



Two-year-long high-time-resolution apportionment of primary and secondary carbonaceous aerosols in the Los Angeles Basin using an advanced total carbon–black carbon (TC–BC(λ)) method

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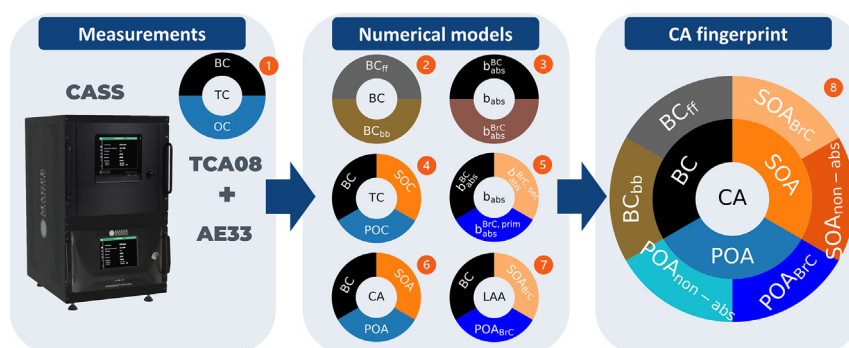
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HIGHLIGHTS

- A new method for carbonaceous aerosol apportionment into six components
- Focus on the primary or secondary origin and light absorption properties
- Long-term (2 years) measurement campaign in two locations in the Los Angeles Basin
- High-time-resolution apportionment allows studying diurnal profiles.
- Comparable results on both sites with similar seasonal patterns

GRAPHICAL ABSTRACT



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ABSTRACT

In recent years, carbonaceous aerosols (CA) have been recognized as a significant contributor to the concentration of particles smaller than $2.5 \mu\text{m}$ (i.e., $\text{PM}_{2.5}$), with a negative impact on public health and Earth's radiative balance. In this study, we present a method for CA apportionment based on high-time-resolution measurements of total carbon (TC), black carbon (BC), and spectral dependence of absorption coefficient using a recently developed Carbonaceous Aerosol Speciation System (CASS). Two-year-long CA measurements at two different locations within California's Los Angeles Basin are presented. CA was apportioned based on its optical absorption properties, organic or elemental carbon composition, and primary or secondary origin. We found that the secondary organic aerosols (SOA), on average, represent >50 % of CA in the study area, presumably resulting from the oxidation of anthropogenic and biogenic volatile organic components. Remarkable peaks of SOA in summer afternoons were observed, with a fractional contribution of up to 90 %. On the other hand, the peak of primary emitted CA, consisting of BC and primary organic aerosol (POA), contributed >80 % to the CA during morning rush hours on winter working days. The light absorption of BC dominated over the brown carbon (BrC), which contributed to 20 % and 10 % of optical absorption at the lower wavelength of 370 nm during winter nights and summer afternoons, respectively. The highest contribution of BrC, up to 50 %, was observed during the wildfire periods. Although the uncertainty levels can be high for some CA components (such as split between primary emitted and secondary formed BrC during winter nights), further research focused on the optical properties of CA at different locations may help to better constrain the parameters used in CA

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apportionment studies. We believe that the CASS system combined with the apportionment method presented in this study can offer simplified and cost-effective insights into the composition of carbonaceous aerosols.

1. Introduction

Carbonaceous aerosols (CA) are characterized by extreme diversity and comprise a large fraction of ambient fine particulate matter (PM_{2.5}), which acts as an atmospheric pollutant with critical local, regional, and global importance. The composition of CA provides a characteristic “fingerprint” that indicates the sources of airborne particulate matter. Role of CA in different atmospheric processes such as radiative forcing (Bond et al., 2013; IPCC, 2013), heterogeneous reactions, cloud formation, and regional visibility degradation, along with their potential adverse impact on human health (Daellenbach et al., 2020; Tomašek et al., 2021; WHO, 2021), has resulted in increasing attention in the scientific community. Recent epidemiological and toxicological studies have indicated that primary emitted and secondarily formed aerosols from anthropogenic precursors may be relatively more hazardous than other PM_{2.5} components (Chowdhury et al., 2022). Furthermore, the radiative effect of CA is the most uncertain among all climate forcers (Ferrero et al., 2021b; Hems et al., 2021; June et al., 2020; Liu et al., 2020; Saleh, 2020; Sun et al., 2021). Owing to the complex chemical and physical properties of CA, the underlying processes controlling the overall impact of CA on climate and human health are still unclear. A lack of long-term, highly time-resolved data on CA components represents an additional limiting factor when studying the impact of specific constituents and their synergistic effects. Thus, adequate online and high-time-resolution apportionment methods for CA are needed to identify their main sources and formation mechanisms and to identify the components with the highest impact on public health and climate forcing.

The use of different measurement techniques (optical and thermo-optical) to determine CA and its components can provide a comprehensive set of information (Massabò and Prati, 2021). Standardized thermo-optical measurements, developed by Huntzicker et al. (1982) and updated with several changes in thermal protocols (such as IMPROVE (Chen et al., 2015; Chow et al., 1993), NIOSH (Birch and Cary, 1996), and EUSAAR2 (Cavalli et al., 2010)), are generally used to quantify the aerosol carbon content in the elemental (EC–elemental carbon) and organic forms (OC–organic carbon). Standardized laboratory OC–EC analyses are time- and manpower-consuming and are limited to high-time-resolution short-term campaigns or longer campaigns with lower time resolutions from 24 h up to a week. Further, these measurements are prone to artifacts owing to the charring of organic compounds, which introduces different uncertainty levels depending on the PM composition (Massabò et al., 2016; Zhang et al., 2021). High-time-resolution determination of non-refractory submicron aerosols, focusing on the source apportionment of organic aerosols, is typically performed using an Aerosol Chemical Speciation Monitor (ACSM) coupled with positive matrix factorization (PMF) analysis (Fröhlich et al., 2015; Hopke et al., 2020). This analysis requires skilled professionals, limiting its wider applicability for long-term measurements through national air quality monitoring networks. Recently, the simplified TC–BC(λ) method (Rigler et al., 2020) was introduced for real-time, high-time-resolution determination of total carbon (TC) and black carbon (BC). The Carbonaceous Aerosol Speciation System (CASS, Aerosol d.o.o., Slovenia, EU) was used for this method, where the thermal approach of the Total Carbon Analyzer TCA08 (Rigler et al., 2020) for TC determination was coupled with the optical method of the Aethelometer AE33 (Drinovec et al., 2015) for multiwavelength absorption measurements for the determination of black carbon (BC) and brown carbon (BrC). The advantages of using CASS compared to online and offline OC/EC analyzers include a high time resolution, no sampling dead time, and online filter-loading effect compensation for BC measurements. As the thermal measurements are performed without a fragile quartz cross oven, high-purity gases, and a catalyst, they are suitable for field campaigns (Rigler et al., 2020).

This work presents the first long-term field campaign using CASS for the highly time-resolved apportionment of CA by incorporating various already established techniques for the apportionment of sources and species. The characterization of CA and its sources and formation mechanisms in the Los Angeles (LA) Basin have been widely studied (Bahreini et al., 2012; Docherty et al., 2008; Hayes et al., 2013; Polidori et al., 2007; Saffari et al., 2016; Soleimanian et al., 2020; Turpin and Huntzicker, 1995; Zhang et al., 2013). However, most of these studies were based on short-term measurement campaigns lasting up to only a few months. In contrast, in this study, a two-year-long CA measurement campaign with a newly developed set of instrumentation was presented at two contrasting sites in the LA Basin. High-time-resolution measurements of TC, BC, and the implementation of a novel approach presented in this paper allowed us to study the diurnal, seasonal, and day-of-week trends of primary, secondary, light-absorbing, and non-absorbing CA components. The results are presented along with complementary air quality measurements (such as gaseous pollutants, ultrafine particles, and PM_{2.5}) to further corroborate the observed trends.

1.1. Carbonaceous components and terminology

Specific attention needs to be paid to the use of appropriate terminology while comparing various CA component measurement techniques based on their chemical and physical properties (Table 1). The terminology used in this study is summarized in this section. Carbonaceous aerosol (CA) or carbonaceous matter (CM) includes an organic fraction, organic aerosol (OA), or organic matter (OM), and a refractory, chemically inert, and strongly light-absorbing fraction referred to as elemental carbon (EC, thermal-optical measurement) or black carbon (BC, optical measurement). The masses of carbon atoms in CA and OA are called total carbon (TC) and organic carbon (OC), respectively. An additional fraction of CA is composed of carbonate minerals that contribute to the carbonate carbon (CC). It should be noted that the CC fraction is negligible for PM_{2.5} total carbon measurements, especially in the areas unaffected by mineral dust (Chow and Watson, 2002; Drinovec et al., 2020).

BC and EC are often used interchangeably; nevertheless, in this study, BC was used exclusively to describe the refractory strong-absorbing fraction of CA. BC has a well-defined chemical structure and is exclusively emitted from incomplete combustion; thus, it has only a primary origin (Bond et al., 2013). In this study, EC was used only for the EC-to-BC inter-comparison of the thermal-optical and optical methods. The reader is referred to Petzold et al. (2013) and Rigler et al. (2020) for detailed information on BC and EC terminology and relationship.

In contrast to the refractory fraction of CA, chemical composition of OA is highly diverse and composed of many complex molecular structures. OA is directly emitted as primary organic aerosols (POA) in particulate form by combustion and from biogenic sources, or it can have a secondary origin, namely secondary organic aerosols (SOA), formed due to oxidation of volatile organic compounds (VOCs) in the atmosphere. VOCs can be emitted from biogenic sources, such as isoprene, monoterpenes, and sesquiterpenes (Fry et al., 2018), combustion-related anthropogenic sources (benzene and toluene as traffic-related, and catechol as biomass burning-related VOC); or volatile chemical products (VCPs) (Seltzer et al., 2021). Although several pathways of SOA formation have been discussed in the published literature, two major pathways are commonly accepted: the photooxidation of VOC, which prevails during daylight hours and peaks around noon (Saffari et al., 2016; Wu et al., 2019; Zhang et al., 2018), with hydroxyl radicals (OH) and ozone (O₃) as the main oxidant species (He et al., 2021). The second pathway of SOA formation, especially evident during winter nights, is driven by aqueous-phase reactions when NO₃ radicals act as the dominant oxidants (He et al., 2021; Jiang et al., 2019; Mayorga et al., 2021;

Table 1

The terminology describing components of carbonaceous aerosol determined by various measurement techniques based on its chemical and physical properties.

AAE _{bb}	Absorption Ångström exponents for biomass burning BC component
AAE _{BC}	Absorption Ångström exponents of pure BC
AAE _{BrC}	Absorption Ångström exponents of brC
AAE _{ff}	Absorption Ångström exponents for fossil fuel BC component
b _{abs} (λ)	Wavelength-dependent optical absorption coefficient (m ⁻¹)
b _{BC} (λ)	Wavelength-dependent optical absorption coefficient on BC (m ⁻¹)
b _{BrC} (λ)	Wavelength-dependent optical absorption coefficient on brC (m ⁻¹)
b _{BrC, prim} (λ)	Wavelength-dependent optical absorption coefficient on primary brC (m ⁻¹)
b _{BrC, sec} (λ)	Wavelength-dependent optical absorption coefficient on secondary brC (m ⁻¹)
BC	Black carbon (μg/m ³)
BC _{bb}	Biomass burning BC component (μg/m ³)
BC _{ff}	Fossil fuel BC component (μg/m ³)
BrC	Brown carbon or light-absorbing OA (μg/m ³)
CA	Carbonaceous aerosol; also carbonaceous matter, CM (μg/m ³)
CC	Carbonate carbon (μg/m ³)
EC	Elemental carbon (μg/m ³)
LA	Los angeles
LAA	Light-absorbing aerosols, the sum of BC, brC and CC (μg/m ³)
MAC _{BC}	Mass absorption cross section for BC (m ² /g)
MAC _{BrC, prim}	Mass absorption cross section for poa _{brC} (m ² /g)
MAC _{BrC, sec}	Mass absorption cross section for soa _{brC} (m ² /g)
OA	Organic aerosol; also organic matter, OM (μg/m ³)
OA/OC	Organic aerosol to organic carbon ratio, equal to OM/OC
OA _{non-abs}	Non-light-absorbing OA (μg/m ³)
OC	Organic carbon, the carbon content in OA (μg/m ³)
(OC/EC) _{prim}	Primary OC-to-EC ratio used for separation between POC and SOC
OM/OC	Organic matter to organic carbon ratio, equal to OA/OC
PBL	Planetary boundary layer
PM _{2.5}	Fine particulate matter with aerodynamic diameter below 2.5 μm (μg/m ³)
POA	Primary organic aerosol (μg/m ³)
POA/POC	Primary organic aerosol to primary organic carbon ratio
POA _{BrC}	Primary brC (μg/m ³)
POA _{non-abs}	Primary non-light-absorbing OA (μg/m ³)
POC	Primary organic carbon, the carbon content of POA (μg/m ³)
SOA	Secondary organic aerosol; also secondary CA (μg/m ³)
SOA/SOC	Secondary organic aerosol to secondary organic carbon ratio
SOA _{BrC}	Secondary brC (μg/m ³)
SOA _{non-abs}	Secondary non-light-absorbing OA (μg/m ³)
SOC	Secondary organic carbon, the carbon content of SOA (μg/m ³)
TC	Total carbon, the carbon content in CA (μg/m ³)
VOC	Volatile organic compounds (ppm)

Saffari et al., 2016; Soleimanian et al., 2020; Wu et al., 2019; Zhang et al., 2018, 2020). As all of the available VOCs are usually not oxidized into SOA owing to lack of oxidant availability, the remaining VOCs have potential for SOA formation (Liu et al., 2021). Therefore, reducing anthropogenic VOC emission does not necessarily result in SOA reduction. For example, (Via et al., 2021) recently reported increased SOA levels in Barcelona regardless of anthropogenic pollutant reduction.

Organic aerosols can be further divided into light-absorbing OA, also known as brown carbon (BrC) (Andreae and Gelencsér, 2006; Liu et al., 2020), and non-light-absorbing OA (OA_{non-abs}), both of which have a possible primary and secondary origin (POA_{BrC}, SOA_{BrC}, POA_{non-abs}, SOA_{non-abs}, respectively). While OA_{non-abs} has a cooling effect due to the scattering of sunlight, BrC absorbs solar radiation mainly in the ultraviolet region (Laskin et al., 2015; Moise et al., 2015). Total of BrC and BC, together with CC, represents the light-absorbing part of CA, known as light-absorbing aerosols (LAA). BC light absorption is relatively well-characterized and it is the second most important anthropogenic climate-forcing agent after CO₂ (Bond et al., 2013; IPCC, 2013). In contrast, BrC can significantly enhance light absorption at shorter wavelengths (Andreae and Gelencsér, 2006; Sun et al., 2021).

2. Materials and methods

2.1. Sampling period and sites

Measurements were conducted at two different sites in the LA Basin, as shown in Fig. B.1 (Supplement B). Central LA site is in the downtown LA

area surrounded by highways and densely populated areas affected mainly by primary sources. The station in Riverside is located in the inland region of the LA Basin (approximately 75 km to E from downtown LA) and is subjected to secondary particle formation and aging processes as well as primary combustion particles.

Sampling was conducted from March 2018 to March 2020. Mild winters and hot summers are typical of the LA Basin. The monthly median ambient temperature ranged from 12 °C to 25 °C in Central LA and from 10 °C to 27 °C in Riverside (Fig. B.2, Supplement B) during the study period. At the same time, the monthly median relative humidity varied between 45 % and 75 % in Central LA and between 32 % and 72 % in Riverside. Calm winds are typical at night for both the stations, with wind speeds of approximately 1 m/s (Fig. B.3, Supplement B). Higher wind speeds of up to 4 m/s were observed in the afternoon during spring, summer, and fall, while the change in wind speed in afternoon was not as remarkable in winter. In Central LA, the wind shifts from westerly/southwesterly during the day to northerly/northeasterly at night. There are no considerable changes in the wind direction in Riverside as it is located further inland. Meteorological data were obtained from reference meteorological monitors operated by the South Coast AQMD at the same monitoring sites (Central LA and Riverside).

2.2. Measurement and setup

2.2.1. TC-BC(λ) method

Measurements of TC and BC(λ) were performed at both sites using the Carbonaceous Aerosol Speciation System (CASS, Aerosol d.o.o., Slovenia, EU), which comprises of a Total Carbon Analyzer TCA08 (Rigler et al., 2020) in tandem with an Aethalometer AE33 (Drinovec et al., 2015). TCA08 was operated at a 1-h time resolution, sampling the PM_{2.5} fraction at 16.7 L min⁻¹. TCA08 measures the concentration of TC by the rapid combustion of PM collected on a quartz filter. The sample was heated almost instantaneously to 940 °C, at which the carbonaceous compounds were efficiently combusted to CO₂. The pulse of CO₂ created during the combustion phase of the analysis was detected as a large transient increase above the CO₂ level in ambient air used as the carrier gas. The limit of detection (LoD) of TCA08 is 0.3 μg/m³. To minimize the VOC adsorption (positive) sampling artifact and quantify its magnitude, a denuder was used with TCA08, which was tested regularly for efficiency and replaced if necessary. Detailed instrument performance, maintenance procedures, and specifications have been published elsewhere (Rigler et al., 2020; TCA08, 2022).

Tandem Aethalometer AE33 measures the aerosol light absorption and corresponding equivalent BC concentration at seven wavelengths (namely 370, 470, 520, 590, 660, 880, and 950 nm) with LoD equal to 0.03 μg/m³. Sample was collected on a TFE-coated glass fiber filter with a flow rate of 5 L min⁻¹ and a PM_{2.5} size-selective inlet. Light attenuation was measured at a time resolution of 1 min.

A multiple scattering parameter C is used to convert the attenuation coefficient (b_{ATN}) measured by the Aethalometer to the absorption coefficient (b_{abs}):

$$b_{abs}(\lambda, t) = \frac{b_{ATN}(\lambda, t)}{C} \quad (1)$$

where b_{ATN} and b_{abs} are wavelength- and time-dependent, as indicated by the index (λ, t). C is applied to account for the multiple scattering effects in the filter matrix, and mostly describes the characteristics of the filter tape used in the instrument. Yus-Díez et al. (2021) reported the wavelength dependence of C for remote sites, characterized by high single-scattering albedo, while it was not considerable for urban and urban background sites. Consequently, a constant, wavelength-independent C value of 1.39 was used in this study, recommended by the manufacturer based on the use of tape 8060.

AE33 uses a “dual-spot” methodology to correct the filter-loading effect in real time (Drinovec et al., 2015). The mass absorption cross section

(MAC_{BC}) is used to convert the absorption coefficient to the equivalent BC mass as shown in the Eq. (2).

$$BC(t) = \frac{b_{abs}(880 \text{ nm}, t)}{MAC_{BC}(880 \text{ nm})} \quad (2)$$

MAC_{BC} can be site-specific and, if available, should be taken from the existing literature for a specific site or estimated based on standardized collocated measurements. In this study, a default value of 7.77 m²/g was used for MAC_{BC} (880 nm) in Eq. (2) as provided by the manufacturer. It was later evaluated as suitable based on the offline EC measurements on 24 h time-integrated filters with IMPROVE A protocol with reflectance correction (Fig. B.4, Supplement B).

The OC fraction of carbonaceous aerosols was calculated as the difference between TC and BC:

$$OC(t) = TC(t) - BC(t). \quad (3)$$

For simplification, BC was used instead of the equivalent elemental carbon $eEC = bBC$ (Rigler et al., 2020). The determined proportionality parameter b is site- and source-specific and depends largely on the thermal protocol used to determine the EC fraction using a conventional OC/EC method (Ahmed et al., 2009; Jeong et al., 2004; Spada and Hyslop, 2018; Zhang et al., 2021). For example, Zhang et al. (2021) reported a 12 % mean bias of EC measurements in inter-model intercomparison using the same thermal protocol IMPROVE A. Based on the results in Fig. B.4, Supplement B, the difference between BC and offline EC is below the expected uncertainty of EC measurements. Thus, b was considered as unity in this study.

The CA concentration is composed of BC and OA as shown in the Eq. (4).

$$CA(t) = OA(t) + BC(t) \quad (4)$$

where the site-specific OA/OC ratio can transform OC to OA mass. If the OA/OC ratio is known, the highly time-resolved CA can be directly computed from the CASS measurements of TC(t) and BC(t) as shown in the Eq. (5).

$$CA(t) = TC(t) \cdot \left(\frac{OA}{OC} \right) - BC(t) \cdot \left[\left(\frac{OA}{OC} \right) - 1 \right] \quad (5)$$

2.2.2. Complementary / collocated measurements

Offline OC and EC concentrations were measured using the thermal optical reflectance (TOR) method on PM_{2.5}, collected every 3rd day on quartz filters as part of the Chemical Speciation Network (CSN) (Gorham et al., 2021).

Concentrations of levoglucosan were measured using gas chromatography mass spectrometry (GC-MS) on PM_{2.5} samples collected every 6th day on quartz filters as part of the fifth iteration of the Multiple Air Toxics Exposure Study V ("MATES V", 2021).

Hourly concentrations of PM_{2.5}, CO, and NO_x were measured using Met One BAM 1020, Teledyne 300EU, and Teledyne T500U instruments, respectively.

A water-based condensation particle counter (CPC) (Teledyne Advance Pollution Instrumentation, TAPI, Model 651, USA) was used to measure the total particle concentration in the range of 7–600 nm particle diameter at 1-min time resolution (referred to as UFP hereafter). The concentrations were averaged over an hourly time resolution. The hours with <75 % data completeness were discarded from further analysis.

2.2.3. Data analysis

The CASS measurements were performed at minute and hourly time resolutions for BC(t) and TC(t), respectively. Following the standard operational procedure, the first two TCA08 analyses after restarting the instrument were removed from the dataset, and filter integrity was checked regularly. Additionally, a denuder efficiency test was performed several times during the campaign.

Rare cases with a frequency ≤ 1 % in all situations when the measured BC(t) was higher than TC(t) were also discarded. A possible reason is that some large particles come through the cyclone and cause an immediate strong light attenuation in the Aethalometer, which affects the 1-h average. After data validation, 2-h time-averaging was used for all CASS data to minimize possible measurement variations between the combustion chambers of the TCA08.

All the observations were reported in local time (Pacific Daylight Saving Time (PDT)) to properly describe the diurnal behavior of anthropogenic aerosol sources between different seasons.

Data manipulation and graphical presentation were done using python libraries: pandas, numpy (Harris et al., 2020), scipy, matplotlib, and basemap. The reduced major axis regression (RMA), implemented in the pylr python library, was used for the regression analyses to introduce error of the independent variables in the regression.

2.3. Carbonaceous aerosol apportionment

The determination of different components of carbonaceous aerosols relies on the specific information available in the measured dataset. Simultaneous measurements of BC and TC resulted in a high-time-resolution OC dataset. Spectrally resolved optical absorption measurements allowed for further differentiation of BrC and BC, which are closely linked to emission sources. Further information on the primary and secondary components takes advantage of highly time-resolved measurements, which provide important insights in the temporal behavior of different components. By applying different apportionment and numerical models from published studies, the CA was finally apportioned into six components as shown in the Eq. (6).

$$CA(t) = BC_{ff}(t) + BC_{bb}(t) + POA_{non-abs}(t) + POA_{BrC}(t) + SOA_{non-abs}(t) + SOA_{BrC}(t) \quad (6)$$

We used eight steps (Fig. 1) to apportion CA into six components. In Step 1, the TC(t) - BC(t) method is used to obtain OC(t), as explained in Section 2.2.1 (Eqs. (3)–(5)).

In Step 2, the widely used Aethalometer model (Sandradewi et al., 2008; Zotter et al., 2017) was applied to apportion BC(t) to its fossil fuel (BC_{ff}(t)) and biomass burning (BC_{bb}(t)) components. The Aethalometer model has an analytical solution, as explained in detail in Supplement A.1. The model has two free parameters, an a priori assumed AAE pair (AAE_{ff}-AAE_{bb}), which describes the specific optical characteristics of both the BC sources, fossil fuel, and biomass burning. The source-specific AAE values used for source apportionment were representative of the location and type of combustion. In our study, levoglucosan measurements, together with the Fuller approach, were used to determine site-specific values for AAE_{ff} and AAE_{bb} (Favez et al., 2010; Fuller et al., 2014; Helin et al., 2018; Martinsson et al., 2017; Titos et al., 2017). Finally, the most appropriate choice of the AAE pair for both sites was 1.15 and 2.05 for AAE_{ff} and AAE_{bb}, respectively (Fig. A.1, Supplement A).

The BrC model was used in Step 3 to separate the wavelength-dependent optical absorption of BC and BrC (Chow et al., 2018; Gilardoni et al., 2020; Massabò et al., 2015; Qin et al., 2018; Tian et al., 2019; Wang et al., 2016, 2020; Wu et al., 2021; Zhang et al., 2020). Based on the assumption that BC is the only light absorber at 880 nm, AAE_{BC} remains as the only free parameter. As diesel exhaust represents the nearest approximation of pure BC and it is expected that fossil fuels will not contribute to BrC (Massabò et al., 2015), AAE_{BC} was assumed to be equal to AAE_{ff} from the Aethalometer model. The details of the BrC model implementation are provided in Supplement A.2.

In Step 4, the EC tracer method (Turpin and Huntzicker, 1995) was used to split the OC(t) based on its origin into primary (POC(t)) and secondary (SOC(t)) components. In this study, we used BC as the optically determined EC. Therefore, the method will be referred to as "BC tracer method" hereafter. This method has one free parameter, the (OC/BC)_{prim} ratio, which is expected to be site (source)- and season-dependent. The minimum R-

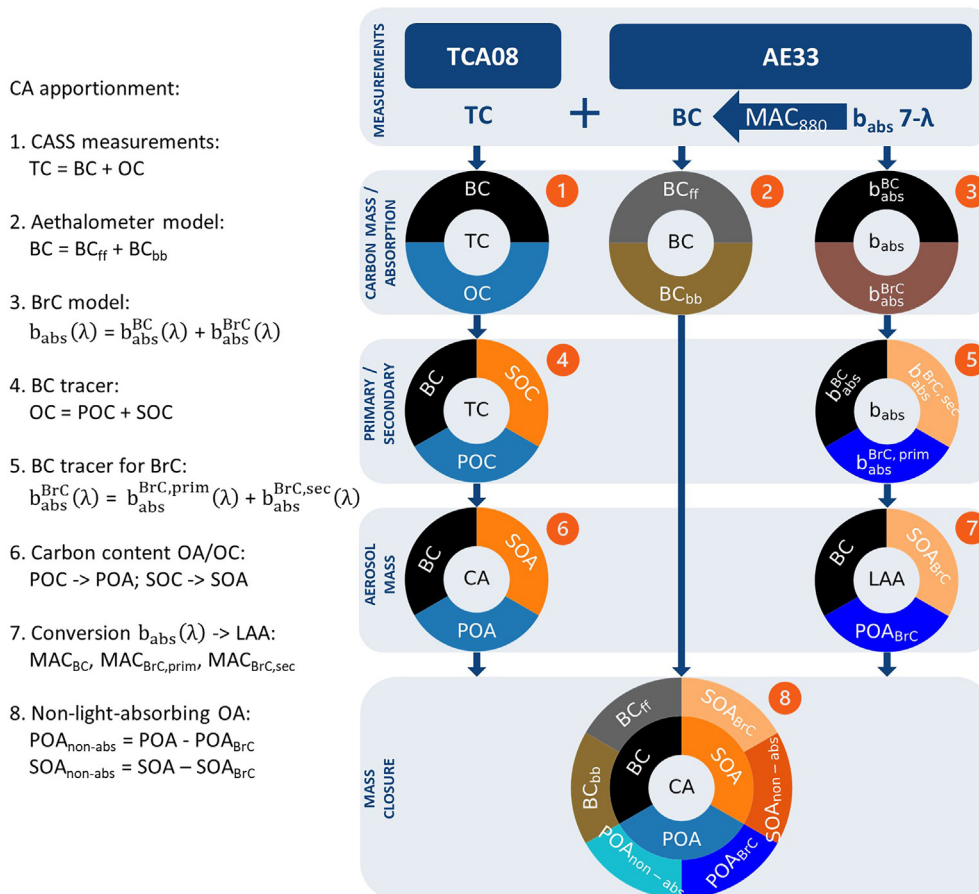


Fig. 1. Flowchart for CA apportionment to six components using the advanced TC-BC method.

squared (MRS) method was used for optimal (OC/BC)_{prim} determination (Hu et al., 2012; Millet et al., 2005; Wu et al., 2019; Wu and Yu, 2016). The main assumption of this method is that BC and POC are emitted from the same source, and they should be well correlated, while the correlation between BC and SOC should be low because of different formation pathways. The details of the implementation are provided in Supplement A.3.

The modified BC tracer method (Liakakou et al., 2020; Wang et al., 2019a, 2019b, 2020) was used in Step 5 to split the light absorption of BrC into its primary or secondary fractions. A detailed description of this methodology is provided in Supplement A.4. Briefly, the method is based on the assumption that the only light-absorbing material formed secondarily is BrC, which can be defined by the same principle used in the BC tracer method for the POC/SOC split.

In Step 6, the POA(t) and SOA(t) mass concentrations were estimated based on the POC(t) and SOC(t) mass concentrations using the specific OA/OC ratio. The OA/OC ratio is site-dependent, and is usually lower for fresh traffic emissions and higher for aged, oxygenated OA (Table A.1, Supplement A). Turpin and Lim (2001) reported minor differences in OA/OC ratios between sites in the Central LA and Riverside (1.65 and 1.77, respectively). In general, Central LA is more exposed to primary emissions with a lower OA/OC ratio, while Riverside is located in a downwind area and receptors of more aged and photochemically processed aerosols. To consider these potential differences, we used different OA/OC ratios for primary and secondary OA as suggested in a study by Docherty et al. (2008), where the ratios 1.2 and 1.8 for POA/POC and SOA/SOC, respectively, were used in the LA Basin. The POA(t) and SOA(t) mass concentrations were estimated from their carbon content as shown in the Eq. (7).

$$\text{POA}(t) = \text{POC}(t) \cdot \left(\frac{\text{POA}}{\text{POC}} \right) \text{ and } \text{SOA}(t) = \text{SOC}(t) \cdot \left(\frac{\text{SOA}}{\text{SOC}} \right) \quad (7)$$

In Step 7, the mass absorption cross section (MAC) from published studies was used to estimate the mass concentration of POA_{BrC}(t) and SOA_{BrC}(t) from the optical absorption $b_{\text{abs}}^{\text{BrC,prim}}(\lambda)$ and $b_{\text{abs}}^{\text{BrC,sec}}(\lambda)$:

$$\text{POA}_{\text{BrC}}(t) = \frac{b_{\text{abs}}^{\text{BrC,prim}}(\lambda, t)}{\text{MAC}_{\text{BrC,prim}}(\lambda)} \text{ and } \text{SOA}_{\text{BrC}}(t) = \frac{b_{\text{abs}}^{\text{BrC,sec}}(\lambda, t)}{\text{MAC}_{\text{BrC,sec}}(\lambda)} \quad (8)$$

Usually, the lowest wavelength ($\lambda = 370$ nm for the Aethalometer) is the most appropriate channel for the BrC mass concentration estimation because the strongest absorption signal from BrC is observed at this wavelength. Owing to the complex and highly varying chemical composition of BrC, complete quantitation of its mass is impossible using current analytical methods (Lack and Cappa, 2010; Laskin et al., 2015; Tian et al., 2019), leading to a wide range of possible MAC_{BrC} reported in the literature (Table A.2, Supplement A). The different chemical compositions of primary and secondary BrC lead to different MAC values (Kumar et al., 2018; Qin et al., 2018; Wang et al., 2019b; Zhang et al., 2020). In this study, MAC values of 5.5 m²/g and 2.4 m²/g were used for primary and secondary BrC, respectively. These MAC values were obtained from chamber experiments reported by Kumar et al. (2018) and were later evaluated as suitable for field studies in the work of Zhang et al. (2020).

The first seven steps result in the mass of light-absorbing organic aerosol and the mass of the total OA apportioned to their primary and secondary origin. If all OA would absorb light, OA_{BrC} (Eq. (8)) is equal to OA (Eq. (7)). However, the difference between OA and OA_{BrC} implies the presence of a non-light-absorbing fraction of OA. In the last step (Step 8), the non-light-absorbing components of the primary and secondary aerosols were estimated based on the difference between the results from Eqs. (7) and (8).

$$\text{POA}_{\text{non-abs}}(t) = \text{POA}(t) - \text{POA}_{\text{BrC}}(t) \quad (9)$$

$$\text{SOA}_{\text{non-abs}}(t) = \text{SOA}(t) - \text{SOA}_{\text{BrC}}(t) \quad (10)$$

2.4. Uncertainty estimation

The final uncertainty of the advanced TC-BC method depends on the uncertainties of the measurements, namely the precision and accuracy, uncertainties of the applied assumptions, and uncertainties of the conversion factors (OA/OC, MAC) used in the calculations. In this section, the uncertainties of CASS measurements are estimated using independent standard measurements and combined with known uncertainties from the literature when independent validation is not possible. Uncertainties are then propagated for every step of the methodology presented in Fig. 1, and covariance is considered if the variables are correlated (Eq. (11)).

$$\sigma_C = \sqrt{\sigma_A^2 + \sigma_B^2 \pm 2\sigma_{AB}} \text{ if } C = A \pm B \quad (11)$$

where σ_A^2 and σ_B^2 are the variances of variables A and B, respectively, and σ_{AB} is the covariance between A and B.

A detailed evaluation of the uncertainty of TC, BC, and OC, determined using Total Carbon Analyzer TCA08 and Aethalometer AE33, was provided by Rigler et al. (2020). Briefly, the uncertainty of TC concentrations measured using TCA08 was estimated to be up to 10 % for the measured range of concentration, while the uncertainty for BC concentration measured using AE33 was considered to be 25 %, where the largest part of uncertainty arises from the selected MAC_{BC} and C values (Eqs. (1) and (2)). In this study, the high-time-resolution dataset measured using CASS was compared to the standardized offline OC/EC measurements performed using IMPROVE A thermal protocol on high-volume filter samples collected every 3rd day at both measurement sites (Fig. B.4, Supplement B). The highest difference in the slope from Fig. B.4, Supplement B, represents the uncertainty for Step 1 of the presented approach: 12 %, 15 %, and 6 % for $\text{TC}_{\text{offline}}\text{-TC}_{\text{CASS}}$, $\text{OC}_{\text{offline}}\text{-OC}_{\text{CASS}}$ and $\text{EC}_{\text{offline}}\text{-BC}_{\text{CASS}}$, respectively.

In Step 2 of the advanced TC-BC method, BC is apportioned to two sources, BC_{ff} and BC_{bb} , using the Aethalometer model. The performance assessment of the Aethalometer model by means of ^{14}C analysis, published by Zotter et al. (2017), estimated the uncertainty to be <10 %. Without the independent measurements of biomass burning and traffic contribution to BC, the uncertainty could be higher, up to 20 % (Healy et al., 2017). Nevertheless, the characteristic AAE_{ff} and AAE_{bb} values used in this study were determined by combining two independent measurements: NO_x and levoglucosan tracer methods (Fig. A.1, Supplement A). Consequently, the uncertainties in BC_{ff} and BC_{bb} were estimated to be 10 % in this study.

The BrC model was used in Step 3 to determine the absorption coefficient at 370 nm. Zhang et al. (2020) performed a sensitivity test of the BrC model for different AAE_{BrC} : 0.9, 1.0, and 1.1, leading to approximately 11 % uncertainty in absorption of BrC at 370 nm. In our calculations, AAE_{BrC} was equal to AAE_{ff} and was fixed at 1.15. The sensitivity test of the BrC model using $\text{AAE}_{\text{BrC}} = 1.10$ and $\text{AAE}_{\text{BrC}} = 1.20$ on our data yielded a discrepancy of 5 % in absorption coefficient of BrC at 370 nm, which is our estimated uncertainty for BrC absorption in Step 3.

The BC tracer method based on the MRS approach was applied in Step 4, which was used to split the OC into primary and secondary fractions. The results of SOC fraction were sensitive to the magnitude of the uncertainty of BC and OC measurements. Based on the work reported by Wu and Yu (2016), the uncertainty of SOC was estimated to be 17 %. Considering the positive correlation between OC and SOC, the uncertainty of POC is propagated by subtraction of SOC from OC, and was estimated to be 25 %.

Similar methodology as reported by Wu and Yu (2016) was used for the uncertainty estimation of the BC tracer model for the determination of the primary and secondary components of BrC absorption in Step 5. Based on the uncertainty of AAE_{BrC} in the brown carbon model above and the work of Wu and Yu (2016), the uncertainty of light absorption on secondary BrC was estimated to be 5 %. The light absorptions of BrC and secondary

BrC were positively correlated, and consequently, the uncertainty of light absorption on primary BrC was estimated to be 6 %.

The uncertainty estimation for organic aerosol mass from organic carbon measurements used in Step 6 is thoroughly discussed in the works of Aiken et al. (2008) and Turpin and Lim (2001). Turpin and Lim (2001) estimated the uncertainty of average molecular weight per carbon weight to be <5 %, and Aiken et al. (2008) reported the reconstruction of OM/OC values to have an average error of 6 %. Use of these values for our estimation resulted in 26 % and 18 % uncertainty in POA and SOA, respectively.

Unlike BC, whose light properties are well known and constant across the visible wavelength range and different emission sources, BrC is composed of a wide range of chemical compounds strongly depending on their sources and formation pathways, which exhibit highly variable, spectrally dependent optical properties. In Step 7, constant conversion factors (source- and season-independent) were assumed to convert the primary and secondary BrC absorption to mass concentration. To the best of our knowledge, there are no available data on the primary and secondary mass absorption cross sections for BrC in the LA Basin. Consequently, the constant values of $\text{MAC}_{\text{BrC,prim}} = 5.5 \text{ m}^2/\text{g}$ and $\text{MAC}_{\text{BrC,sec}} = 2.4 \text{ m}^2/\text{g}$ at 370 nm were obtained from the study by Kumar et al. (2018). To estimate the uncertainty of the MAC values, the standard deviation analysis from Kumar et al. (2018) was followed, which resulted in 22 % uncertainty for $\text{MAC}_{\text{BrC,prim}}$, and 63 % uncertainty for $\text{MAC}_{\text{BrC,sec}}$. This resulted in 23 % and 63 % uncertainties for POA_{BrC} and SOA_{BrC} , respectively.

Following the uncertainties in all steps mentioned above and considering their propagation, the uncertainties of $\text{POA}_{\text{non-abs}}$ and $\text{SOA}_{\text{non-abs}}$, the last step in the advanced TC-BC method, were estimated to be 28 % and 20 %, respectively. The uncertainties of all the components are listed in Table B.1, Supplement B.

3. Results and discussion

3.1. Overview of measurements

An overview of the two-year TC and BC concentration measurements using CASS is shown in Fig. 2a,b. The median BC [first quartile, third quartile] concentrations were $0.82 [0.46, 1.45] \mu\text{g}/\text{m}^3$ and $0.72 [0.41, 1.35] \mu\text{g}/\text{m}^3$ at Central LA and Riverside, respectively. While BC concentrations were slightly lower at Riverside than in Central LA, TC concentrations were slightly higher at Riverside, with median values of $3.50 [2.51, 5.07] \mu\text{g}/\text{m}^3$ and $3.54 [2.43, 5.14] \mu\text{g}/\text{m}^3$ at Central LA and Riverside, respectively. The TCA08 instrument maintenance was the reason for the long periods of missing TC data for Riverside (Fig. 2b).

Similar diurnal patterns of BC were observed for all seasons at both sites (Fig. 2c-j), with peaks during morning traffic rush hours and at night; the latter was observed particularly during cold seasons. In contrast, diurnal patterns of TC were found to be seasonally dependent at both sites. Wintertime TC peaks were observed during the nighttime, while summertime TC peaks were observed around noon. During winter, the enhanced nighttime TC concentrations can be explained by the combined effects of lower planetary boundary layer (PBL) heights, enhanced biomass burning activities for residential heating, and aqueous-phase SOA formation. The summertime mid-day TC peaks were mainly attributed to SOA formation owing to enhanced photooxidation. The summertime mid-day TC peak in Riverside is wider than the TC peak in Central LA. The earlier appearance may be attributed to high diesel truck activity owing to a high density of commercial warehouses in Riverside. The peak also lasts longer due to the Riverside downwind location and its higher potential to form secondary aerosols. Further discussion of the SOA contribution and its formation is presented in the Section 3.2.

The daily average values of the CASS measurements (BC, OC, and TC) were compared to the offline OC/EC analyzer results (every 3rd day, Fig. B.4, Supplement B). The slopes of the linear regression were 0.98, 1.15, and 1.07 for BC, OC, and TC, respectively, in Central LA, and 1.06, 1.15, and 1.12, respectively, in Riverside. These results demonstrate the

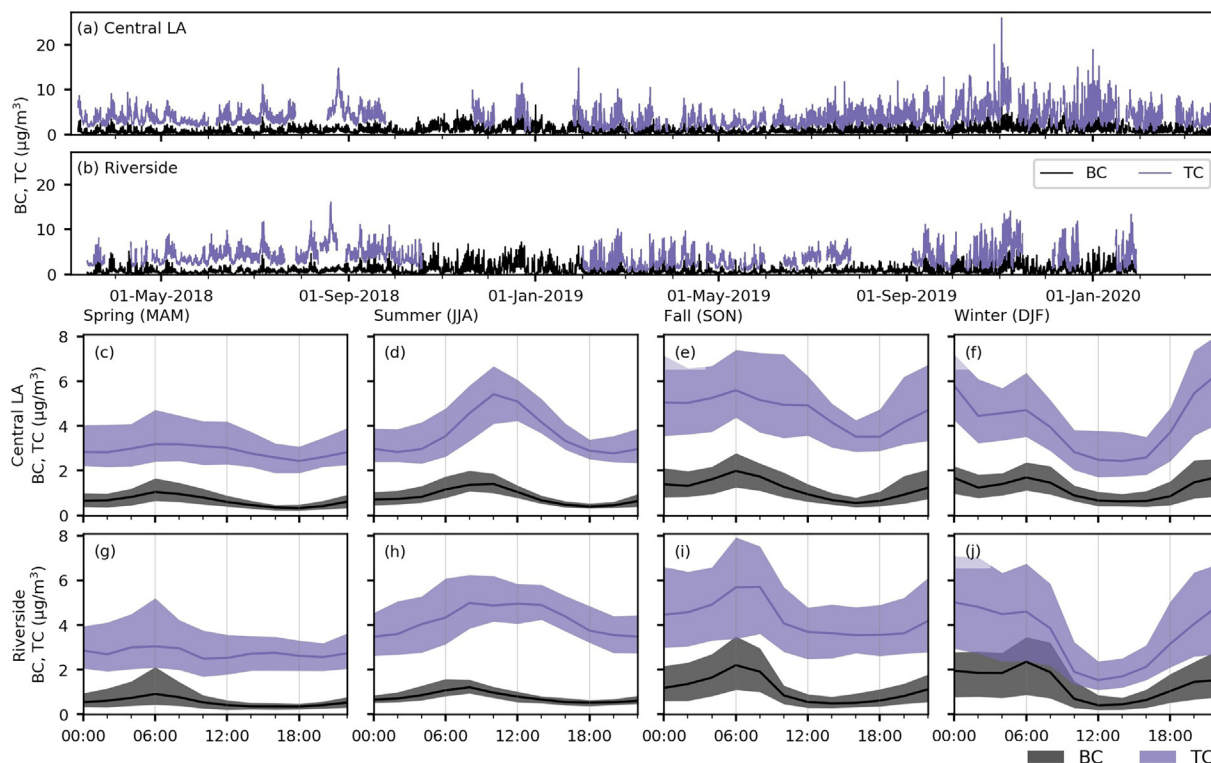


Fig. 2. Two-year-long measurements with CASS in Central LA (a) and Riverside (b) and diurnal profiles of BC and TC by season in Central LA (c–f) and Riverside (g–j). The lines represent median values, and the borders of the shaded area are the first and third quartiles in diurnal plots.

agreement between the newly developed CASS and the conventional offline measurements.

3.2. Advanced apportionment of carbonaceous aerosols

The results of the CA apportionment to six components (Eqs. (3)–(10)) are presented as typical diurnal profiles in Fig. 3, where the results are split between sites and seasons. An extended split between working days, Saturdays, and Sundays is shown in Figs. B.6 and B.7 (Supplement B). The highest seasonal median CA concentrations of $7.8 \mu\text{g}/\text{m}^3$ were found in the summer afternoon in Riverside (Fig. 3j). In contrast, the highest summer afternoon and winter night peaks are comparable ($7.1 \mu\text{g}/\text{m}^3$ and $7.2 \mu\text{g}/\text{m}^3$) in Central LA (Fig. 3b,d).

In general, BC_{ff} and $\text{POA}_{\text{non-abs}}$ had similar diurnal trends at both sites, as shown in Fig. 3, with morning and evening rush hour peaks in all seasons, suggesting that traffic is the major source of $\text{POA}_{\text{non-abs}}$. The evening peak is less considerable in the warmer part of the year owing to longer days and, consequently, a higher PBL at the time of the evening traffic rush hour. Traffic-related peaks can also be observed on Saturdays, while the Sunday profiles are flatter (Figs. B.6 and B.7, Supplement B), all of which are consistent with the typical traffic patterns in the basin. BC_{ff} 's diurnal peak concentrations on Sundays are lower by 48 % and 29 % than those on working days in Central LA and Riverside, respectively (Fig. B.7, Supplement B). We observed a comparable decrease in the Sunday diurnal peak of $\text{POA}_{\text{non-abs}}$ concentrations as well: 54 % and 27 % in Central LA and Riverside, respectively. Previous studies have reported that only a 5–10 % emissions reduction from gasoline-powered vehicles is expected on the weekends in the LA Basin (Bahreini et al., 2012; Hayes et al., 2013). On the other hand, BC_{ff} emitted by diesel vehicles was found to be reduced by 60–80 % on weekends in California, suggesting commercial vehicles are primarily responsible for high BC_{ff} and $\text{POA}_{\text{non-abs}}$ peak concentrations.

The BC_{bb} contribution to CA was negligible in spring, summer, and fall, but contributes up to 4 % and 8 % of CA during winter nights in Central LA and Riverside, respectively (Fig. 3h,p). POA_{BRC} has a diurnal pattern similar

to that of BC_{bb} , with the highest contribution during winter nights and a negligible contribution during other periods.

The diurnal pattern of the SOA in Fig. 3 exhibits a similar pattern at both sites. During summer afternoons and winter nights, SOA contributed up to 80 % and 40 % of CA, respectively (Fig. 3f,n,p). The lowest fraction of SOA to CA was observed during the morning rush hour in all the seasons (Fig. 3). SOA formation by photooxidation is responsible for the vast peaks in the afternoons, especially during the warm seasons. Recently, nighttime SOA formation, driven by aqueous-phase reactions, has also been recognized as a vital source of SOA (He et al., 2021; Jiang et al., 2019; Kumar et al., 2018; Mayorga et al., 2021; Saffari et al., 2016; Soleimanian et al., 2020; Wu et al., 2019; Zhang et al., 2018, 2020), which is also evident from our results. Tobler et al. (2021) marked the SOA formed during the night as low oxidized oxygenated OA (LO-OOA). Later in the day, LO-OOA can be further oxidized by photochemical aging into more oxidized oxygenated OA (MO-OOA). In our study, the highest median SOA concentrations were $4.7 \mu\text{g}/\text{m}^3$ and $6.1 \mu\text{g}/\text{m}^3$ in Central LA and Riverside, respectively, which were found during summer afternoons (Fig. 3b,i). Considering the higher PBL in summer afternoons than in winter nights, the amount of SOA formed by photooxidation is remarkable.

Using radiocarbon analyses, Zhang et al. (2011) reported that SOA in LA contains more fossil carbon from anthropogenic VOC precursors and less modern carbon from biogenic VOCs than samples from Atlanta. Considering that biogenic VOC oxidation is faster than reactions with anthropogenic aromatics, the authors concluded that the presence of biogenic VOC was low in LA. Recently, Liu et al. (2021) concluded that the SOA formation potential with the remaining unoxidized precursors is usually much higher in Beijing than in LA. Regardless of the previously reported lower levels of gasoline vehicle emissions during weekends (Bahreini et al., 2012; Hayes et al., 2013), the SOA levels remained unchanged (for example, Figs. B.6c–II,f–II, Supplement B). This suggests the increasing importance of non-combustion-related sources (such as consumer, commercial, and industrial products) in LA. Khare and Gentner (2018) reported a decrease in potential SOA

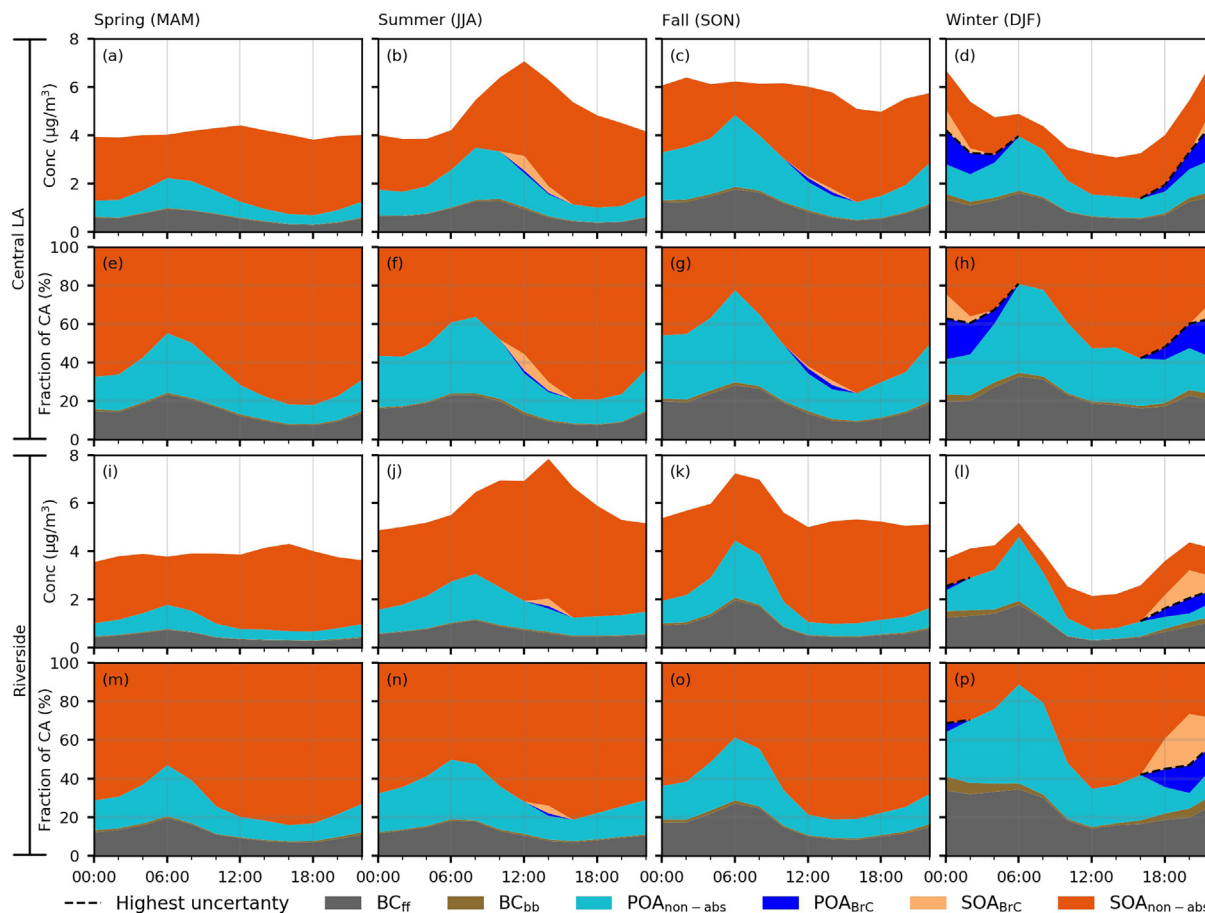


Fig. 3. Diurnal profiles of CA apportioned to BC_{ff} , BC_{bb} , $POA_{non-abs}$, POA_{BrC} , $SOA_{non-abs}$, and SOA_{BrC} in Central LA (a-h) and Riverside (i-p). Results are separated into seasons: (a, e, i and m) for spring, (b, f, j and n) for summer, (c, g, k and o) for fall, and (d, h, l and p) for winter. Graphs (a-d) and (i-l) contain medians, and relative fractions are shown in (e-h) and (m-p). The black dashed line represents the split between POA_{BrC} and SOA_{BrC} during winter nights, where the highest uncertainty is expected to appear.

from on-road gasoline vehicles by nearly 90 % owing to the continued implementation of stricter emission standards in the last 30 years.

Many studies have been performed in late spring (May and June 2010), where photo-oxidation plays a significant role in SOA formation; however, nighttime SOA formation has been neglected (Bahreini et al., 2012; Hayes et al., 2013; Saffari et al., 2016; Zhang et al., 2011). Our results (Fig. 3) show that nighttime SOA formation is present throughout the year (also during summer nights). Fry et al. (2018) recognized the nighttime SOA formed by reactions between NO_3^- and biogenic VOCs as an essential source of coupled anthropogenic-biogenic SOA in southeastern USA. Li et al. (2020) reported that the MACs of biogenic SOA were nearly an order of magnitude lower than those of SOA formed from anthropogenic precursors. Recently, He et al. (2021) confirmed that SOA formed from biogenic VOC and NO_3^- are non-light-absorbing. As shown in Fig. 3, most SOA in spring, summer, and fall are non-light-absorbing ($SOA_{non-abs}$). Consequently, we assumed that the biogenic VOC played an important role in air quality at considered sites.

We found a significant fraction of SOA_{BrC} on winter nights, which can account for up to 20 % of CA (Fig. 3h,p) and can be associated with precursors from biomass burning. Finewax et al. (2018) reported that catechol, a biomass-burning-related VOC, can react with NO_3^- and OH $\cdot$ and form a considerable amount of the SOA product 4-nitrocatechol, which absorbs light at lower wavelengths (Li et al., 2020). Chen and Bond (2010) found that approximately 98 % of biomass burning OC could be extracted from filters using methanol. Soleimani et al. (2020) and Zhang et al. (2013) reported that methanol extracts have a higher absorption efficiency than water extracts. In our study, SOA_{BrC} appeared late in winter evenings. Usually, SOA_{BrC} and POA_{BrC} lose the ability to absorb light with aging and under

sunlight-induced photobleaching, which destroys specific chromophores (Chen et al., 2021). Chen et al. (2021) named the process “whitening” of OC, and the process is also evident from our results; both SOA_{BrC} and POA_{BrC} disappeared in winter mornings (Fig. 3d,l). Similarly, Rastogi et al. (2021) reported that SOA_{BrC} formed during the daytime is less light absorbing because photolysis or oxidation can rapidly bleach BrC chromophores by breaking the unsaturated bonds and decomposing them into colorless carboxylic acids. As the split between POA_{BrC} and SOA_{BrC} was recognized as the most uncertain point of the results in Fig. 3, the split in winter nights is marked with a dashed line to alert the reader again about the potential uncertainties.

In our study, a minor but marked SOA_{BrC} contribution to CA was observed at both sites during the summer afternoons, which was not related to biomass burning (Fig. 3f,n). While biomass burning related POA_{BrC} and SOA_{BrC} contributed up to 26 % of the light absorption at 370 nm during winter nights (Fig. B.8d,h, Supplement B), the average fraction of light absorption by BrC in summer afternoon was 11 % (Fig. B.8b,f, Supplement B). Similar to our results, Cappa et al. (2019) reported a 10 % peak in BrC fractional contribution to light absorption at 405 nm in Fontana in July 2015. Similarly, Zhang et al. (2013) reported the highest BrC absorption in the middle of the day during the summer campaign from mid-May to mid-June 2010 in Pasadena (11 km to NE from downtown LA) and Riverside, which correlated with water-soluble OC concentrations in a timely manner.

In addition to domestic heating as the major source of BrC in urban or rural environments, wildfires can represent another potential source. Therefore, BrC can be used as a good marker for wildfire plumes. Although light absorption on BrC coming from biomass burning for winter heating

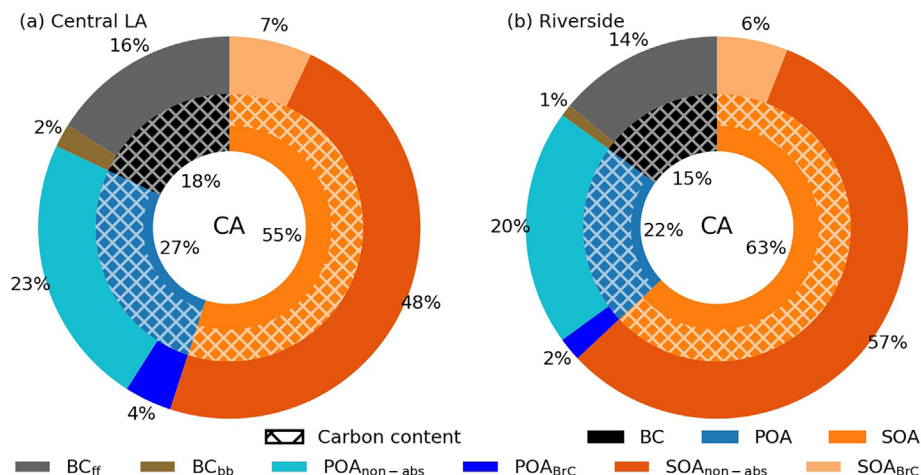


Fig. 4. Two-year average CA fingerprint in Central LA (a) and Riverside (b). The inner ring contains CA apportionment in three components - BC, POA and SOA. The hatches in the inner ring mark the mass fractions of carbon content in BC, POA and SOA (i.e., BC, POC and SOC) in the radial direction. The outer ring includes CA apportionment into six components: BC_{ff} , BC_{bb} , $POA_{non-abs}$, POA_{BrC} , $SOA_{non-abs}$ and SOA_{BrC} .

demand or afternoon summer formation has a typical diurnal cycle (Fig. B.8, Supplement B), wildfires are sporadic, and therefore, they cannot be seen on a typical diurnal profile, although they can cause a high, >50 % fractional contribution to the light absorption on BrC at 370 nm (Fig. B.9 a, b, Supplement B). The fingerprints of the three wildfires were detected in the LA Basin in October 2019 (Fig. B.9c-f, Supplement B). The plume from the Saddleridge and Getty wildfires impacted the Central LA site on 11th and 28th of October 2019, and the Sandalwood wildfire affected the measurements in the Riverside site on 10th of October 2019. The CA fingerprints from the Saddleridge and Getty fires are presented in Fig. B.8f,g, Supplement B, while TCA08 at the Riverside did not work because of maintenance when the plume from the Sandalwood fire reached the Riverside site. During both fires, higher fractions of BC_{bb} , POA_{BrC} , and SOA_{BrC} were observed in the Central LA compared to the general CA fingerprint shown in Fig. 4.

The highest secondary CA contribution of up to 80 % was observed during spring, summer, and fall afternoons, consistent with the observations of the study Docherty et al. (2008) performed in Riverside in the summer of 2005. A minor difference in the peak contribution was found between both sites and on weekdays. The winter afternoon secondary CA share was lower by 50 % on working days (Figs. B.7a-IV,d-IV, Supplement B) and approximately 70 % on Sundays (Figs. B.7c-IV,f-IV, Supplement B). The highest contribution of primary CA ($BC_{ff} + BC_{bb} + POA_{BrC} + POA_{non-abs}$) was found during morning rush hours on winter working days, with a share higher than 80 % in Central LA and a share up to 90 % in Riverside (Figs. B.7a-IV,d-IV, Supplement B). The peak of primary CA on Sunday winter mornings was considerable lower, with a relative contributions of approximately 50 % and 60 % in Central LA and Riverside, respectively (Figs. B.7c-IV,f-IV, Supplement B). These values are slightly higher than those reported by Docherty et al. (2008). Minimum SOA contributions of ~45 % were observed during morning peak traffic periods.

3.3. Summary of CA apportionment

A general overview of two-year long CA apportionment is shown in Fig. 4. The BC_{ff} presents 16 % and 14 % fractions of CA in Central LA and Riverside, respectively. The $SOA_{non-abs}$ was a dominant CA component at both sites, with an average share of 48 % in Central LA and 57 % in Riverside. The average contribution of SOA_{BrC} to CA was comparable for both sites: 7 % in Central LA and 6 % in Riverside. Chen et al. (2021) recently reported a similar pattern for other sites in the USA IMPROVE network, where most of the time non-light-absorbing OC dominated the OC mass.

The higher SOA share for Riverside is reasonable because of its downwind location, while the Central LA site is located in downtown LA and is

more exposed to primary emissions, mainly from traffic. SOA contributed to 67 % and 74 % OA in Central LA and Riverside, respectively, which is consistent with the results of Docherty et al. (2008), where $SOA > POA$ in Riverside in 2005 was confirmed using five different methods. Considering the carbon content in aerosol mass, the SOC fraction of OC was slightly lower than the corresponding fraction of SOA in OA: 57 % in Central LA and 66 % in Riverside (see the hatched area in inner rings in Fig. 4). Comparable values for SOC fraction in OC for Central LA were reported in work by Saffari et al. (2016) as 55 % SOC in the warm season and 57 % in the cold season.

Fig. B.12, Supplement B, shows that carbonaceous aerosol represents a significant fraction of $PM_{2.5}$, which can comprise between 34 % and 50 % of total $PM_{2.5}$ mass in summer and fall, respectively, in Central LA (Fig. B.12a-d, Supplement B), and between 46 % and 53 % in summer and fall, respectively, in Riverside (Fig. B.12e-h, Supplement B). The time series of CA compared to $PM_{2.5}$ concentrations are shown in Fig. B.13, Supplement B. Additionally, Fig. B.14, Supplement B, contains a split between working days, Saturdays, and Sundays. The highest non-carbonaceous matter contributions to $PM_{2.5}$ mass were found during summer for both sites, most probably related to the inorganic secondary aerosol formation.

3.4. CA apportionment validation

To confirm validity of the CA apportionment results, each apportioned CA component was compared with other available tracers for different aerosol sources and atmospheric processes measured using independent methods. The choice and usage of tracers are explained in this section.

We validated the Aethalometer model by comparing BC_{ff} and BC_{bb} results with NO_x and CO concentrations as traffic tracers and levoglucosan concentrations as marker for biomass burning. We used hourly data to explore the association between NO_x and CO against BC_{ff} and BC_{bb} (Fig. 5a, c,e,g); however, the comparisons of levoglucosan against BC_{ff} and BC_{bb} data were done using daily averages (Fig. 5b,f), given the time-integrated nature of levoglucosan data. BC_{ff} correlated well with NO_x and CO and BC_{bb} with levoglucosan at both sites, suggesting common emission sources for BC_{ff}/NO_x , BC_{ff}/CO , and $BC_{bb}/levoglucosan$ pairs. The R^2 for all six regression lines was found to be ≥ 0.74 , consistent with other studies; for example, Mbengue et al. (2020) reported an R^2 value of 0.77 between BC_{bb} and levoglucosan, and Fuller et al. (2014) reported an R^2 of 0.79 for the same comparison. In our study, there was no correlation between BC_{bb} and NO_x and BC_{ff} and levoglucosan, with R^2 values of 0.26 for both sites. Fig. B.5, Supplement B, shows the diurnal profiles of BC_{ff} and BC_{bb} in different seasons. BC_{ff} has morning and afternoon rush hour peaks, while BC_{bb} was observed only during the nighttime in winter and fall. The morning

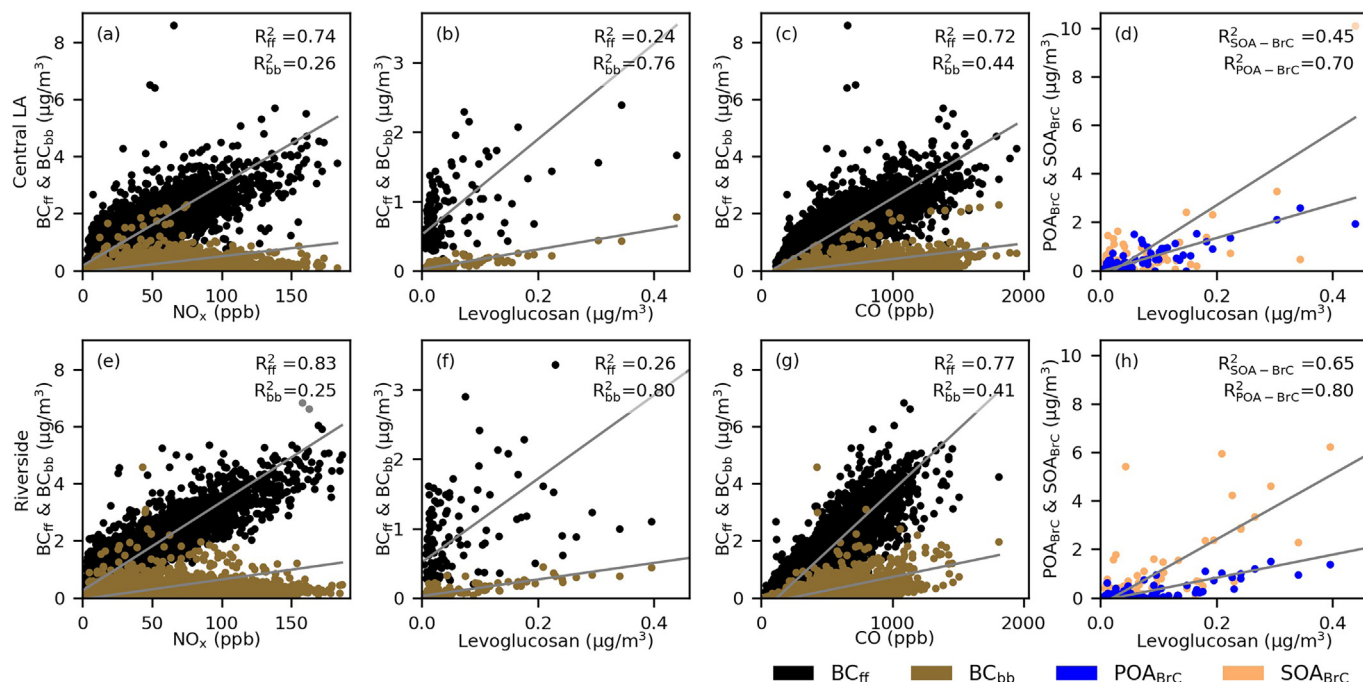


Fig. 5. Validation of Aethalometer model results BC_{ff} and BC_{bb} with NO_x , levoglucosan and CO in Central LA (a,b,c) and Riverside (e,f,g). Hourly values are used in correlations with NO_x and CO (a,c,e,g) and daily averages with levoglucosan (b,f). Regressions between POA_{BrC} and SOA_{BrC} against levoglucosan are added for Central LA (d) and Riverside (h). The regression details (slopes and intercepts), together with R^2 , are collected in Table B.2, Supplement B.

peak of BC_{ff} was higher because of the lower PBL in all seasons, and the summer afternoon BC_{ff} peak was missing due to longer days (and higher PBL at that time). BC_{bb} concentrations peaked only during winter nights.

The evaluation of POC and SOC split accuracy is challenging because of the lack of direct SOC measurements (Wu and Yu, 2016). Therefore, the BC tracer model results were compared with NO_x and CO as tracers for primary emissions and O_3 as a tracer for daytime photochemistry. The agreement between the BC tracer model results and trace gases was assessed using diurnal profiles (Fig. 6). Ultrafine particles (UFP) were used as an additional parameter because UFP can have a primary and secondary origin; therefore, they can be partially compared to both POC and SOC, as shown in Fig. 6i-l,u-x). However, it should be noted that UFP can also result from the inorganic fraction of secondary-formed particles. Detailed results, split into working days, Saturdays, and Sundays, are shown in Figs. B.10 and B.11, Supplement B.

SOC and POC showed distinct diurnal profiles during all seasons and at both the sites. We found similar diurnal patterns of POA, NO_x , and CO in all seasons (Fig. 6), suggesting common primary emission sources (mainly traffic) for all the three species. A higher morning rush hour peak for all the three species was observed in fall and winter than in spring and summer. NO_x is reported to be a better tracer for diesel engines, whereas nearly all CO emissions are from gasoline vehicles (Bahreini et al., 2012). In Figs. B.10 and B.11, Supplement B, we can see that the morning peak in NO_x concentrations is sharper during weekdays than on Sundays, whereas the difference in the peak CO concentrations in the morning is not as distinct between weekdays and Sundays. This suggests a different vehicle fleet composition during weekdays versus Sundays, with lower emissions from commercial diesel vehicles on Sundays. POC also showed a midnight peak, especially pronounced during the cold seasons (fall and winter), mainly due to lower PBL heights and enhanced residential wood-burning activities.

According to its photochemical origin, the ozone concentration peaked at mid-day and in the early afternoon. The highest peaks were formed during summer and the lowest during winter, according to the different intensities of solar radiation (see Fig. 6). The SOC concentration followed a similar diurnal pattern from spring to fall, while the winter diurnal variation was different, as shown in Fig. 6, suggesting different formation

pathways in the cold season. Significantly higher summer afternoon O_3 concentrations were observed in the Riverside than in the Central LA (Fig. 6r vs. Fig. 6f), which indicates that ozone production is VOC-limited in the central region. On the other hand, more VOCs are available in rural areas from biogenic sources, which might be the reason for the higher SOC concentration in the Riverside (Fig. 6n vs. Fig. 6b). We did not observe any considerable difference in afternoon peak O_3 and SOC concentrations between working days and weekends, as shown in Figs. B.10 and B.11, Supplement B, supporting the importance of biogenic sources for both components. O_3 can only be partially compared to the SOC concentrations (Fig. 6e-h,q-t) because the nighttime peaks in SOC concentrations during the winter are independent of photochemical activities and are likely formed through aqueous-phase reactions, as discussed above.

The UFP diurnal profile had three peaks (morning, afternoon, and evening) in spring and fall (Fig. 6i,k,u,w) and two peaks (morning and evening) in winter (Fig. 6l,x). In summer, UFP showed two peaks (morning and afternoon) at both sites, while the afternoon peak in Central LA occurred slightly earlier during the day (Fig. 6j,v). Morning UFP correlated well with the morning peak of POA and two primary tracer gases (i.e., NO_x and CO) during all four seasons. In afternoon, the UFP peaks in spring, summer, and fall correlate well with the O_3 and SOA afternoon peaks. On the other hand, there was no afternoon peak in UFP concentrations in winter, which is comparable to the SOA variation pattern.

Fig. 7 illustrates the two-year-long correlations between POC/SOC and primary (i.e., NO_x , CO, and BC) and secondary (O_3) aerosol tracers. Correlations improved considerably if, instead of OC, only POC or SOC were used against the chosen tracers. A high R^2 was found for correlations between POC and primary tracers: $R^2 \geq 0.69$ for POC against NO_x (Fig. 7a,f), $R^2 \geq 0.69$ for POC against CO (Fig. 7b,g), and $R^2 \geq 0.93$ for POC against BC (Fig. 7c,h). The R^2 value of the regression line between SOC and O_3 was low, confirming that O_3 was only partially related to SOC (Fig. 7d,i). Hayes et al. (2013) reported R^2 of 0.53 between SOA and O_3 in Pasadena, but only the summer months were included in the study (May and June 2010). Wu et al. (2019) used O_3 to validate SOA in Guangzhou, China. They showed a significantly worse correlation for the winter months ($R^2 < 0.11$), but again, a good correlation $R^2 = 0.73$ in summer. We found a similar pattern in our dataset (Fig. 7e,j): the highest R^2 values for

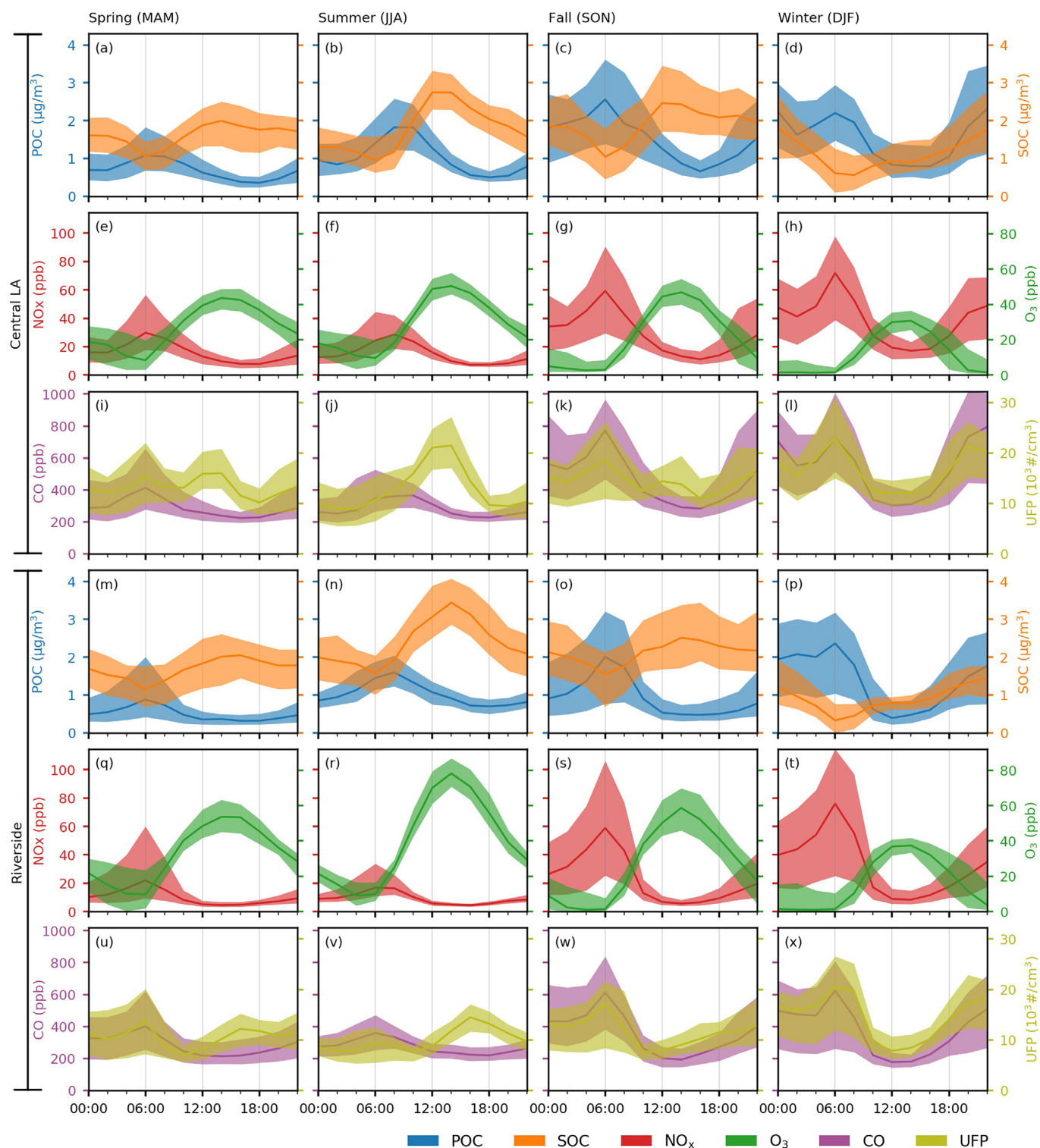


Fig. 6. Diurnal profiles of POC, SOC and their tracers in Central LA (a-l) and Riverside (m-x). POC and primary tracer gases NO_x and CO are on the left y-axis, while the right y-axis contains SOC, O_3 as a secondary trace gas, and UFP as a combined primary and secondary tracer. Results are split between seasons (columns). The strong line represents median values and the shaded area shows the lower and upper quartile.

the association between SOA and O_3 were found in summer (0.59 and 0.62 in Central LA and Riverside, respectively), while R^2 falls below 0.12 in winter months (Fig. 7e,j). Such seasonal dependence was not observed for correlations between POA and primary emission tracers (i.e., NO_x , CO, and BC).

A modified BC tracer model that splits BrC into its primary or secondary origin (POA_{BrC} and SOA_{BrC}) is even more challenging to evaluate. POA_{BrC} is a direct consequence of enhanced biomass burning during winter nights; therefore, a good correlation with levoglucosan is expected. However, SOA_{BrC} can also be formed by the oxidation of precursors coemitted from

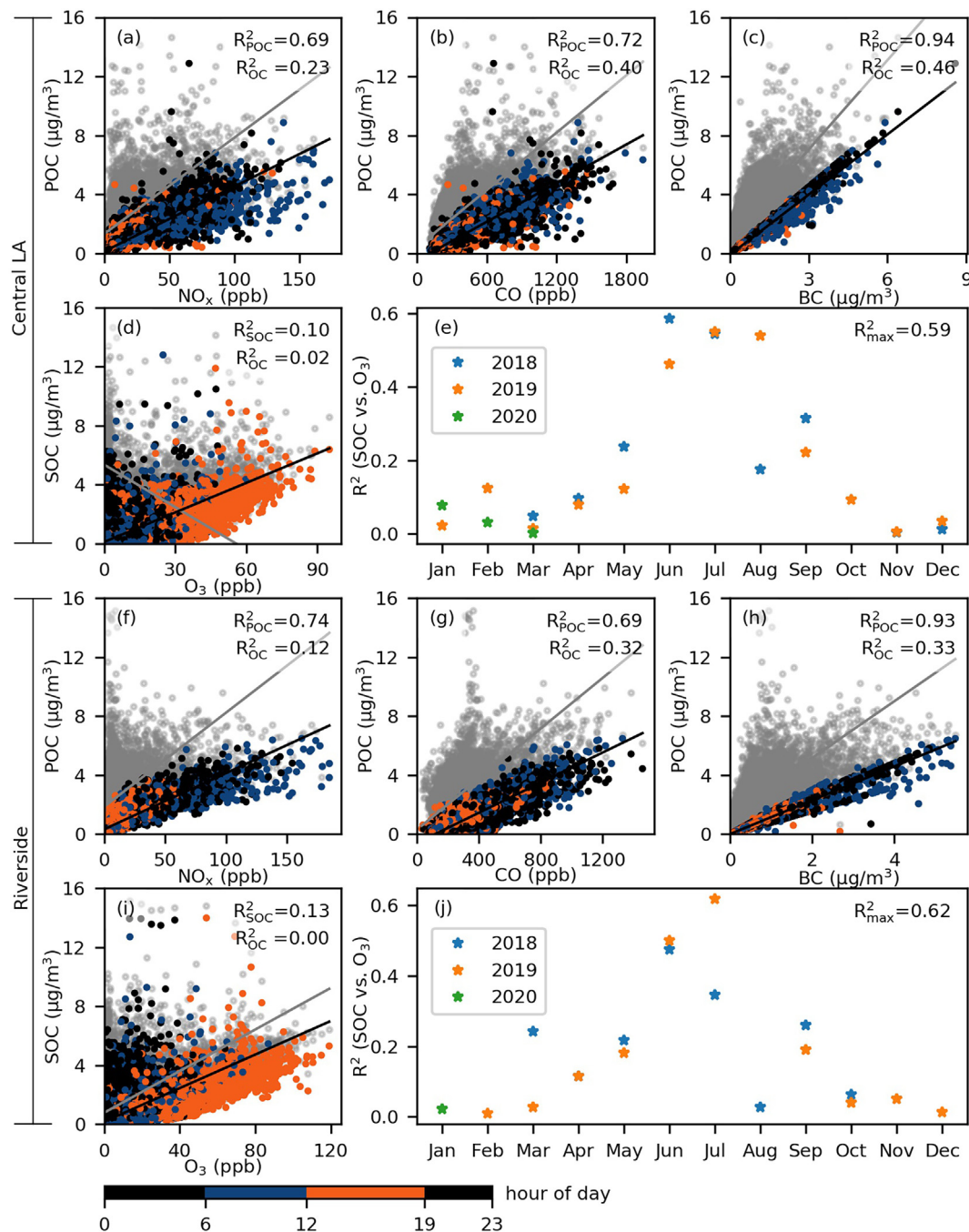


Fig. 7. Validation of POC and SOC split for Central LA (a-e) and Riverside (f-j). Scatter plots (a-d) and (f-i) contain two regressions: total OC against chosen tracer with gray dots and POC or SOC regression against chosen tracer with colored dots where the color scale represents part of the day in hours. The strong monthly dependence of the R² value between SOC and O₃ is presented in graphs (e) and (j), where colors mark the year of the observation. The regression details (slopes and intercepts), together with R₂, are collected in Tables B.3 and B.4, Supplement B.

biomass burning. An additional pathway of SOA_{BrC} formation is present in the summer afternoons, independent of the biomass burning emissions. Due to the existence of multiple formation pathways, the correlation between SOA_{BrC} and levoglucosan is expected to exist, but is weaker than the correlation between POA_{BrC} and levoglucosan (Fig. 5d,h).

4. Limitations and recommendations

The presented method for high-time-resolution CA apportionment contains ten free parameters, which can be site- or regional-specific and may vary seasonally. Although the proposed approach may offer characterization of CA species and sources in near real-time, when these parameters

are well defined and cautiously chosen for a specific measurement location, they would require short-term complementary measurements and validation to decrease the uncertainty. While we were able to fix six free parameters (including AAE_{ff}, AAE_{bb}, AAE_{BC}, b, (OC/EC)_{prim}, MAC_{BC}) specifically for the considered sites, other four parameters (POA/POC, SOA/SOC, MAC_{BrC,prim}, MAC_{BrC,sec}) were obtained from the literature and were considered the main source of uncertainties in our approach. By adjusting all free parameters to the local aerosol characteristics, the proposed method has the potential to study CA worldwide.

Starting with the equivalent BC measurements by the Aethalometer, the MAC and C values represent the highest uncertainty. Cross-validation with offline measurements is recommended to ensure compliance with

standardized EC determination. Corrections of MAC_{BC} or proportionality parameter b are recommended, especially if the difference between BC and EC exceeds 10 %. However, it has to be pointed out again that standardized measurements are also affected by some level of uncertainty (Zhang et al., 2021).

Using the wavelength-independent multiple scattering coefficient C is acceptable for urban or urban background stations (Yus-Díez et al., 2021). When using wavelength-independent C , the magnitude of C does not affect the Aethalometer source apportionment to BC_{ff} and BC_{bb} , nor the proportion between light absorption on BC and BrC, only the magnitude of the absorption coefficient b_{abs} is affected (Ferrero et al., 2021a). Therefore, site-specific correction of C is strongly recommended, especially for climatological studies (Ferrero et al., 2021b). Several studies have been published on the C value for different filter tapes using Aethalometers (Bernardon et al., 2021; Ferrero et al., 2021a, 2021b; Kumar et al., 2018; Massabò et al., 2015). Since M8060 filter tape was used in the AE33 in 2017, its optical properties have been published in only one study (Yus-Díez et al., 2021) to the best of our knowledge. Based on this study, using the manufacturer's default C value could lead to an overestimation of the absorption coefficient.

The Aethalometer model source apportionment of BC to BC_{ff} and BC_{bb} is sensitive to the chosen pair of parameters AAE_{ff} and AAE_{bb} . It is recommended to find the optimal site-specific pair of values by using the colocated measurements of levoglucosan as a biomass burning marker (Fuller et al., 2014) or radiocarbon ^{14}C as a fossil fuel tracer (Zotter et al., 2017). Usually, the AAE_{ff} - AAE_{bb} pair is characteristic of a wider region, assuming that the fuels do not vary significantly inside the area. Aethalometer model is best suited for application in urban environments with two dominant sources of BC, namely biomass and fossil fuel combustion. The results of the Aethalometer model should be interpreted carefully in the presence of other fuel types.

To reduce the possible uncertainty of the BC tracer model to split OC in SOC and POC, the MRS method (Wu et al., 2019; Wu and Yu, 2016) is recommended to use because the parameter $(OC/BC)_{prim}$ is not predefined but estimated from the data. In our study, $(OC/BC)_{prim}$ was assessed separately for every season to further reduce potential uncertainty. The BC tracer model is limited to the analysis of local aerosols because it takes advantage of the differences between the temporal evolution of primary sources and secondary formation processes. If local air quality is significantly exposed to pollution transport, Wu et al. (2019) recommended building a separate BC tracer model for episodes strongly affected by transported aerosols.

The constant POA/POC and SOA/SOC, taken from a study conducted in the LA Basin (Docherty et al., 2008), were used in our study to convert organic carbon to organic aerosol mass. It must be mentioned that the uncertainty increases for high-time-resolution data with changing emission sources. For example, higher OA/OC ratios are expected for aerosols impacted by woodsmoke in winter evenings at both sites. Therefore, the use of seasonally and source-dependent OA/OC (or POA/POC, SOA/SOC) ratios would decrease the uncertainty in the conversion of organic carbon to organic aerosol mass in future studies.

The $MAC_{BrC,prim}$ and $MAC_{BrC,sec}$ parameters were taken from the literature (Kumar et al., 2018) and considered as a potential source for the highest level of uncertainty in our high-time resolution approach. Consequently, the split between POA_{BrC} and SOA_{BrC} during the nights in the colder part of the year must be considered carefully, because both components have a similar diurnal pattern. This point is marked with a dashed line in Fig. 3 to alert the reader about the potential higher uncertainty. However, a growing number of studies are focusing on BrC and its physical and chemical properties in recent years (Cappa et al., 2020; Chen et al., 2021; Gilardoni et al., 2020; Hettiyadura et al., 2021; Huang et al., 2022; Izhar et al., 2020; Li et al., 2020; Liakakou et al., 2020; Liu et al., 2020, 2021; Rastogi et al., 2021; Sun et al., 2021; Wang et al., 2020; Wu et al., 2021; Zhang et al., 2020), which promises that the highest uncertainty of $MAC_{BrC,prim}$ and $MAC_{BrC,sec}$ could be reduced in coming years.

5. Conclusions

Different carbonaceous aerosol apportionment methods in a concise and advanced apportionment technique were integrated for the first time in this study. The proposed approach relies on high-time-resolution measurements of TC and BC concentrations using a recently developed CASS system. Long-term (i.e., two years), high-time-resolution CA measurement and apportionment were performed at two contrasting sites in the LA Basin, focusing on primary and secondary aerosols and their ability to absorb light. Similar temporal patterns were observed at both sites: the morning rush hour traffic, especially in winter, resulted in the contribution of primary emitted carbonaceous aerosols ($BC_{ff} + BC_{bb} + POA_{non-abs} + POA_{BrC}$) up to 90 % of the total CA. On the other hand, secondary formed SOA ($SOA_{non-abs} + SOA_{BrC}$) is a dominant component of CA in summer afternoons when their contribution can reach 80 % of the total CA, but is also not negligible during nights. The results were in good agreement with the previously reported studies focusing on carbonaceous aerosol composition and sources. The presented measurement system and methodology have high potential to be implemented for real-time analyses worldwide if the free parameters are carefully chosen for each location, considering the methodology limitations and recommendations.

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CRedit authorship contribution statement

Matic Ivančič: Conceptualization, Data curation, Methodology, Software, Visualization, Writing – original draft, Writing – review & editing. **Asta Gregorič:** Conceptualization, Methodology, Supervision, Writing – review & editing. **Gašper Lavrič:** Data curation, Investigation, Project administration. **Bálint Alföldy:** Methodology, Writing – review & editing. **Irena Ježek:** Writing – review & editing. **Sina Hasheminassab:** Conceptualization, Data curation, Investigation, Writing – review & editing. **Payam Pakbin:** Conceptualization, Data curation, Investigation, Project administration, Writing – review & editing. **Faraz Ahangar:** Conceptualization, Data curation, Investigation, Writing – review & editing. **Mohammad Sowlat:** Conceptualization, Data curation, Investigation, Writing – review & editing. **Steven Boddeker:** Conceptualization, Data curation, Investigation, Writing – review & editing. **Martin Rigler:** Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: At the time of the research, Matic Ivančič, Asta Gregorič, Gašper Lavrič, Bálint Alföldy, Irena Ježek, and Martin Rigler were also employed by the manufacturer of the Aethalometer and Total carbon analyzer instruments. Other authors declare no conflict of interest. The views expressed in this document are solely those of the authors and do not necessarily reflect those of the South Coast AQMD.

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