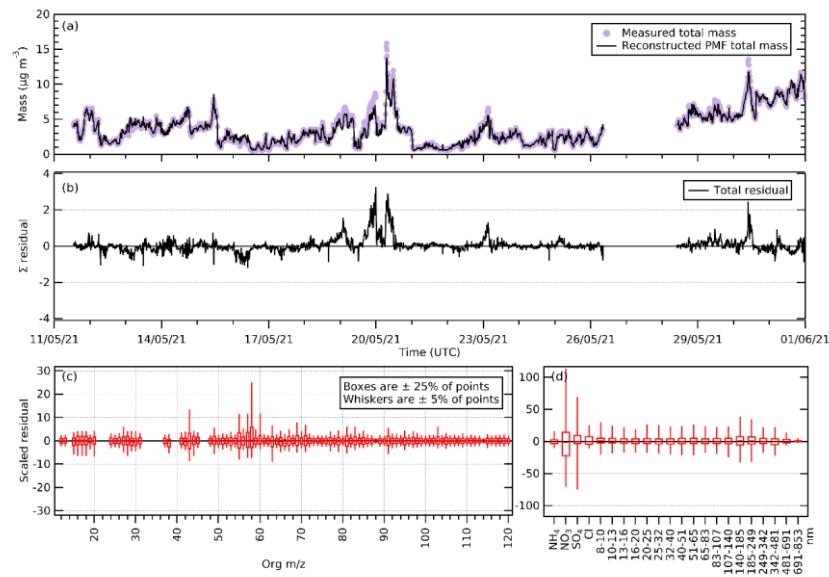
Determination of PMF solution

PMF analysis in each period were run unconstrained by varying the number of factors (p) from 2 to 8 factors and using varied seed values (min = 0; max = 20; delta = 1). The optimum p is selected first based on the lowest residuals and local minima (Q/Q_{exp}) of the PMF solutions. With the introduction of inorganic species mass concentration and particle number size distribution (PNSD) variables, we suggest that the PMF solution also must include at least two factors that show a significant signal of particle size distribution, or size-driven factors. A minimum of two size-driven is required in order to study new particle formation and growth. Lastly, the lowest Q/Q_{exp} should not be accepted if it contains redundant factors with very similar organic and inorganic profile. The diurnal cycle of each factor and correlation with other chemical species (gas and aerosol species) are also done to confirm the PMF solution. After the optimum p and seed value are chosen, the rotationality of the solution is explored by performing PMF run with varied rotation (f_{peak}) values (min = -1, max = +1, delta = 0.2).

For each period, a 4-factor solution was picked as the best fit (see Table S3 for the statistical summary). The measured and total reconstructed PMF mass time series, total residuals time series, and scaled residuals of PMF variables are shown in Fig. S11 (May), Fig. S12 (June), and Fig. S13 (September). We can observe that the PMF solutions that were solved by PMF analysis from hybrid PMF input have reduced number of converging solutions unlike regular PMF analysis with only organic spectrum. As we introduce extra variables to the input, more constraints are introduced to the PMF analysis, and thus increasing the number of variables that needs to be considered into the PMF model fit, limiting the number of convergences. NO_3 and SO_4 represent the largest contributor of residuals as can be seen in the scaled residual plots in Fig. S11 (May), Fig. S12 (June), and Fig. S13 (September).
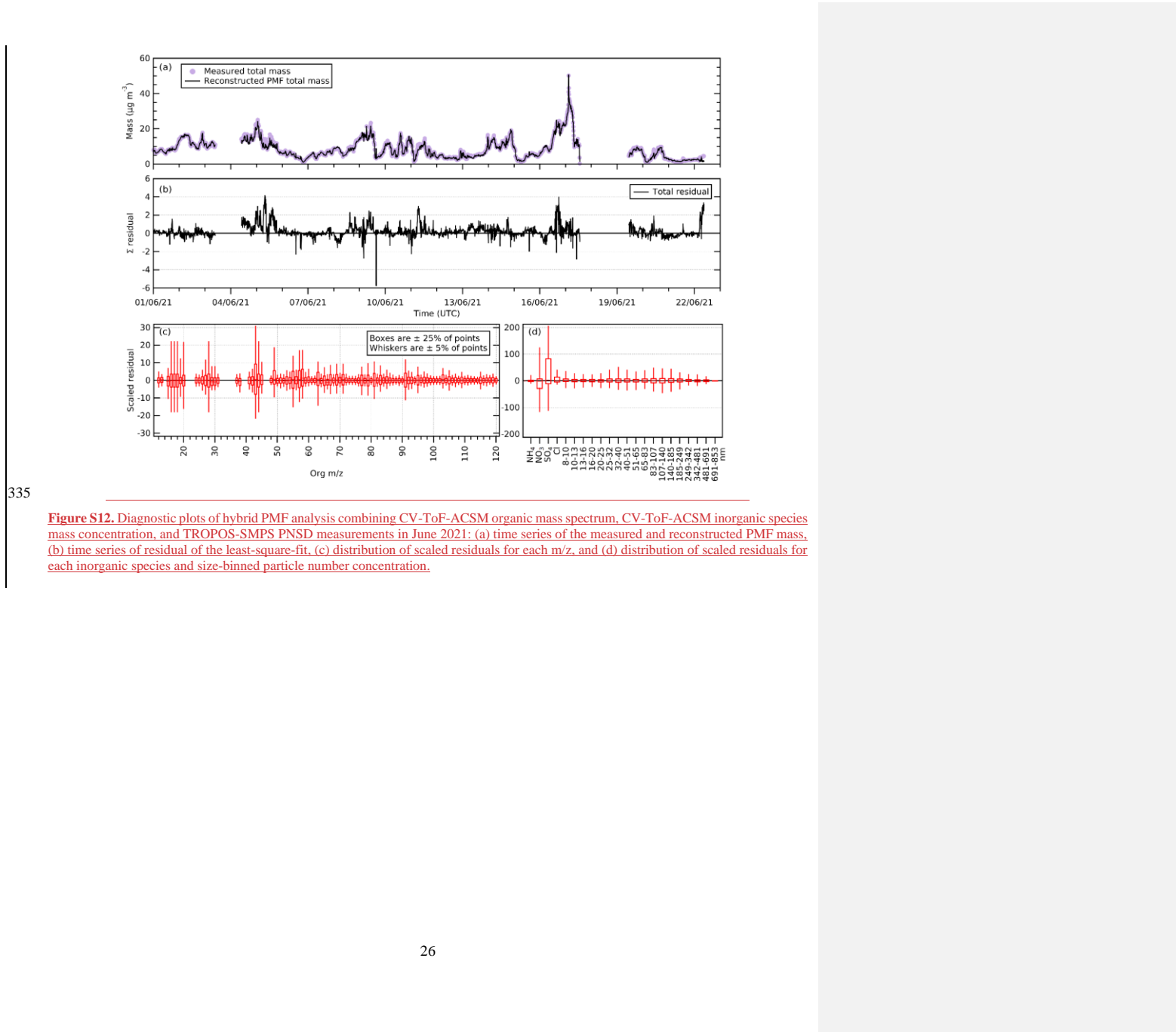
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Table S3. Diagnostic plots of hybrid PMF analyses in May 2021, June 2021, and September 2021, combining CV-ToF-ACSM organic mass spectrum, CV-ToF-ACSM inorganic species concentration, and TROPOS-SMPS PNSD measurements: (a) Q/Q_{exp} vs. number of factors, (b) Q/Q_{exp} vs. seed value, (c) Q/Q_{exp} vs. f_{peak} value, and (d) correlation of time series and mass spectra among PMF factors (R time series vs. R profiles). The number of factors, seed value, f_{peak} value, Q/Q_{exp}, and the reasoning of the chosen PMF solutions are listed below the plots. If not stated, the default values for seed and f_{peak} are zero.

| Plots*/ values chosen	May 2021	Jun 2021	Sep 2021
(a) Q/Q_{exp} vs. p			
(b) Q/Q_{exp} vs. seed			
(c) Q/Q_{exp} vs. f_{peak}			
(d) Un-centered R time series vs. R profiles			
p	4	4	4
seed	1	5	0
f_{peak}	0 (no significant change in rotational changes)	0 (no significant change in rotational changes)	0 (no significant change in rotational changes)

24

Q/Q$_{exp}$	12.62	21.27	10.82
Comments	Although solutions with p > 4 have lower Q/Q$_{exp}$, 4-factor solution was chosen because it does not generate redundant factors with same organic and inorganic compositions unlike factors with p > 4. It resolves two size-driven factors, and every factor has distinctive particle size distribution and inorganic composition. One POA (HOA) and three OOA factors (one MO-OOA and two LO-OOA) are also generated.	This PMF solution was chosen because it is solution with the highest number of factors that converged. It resolves two size-driven factors, and every factor has distinctive particle size distribution and inorganic composition. One POA (HOA) and three OOA factors (one MO-OOA and two LO-OOA) are also generated.	This PMF solution was chosen because it is solution with the highest number of factors that converged. It resolves two size-driven factors, and every factor has distinctive particle size distribution and inorganic composition. One POA (HOA) and three OOA factors (one MO-OOA and two LO-OOA) are also generated.

330 **Figure S11.** Diagnostic plots of hybrid PMF analysis combining CV-ToF-ACSM organic mass spectrum, CV-ToF-ACSM inorganic species mass concentration, and TROPOS-SMPS PNSD measurements in May 2021: (a) time series of the measured and reconstructed PMF mass, (b) time series of residual of the least-square-fit, (c) distribution of scaled residuals for each m/z, and (d) distribution of scaled residuals for each inorganic species and size-binned particle number concentration.

Figure S12. Diagnostic plots of hybrid PMF analysis combining CV-ToF-ACSM organic mass spectrum, CV-ToF-ACSM inorganic species mass concentration, and TROPOS-SMPS PNSD measurements in June 2021: (a) time series of the measured and reconstructed PMF mass, (b) time series of residual of the least-square-fit, (c) distribution of scaled residuals for each m/z, and (d) distribution of scaled residuals for each inorganic species and size-binned particle number concentration.

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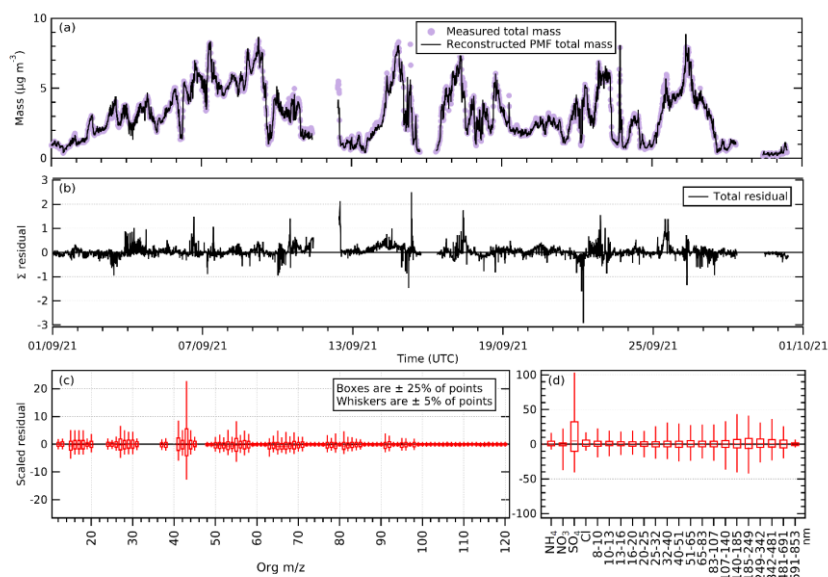
Figure S13. Diagnostic plots of hybrid PMF analysis combining CV-ToF-ACSM organic mass spectrum, CV-ToF-ACSM inorganic species mass concentration, and TROPOS-SMPS PNSD measurements in September 2021: (a) time series of the measured and reconstructed PMF mass, (b) time series of residual of the least-square-fit, (c) distribution of scaled residuals for each m/z, and (d) distribution of scaled residuals for each inorganic species and size-binned particle number concentration.

345 ~~, increase slightly during the day due to photochemical activity and then concentrated in the boundary layer after sunset. It decreases around the midnight until morning due to absence of photochemistry. The OA F1 plumes mostly arrive from the eastern and northern sector in Cabauw.~~

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~~**S4.** **Correlation of chloride-sulfate and potassium-organic species**~~

~~Chloride (Cl) and potassium (K) generally only contribute a trace amount of mass in the aerosol (see Fig. 3, Fig. S1, and Fig.~~
350 ~~S2). Nonetheless, source apportionment of ACSM species and PMF factors showed some interesting patterns with chloride and potassium species. Most of the time, chloride is a visible minority to factors that are abundant in sulfate. In nucleation-mode F6, which is mostly composed of ammonium sulfate, a trace of chloride (0.1% to 6.0%) can be found. Such appearance is also observed for the sulfate-containing size-driven factors (i.e., F4 in May, F3 in June, and F3 in September), where chloride is 0.6% to 3.6% of the total factor mass. The chloride across periods may arrive from sea salt aerosols, although its sources~~
355 ~~varied as seen in Fig. S8. This is broadly consistent with the dominant source of sulfate being the port region, where sea spray can be a source of the co-occurring chloride.~~

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360 A trace amount of potassium was frequently found on factors related to OA. When the OA in F6 is higher during summer (June), a significant amount potassium (2.1%) can be found in the factor. This appearance can also be observed in factors that are dominated by OA or in OA+IA mixed factors (e.g., F5, some F4, F3, and F1) where the potassium concentration ranges from 0.8% to 6.2% of the total mass. Such correlation was also confirmed by the similar pollution rose of the ACSM organic and potassium species (see Fig. S8). This suggests that the potassium originated from the same source as the emissions of organic compounds, perhaps indicative of a woodsmoke contribution from biomass burning (Pio et al., 2008; Urban et al., 2012; Pachon et al., 2013).

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