

Impacts of summertime photochemical aging on the physicochemical properties of aerosols in a Paris suburban forest region

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Abstract.

Organic aerosols (OA) play a significant role in influencing both climate and human health. However, in source–receptor
modeling, a large fraction of OA is typically attributed to highly aged, atmospherically processed species collectively
referred to as oxygenated organic aerosol (OOA). However, the formation pathways and evolution of OOA as well as their
30 impacts on aerosol optical properties, remain poorly understood. To address this knowledge gap, an experiment was
conducted in a suburban site in the Paris region to study the evolution of OOA and their optical properties. Our results show
that in regionally transported air masses with mixed biogenic and anthropogenic emissions, the formation of OOA through
photochemical processes explains most of the increase in submicron particle mass. Meteorological conditions played a
critical role: under dry and strong solar radiation conditions, rapid formation of more-oxidized OOA (MO-OOA) was
35 observed. The production of MO-OOA importantly contributed to the brown carbon (BrC) increase during the daytime,
enhancing short-wavelength light absorption by an average of ~35% following ~24 h of photochemical aging. Conversely,
under humid, low-radiation conditions, the OA composition shifted toward less-oxidized OOA (LO-OOA). Suppressed
photochemistry limited MO-OOA production, resulting in a lower overall OA oxidation state. These findings highlight the

role of photochemistry in shaping both the chemical evolution and resultant optical properties of OA, underscoring the need to consider meteorological dynamics when evaluating aerosol–climate interactions in suburban forest environments.

1. Introduction

Atmospheric aerosols are complex combinations of different chemical species and have an important impact on the climate system by scattering and absorbing atmospheric radiation (Ravishankara et al., 2015) and by interacting with clouds (Farmer et al., 2015). They also negatively affect air quality by reducing visibility, causing respiratory problems, and damaging ecosystems (Manisalidis et al., 2020). Urban areas, with their intensive resource use, are major contributors to anthropogenic aerosol emissions globally (Zhang et al., 2020; Papachristopoulou et al., 2022; Franklin et al., 2025). Therefore, characterizing the physicochemical properties of aerosols is crucial for understanding their impact on climate, air quality, and human health, ultimately informing strategies for mitigation and environmental protection.

Aerosols contain various components varying from volatile to refractory materials. Globally, Organic Aerosols (OA) often comprise the dominated mass fraction of submicron aerosols, while other components include soot (also known as Black Carbon (BC)), inorganic salts (such as sulfates, nitrates, and ammonium), metals, and other elements (Seinfeld and Pandis, 2016). OA can be classified into primary OA (POA) and secondary OA (SOA) compounds. POA compounds are hydrocarbon components emitted from primary sources such as biomass burning, cooking, and transport (e.g. (Allan et al., 2010; Lu et al., 2011)), while SOA compounds are formed through atmospheric chemical reactions involving the oxidation of gas precursors such as volatile organic compounds (VOCs) (Kroll and Seinfeld, 2008). Source apportionment analysis on OA based on mass spectra from widely used instruments such as the Aerodyne Aerosol Mass Spectrometer (AMS) (Jayne et al., 2000) or Aerosol Chemical Speciation Monitor (ACSM) (Ng et al., 2011) can provide insight into its primary and secondary components. The Positive Matrix Factorization (PMF) analysis of AMS/ACSM (Ulbrich et al., 2009; Zhang et al., 2011) derived POA typically includes hydrocarbon-like OA (HOA), biomass burning OA (BBOA), and cooking-related OA (COA), while the SOA (also referred as oxygenated OA (OOA), often used as a proxy for SOA) is often typically separated into Less-Oxidized OOA (LO-OOA) and More-Oxidized OOA (MO-OOA). At some measurement sites, specific components like peat-emitted OA, shipping-related OA, or sea spray-related OA can also be identified (Lin et al., 2020; Fossum et al., 2024; Schmale et al., 2013). Previous AMS/ACSM studies revealed that the OOA dominated the total submicron OA mass in the European region with a yearly average fraction of more than 70%, while the contribution from solid-fuel related POA is about 16% yearly on average and mostly during the winter months (Chen et al., 2022). The chemical characteristics and evolution of OA have significant impacts on aerosol optical properties. Particulate organic nitrate (pON), an important component of OA primarily emitted or formed through the oxidation of VOCs oxidation in the presence of NO_x radicals and atmospheric oxidants, can substantially contribute to the total light-absorbing brown carbon (BrC) loadings (Laskin et al., 2015). Studies show that the contribution of light absorption by BrC may be enhanced due to

the increase of nitrogenous organic aerosols during photochemical aging (Yang et al., 2021; Jiang et al., 2022; Cappa et al., 2020). However, bleaching of BrC through **intense** photooxidation processes has also been documented, with significant **temporal** variability depending on factors such as oxidant concentrations and ambient relative humidity (RH) (Liu et al., 2021; Zhao et al., 2015). **The variability of OOA also influences the aerosol hygroscopicity, and the** complex aging process of OOA introduces significant uncertainty in **representing** the cloud condensation nuclei (CCN) activity of atmospheric aerosols (Mei et al., 2013; Wang et al., 2022). Given all these factors, understanding the aging process of OA is crucial to better constrain their role in the atmosphere.

Paris is one of the most developed and densely populated megacities in Europe, facing significant air pollution challenges. In the past decades, extensive research has been conducted to identify and characterize the properties of particulate pollutants in the Paris region (e.g. (Beekmann et al., 2015)). Previous aerosol mass spectrometer studies (Stirnberg et al., 2021; Bressi et al., 2013; Petit et al., 2015; Healy et al., 2013) indicate that Paris is often affected by the mid-range to long-range transport pollutants attribute to the flat orography of the city. Previous AMS Positive Matrix Factorization (PMF) analysis during summertime have shown that, in addition to the significant contributions from the continental polluted air mass to the total **particulate matter with aerodynamic diameter less than 1 μm (PM_{10})**, Paris **peri-urban area** is also influenced by emissions from the Atlantic Ocean (Crippa et al., 2013). Zhang et al. (2019) observed a significant increase in LO-OOA related to the mixture of anthropogenic and biogenic emissions in Paris **peri-urban area** during the summer, but the formation mechanism remains poorly understood. This knowledge gap is potentially because previous studies in the Paris region mostly concentrated on developed areas. As Paris is surrounded by forest regions, it is important to address the issue of how the mixture of anthropogenic and biogenic emissions impacts secondary aerosol properties in this region. Furthermore, it is reported that the Ozone (O_3) has become an important pollutant in the urban areas, and the decreasing of Nitrogen Oxides (NO_x) may contribute to the increases in European urban O_3 concentrations in the future (Grange et al., 2021). Measurements in a suburban forest region in China indicate that the oxidation of Biogenic VOCs (BVOCs) by O_3 may lead to enhanced formation of LO-OOA (Gao et al., 2023). Therefore, characterizing the evolution of aerosol physicochemical properties during transport is crucial, given the changing atmospheric oxidation capacity. **To address these issues, the Atmospheric Chemistry of the Suburban Forest (ACROSS) project was designed to understand the complex chemistry of the urban and forest emissions in and around Paris (Cantrell and Michoud, 2022). In this study, we present an analysis of ground-based observations to provide insights on the evolution of aerosol compositions as a function of photochemical processes, with a focused analysis of their subsequent effects on aerosol optical properties under ambient conditions.**

100 2. Experimental methods and data analysis

2.1 Atmospheric Chemistry of the Suburban Forest (ACROSS) project

A ground-based experiment was conducted in a suburban forest area of Paris (Rambouillet forest) within the framework of the ACROSS project (Cantrell and Michoud, 2022). It was composed of approximately 70% oak, 20% pine, and 10% beech and chestnut trees. The canopy height of the trees in the Rambouillet forest was on the order of ~20 - 25 m. During the campaign, multiple containers were placed side by side in a clear area (with a size of 26.5 m × 26.3 m, ~ 697 m²) within the Rambouillet forest (48.7 N, 1.7 E) which was ~50 km south-west from the centre of Paris. The broader ACROSS Rambouillet experiment, encompassing both near-ground (~5 m) and above-canopy (on a ~40-m-high tower) measurements, was conducted from June 13th to July 25th, 2022. As it will be discussed in the following sections, in this study, the scope is confined to near-ground measurements as most of the measurement results in this study were only available at the near-ground level. The analysis period is refined to June 29th to July 20th, ensuring instrument availability.

2.2 Particulate phase measurements

2.2.1 High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-AMS)

The **Non-Refractory PM₁** (NR-PM₁) compositions, including organic (OA), sulfate (SO₄), nitrate (NO₃), ammonium (NH₄), and chloride (Chl), was characterised through an Aerodyne HR-AMS (Decarlo et al., 2006). Briefly, particles enter the AMS through a critical orifice and an aerodynamic lens, forming a narrow particle beam. The particle size (vacuum aerodynamic diameter) is determined in a Particle Time-of-Flight (PToF) region through the flight time of particles. NR components are subsequently vaporized on a metallic surface, ionized by electron impact ionization (EI, 70 eV), and analysed by Time-of-Flight Mass Spectrometry (ToF-MS) under high vacuum. During the campaign, the HR-AMS conducted measurements with a flow rate of ~0.1 L min⁻¹, drawn from the main 3 L min⁻¹ flow from a PM_{2.5} cyclone and through a Nafion dryer. The HR-AMS sampled intermittently, alternating between near-ground and above-canopy measurements every 5 minutes. This study focuses exclusively on data collected at near-ground level. The HR-AMS was operated alternatively among two modes: V-mode and PToF mode. The Ionization Efficiency (IE) and the Relative Ionization Efficiency (RIE) of the HR-AMS were calibrated using mono-disperse (300 nm), nebulized ammonium nitrate and ammonium sulfate particles, and the IE and RIE results were presented in Table S1. A Composition-Dependent Collection Efficiency (CDCE) was applied to the final results (Middlebrook et al., 2012). Background CO₂ in the HR-AMS was corrected by calibrating the measured CO₂ in filtered air against external measurements obtained with a cavity ringdown spectrometer (CRD, Picarro G2302).

The mass concentrations of different NR-PM₁ species and high-resolution mass spectra analysis were processed from the V-mode results. Elemental ratios of OA, including oxygen-to-carbon (O:C), hydrogen-to-carbon (H:C), and nitrogen-to-carbon

(N:C), as well as the organic mass to organic carbon (OM:OC), were derived from high-resolution mass spectra using the “Improved-Ambient (I-A)” method (Canagaratna et al., 2015). The contribution of pON to the total HR-AMS measured NO₃ is estimated following the method described by Day et al. (2022), as shown in equation (1):

$$f_{\text{pON}} = \frac{(R_{\text{ambient}} - R_{\text{NH}_4\text{NO}_3})(1 + R_{\text{pON}})}{(R_{\text{pON}} - R_{\text{NH}_4\text{NO}_3})(1 + R_{\text{ambient}})} \quad (1)$$

135 Where f_{pON} is the estimated fraction between the pON mass concentration and the total HR-AMS measured NO₃, and R_{ambient} , $R_{\text{NH}_4\text{NO}_3}$, and R_{pON} are the ratios between NO₂⁺ and NO⁺ for ambient, pure NH₄NO₃, and pure pON (determined as 2.75), respectively.

The source apportionment analysis of OA was performed on the high-resolution OA mass spectral matrix for m/z 12–120 in V mode from the HR-AMS using the PMF Evaluation Tool (PET) (Ulbrich et al., 2009). Though a Biomass Burning (BB) event was observed on the evening of July 20th (presented in the time-series results in Figure 2), it only lasted for few hours and the unconstrained PMF analysis is unable to derive a distinct BB factor for this event. To avoid biasing the PMF solution, results from this period were excluded from the PMF analysis in this study. A six-factor solution with fPeak = 0 was chosen as the optimal solution. Although the mass spectra of the OOA factors were highly similar (Pearson correlation coefficient $r > 0.8$), their time series remained distinct, with $r < 0.6$ in the six-factor solution. The spectra of the six factors were comparable to those from previous summer AMS PMF study in Paris urban area (Crippa et al., 2013) documented in the AMS spectral database (Jeon et al., 2023), and the comparison is presented in Table S2 in the supplementary.

2.2.2 Aethalometer

150 The PM₁ aerosol optical absorption coefficient (units of Mm⁻¹ = 10⁻⁶ m⁻¹) at seven different wavelengths (370, 470, 520, 590, 660, and 880 and 950 nm) was measured by a dual-spot aethalometer (AE33, Magee Sci.) (Drinovec et al., 2015) at the Portable Gas and Aerosol Sampling UnitS (PEGASUS) mobile platform (Formenti et al., 2025) which was positioned close to the HR-AMS container. The AE33 was operated at a flow rate of 5 L min⁻¹ and connected to a PM₁ cyclone and a Nafion drier. The whole inlet system has a total flow rate of around 38 L min⁻¹. The AE33 measures the light attenuation coefficient (σ_{atn}) through a filter tape, which was sampled at 1-minute intervals. The spectral aerosol absorption coefficient is determined as:

$$\sigma_{\text{abs}} = \frac{\sigma_{\text{atn}}}{C_{\text{ref}}} \quad (2)$$

Where C_{ref} is the multiple scattering correction factor. While the filter-based AE33 quantifies σ_{abs} via transmittance attenuation from deposited particles, its accuracy is compromised by multi-scattering interactions within the filter matrix, including variable aerosol loading and filter leakage (Yus-Díez et al., 2021). A wavelength-independent C_{ref} of 3.38 has been applied to correct the final absorption coefficient results, and more details about the corrections of AE33 results during the

ACROSS campaign are presented in Di Antonio et al. (2024) and Di Antonio et al. (2025). The light absorbing equivalent Black Carbon (eBC) mass concentration is derived from the multiple scattering corrected 880 nm channel results using a mass absorption cross section (MAC) of $7.77 \text{ m}^2 \text{ g}^{-1}$ (Petzold et al., 2013; Bond et al., 2013). Due to anomalous peaks at 370 nm were observed when fresh filter tape was brought into the analytical airflow during the experiments, the results from 370 nm were excluded from this study, while other wavelengths remained unaffected.

To determine the absorption contributed by the BrC, firstly, the Absorption Ångström exponent (AAE) is calculated through:

$$AAE_{\lambda_1/\lambda_2} = -\frac{\ln(\sigma_{\text{abs},\lambda_1}/\sigma_{\text{abs},\lambda_2})}{\ln(\lambda_1/\lambda_2)} \quad (3)$$

Where $\sigma_{\text{abs},\lambda_1}$ and $\sigma_{\text{abs},\lambda_2}$ represent the absorption coefficient measured at wavelengths λ_1 (470 nm) and λ_2 (880 nm), respectively. The BrC absorption coefficient is determined in the assumption that absorption at 880 nm is contributed by BC only and the AAE for BC is 1. Henceforth, the σ_{abs} contributed by BC at 470 nm can be derived as:

$$\sigma_{\text{abs BC},470} = \sigma_{\text{abs},880\text{nm}} \cdot \left(\frac{470}{880}\right)^{-AAE_{470/880}} \quad (4)$$

Then the σ_{abs} of BrC at 470 nm can be estimated as:

$$\sigma_{\text{abs BrC},470} = \sigma_{\text{abs},470} - \sigma_{\text{abs BC},470} \quad (5)$$

A Single Particle Soot Photometer (SP2, DMT) was employed to characterise the BC mixing state but was only operational for a limited period during the campaign due to a technical issue, with data available partially between 11th July and 19th July. The coating thickness of BC particles was derived from the SP2 results using leading-edge only (LEO) method (Gao et al., 2007), and the mass ratio between the non-BC coating material and BC core material (MR) was $1.65 (\pm 1.38)$, assuming densities as 1.8 g cm^{-3} for BC and 1.6 g cm^{-3} for non-BC coating. According to Liu et al. (2017), when MR is less than 3, the lensing effect becomes less pronounced. Therefore, the lensing effect of BC can be considered negligible in this study.

2.2.3 Total PM₁ mass concentration calculation

The total PM₁ mass concentration was determined as the sum of the NR-PM₁ and eBC mass concentration measured by the HR-AMS and the AE-33, respectively. Although the HR-AMS was operated downstream of a PM_{2.5} cyclone, its aerodynamic lens transmits only submicron particles. The two sampling inlet systems showed comparable line loss rates for PM₁, with maximum losses estimated at approximately 6% for PM₁ in both inlet systems following the method described in Von Der Weiden et al. (2009).

2.3 Gas phase measurements

The nitrogen oxides (NO_x, NO_x = NO + NO₂) and total gas-phase nitrogen species (NO_y) concentrations were measured by the MPIC thermal dissociation cavity ringdown spectroscopy (TD-CRD) instrument at 405 nm (Friedrich et al., 2020), and more details about the operations of the MPIC TD-CRD during ACROSS project are described in Andersen et al. (2024).

NO₂ concentration was measured by a chemiluminescence analyzer (HORIBA APNA 370). The O₃ and CO concentrations were measured using a commercial monitor (HORIBA APOA-370) and a CRD (Picarro G2302) at PEGASUS platform, respectively. VOCs were characterised through the Proton Transfer Reaction Time-of-Flight Mass Spectrometer (PTR-MS, KORE Inc.). The instrument operated in the PEGASUS mobile lab in H₃O⁺ mode with a drift tube pressure of 1.30 mbar and a temperature of 40°C, along with a drift tube voltage of 397V, resulting in an E/N ratio of 134.2 Td. Air samples were drawn at a flow rate of approximately 300 mL min⁻¹ through a 3-meter-long Silcosteel® coated stainless steel tube (2.1 mm inner diameter). The PTR-MS conducted full mass scan mode analysis (10 – 270 amu). The PTR-MS was calibrated during the campaign using a NPL (National Physical laboratory) VOC standards for PTR-MS every three days. Water dependencies of various compounds were determined by performing calibration at various relative humidity before and after the campaign using the same NPL standard cylinder. Non-calibrated compounds were retrieved from reactor conditions, rate constants, fragmentations, and ion transmissions determined using the same NPL standard cylinder. An automated zero procedure was performed every hour for 10 min by sampling humid zero air generated by passing ambient air through a catalytic converter. OH radicals were measured through the Chemical Ionisation Mass Spectrometry (CIMS, LPC2E), and more details about the instrument was described in (Kukui et al., 2008). Briefly, the CIMS determines OH radical concentrations by chemically converting sampled OH into H₂SO₄ by addition of SO₂ in a chemical conversion reactor in the presence of water vapour and oxygen (Eisele and Tanner, 1991). H₂SO₄ is detected by the mass spectrometer as HSO₄⁻ ion. To distinguish this signal from ambient H₂SO₄, the conversion process uses isotopically labelled ³⁴SO₄ leading to the formation of H₂³⁴SO₄.

2.4 Other supporting measurements

The surface downwelling shortwave radiation and wind parameters were measured by a net radiometer (Kipp & Zonen, CNR4: 192119) and a wind monitor (Young, 05103: 4655) mounted on the tower. As the measurements were conducted in a clear area with no trees, the tower-top observations were considered representative of near-surface atmospheric conditions relevant for radiation and wind.

2.5 Relative anthropogenic photochemical age estimation

Photochemical processing of the mixed anthropogenic–biogenic air masses arriving at the measurement site was evaluated using the ratio between NO_x and NO_y as proposed by Kleinman et al. (2003); Kleinman et al. (2007), as done in previous ground-based measurement studies (Hayes et al., 2013; Ensberg et al., 2014). The relative anthropogenic photochemical age ($t_{\text{anthrop-photo}}$) in this study is calculated following the method described by Nault et al. (2018):

$$t_{\text{anthrop-photo}} = \frac{\ln \left(\frac{[\text{NO}_x]}{[\text{NO}_y]} \right)}{k_{\text{OH}+\text{NO}_2} [\text{OH}]_{\text{avg}}} \quad (6)$$

Where [NO_x] and [NO_y] are the measured concentrations of NO_x and NO_y, respectively, [OH]_{avg} is the average measured OH concentration during the campaign period, which is $1.6 (\pm 1.3) \times 10^6$ molecules cm⁻³. $k_{\text{OH}+\text{NO}_2}$ is the rate coefficient

of OH with NO₂ and is assumed to be $9.2 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (Mollner et al., 2010). The estimated $t_{\text{anthrop-photo}}$ was constrained to the period of 6:00 – 20:00 European Summer Time (EST) according to the diurnal trend of the radiation intensity (presented in Figure 3(a) and 3(e)).

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The results are expressed as “relative anthropogenic photochemical age” since the method mainly captures the aging of anthropogenic pollutants in the mixed anthropogenic–biogenic air masses arriving at the site. In addition, the potential short lifetime of NO_y in the forest (Andersen et al., 2024) may compromise the accuracy of absolute photochemical age calculation. Only the calculated $t_{\text{anthrop-photo}}$ within 1 day (24 hours) was used here to reduce the uncertainty of the estimated $t_{\text{anthrop-photo}}$ due to the potential short lifetime of HNO₃ and other oxidised reservoirs via deposition in the forest (Nguyen et al., 2015; Romer et al., 2016).

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2.6 UK Met Office NAME dispersion model

Potential source regions were identified using the UK Met Office Numerical Atmospheric-dispersion Modelling Environment (NAME) dispersion model (Jones et al., 2007). The model calculates the integrated historical air mass contribution over 24 hours by back-tracking tracer particles (released at 1 g s^{-1} from the sampling site) on a $0.25^\circ \times 0.25^\circ$ horizontal grid within the boundary layer every four hours. The model distinguishes between air masses primarily influenced by local sources and those transported regionally from broader areas. The potential air mass sources are classified into five main regions (presented in Figure 1(a)) according to the CAMS EAC4 (ECMWF Atmospheric Composition Reanalysis 4) global reanalysis PM₁ spatial distribution results (presented in Figure 1(b)) (Inness et al., 2019) during the campaign period:

(1) The Ile-de-France region (IDF (local), $48^\circ - 50^\circ \text{ N}$, $1^\circ - 3^\circ \text{ E}$) represents the local emission from the Paris region; (2) The Northeast (NE) region ($50^\circ - 54^\circ \text{ N}$, $1^\circ - 10^\circ \text{ E}$) is identified as a source of anthropogenic polluted continental air masses, evidenced by significantly elevated PM₁ concentrations in this area; (3) The Northwest (NW) region ($50^\circ - 54^\circ \text{ N}$, $-5^\circ - 1^\circ \text{ E}$) represents the source of polluted maritime air masses originating from the English Channel and the United Kingdom (UK); (4) The Southwest (SW) region ($44^\circ - 50^\circ \text{ N}$, $-5^\circ - 3^\circ \text{ E}$, exclude the IDF region) is characterized as a source of low-pollution maritime air masses, as evidenced by persistently low PM₁ concentrations over Southwest France despite several wildfire activities (the spatial distribution of fire points information during the experiment period is presented in Figure S2); and (5) The Southeast (SE) region ($44^\circ - 48^\circ \text{ N}$, $3^\circ - 10^\circ \text{ E}$) represents another source of polluted continental air mass due to the high PM₁ concentration over Southeast France and North Italy. The air mass examples are presented in Figure S1 in the supplementary.

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3.1 Overview of meteorology and campaign conditions

Figure 2(a) presents the time series of temperature and RH, PM₁ composition, and the fractional contributions of different air masses throughout the whole campaign period. The average mass concentrations of PM₁ species and the normalised OA under different air mass dominated periods are displayed in Figure 2(b) and (c). While the contribution from the local emissions (IDF air mass) was significant, external air masses also had a substantial impact on PM₁ mass concentrations. The SE air mass-dominated period was excluded from further analysis due to its short duration during the campaign. The NE air masses brought higher average aerosol mass loadings compared to the other sectors, in agreement with the previous summertime studies in Paris, indicating that the continental air mass is generally more polluted (Crippa et al., 2013). The continental air masses also typically resulted in the highest temperatures and the lowest RH. In contrast, air masses originating from oceanic influence, whether from the SW or NW sectors, resulted in lower aerosol loadings in the Paris region, while higher RH and lower temperatures prevailed. The ECMWF CAMS reanalysis shows higher average PM₁ concentrations over the Southwest France due to the forest fires burning during the summer of 2022 (Menut et al., 2023). Although an in-situ PM₁ mass concentration spike occurred on the evening of 20 July when the SW air mass dominated, measurement data and back-dispersion analysis confirm that BB particulates from Southwest France were absent at the site for the rest of the study.

Figure 3 presents the diurnal variations of the $t_{\text{anthrop-photo}}$, CO concentration, eBC mass concentration, temperature, downward shortwave radiation, RH, OH and NO_x concentrations under the different external air masses dominated periods. The BB event on the evening of July 20th was excluded from the analysis. Based on the diurnal trends in meteorological parameters, increases in radiation intensity during the day were inversely correlated with decreases in RH, which reached its lowest level in the late afternoon. As shown in Figure 3(a) and 3(g), the diurnal trend of $t_{\text{anthrop-photo}}$ was similar to the observed OH concentration and radiation intensity diurnal trend, reinforcing its robustness as a photochemical indicator. Due to the weaker radiation intensity or the potential shorter transport distance, the average $t_{\text{anthrop-photo}}$ and OH concentration of the SW air mass dominated period were lower compared to the other air masses dominated periods. Since the measurements were conducted away from urban emission sources, the diurnal average eBC mass concentration was with no discernible peak during rush hours, and there was only limited increase in NO_x concentrations during the morning rush hours during NE and NW periods. The daytime decrease of CO concentration during NW and SW periods was due to boundary layer dilution, with lowest CO concentrations at midday. In contrast, the NE period showed no diurnal variation of CO, suggesting the accumulation of regionally transported pollutants from surrounding areas at the suburban forest site.

3.2 Source apportionment of organic aerosols

Figure 3 presented the average mass spectra of the resolved six PMF OA factors: one Hydrocarbon-like OA (HOA) and five OOA factors. The Pearson correlation coefficient (r) between the HR-AMS PMF factors and the external tracers is presented in Figure 4. The time series of the PMF-derived OA factors between June 29th and July 20th, 2022, is presented in Figure 2(a). Figure 3(i) shows the diurnal variations of the OA factors, and Figure 5 presents the mass fractions of the OA factors according to the dominated air mass periods. The comparison between below- and above-canopy PMF results is provided in the supplementary, showing that the trends of NR-PM₁ and PMF for below- and above-canopy were consistent during the daytime throughout the campaign. Thus, the influence of localized fresh plumes and nearby human activities was minimal since the boundary layer was well mixed during the daytime during the campaign period, supporting our subsequent findings on regional pollution within the boundary layer during the daytime.

The OOA factors accounted for over 90% of total OA during the campaign, contributing a larger mass fraction than in previous studies conducted in the Paris urban area or its surroundings (Crippa et al., 2013; Petit et al., 2015; Zhang et al., 2019). As expected, the HOA factor has the lowest O:C ratio (0.15) and the highest fraction of C_xH_y fragments, notably at m/z 41, 43, 55, and 57. Temporal variability shows sporadic enhancements associated with occasional vehicular activity in the vicinity of the site. However, HOA only exhibited moderate correlation with eBC ($r = 0.55$) and with NO_x ($r = 0.49$). This may be due to the remote location of the measurement site, primary anthropogenic emission sources were limited near the site.

LO-OOA1 and LO-OOA2 exhibited very similar mass spectral profiles but distinct temporal patterns, with LO-OOA1 peaking during the daytime and LO-OOA2 during the nighttime. The correlation analysis indicates that they were associated with secondary formation from a mixture of biogenic precursors: while LO-OOA1 exhibited fair correlation with isoprene ($r = 0.43$), LO-OOA2 correlated more strongly with monoterpene ($r = 0.79$). The moderate correlation between LO-OOA1 and isoprene was to be expected in such a temperate forest, given the typical mixtures of BSOA precursors and the differing lifetimes of aerosol- and gas-phase compounds. Since monoterpenes emitted from local vegetation can form SOA through ozonolysis, OH- or NO₃- initiated reactions at night (Lee et al., 2016), this explains the nighttime peak of LO-OOA2. Good correlation ($r = 0.63$) was observed between LO-OOA3 and the sum of methyl vinyl ketone (MVK) and methacrolein (MACR), while a fair correlation ($r = 0.45$) was found between LO-OOA2 and MVK + MACR. Isoprene epoxydiols (IEPOX)-OOA was not identified through the HR-AMS results during the experiment period, as the mass spectral profiles of both LO-OOA1 and LO-OOA2 lacked the characteristic enhancement at m/z 82, a known tracer signal for IEPOX-OOA (Hu et al., 2015). However, both OOA factors exhibited pronounced contributions at m/z 91.05, attributed to C₇H₇⁺ fragments likely from thermal decomposition of dimers and oligomers on the vaporizer (Riva et al., 2016). These two biogenic-related LO-OOA factors contributed approximately 40% to 50% of the total OA mass concentration throughout the campaign period.

315 The diurnal trend shows that the LO-OOA3 concentration started increasing from the evening at around 8 pm and reached the peak in the early morning (between 6 and 8 am). The moderate positive correlation between LO-OOA3 and RH ($r = 0.45$) and Chl ($r = 0.4$) suggested that this OOA factor may be influenced by marine air masses. This interpretation is further supported by the larger mass fraction of LO-OOA3 observed during marine air mass-dominated periods (SW and NW periods) compared to continental periods (NE periods). However, no significant methanesulfonic acid (MSA) fragments
320 were detected at m/z 79, 95, or 96. Consequently, the similarity between the LO-OOA3 mass spectral profile and the marine OOA factor previously reported in Paris was limited (Table S1). These results suggest that the marine influence at our site was dominated primarily by inorganic sea-salt Chl and its processed products, rather than by MSA-related organic aerosol. The highest N:C ratio among all the OOA factors for LO-OOA3 was observed suggesting that LO-OOA3 importantly contributed to the nitrogen-containing organics. However, the correlation between LO-OOA3 and pON was poor ($r = 0.06$).
325 The mass spectral profile shows that the most abundant nitrogen-containing fragments were CHN^+ (m/z 27.01) and CH_4N^+ (m/z 30.03), which together contributed approximately 6% to the total LO-OOA3 signal. The presence of CH_4N^+ suggested that LO-OOA3 likely contained a contribution of reduced-N compounds such as organic amines (Ge et al., 2024). The LO-OOA3 likely originated from aqueous-phase chemistry under marine air mass dominance, where elevated RH ($> 80\%$) at night-time promoted partitioning of nitrogen-containing organics into hygroscopic aerosol phases. Chen et al. (2019) also
330 shows that the high RH condition promoted the formation of organic amines particles. At this suburban forest site, reduced nocturnal oxidant levels, especially during SW air mass periods, facilitated the accumulation of nitrogen-enriched LO-OOA3. In contrast, daytime photo-oxidation driven by OH radicals and secondary oxidants (e.g., O_3) effectively degraded LO-OOA3, as evidenced by strong inverse correlations between LO-OOA3 and photochemical-related OVOCs (e.g. with MVK+MACR: $r = -0.69$).

335 LO-OOA4 exhibited a good correlation with sulfate ($r = 0.67$) and moderate correlation with inorganic nitrate ($r = 0.42$). The wind rose analysis (shown in Figure S8 in the supplementary) reveals that LO-OOA4 predominantly originated from anthropogenic polluted air masses advected from the NE and NW regions. Consequently, during the SW period, LO-OOA4 contributed only 6% to the total OA mass concentration. In contrast, its contribution increased to 15% and 13% with the
340 increasing pollution level during the NW and NE periods, respectively.

he MO-OOA was with the highest average O:C ratio (0.86) among all the factors, and dominant peaks were presented at m/z 28 (CO^+) and 44 (CO_2^+). The good correlation between MO-OOA and isoprene was attributed to under daytime conditions, both elevated isoprene emissions and the oxidation of various precursors leading to MO-OOA formation occurred
345 simultaneously. The significant increase in MO-OOA observed during the afternoon, despite boundary layer dilution, indicates that summertime MO-OOA formation was strongly driven by active photochemical processes. Due to the reduction of photochemical activity during the SW period, the mass fraction of MO-OOA during the SW period was smaller than the

fraction during the other periods. The wind rose analysis shows that the MO-OOA was contributed significantly from the anthropogenic polluted NE regions.

350 3.3 Evolution of aerosol compositions due to photochemical aging

Figure 7 illustrates the evolution of O_x ($O_3 + NO_2$) mixing ratio, O:C ratio, and NR- PM_{10} components concentrations normalised to eBC as a function of $t_{\text{anthrop-photo}}$. The air masses arriving at the measurement site were enriched with anthropogenic primary carbonaceous aerosols and subsequently modified by secondary processes. Concentrations of compounds presumed to be associated with anthropogenic sources were normalised by eBC to account for dilution, providing an indicator of secondary processing. The results are averaged into four-hour intervals along $t_{\text{anthrop-photo}}$ to illustrate their evolution. To quantify the relative photochemical-age-dependent evolution of particulate phase components, an exponential fitting was applied to the factors that showed significant correlation with $t_{\text{anthrop-photo}}$:

$$y = A \cdot \exp(B \cdot t_{\text{anthrop-photo}}) \quad (7)$$

Where the coefficient B quantifies the relative hourly change rate of each factor. As discussed previously in Section 2.5, the absolute photochemical age calculation may be uncertain. Therefore, the hourly change rate reported in this study was used to assess the relative variations in parameters. The fitting results are summarized in Table S3. The uncertainty of coefficient B , reported as its standard deviation, reflects the variability inherent to the regression analysis.

The correlation between $t_{\text{anthrop-photo}}$ and O_x concentrations shown in Figure 7(a) indicate that the photochemical process in summer has a significant impact on the formation of O_x throughout the experiment period. This agrees with the previous study in Beijing during summertime (Chen et al., 2021) and suggests that increased photochemical aging leads to greater consumption of VOCs, which in turn accelerates NO_x cycling and promotes the accumulation of tropospheric O_3 . The NE period showed higher average O_x concentrations compared to the NW and SW periods during the relative ~24-hour photochemical aging period.

The normalised PM_{10} concentration, shown in Figure 7(b) as a function of $t_{\text{anthrop-photo}}$, exhibited a consistent increase across all three periods with higher $t_{\text{anthrop-photo}}$, and the normalised OA mass concentration doubled following a relative ~24-hour photochemical aging process as presented in Figure 7(c). The relative increasing rate of PM_{10} was $3.8 (\pm 0.5) \% h^{-1}$, $2.5 (\pm 0.3) \% h^{-1}$, and $2.9 (\pm 0.7) \% h^{-1}$ for SW, NW and NE periods, respectively. While the relative production rate of OA was significant higher and was $5.0 (\pm 0.5) \% h^{-1}$, $3.5 (\pm 0.3) \% h^{-1}$, and $3.7 (\pm 1.0) \% h^{-1}$ for SW, NW and NE periods, respectively. This higher OA production rate compared to the average PM_{10} production rate, combined with no significant relative increase of other aerosol components (sulfate, and organic and inorganic nitrate; see Figure 7(d, e, f)). This finding aligns with previous studies in Europe, which have shown that OOA formation substantially contributes to summer PM_{10}

levels (Chen et al., 2022; Zhang et al., 2019). The increasing trend of OA also agreed with the results previously observed in urban plumes from Paris, Mexico City, and Seoul (Freney et al., 2014; Decarlo et al., 2010; Nault et al., 2018) during photochemical process. However, a slight increase in the average bulk O:C ratio as a function of $t_{\text{anthrop-photo}}$ was observed only during the NW period. Indeed, the average bulk O:C ratio did not show a corresponding increase with $t_{\text{anthrop-photo}}$ during the SW and NE period. On the contrary, a slight decrease was observed at higher $t_{\text{anthrop-photo}}$ during the NE period. The relatively high O:C ratio at $t_{\text{anthrop-photo}} = 0$ suggests that the observed regional background OA was already oxidised. With further photochemical processing, the evolution of O:C may become less significant, as reported in other field studies in remote station where oxidation indicators reached a steady state rather than continuing to rise with photochemical age (Irei et al., 2015). Furthermore, the decrease in O:C during the NE period was likely caused by the additional contribution of LO-OOA from photochemical processes, which diluted the overall oxidation level and lowered the average bulk O:C ratio.

However, there was a slight increase in the average bulk O:C ratio as a function of $t_{\text{anthrop-photo}}$ during the NW period. Indeed, the average bulk O:C ratio did not show a corresponding increase with $t_{\text{anthrop-photo}}$ during the SW and NE period; instead, a slight decrease was observed at higher $t_{\text{anthrop-photo}}$ during the NE period. The relatively high O:C ratio at $t_{\text{anthrop-photo}} = 0$ suggests that the observed regional background OA was already oxidised. With further photochemical processing, the evolution of O:C may become less significant, as reported in other field studies in remote station where oxidation indicators reached a steady state rather than continuing to rise with photochemical age (Irei et al., 2015). Furthermore, the decrease in O:C during the NE period was likely caused by the additional contribution of LO-OOA from photochemical processes, which diluted the overall oxidation level and lowered the average bulk O:C ratio.

The sulfate concentrations exhibited minimal variation with $t_{\text{anthrop-photo}}$ here, regardless of the period, likely due to the limited availability of SO₂ precursors in the Rambouillet remote measurement site. Previous studies have demonstrated rapid conversion of SO₂ into sulfate via aging processes in urban areas (Wu et al., 2022; Chen et al., 2021) or near emission sources (Yu et al., 2020). Concerning particulate nitrate, which was over 80% attributed to pON on average during the experiment period, has shown distinct behaviours between its inorganic and organic fractions. For inorganic nitrate compounds, concentrations in the NW and SW period slightly decreased with increasing $t_{\text{anthrop-photo}}$, whereas those in the NE period exhibited a minor increasing trend. It is likely that this variation was due to the inhomogeneous availability of NO_x concentrations during different periods. The SW period showed a slight increase in the pON concentration with $t_{\text{anthrop-photo}}$ increases, while the NE and NW periods displayed a decreasing trend. This difference was due to depletion of primary pON and concurrent formation of secondary pON during photochemical aging, and this relationship will be further explored through linking to the trend of PMF-derived factors.

410 3.4 Evolution of PMF-derived OA factors due to photochemical aging

Figure 8 shows the evolution of the concentrations of HR-AMS PMF-derived factors (normalised and non-normalised by eBC), as well as gas-phase components measured by PTR-MS, as a function of $t_{\text{anthrop-photo}}$. Primary anthropogenic VOCs (Toluene + Benzene) were normalised against ΔCO to account for dilution. The background CO was defined as the 5th percentile of the entire campaign period (with BB influenced period removed) and was estimated to be 52 ppb. The evolution of absolute particulate and gas-phase concentrations is presented in Figure S11 in the supplementary. For the primary OA compounds, the HOA shown a decreasing trend with the increase of $t_{\text{anthrop-photo}}$ during the NE and NW periods. Same decreasing trend was also observed for the primary anthropogenic VOCs (Toluene + Benzene). During the SW period, HOA concentrations exhibited a slight increase, and the Toluene + Benzene concentrations remained independent of $t_{\text{anthrop-photo}}$. Previous studies in the polluted urban areas have shown that strong photochemical processes lead to the oxidation of the HOA and traffic related primary VOCs (Wu et al., 2022; Chen et al., 2021). However, reduced radiation levels decreased the photochemical oxidation rate of primary traffic-related pollutants, potentially leading to their accumulation in suburban forested areas. As HOA has shown some correlation with the pON ($r = 0.35$), this may explain that the decline in pON concentration with $t_{\text{anthrop-photo}}$ was driven by photodepletion of primary pON during intense photochemical activity, while the photo loss of primary pON during the SW period was slower than the other periods.

425 The biogenic-related LO-OOA1 and LO-OOA2 were not normalised to eBC here, as this could overestimate their relative abundance. LO-OOA1 showed an increasing trend during all three periods. As shown in Figure 8(h), the ratio of isoprene to MVK+MACR decreased during the SW period, while its variation was limited during the NE period. This was likely due to both enhanced daytime isoprene emissions and more active photochemical process of MVK+MACR under the strong solar radiation and high temperatures characteristic of the NE period. All the periods illustrated a close relative production rate of around for LO-OOA1 which was $6.1 (\pm 2.8) \% \text{ h}^{-1}$, $8.7 (\pm 3.6) \% \text{ h}^{-1}$ and $6.9 (\pm 3.0) \% \text{ h}^{-1}$ for SW, NW, and NE period, respectively. However, LO-OOA2 showed no clear correlation with $t_{\text{anthrop-photo}}$. As discussed in Section 3.2, LO-OOA2 can likely be attributed to SOA formation from locally emitted monoterpenes. As the Boundary Layer Height (BLH) increased during the daytime, LO-OOA2 was progressively diluted. Therefore, the variation of LO-OOA2 did not correspond to the evolution of $t_{\text{anthrop-photo}}$.

440 During the NE period, LO-OOA3 exhibited a clear decreasing trend with increasing $t_{\text{anthrop-photo}}$ at a relative rate of $-2.9 (\pm 1.4) \% \text{ h}^{-1}$, whereas no distinct trend was observed in the other periods. Elevated OH radical and secondary oxidant concentrations during the NE period likely enhanced oxidative depletion of nitrogen-enriched LO-OOA3 relative to other periods. While continental pollution-related LO-OOA4 demonstrated a strong dependence on photochemical processes, its variability may also be influenced by dominant air masses, as the SW period was with lower average normalised mass concentrations compared to other periods. The MO-OOA showed strong correlation with the photochemical process. The

relative production rates for the NE and NW periods were $6.4 (\pm 1.3) \% \text{ h}^{-1}$, $6.4 (\pm 1.5) \% \text{ h}^{-1}$, and they were higher than the relative production rate during the SW periods ($4.8 (\pm 2.1) \% \text{ h}^{-1}$). The normalised mass concentrations of MO-OOA during the NE and NW period were significantly higher than the concentration during the SW period after a relative ~24-hour photochemical aging. Limited formation of MO-OOA during the SW period led to a lower average bulk O:C ratio compared to other periods. Moreover, our findings indicate that highly oxidized particulate species were not favoured under conditions of low radiation and high relative humidity. In addition, LO-OOA4 and MO-OOA also exhibited a correlation with pON ($r = 0.34$ and 0.3 , respectively), suggesting that LO-OOA4 and MO-OOA importantly contributed to secondary pON formation during photochemical aging. Thereby, the concurrent depletion of HOA and formation of LO-OOA4 and MO-OOA likely govern the observed variations in total pON concentrations throughout the photochemical aging process.

3.5 The impact of photochemical aging on aerosol optical properties

Figure 9 illustrates the increasing contribution of BrC to the total aerosol light absorption coefficient at 470 nm as a function of $t_{\text{anthrop-photo}}$, particularly during the NE and NW periods. As $t_{\text{anthrop-photo}}$ increased from around 2 hours to nearly 24 hours, the average BrC absorption fraction rose from about 17% to 23% in the NE period and from roughly 18% to 26% in the NW period. To identify and quantify the contribution of different OA factors to the total $\sigma_{\text{abs BrC},470}$, a Multiple Linear Regression (MLR) analysis was applied using the OA factors from the PMF analysis during the whole experiment period (with BB period removed). The p -test ($p < 0.01$) was also applied to assess the statistical significance of each parameter. The MLR relationship between $\sigma_{\text{abs BrC},470}$ and PMF-derived factors are formulated as:

$$\sigma_{\text{abs BrC},470} = a_0 + \sum_i a_i [C_i] \quad (8)$$

Where a_0 represents the intercept, and a_i represents the regression coefficient for each PMF-derived factor C_i . These regression coefficients can be associated with the Mass Absorption Coefficients (MAC) of each PMF-derived factor. The Variance Inflation Factors (VIF) for all factors were below 5, indicating that multicollinearity was not a concern. The partial correlation remained unchanged after variable standardization.

Table 1 presents the results of the regression factors of the MLR analysis between $\sigma_{\text{abs BrC},470}$ and PMF-derived factors. The correlation coefficient is also presented to illustrate the contribution of each PMF-derived factor to the total BrC absorption during the whole experiment period. Interestingly, the LO-OOA3 and MO-OOA, which have the highest nitrogen content among all factors, also depict high MAC (regression coefficients). Nonetheless, their correlations with BrC differ markedly: LO-OOA3 displayed a significant negative partial correlation, whereas MO-OOA was strongly positively correlated. The HOA and LO-OOA4 also showed high MAC which were $0.47 \text{ m}^2\text{g}^{-1}$ and $0.30 \text{ m}^2\text{g}^{-1}$, respectively, and they exhibited fair correlation with BrC. The MAC reported here was close to the results from other suburban areas, for example, Jiang et al. (2022) observed MAC values of $0.4 - 0.8 \text{ m}^2\text{g}^{-1}$ at 375 nm for OA with O:C ratios between 0.4 and 0.6. In contrast, our MAC

value was lower than the MAC observed near emission source, for example, Washenfelder et al. (2015) reported a MAC of
475 $1.35 \text{ m}^2 \text{ g}^{-1}$ at 365 nm for BB emitted OA. It is interesting to note that HOA, LO-OOA4 and MO-OOA also exhibited
correlation with the pON, typically associated as an important component of BrC (Laskin et al., 2015).

Combined with the photochemical aging process discussed in Section 3.3, the decline in HOA concentration with
photochemical aging during the NE and NW period demonstrated a reduced contribution of primary BrC following a relative
480 ~ 24 -hour photochemical aging process. The photochemical process also suppressed the formation of LO-OOA3 or oxidized
it into MO-OOA, particularly during the NE period. Conversely, the increase in BrC absorption fraction as a function of
 $t_{\text{anthrop-photo}}$ highlighted the production of more secondary BrC. This suggested that photochemical aging-driven formation
of MO-OOA dominated the contribution to enhancement of the overall BrC absorption contribution at short wavelength,
particularly during high solar radiation periods (NE and NW periods) in summer. Previous studies also demonstrated that the
485 photochemical process promoted the enhancement of the secondary BrC absorption in urban (Li et al., 2023) and remote
areas (Wu et al., 2024). The persistence of secondary BrC in remote regions demonstrated their enhanced summertime
production efficiency, thus amplifying their direct radiative effects through solar radiation interactions. The weak absorption
capacity of LO-OOA1 and LO-OOA2 suggested that these PMF-derived factors exhibited negligible short-wavelength
absorption. While LO-OOA1 and LO-OOA2 were predominantly associated with Biogenic SOA (BSOA) derived from
490 isoprene and monoterpene oxidation, they typically displayed limited light absorption properties due to the prevalence of
non-chromophoric oxygenated products (Flores et al., 2014; Laskin et al., 2015). Previous study in a suburban forest area in
the US also finds that BSOA was not correlated with the BrC absorption at short wavelengths (Washenfelder et al., 2015).

Conclusions

495 In this paper, we present a study in a suburban forest region of a European megacity in summer to demonstrate the impacts
of photochemical processes on aerosol properties in regionally transported air masses containing a mixture of anthropogenic
and biogenic emitted compounds. Based on the detailed mass spectra of the HR-AMS, we resolved primary and secondary
OA sources via PMF analysis, enabling quantitative tracking of the evolution of OA during photochemical aging. The
evolution of individual PMF-derived OA factors was further examined in relation to aerosol optical properties to determine
500 their respective contributions to BrC. Throughout the entire experiment, OA dominated the total submicron aerosol mass. An
increase in OA with relative anthropogenic photochemical age was primarily driven by the production of OOA. The
production rates of different OOA types varied with meteorological conditions: dry air masses from NE continental regions
coincided with strong solar radiation, while SW marine air masses were associated with humid, low-radiation conditions.
OOA formed under humid, low-radiation conditions exhibited a lower oxidation state, reflected in reduced average bulk O:C
505 ratios, with LO-OOA accounting for a substantially larger fraction of total OA. By contrast, intense photochemical activity
under dry, high-radiation conditions promoted rapid formation of MO-OOA. Although such strong photochemistry depleted
primary anthropogenic OA and nitrogen-enriched LO-OOA, this was offset by enhanced production of MO-OOA and

subsequent secondary BrC formation. Consequently, the fraction of total BrC associated with short-wavelength absorption increased with relative anthropogenic photochemical age. This highlights the critical need to incorporate BrC formation mechanisms into models to accurately simulate direct radiative effect (Drugé et al., 2022).

Author Contribution

VM and CC designed the ACROSS Rambouillet experiments; CY performed the data analysis and wrote the paper; PF and VM provided guidance with the analysis and writing; CY, PF, JB, CDB, LDA, TS, STA, PD, GNTET, JNC, AK, CX, CD, MCi, MCa, CC and VM performed experiments; JB performed the operation and data analysis of the HR-AMS; CY and JB performed the HR-AMS PMF analysis; CDB and LDA performed the operation and data analysis of AE33; TS, STA, PD, GNTET and JNC performed the operation and data analysis of TD-CRD; AK and CX performed the operation and data analysis of CIMS; CD, OG and JCE performed the operation and data analysis of the meteorological data measurements; VM, HB, and AB performed the operation and data analysis of PTR-MS; CY and HW performed the back dispersion analysis of UK Met Office NAME dispersion model; CG coordinate the technical aspect of the Rambouillet experiments; FM, MCa, ABe and PZ contributed to the design and preparation of measurement infrastructures at the Rambouillet site; JDA, DL and YW contributed to the data analysis and discussions.

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The below-canopy measurement data for Ramouillet site measurements during ACROSS project is available from the AERIES website (<https://across.aeris-data.fr/>, last access: 01/04/2025): which includes NR-PM1 data from HR-AMS (Brito and Riffault, 2023), NO_x, NO_y and O₃ data (Crowley, 2024). OH data from CIMS (Kukui, 2023), eBC and multi-wavelength absorption data from AE33 (Di Antonio and Di Biagio, 2024), VOC data from LISA PTR-MS data (Michoud and Bouzidi, 2024), and meteorological data (Denjean, 2023).

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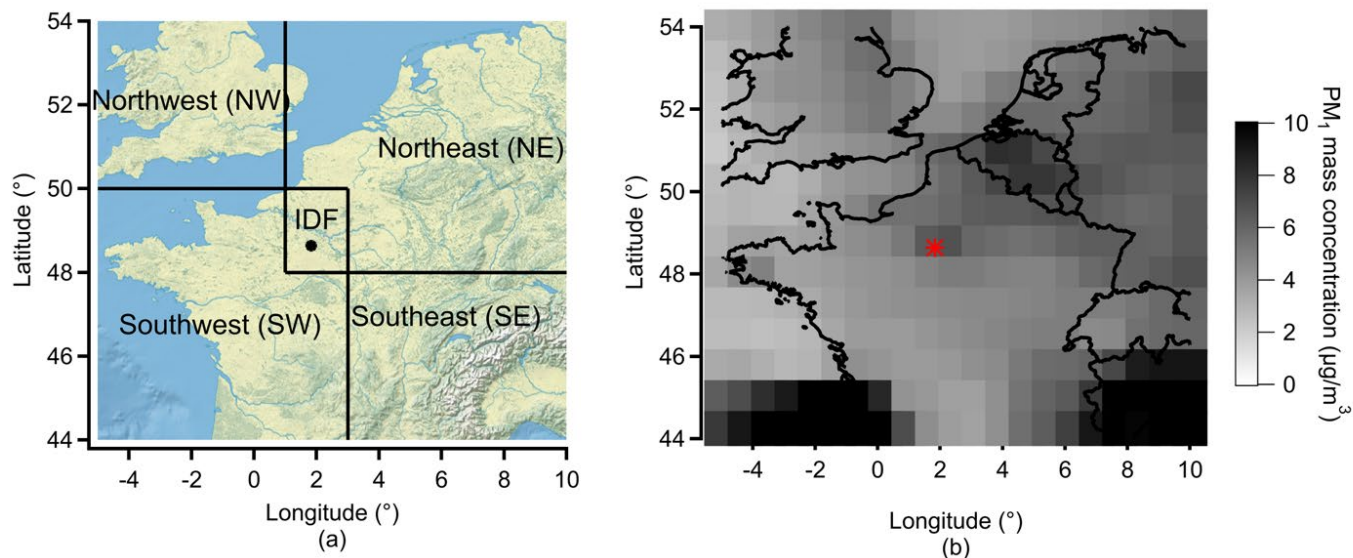


Figure 1: (a) Classification of the potential air mass source regions; (b) ECMWF CAMS EAC4 (ECMWF Atmospheric Composition Reanalysis 4) reanalysis PM_{10} spatial distribution during the ACROSS campaign period. The dot in the figure represents the location of the Rambouillet measurement site. (the map information is from © Google Maps).

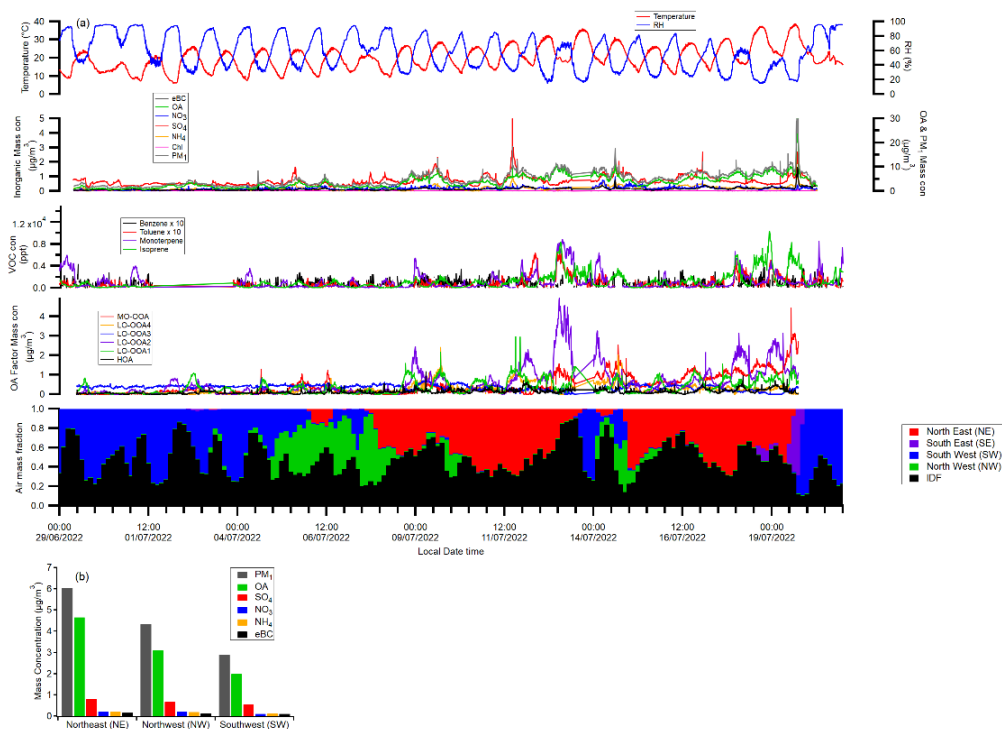


Figure 2: (a) Time series of temperature, RH, PM_{10} , VOC, PMF OA factors and historic air mass fractions; (b) The average PM_{10} composition mass concentrations under different external air mass dominated periods.

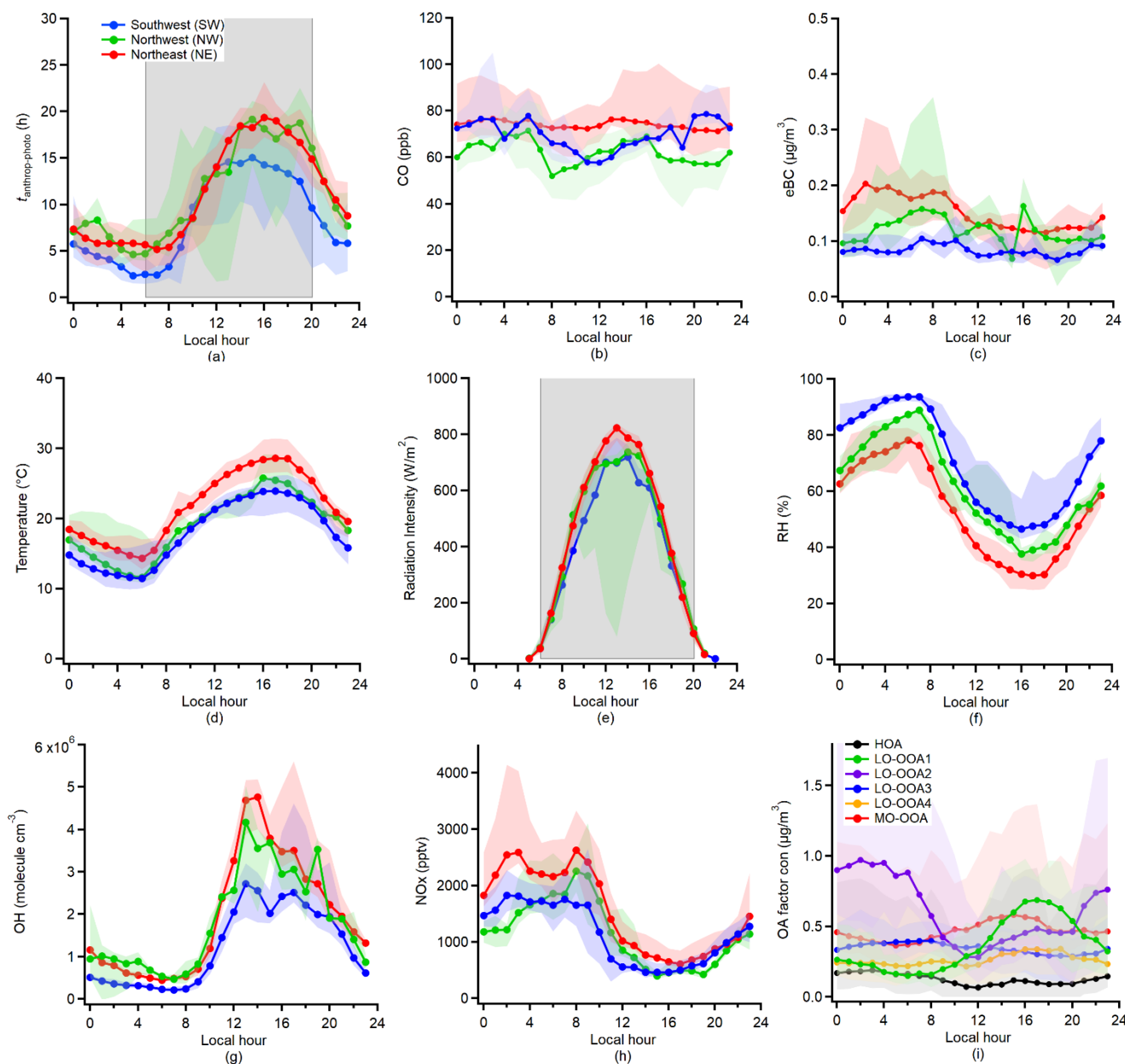


Figure 3: Diurnal variation of the (a) Relative anthropogenic photochemical age ($t_{\text{anthrop-photo}}$); (b) CO mixing ratio; (c) eBC mass concentration; (d) Temperature; (e) Radiation Intensity; (f) RH; (g) OH concentration; (h) NO_x concentration; (i) PMF OA factors. The grey shades in (a) and (e) indicate the periods for the photochemical aging analysis. The lower and upper whiskers in the figure are the 25th and 75th percentiles, respectively.

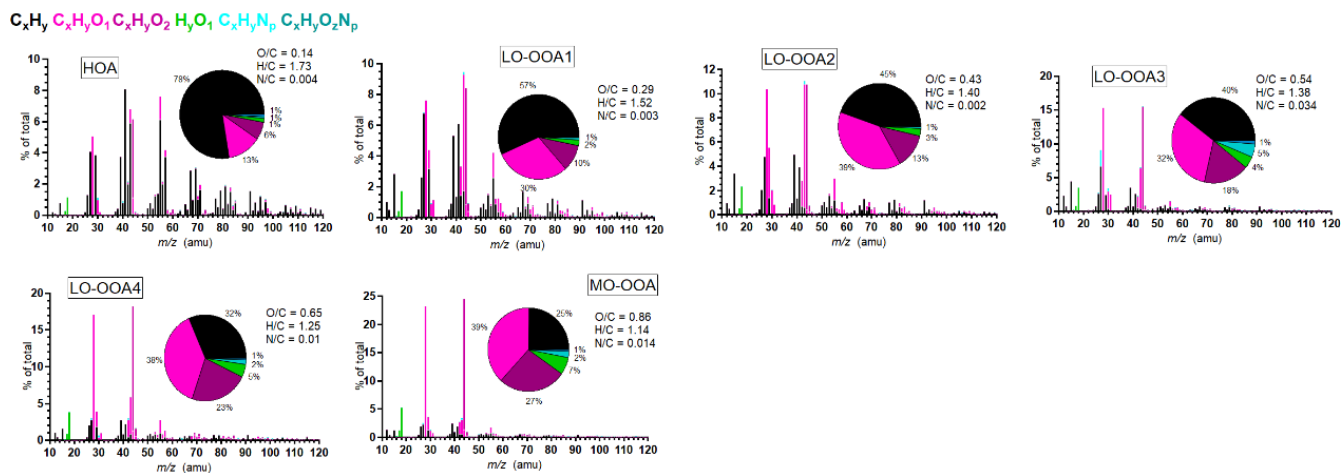


Figure 4: Average mass spectra for the PMF OA factors.

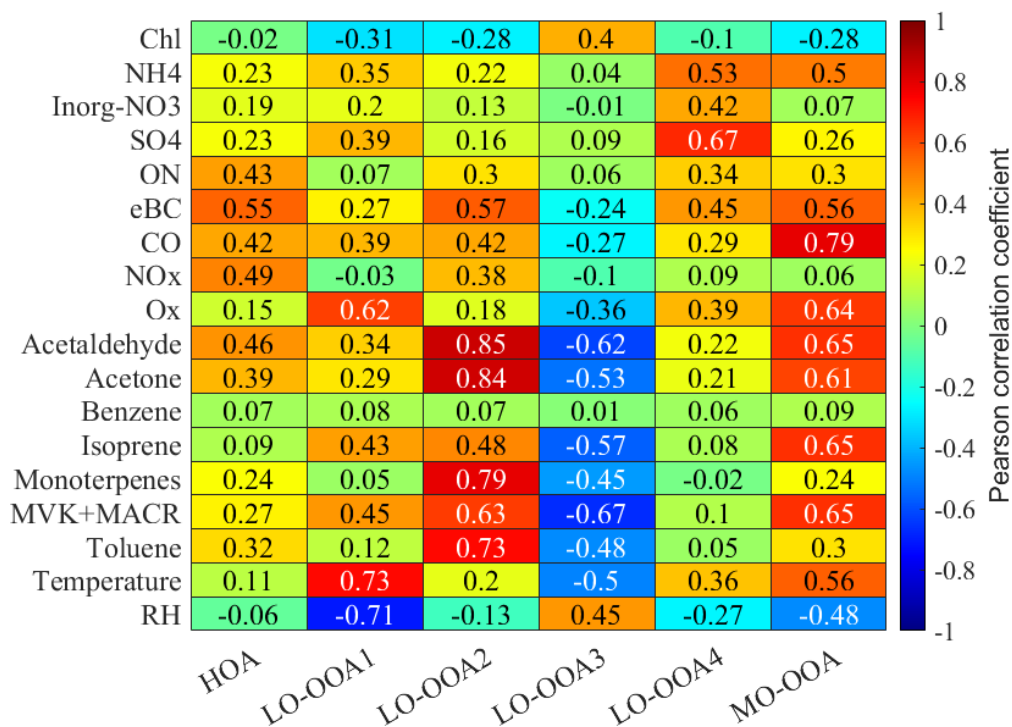


Figure 5: Pearson correlation coefficient (r) between the PMF OA factors and the external tracers.

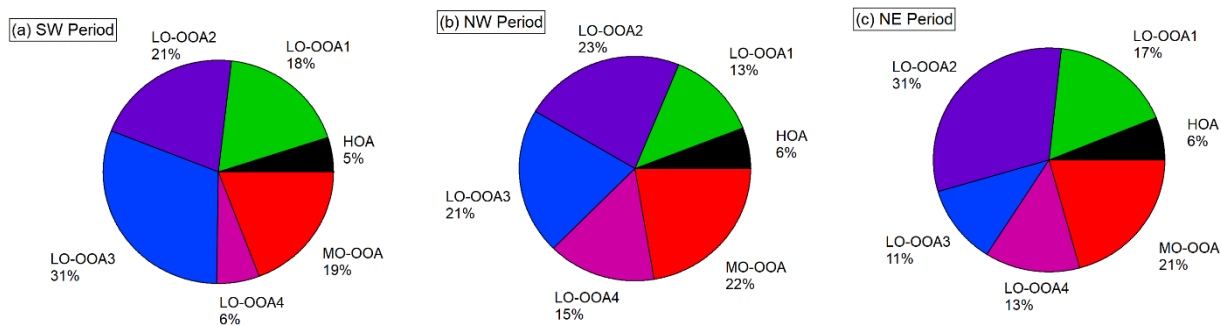


Figure 6: Pie charts for the mass fractions of different PMF OA factors during the three different air mass dominated periods

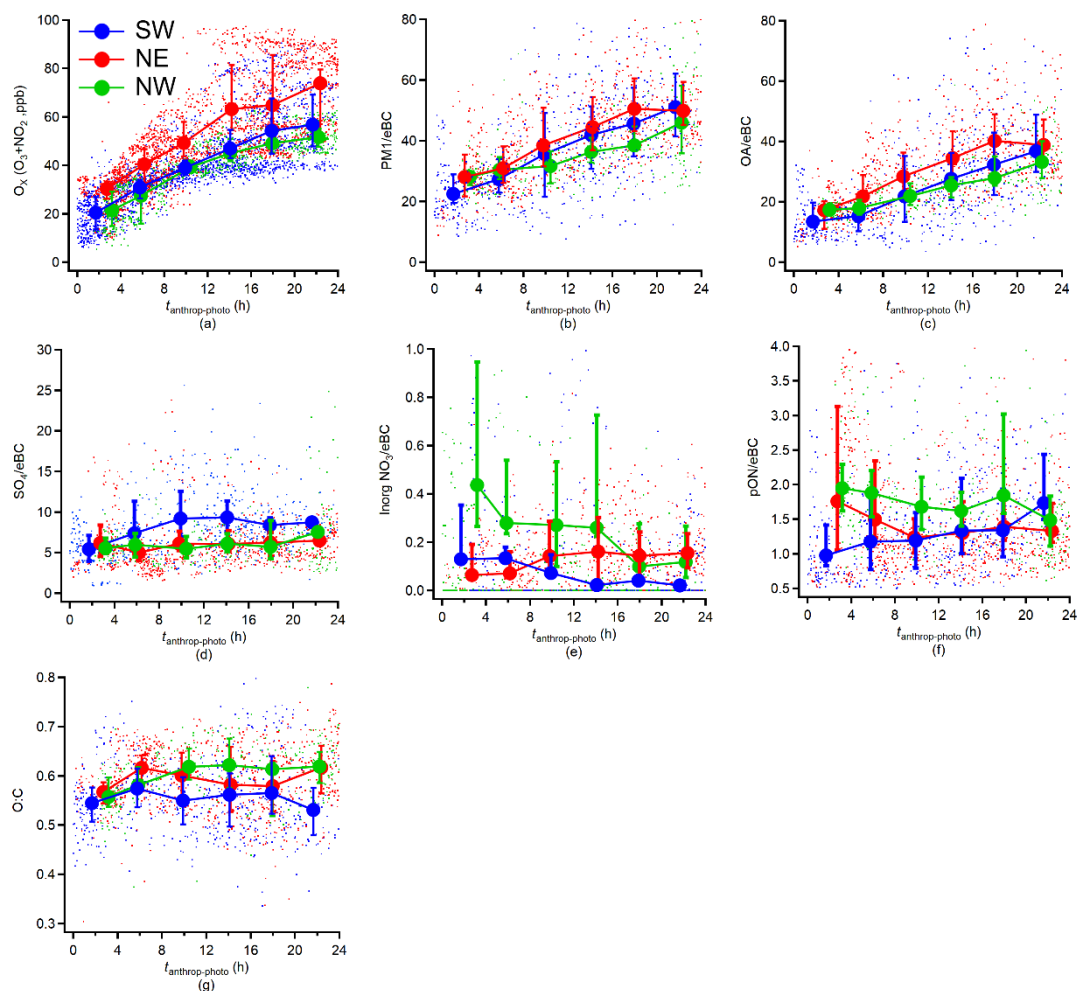
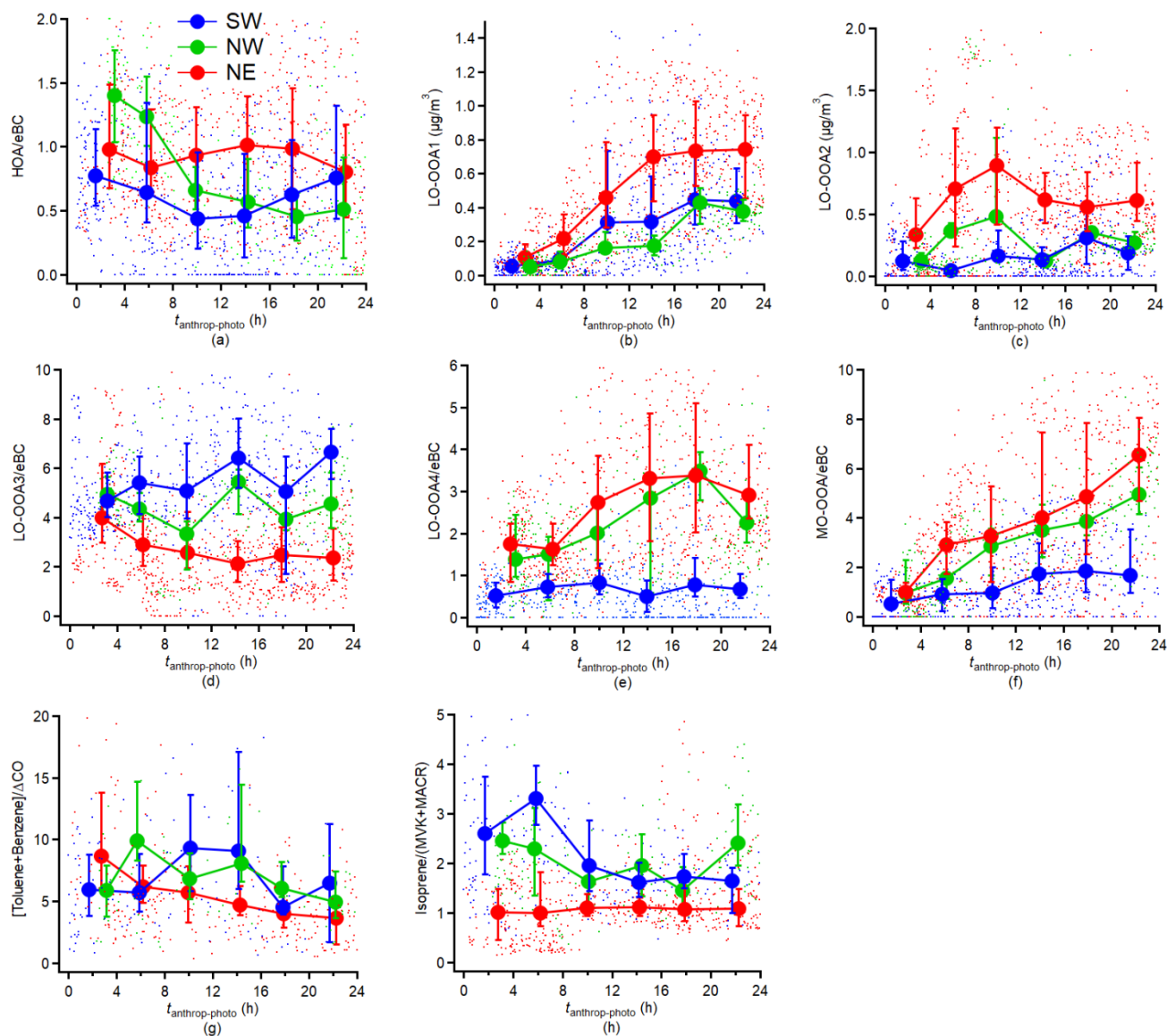


Figure 7: Variations in aerosol compositions concentrations: (a) O_x (O_3+NO_2) (b) PM_1 (c) OA (d) Sulfate (e) Inorganic nitrate (f) particulate Organic Nitrate (pON) (g) O:C ratio measured by HR-AMS as a function of $t_{\text{anthrop-photo}}$. The results are averaged into four-hour intervals along $t_{\text{anthrop-photo}}$ and the error bar indicates the 25th and 75th percentiles, respectively.



865 **Figure 8: Variations in (a-f) HR-AMS PMF-derived factors normalised or non-normalised concentrations; (g) Sum of Toluene and Benzene normalised concentration; (h) ratio between isoprene and MVK+MACR as a function of $t_{\text{anthrop-photo}}$. The results are averaged into four-hour intervals along $t_{\text{anthrop-photo}}$ and the error bar indicates the 25th and 75th percentiles, respectively.**

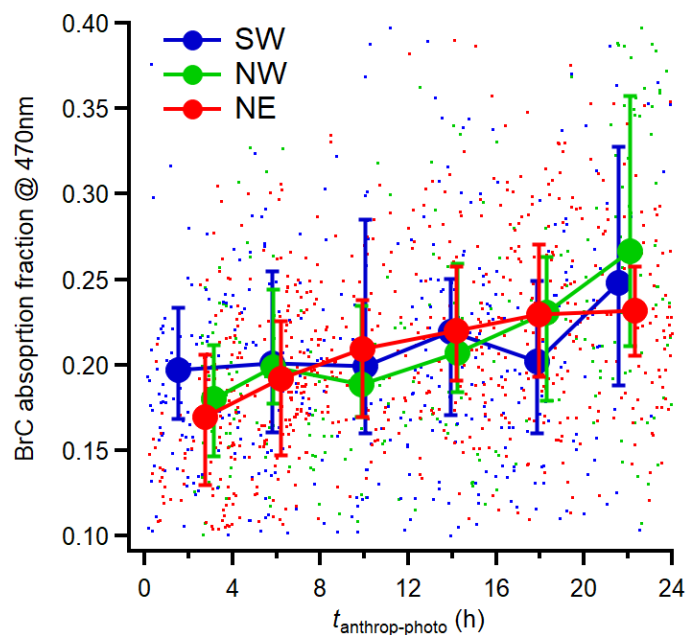


Figure 9: Variations of absorption fraction of BrC at 470 nm as a function of $t_{\text{anthrop-photo}}$. The results are averaged into four-hour intervals along t_{photo} and the error bar indicates the 25th and 75th percentiles, respectively.

$\sigma_{\text{abs BrC},470}$ ($R^2 = 0.54$)		
HR-AMS PMF factor	Regression coefficient	Partial correlation coefficient
a_i		
HOA	0.47	0.53
LO-OOA1	-	-
LO-OOA2	0.04	0.58
LO-OOA3	0.57	-0.25
LO-OOA4	0.30	0.55
MO-OOA	0.40	0.86
Intercept		-0.13

Table 1. Results of multiple linear regression (MLR) between $\sigma_{\text{abs BrC},470}$ and individual PMF-derived factors. The final regression excludes the LO-OOA1 due to its negative regression coefficient value (-0.06). The Variance Inflation Factors (VIF) for HOA, LO-OOA2, LO-OOA3, LO-OOA4, and MO-OOA were 1.48, 1.16, 1.71, 2.27 and 1.31, respectively. Results include all the PMF-derived factors are presented in Table S2 in the supplementary.