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One-year measurements of secondary organic aerosol (SOA) markers
in the Paris region (France): concentrations, gas/particle partitioning
and SOA source apportionment

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Abstract

Twenty-five biogenic and anthropogenic secondary organic aerosol (SOA) markers have been measured over a one-year period in both gaseous and PM₁₀ phases in the Paris region (France). Seasonal and chemical patterns were similar to those previously observed in Europe, but significantly different from the ones observed in America and Asia due to dissimilarities in source precursor emissions. Nitroaromatic compounds showed higher concentrations in winter due to larger emissions of their precursors originating from biomass combustion used for residential heating purposes. Among the biogenic markers, only isoprene SOA marker concentrations increased in summer while pinene SOA markers did not display any clear seasonal trend. The measured SOA markers, usually considered as semi-volatiles, were mainly associated to the particulate phase, except for the nitrophenols and nitroguaiacols, and their gas/particle partitioning (GPP) showed a low temperature and OM concentrations dependency. An evaluation of their GPP with thermodynamic model predictions suggested that apart from equilibrium partitioning between organic phase and air, the GPP of the markers is affected by processes suppressing volatility from a mixed organic and inorganic phase, such as enhanced dissolution in aerosol aqueous phase and non-equilibrium conditions. SOA marker concentrations were used to apportion secondary organic carbon (SOC) sources applying both, an improved version of the SOA-tracer method and positive matrix factorization (PMF). Total SOC estimations agreed very well between both models, except in summer and during a highly processed Springtime PM pollution event in which systematic underestimation by the SOA tracer method was evidenced. As a first approach, the SOA-tracer method could provide a reliable estimation of the average SOC concentrations, but it is limited due to the lack of markers for aged SOA together with missing SOA/SOC conversion fractions for several sources.

Keywords: Aerosol; SOA; Tracers; Source apportionment; PMF; Gas/particle partitioning

1. Introduction and objectives

Aerosols (particulate matter, PM) have significant impacts on air quality and climate. The organic fraction (organic aerosol (OA)) contributes about 20 to 90% of the PM mass in ambient air. OA originates either from anthropogenic or natural sources and from both, primary (POA, directly emitted into the atmosphere) and secondary processes (SOA, formed in the atmosphere). SOA results from the condensation and coagulation of (photo-)oxidized volatile and/or semi-volatile organic compounds (VOCs and SVOCs) (Carlton et al., 2009; Hallquist et al., 2009; Kroll and Seinfeld, 2008; Ziemann and Atkinson, 2012). It accounts for a major fraction of OA (up to 90%) (Srivastava et al., 2018b; Zhang et al., 2007, 2011), making its characterization and apportionment essential in terms of air quality and climate impacts. However, the comprehension and identification of the large number of SOA sources is still difficult to achieve, while the SOA prediction by air quality models in the atmosphere remains highly uncertain (Bessagnet et al., 2016).

Several previous studies have shown that a detailed chemical characterization of OA at a molecular level can provide insights into the OA sources as several organic compounds have been identified and recognized as tracers (or markers) of specific sources or chemical (trans-)formation processes (Srivastava et al., 2019, 2018a, 2018b, 2018c and references therein). For instance, for primary sources, levoglucosan is commonly used to trace biomass burning emissions, polyols for biogenic emissions (fungal spores), hopanes for vehicular emissions, etc. (Cass, 1998; Samaké et al., 2019a, 2019b; Schauer et al., 1996; Simoneit et al., 1999). Similarly, key organic species have been identified as characteristic of secondary sources or, as typical oxidation by-products of specific SOA precursors. They are commonly referred to SOA tracers (markers) as they can be used to apportion biogenic and anthropogenic SOA sources (Kleindienst et al., 2007a). Biogenic SOA markers notably include pinene (α - and β -pinene) oxidation by-products such as cis-pinonic acid, pinic acid (Christoffersen et al., 1998;

Jang and Kamens, 1999; Mutzel et al., 2016; Yu et al., 1999; Zhang et al., 2018), 3-methylbutane-1,2,3-tricarboxylic acid (MBTCA) (Mutzel et al., 2016; Szmigielski et al., 2007) and 3-hydroxyglutaric acid (Claeys et al., 2007). Several other pinene SOA markers have also been reported and used for source apportionment (Jaoui et al., 2005) (Table 1). Isoprene SOA markers include α -methylglyceric acid, 2-methylthreitol and 2-methylerythritol (Claeys et al., 2004, 2004; Edney et al., 2005) while a common sesquiterpene SOA marker is β -caryophyllinic acid formed from the oxidation of β -caryophyllene (Jaoui et al., 2007). Anthropogenic SOA markers are generally less source (precursor) specific. For instance, succinic acid has been identified as a photooxidation product of cyclic olefins but it is also directly emitted by vehicle engines (Hatakeyama et al., 1987; Kawamura and Kaplan, 1987). Typical toluene oxidation products are 2,3-dihydroxy-4-oxopentanoic acid (DHOPA), nitrophenols and methylnitrophenols (Forstner et al., 1997; Kleindienst et al., 2004). Note that DHOPA is also formed from the oxidation of benzene, o,m,p-xylenes, ethylbenzene, 1,3,5-trimethylbenzene (TMB), and 1,2,4-TMB in addition to toluene (Al-Naiema et al., 2020). Phthalic acid has been proposed as SOA marker for the photooxidation of naphthalene and methyl-naphthalenes (Kleindienst et al., 2012). All these SOA precursors are both emitted by biomass burning and fossil fuel combustions. Nitroguaiacols and methylnitrocatechols are considered as specific by-products of the phenolic compounds oxidation (Iinuma et al., 2010; Yee et al., 2013), precursor species largely emitted by biomass burning (Bruns et al., 2016; Iinuma et al., 2010). In addition, phthalic acid, nitrophenols, methyl-nitrophenols and methylnitrocatechols might be also directly emitted during the biomass burning combustion process (Wang et al., 2017; Lu et al., 2019; Mkoma and Kawamura, 2013).

As defined, a tracer should be unique to the source (precursor) of origin, formed in reasonably high yields to induce quantifiable concentrations in the ambient air, stable in the atmosphere,

and so be conserved between its emission/formation and its collection at a receptor location. It should also have a low vapour pressure, and so, be mainly associated with the particulate phase, to minimize possible underestimation from loss of the gaseous phase. However, as already mentioned above for source specificity, all these conditions are rarely (and probably never) fulfilled and, in this case, the term ‘marker’ is more appropriate. In fact, such compounds may react in the atmosphere by photochemical processes involving sunlight and atmospheric oxidants (O_3 , NO_x , radicals OH, NO_3). For most of the known SOA markers, information about their stability or atmospheric lifetime are scarce or not available. They are usually based on empirical calculations (Nozière et al., 2015) and experimental values are only available for a few of them (e.g. cis-pinonic acid \approx 2.1–3.3 days (Lai et al., 2015; Witkowski and Gierczak, 2017); β -caryophyllonic acid \approx 1.5 h in gaseous phase (Witkowski et al., 2019) and MBTCA \approx 1.2 days (Kostenidou et al., 2018). SOA markers are typically semi-volatile compounds but their gas/particle partitioning (GPP) is still poorly documented (Al Naiema and Stone, 2017; Bao et al., 2012; Isaacman-VanWertz et al., 2016; Lutz et al., 2019; Thompson et al., 2017; Xie et al., 2014; Yatavelli et al., 2014) but this parameter is essential for the understanding of their atmospheric fate and is furthermore needed in PM source apportionment. Simple parametrizations based on Raoult and Henry’s laws do not succeed in correctly representing the GPP of the SOA organic markers (Lutz et al., 2019). In addition, models based on single and poly-parameter linear free energy relationships (sp-, ppLFER), which have been applied to predict the GPP of other substance classes in the atmosphere, (Endo and Goss, 2014; Götz et al., 2007; Isaacman-VanWertz et al., 2016; Salthammer and Goss, 2019; Shahpoury et al., 2018, 2016; Tomaz et al., 2016), have rarely been used to study SOA markers. Such studies are needed to evaluate the suitability of these models for predicting the GPP of SOA markers.

Finally, SOA markers have been commonly used for source apportionment, in the USA and in Asia but are still poorly documented in Europe (Srivastava et al., 2018a). The SOA formation conditions are expected to be quite different in Europe compared to USA and/or Asia due to the differences in the predominant SOA precursor and emission sources. For example, biogenic emissions in the USA and in China are largely dominated by isoprene (Guenther et al., 2006; Hantson et al., 2017), while other biogenic VOCs, such as monoterpenes, are significantly emitted in Europe (Simpson et al., 1995; Steinbrecher et al., 2009). Similarly, coal combustion contribution to PM (and OA) is largely substantial in China (Huang et al., 2014) but not so much in western Europe while biomass burning for residential heating purposes is commonly used in Europe (Denier van der Gon et al., 2015; Viana et al., 2016). In addition, most of the measurements of SOA markers in Europe were performed in rural or forested areas. This limited information about the influence of anthropogenic sources is clearly a constraint for urban air quality purposes (Srivastava et al., 2018b).

Here, we investigated over a year, the concentrations of 25 SOA markers, in both the particulate and gaseous phases, in the Paris region (France) in order to (1) compare the concentration levels observed with the ones reported in the literature in Europe and worldwide, (2) study emission sources and chemical processes influencing their levels and fate based on their temporal variation and seasonality, (3) evaluate the GPP of the SOA markers and test the underlying processes by comparison with model prediction and (4) apportion the different SOA sources using two models, namely SOA-tracer method and positive matrix factorization (PMF).

2. Experimental methods

2.1. Sampling site and sample collection

PM₁₀ and gaseous phases were collected, every third day, from mid-November 2014 to mid-December 2015 on quartz fiber filters (Tissu-quartz, Pallflex, Ø = 150 mm) and polyurethane foams (PUF, Tisch Environmental, L = 75 mm, placed downstream from the filter), respectively, at the SIRTA facility (Site Instrumental de Recherche par Télédétection Atmosphérique, 2.15° E; 48.71° N; 150 m a.s.l. (meters above sea level); <http://sirta.ipsl.fr>, Fig. S1). This site is located 25 km southwest from the Paris city centre (Haeffelin et al., 2005) and is part of the ACTRIS European program (Aerosol, Clouds and Trace gases Research InfraStructure, www.actris.eu). The location is surrounded by forests, agricultural fields, residential areas and commuting roads, and is representative of the suburban background air quality conditions of the Ile-de-France region (Paris), the most populated area in France (with about 12.2 million inhabitants) (Crippa et al., 2013a; Petit et al., 2014, 2017; Sciare et al., 2011; Zhang et al., 2019). Each sample was collected for 24 h (from 8 am to 8 am, UTC), using a high-volume sampler (DA-80, Digitel, 30 m³ h⁻¹) and the PM sampling head was not heated to avoid any additional sampling artifact (Albinet et al., 2007). Field blanks were collected every 8 to 10 days. Prior to sampling, filters were pre-baked at 500 °C for 12 h and PUFs were cleaned by pressurized solvent extraction (ASE 350, Thermo) using hexane (1 cycle) and acetone (2 cycles): 80 °C, 100 bars, 5 min heat time, 15 min static time (Zielinska, B., 2008). Once collected, particulate and gaseous phase samples (n=130 +15 field blanks) were wrapped in aluminium foils and stored in polyethylene bags at <-18°C until analysis. Shipping of the samples to the different laboratories for analyses have been done by express post using cool boxes (< 5°C). As no denuder (for oxidants or to trap the SVOCs in the gaseous phase) has been used for the samplings, the results could be biased due to some sampling artifacts (positive, overestimation of the concentrations, or negative, underestimation, due to the sorption or desorption on/from the filter of semi-volatile species and/or due to the degradation/formation of chemical species by heterogeneous processes

involving atmospheric oxidants) (Albinet et al., 2010; Goriaux et al., 2006; Mader and Pankow, 2001; Turpin et al., 2000 and references therein).

2.2. Off-line chemical analyses

Particulate phase was extensively characterized for many chemical species (n=175). Elemental and organic carbon (EC/OC) were measured using a Sunset lab analyser following the EUSAAR-2 thermo-optical protocol (Cavalli et al., 2010). Major ions (Cl^- , NO_3^- , SO_4^{2-} , NH_4^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+}) together with methanesulfonic acid (MSA) and oxalate ($\text{C}_2\text{O}_4^{2-}$), were quantified using ion chromatography after filter extraction in ultrapure water (18 M Ω) (Guinot et al., 2007). Both EC/OC and ion analyses fulfilled the recommendations of the European standard procedures EN 16909 and EN 16913, respectively (CEN, 2017a, 2017b). Thirty seven elements, notably including Ca, Ti, Mn, Fe, Ni, Sb, Cu, Zn, V, and Pb, were measured using ICP-AES or ICP-MS (inductively coupled plasma atomic emission spectroscopy or mass spectrometry) after microwave acid digestion (HNO_3 , H_2O_2) at 220°C (Alleman et al., 2010; CEN, 2005; Mbengue et al., 2014). In addition, samples of NIST SRM 1648a (urban particulate matter) were systematically tested as standard reference material to validate the whole extraction procedure. Anhydrosugars, including known biomass burning markers (levoglucosan, mannosan and galactosan) and 3 polyols (arabitol, sorbitol and mannitol) were quantified using LC-PAD (liquid chromatography coupled to pulsed amperometric detection) (Verlhac et al., 2017; Yttri et al., 2015). Polycyclic aromatic hydrocarbons (PAHs) and their oxygenated and nitrated derivatives (oxy- and nitro-PAHs) in the PM_{10} samples were extracted using a QuEChERS-like (Quick Easy Cheap Effective Rugged and Safe) procedure with acetonitrile (ACN) as solvent. As described below, a single extraction for PUF samples was performed for the analysis of SOA markers, PAHs and PAH derivatives. For both phases, 22 PAHs, 27 oxy- and 31 nitro-PAHs were quantified by

UPLC/Fluorescence (ultra-performance LC/Fluorescence detection) and GC/NICI-MS (gas chromatography/negative ion chemical ionization MS), respectively (Albinet et al., 2014, 2013, 2006; Srivastava et al., 2018a; Tomaz et al., 2016). PAH analyses have been performed following the recommendations of European standard procedures EN 15549 and TS 16645 (CEN, 2014, 2008) including the control of extraction efficiency using the NIST SRM 1649b (urban dust). Oxy- and nitro-PAH extraction efficiencies were also checked using the same SRM. All the concentration values obtained were in good agreement with the certified, reference or indicative values from the NIST certificate or with the ones reported in the literature (Albinet et al., 2014, 2013, 2006).

Twenty-five SOA markers were quantified using the extraction and analytical procedures described briefly here and in the Supplementary Material (SM) and as reported previously (Albinet et al., 2019). The list of the chemicals used together with their purity, CAS number and suppliers is also specified (Table S1). SOA markers in PM₁₀ were extracted using a QuEChERS-like extraction procedure as described previously (Albinet et al., 2019). 47 mm filter punches were placed in centrifuge glass tubes ($\varnothing = 16$ mm, L=100 mm, screw cap with PTFE septum face; Duran (Mainz, Germany)), spiked with a known amount (800 ng) of 4 deuterated SOA surrogate standards (Table S2, Fig. S2) and 7 mL of methanol (MeOH) were added for the extraction. The tubes were shaken using a multi-tube vortexer for 1.5 min (DVX-2500, VWR), then centrifuged for 10 min at 4500 rpm (Sigma 3-16 PK). Supernatant extracts (5 ml) were collected and reduced to dryness under a gentle nitrogen stream to remove any trace of MeOH or water and avoid additional consumption of derivatizing reagent. Extracts were then reconstructed into 100 μ L of ACN.

PUF samples were extracted with acetone using pressurized liquid extraction (ASE 350, Thermo; two cycles: 80 °C, 100 bars, 5 min heat time, 15 min static time) (Tomaz et al., 2016). Extracts were reduced under a gentle nitrogen stream to a volume of about 200 μ L

(Zymark, Turbovap II) and adjusted to 2 mL with ACN. Next, a known amount of labelled SOA surrogate standards (100 ng) was added to 500 μ L of the extract and then reduced to dryness under a gentle nitrogen stream and finally dissolved into 50 μ L of ACN. This step was required to eliminate any residual acetone left. Note that the surrogates have not been added before PUF extractions at that time, but extraction tests (n=10) have been performed later, using spiked PUFs with a known amount of several SOA markers (solution of authentic SOA marker standards, Table S1), and showed extraction efficiencies in the range of 20 to 70%, with a standard deviation from 5 to 30%. Reported concentration values here have been corrected from these recovery rates. For molecules with no authentic available standards, correction was done using the known recovery of the most similar compound.

All the extracts have been subjected to derivatization (silylation) using N-methyl-N-trimethylsilyl-trifluoroacetamide (MSTFA) with 1% trimethylchlorosilane (TMCS) (ratio sample extract to derivatizing reagent of 1/1, v/v) for 30 minutes at 60°C. SOA marker analyses were achieved by GC/MS (Agilent 7890A GC coupled to 5975C MS, EI (electron ionization), 70 eV). Authentic SOA marker standards (liquids or solids) were used for the quantification of most of the compounds (Table S1). For molecules with no authentic available standards, quantification was performed using the response factor of the most similar measured compound: 3-(2-hydroxy-ethyl)-2,2-dimethylcyclobutane-carboxylic acid (HCCA) was quantified as pinic acid (PniA); 3-isopropylpentanedioic acid (IPPA), 3-acetylpentanedioic acid (APDA), 3-acetylhexanedioic acid (AHDA), 2-hydroxy-4,4-dimethylglutaric acid (HDGA) were quantified as 3-hydroxyglutaric acid (HGA); 3-methyl-6-nitrocatechol (3M6NC) were quantified as 3-methyl-5-nitrocatechol (3M5NC). All compounds were quantified by internal standard calibration using appropriate deuterated surrogates except methylnitrocatechols (Table S2, (Albinet et al., 2019)).

2.3. SOA markers analysis quality control/quality assurance

Fifteen field blanks for both, particulate and gaseous phases, were collected, stored and analysed simultaneously with the ambient air samples. SOA marker concentrations were corrected from the field blanks when necessary. Overall, field blank concentrations were for most of the compounds below the limit of quantification (LOQ) or represented less than 30% of the average ambient concentrations observed.

LOQs, defined as the lowest concentration of the compound that can be quantified for a signal to noise ratio $S/N = 10$, were estimated using the lowest calibration standard solution (Table S2). Compound concentrations in the samples $< LOQ$ were replaced by $LOQ/2$.

The extraction efficiencies of the SOA markers from PM were also checked using the NIST SRM1649b (urban dust). Results obtained were compared with the only concentration values available in literature (Albinet et al., 2019, Table S3) as there are currently no SRM with certified concentration values for SOA markers. Succinic acid (SuA), phthalic acid (PhA), α -methylglyceric acid (MGA), 2,3-dihydroxy-4-oxopentanoic acid (DHOPA), cis-pinonic acid (PnoA), 3-hydroxyglutaric acid (HGA), pinic acid (PniA), 3-methylbutane-1,2,3-tricarboxylic acid (MBTCA) and β -caryophyllinic acid (CarA) concentrations obtained were in relatively in good agreement with the previously reported values. The differences for 2-Methylerythritol (MET), 3-Methyl-5-nitrocatechol (3M5NC) and 4-Methyl-5-nitrocatechol (4M5NC) were more significant due to the probable inhomogeneity of MET in the SRM 1649b and the fact that both methylnitrocatechols were quantified by external calibration, a procedure which could have introduced additional bias (Albinet et al., 2019). Note that additional and new individual concentration values are given for nitrophenols and nitroguaiacols in this SRM.

2.4. On-line measurements

PM₁₀ were monitored by TEOM-FDMS (1405F model, Thermo) following the technical specifications of the standard method EN 16450 (CEN, 2017c). Black carbon (BC) concentrations were measured using a multi-wavelength aethalometer (AE33, Magee Scientific) and corrected from the filter-loading effect with the real-time compensation algorithm using both simultaneous light attenuation measurements (Drinovec et al., 2017). BC was apportioned into its two main sources, i.e. wood burning (BC_{wb}) and fossil fuel (BC_{ff}) using the “aethalometer model” (Sandradewi et al., 2008). For these calculations, absorption Angström exponents of 1.7 and 0.9 were used for BC_{wb} and BC_{ff}, respectively (Zhang et al., 2019; Zotter et al., 2017). NO_x and O₃ were monitored using T200UP and T400 analysers (Teledyne API), respectively, following the standard operating procedures from the ACTRIS network (CEN, 2012a, 2012b).

Meteorological parameters such as, temperature, relative humidity (RH), wind direction, wind speed and planetary boundary level (PBL) height were measured at the main SIRTA facility located at about 5 km east from the sampling site.

3. Data analysis

3.1. SOA source apportionment

3.1.1. SOA-tracer method

Estimation of the different SOA fractions associated with individual gaseous precursors was achieved applying the SOA-tracer method developed by Kleindienst et al., (2007). In this method, secondary organic carbon (SOC) mass fractions are determined from the concentrations of SOA markers and conversion factors (obtained from smog chamber experiments). This procedure can therefore be applied to calculate SOC loadings from SOA marker concentrations.

From the smog chamber experiments, the SOA mass fraction for each precursor have been calculated using Eq. (1):

$$f_{SOA,prec} = \frac{\sum_i tr_i}{[SOA]} \quad (1)$$

where $f_{SOA,I}$ is the ratio of the sum of the concentrations of all the measured SOA markers $\sum_i tr_i$, to the total SOA concentration formed from the individual class of precursor “prec”. The SOA mass fractions were obtained using gravimetric measurements to convert them into SOC mass fractions (f_{SOC}) using SOA/SOC mass ratios (Eq. (2)).

$$f_{SOC,prec} = f_{SOA,prec} \frac{[SOA]}{[SOC]} \quad (2)$$

Here, SOC mass fractions, from anthropogenic and biogenic origins, were estimated according to a subset of markers analysed following the procedure proposed by Rutter et al., (2014) and described in the SM (Table S6).

The limited number of SOA markers identified for known gaseous organic precursors (so far, only isoprene, α -pinene, β -caryophyllene, naphthalene and monoaromatic VOCs) and the few $f_{SOA/SOC}$ data available in the literature are the main limitations in the application of this method (Srivastava et al., 2018b). Biomass burning SOA is not estimated using the traditional SOA-tracer method. Neglecting this SOA source might lead to significant underestimation of the total wintertime SOC concentrations in Europe due to relatively high contributions (up to 70%) of residential wood burning during the cold season (Ciarelli et al., 2017; Denier van der Gon et al., 2015; Favez et al., 2009; Petit et al., 2014; Puxbaum et al., 2007; Srivastava et al., 2018c; Weber et al., 2019; Zhang et al., 2019). Here, the biomass burning SOA fraction was evaluated using the measured concentrations of methylnitrocatechols, previously demonstrated as secondary photooxidation products of phenolic compounds (e.g., cresols, methoxyphenols) (Iinuma et al., 2010) and known to account for a major fraction of SOA biomass burning (Bruns et al., 2016). Values were taken from the literature (Iinuma et al.,

2010) to calculate f_{SOA} using Eq. (1) with $\sum[tr]_i = 821 \text{ ng m}^{-3}$; $[SOA] = 8293 \text{ ng m}^{-3}$. The SOA mass fraction was converted into SOC mass fraction (f_{SOC}), following Eq. (2), using a SOA to SOC mass ratio of 2, typical for SOA (Aiken et al., 2008). The SOA and SOC mass fractions linked to the oxidation of phenolic compounds emitted from biomass burning finally estimated are detailed in Table S6. Only very recently, biomass burning SOA has been included in the SOA-tracer method with $f_{SOA/SOC}$ for methylnitrocatechols determined from smog chamber experiments with *o*-, *m*- or *p*-cresols as SOA precursors (Al-Naiema et al., 2020). Except for *m*-cresol, the values reported by Al-Naiema et al. (2020) are similar to the ones we evaluated here (e.g. f_{SOA} : 0.0409-0.0489 (this study) vs 0.0410-0.0570) and *m*-cresol = 0.279 in Al-Naiema et al (2020)).

3.1.2. Positive matrix factorization (PMF)

We previously showed that the use of key secondary organic markers into source-receptor models permits the resolution of several SOA sources (Srivastava et al., 2018b, 2018c, 2019, 2019 and references therein). SOA marker concentrations, together with other key species from the extended PM chemical characterization, were included into the data matrix of a PMF analysis performed to apportion the different PM and SOA sources. Finally, a 11-factor output provided the most reasonable solution (Fig.S23 and S24). Briefly, assignments of source were based on the contribution attributed to the marker species in the identified factor. For example, marker species like levoglucosan, 1-nitropyrene, arabitol and sorbitol were used to characterize sources such as biomass burning, primary traffic emissions, and fungal spores, respectively. Secondary markers, such as DHOPA (SOA marker of monoaromatic compounds oxidation) and methylnitrocatechol isomers (SOA from phenolic compounds oxidation) allowed the identification of anthropogenic SOA-1. Bootstrapping of the selected solution showed stable results with ≥ 88 out of 100 bootstrap mapped factors. In addition, the

comparison between the reconstructed and measured PM₁₀ mass also indicated a good agreement (Figure S25), justifying the selection of a 11-factor PMF solution. Details about the PMF analysis and results obtained are reported in the SM (section 9).

3.2. Gas/particle partitioning model

The gas/particle partitioning of organic species in ambient air can be quantified by the gas/particle partitioning coefficient, K_p (Pankow, 1994):

$$K_p = \frac{c_{ip}/c_{PM}}{c_{ig}} \quad (3)$$

where, K_p ($\text{m}^3_{\text{air}} \text{g}^{-1}_{\text{PM}}$) is the temperature-dependent partitioning coefficient, c_{PM} (g m^{-3}) is the concentration of particulate matter in air, c_{ip} is analyte (i) air concentration (ng m^{-3}) in particulate phase, and c_{ig} is that in the gas phase. SOA is a mixture of non-polar compounds and polar material (Pankow, 1994; Saxena and Hildemann, 1996a; Yu et al., 2016). With aliphatic chains or aromatic moiety, the SOA markers studied here have amphiphilic functionalities and are soluble in both, water and organic solvents. These markers are part of the humic-like substances (HuLiS) fraction of OA (Graber and Rudich, 2006; Hallquist et al., 2009; Kitanovski et al., 2020). HuLiS form part of an organic or mixed organic and inorganic phase, which is liquid under most ambient conditions (Hallquist et al., 2009; Shahpoury et al., 2016; Shiraiwa et al., 2013). The octanol-air partitioning coefficient, K_{OA} , has been successfully applied as predictor of gas/particle partitioning for a wide range of mostly non-polar organics, which are absorbed by particulate organic matter (Finizio et al., 1997; Harner and Bidleman, 1998). In this work, we evaluated the suitability of the K_{OA} model to predict the GPP of SOA markers. K_{OA} for each compound was estimated using ppLFER models. This latter combines solute descriptors and so-called system parameters which can be used independently (Endo and Goss, 2014). This approach allows obtaining K_{OA} values for SOA

markers as well as the solute-specific enthalpies of phase transfer that are needed to account for the temperature dependency of estimated partitioning coefficients. This method was chosen for consistency across the target substance list, since experimental K_{OA} and enthalpy values are not available for all SOA markers studied here; this approach was previously used for semi-volatile substituted aromatic species (Tomaz et al., 2016). More details about the applied ppLFER method can be found in section 6 of the SM.

4. Results and discussion

4.1. SOA marker concentrations: comparison with literature data and temporal variations

Annual mean and median of total SOA marker (gaseous + particulate phases) and organic carbon (OC) concentrations, together with minimum, maximum, mean concentrations during the cold (October, November, December, January, February and March) and warm periods (April, May, June, July, August and September), and average particulate fractions (for SOA marker only), are presented in Table 1.

Overall, the concentrations of individual SOA markers observed at SIRTA ranged from few pg m^{-3} , for both, biogenic and anthropogenic compounds, up to $0.1\text{-}1 \mu\text{g m}^{-3}$ for nitroaromatic compounds (NACs) (Table 1). These concentrations were in the same range as those reported worldwide (Tables S4 and S5, particulate phase only).

For the biogenic SOA markers, the concentrations of isoprene SOA markers in PM_{10} at SIRTA (MGA, MTR and MET) were significantly lower than the ones reported in North and South America and in China. This may be the fact that isoprene emissions in Europe are lower than in America and China (Guenther et al., 2006; Hantson et al., 2017). This is also true for some pinene SOA markers such as MBTCA and HGA. Interestingly, significant differences

with the other regions were only observed for these 2nd generation photooxidation products (Claeys et al., 2007; Müller et al., 2012; Szmigielski et al., 2007), while the concentrations of the 1st generation products such as pinic and cis-pinonic acids, were comparable. Finally, except for Hong Kong (Hu et al., 2008), CarA (marker of β -caryophyllene oxidation) concentrations at SIRTA were comparable to worldwide reported values.

For the anthropogenic SOA markers, the concentrations in PM₁₀ observed at SIRTA were all similar to the ones reported worldwide except for the methylnitrocatechols that were largely higher than in China, highlighting a comparably lower proportion of wood burning emissions (for residential heating purposes) in the atmosphere of China than the Paris region.

These results strongly suggest that the emission profiles of the precursors (of SOA markers) and the atmospheric chemical processes involved in the formation and fate of SOA markers are significantly different between Europe and America or Asia. A comparison of the SOA marker concentrations measured at SIRTA (in particulate phase only) with the ones previously reported in Europe is presented in the Supplementary Material (section 2, Fig. S3)..

The comparison of the average total SOA marker concentrations observed during the cold and warm periods gives some clues on the seasonal variations of these compounds (Table 1) which is further discussed afterwards. For biogenic species, the average sum of monoterpene SOA marker concentrations in warm and cold periods were 34 and 26 ng m⁻³, respectively. Although the total monoterpene marker budget varied according to the temperature, with higher concentrations in the warmer periods, the individual compounds did not show the same behaviour. Most of the biogenic marker concentrations were 1.5 times lower in the cold period, except for HDGA, that was quite stable with temperature, and HCCA, MBTCA, and HGA, for which cold period concentrations were 1.5 to 2 times higher than in warm period. For isoprene SOA markers, mean total concentrations were 4.5 times higher (from 1.6 to 7.6 ng m⁻³) during the warm period. Specifically, MGA, MTR and MET concentrations were

about 2.7, 1.6 and 10 times higher in this season than in the cold period. Finally, β -caryophyllinic acid mean concentrations were higher in the colder period (1.5 ng m^{-3}) than in the warmer period (0.4 ng m^{-3}) by a factor of 3.7. As for HCAA, MBTCA and HGA, this difference was mainly due to the high concentrations observed in October/November. This period is discussed in detail in the SM (section S4.3). The high concentrations observed in cold period also suggested that the seasonal trend of biogenic markers did not only depend on the emissions of their precursor.

Anthropogenic SOA marker concentrations were overall higher in cold season than in warm season. SuA, PhA and DHOPA concentrations were respectively 1.9, 2 and 5.8 times higher during the cold period. Nitroaromatic compounds (NACs) dominated over the other markers throughout all seasons. They all showed higher concentrations in the cold period i.e., 1.7 to 245 times higher for the various compounds. Major differences between the cold and the warm periods were observed for 2NPh ($\times 245$) and for 4-NG, 4M5NC and 3M5NC ($\times 20$), obviously due to large emissions of their precursors by biomass burning from residential heating in winter (Bruns et al., 2016; Iinuma et al., 2010). Similar seasonal variations in the concentrations of 4-NG, 4M5NC and 3M5NC were recently reported from an urban site in central Europe, Ostrava (Kitanovski et al., 2020).

The results shown in Table 1 suggest that the precursor emission rates cannot be considered as the only factor influencing SOA marker concentrations. The variations observed in the SOA marker mean concentrations between the warm and the cold periods are probably due other factors, such as gas/particle partitioning and photochemical reactivity, that are strongly dependent on the temperature and sunlight intensity.

The temporal variations in the concentrations of selected biogenic (PnoA, PniA, MBTCA, HGA, MGA and MET+MTR) and anthropogenic (PhA, DHOPA and 3M5NC) SOA markers (gaseous + particulate phase concentrations) are shown in Figs. 1 and 2, respectively, together

with ambient temperature. All other compounds are presented individually in the SM (Figs. S4 to S10). Anthropogenic SOA markers are presented with two primary anthropogenic markers: levoglucosan, a well-known biomass burning molecular marker (Simoneit et al., 1999) and 1-nitropyrene (1-NP) emitted by diesel engines (Keyte et al., 2016; Zielinska et al., 2004a). The latter was used to trace vehicular emissions (Srivastava et al., 2019, 2018a, 2018c) as in 2015, 80% of the total vehicles fleet (cars and heavy duty vehicles) in France was composed by diesel engines (CCFA, 2016) which was supported by the correlations between BC_{ff} and NO_x (Fig. S11 and Fig. S12, $r=0.73$ for both, $n=130$, $p<0.05$).

The concentrations of biogenic SOA marker were expected to increase during the summer period due to the increase of biogenic emissions and photochemical activities (Guenther, 1997; Tarvainen et al., 2005). Here, only isoprene SOA markers (e.g. MGA and MET+MTR) showed clear seasonal variations with higher concentrations observed in summer while no significant seasonal trend could be observed for all the pinene SOA makers. Several previous studies, in China and USA, investigated the temporal variations of the concentrations of biogenic SOA markers in the particulate phase. They showed a systematic summer increase in the concentrations of isoprene SOA marker and a fluctuating seasonal trend for the concentrations of pinene SOA markers (Ding et al., 2016, 2008; Feng et al., 2013). The only study reporting PnoA, PniA and MBTCA seasonal variations in Europe (Mainz, Germany, particulate phase (Zhang et al., 2010) found a general increase of these compounds in summer. The different seasonal trends of these marker families are related to the annual variations in the emissions of their precursor compounds. Monoterpene emissions are regulated almost entirely by the temperature, while isoprene emissions also depend on the light irradiance and the leaf area index (Guenther et al., 2006). Thus, in cold period, monoterpene emissions are still significant, while isoprene emissions are close to zero (Oderbolz et al., 2013). There were no significant correlations ($p > 0.05$) between biogenic

SOA markers and trace gases or meteorological data at SIRTA. Only MGA and MET slightly correlated with temperature ($r = 0.58$ and 0.63 , $p < 0.05$, $n = 130$, $p < 0.05$, Fig. S13). Considering the difference in the factors driving isoprene and monoterpene emissions, the lack of a definite seasonal trend for monoterpene SOA was not surprising.

All anthropogenic SOA markers concentrations were enhanced in colder periods, but no seasonal trend could be observed for PhA and SuA. The concentrations of nitrophenols and nitroguaiacols were only higher in the first part of the year. Significant correlations with levoglucosan have been observed for 2NPh ($r = 0.72$, $p < 0.05$, $n = 130$, Fig. S14) and for methylnitrocatechols (r for 4M5NC, 3M6NC and 3MNC of 0.79 , 0.74 and 0.81 , respectively, $p < 0.05$, $n = 130$, Fig. S14). The increase in the concentrations of the biomass burning related markers under low atmospheric temperature conditions was expected, since in Europe, biomass burning for residential heating is a large source of atmospheric PM (Denier van der Gon et al., 2015; Puxbaum et al., 2007; Viana et al., 2016). No significant correlations between any anthropogenic secondary markers or 1-NP, trace gases and meteorological data were observed (Figs. S13 and S14).

4.2. SOA markers gas/particle partitioning

4.2.1. Field observations

Particulate mass fractions (F_p) of biogenic and anthropogenic SOA markers are shown on Fig. 3. F_p were split by temperature bins based on 3 temperature quartiles: $T < 7^\circ\text{C}$ (25% of the data); $15 > T > 7^\circ\text{C}$ (50% of the data) and $T > 15^\circ\text{C}$ (25% of the data). These temperatures could be considered as representative of the winter, spring and autumn, and summer seasons, respectively.

All the pinene SOA markers, were on average, mainly associated to the particulate phase (Table 1). Compared to the literature, in which F_p values ranged from 0.1 to 0.6, PnoA was

largely in the particulate phase but showed a shift towards the gaseous phase with increasing temperature (F_p from 1 to 0.65 with $T < 7^\circ\text{C}$ and $T > 15^\circ\text{C}$) (Al Naiema and Stone, 2017; Lutz et al., 2019; Yatavelli et al., 2014). Similarly, PniA (median $F_p \approx 0.9$), TerA (median $F_p \approx 0.8$) and HGA (median $F_p > 0.9$) partitioned more to the particulate phase than previously reported (Yatavelli et al. (2014), found $F_p \approx 0.5$ for both PniA and TerA, $F_p \approx 0.7$ for HGA, Kristensen et al. (2016) measured respectively mean $F_p \approx 0.38$ and 0.29 for PniA and TerA). Overall, our observations were in agreement with the literature, showing that PniA is less volatile than PnoA (Lutz et al., 2019; Thompson et al., 2017). Finally, MBTCA was mainly in the particulate fraction (median $F_p \approx 1$) with no change according to the temperature as previously published (Kristensen et al., 2016; Yatavelli et al., 2014). Isoprene SOA markers GPP showed also a low temperature dependency. MGA F_p ranged from 0.85 to 0.90 whatever the temperature range considered. MTR and MET tend to partition slightly in the gaseous phase only above 15°C (average F_p of 0.93 and 0.72, respectively). Except for MTR, these results were in agreement with the measurements performed by (Al Naiema and Stone, 2017) (for MGA average $F_p \approx 0.85$, for MET and MTR average $F_p \approx 0.63$). Finally, β -caryophyllinic acid was observed only in the particulate phase ($F_p = 1$).

Among anthropogenic acid SOA markers, only PhA GPP was significantly affected by temperature. SuA and DHOPA median F_p were above 0.8 in all bins, while PhA median F_p decreased from 0.7 to 0.5 following the temperature increase. Literature data for SuA and PhA are discordant on F_p estimation and temperature dependency, with F_p ranging from 0.5 to 0.9 for SuA (Bao et al., 2012; Limbeck et al., 2001) and from 0.2 to 0.7 for PhA (Al Naiema and Stone, 2017; Kristensen et al., 2016; Limbeck et al., 2001). In agreement with our observations (mean $F_p = 0.84$), (Al Naiema and Stone, 2017) showed that DHOPA was 100% associated to the particulate phase but we observed large variations at temperatures $> 15^\circ\text{C}$.

No common behaviour for NACs GPP could be highlighted. The nitrophenols (2NPh, 4NPh and 2M4NPh) were predominantly partitioned into the gaseous phase (median $F_p < 0.3$). The F_p of 2NPh in this study is similar to the values ($F_p = 0.25$) reported by Cecinato et al., (2005), while their F_p value of 0.82 for 4NPh F_p was higher than the value from SIRTA. Al Naiema and Stone, (2017) reported low 4NPh ($F_p = 0.3$) in agreement with our results. Both NG isomers, namely 4NG and 5NG, were in total opposition with the 90% of the gaseous phase for 4NG, as in Al Naiema and Stone, (2017), and about 80% for 5NG was associated to the particulate phase. 3M6NC and 4M5NC were mainly associated to the particulate phase whatever the T° bin considered ($1 > F_p > 0.9$), as previously reported (Al Naiema and Stone, 2017). Only 3M5NC showed a temperature dependency with a shift to the gaseous phase at higher T° (F_p from 0.1 to 0.5).

Besides temperature, organic carbon (or matter) mass has been found to play a major role in the GPP (Donahue et al., 2012; Odum et al., 1996; Shahpoury et al., 2016; Tomaz et al., 2016). The variation of F_p with OM concentrations is shown on Fig. S16 but no significant links have been observed. Even so strong dependence towards OM mass fraction (f_{OM}) has been reported in the literature for various classes of apolar or moderately polar organics, it cannot be expected for strongly polar organics which form H-bonds and even less in mixed organic and inorganic (aqueous) phases, where the solute's solubility in water becomes a significant parameter.

These results showed that all the SOA markers studied here, including the compounds usually considered as semi-volatiles, were predominantly associated to the particulate phase. This might be explained by the very polar functional groups of several of the targeted SOA markers in this study. For instance, the very polar and ionisable (carboxyl) functional groups of alkanolic acids causes strong decreases in their volatility (Yatavelli et al., 2014) and can explain their large sorption to the atmospheric PM as previously observed for low molecular

weight dicarboxylic acids (Bilde et al., 2015; Booth et al., 2010; Falkovich et al., 2004; Huisman et al., 2013; Limbeck et al., 2001; Mochida et al., 2003; Saxena and Hildemann, 1996b). In the accumulation mode and below, the difference between the aqueous phase pH and the substance pK_a may cause partial to complete dissociation of organic acids in the pK_a range 2-5 (Ahrens et al., 2012; Shahpoury et al., 2018) (Table S6). The temperature and the OM concentrations dependence of the GPP in this study was generally low. This suggests that adsorption is not determining the GPP of SOA markers, but absorption and eventually additional other processes should be considered in order to understand the GPP.

4.2.2. Gas/particle partitioning model evaluation

Detailed results about the GPP model evaluation are presented in the SM in section 6 (Fig. S17). The K_{oa} model applied in this study provided the best GPP predictions for 3- and 4M5NC, covering the observed range of K_p (one order of magnitude) and with relatively small deviation from the observed values, i.e. root mean square errors (RMSE, Table S6) of ≤ 0.56 and predicting 70 - 89% of the observed values within one order of magnitude. The model predictions were rather diverse for all other compounds, as the observed variation of K_p across the samples was not fully captured by the model. The model covered the central values for the range of observed K_p for 4- and 5NG, 2M4NP, 4NP, PniA, IPPA, APDA, HGA, MTR, and MET (30 - 68% of the values predicted within one order of magnitude). The K_p values of HCCA, TerA, PnoA, DHOPA (6 - 49% of values predicted within one order of magnitude) and MGA, SuA, and 3M6NC (none within one order of magnitude) were systematically underestimated by 1 or 2 orders of magnitude, while the K_p values of PhA, HDGA, AHDA (26-62% of the values predicted within one order of magnitude), and CarA and MBTCA (none within one order of magnitude) were systematically overestimated by 1 or 2 orders of magnitude.

The particularly poor predictions for the acids SuA and MGA (RSME = 2.8 and 2.7, respectively, and $\leq 1\%$ of K_p values predicted within one order of magnitude) may be explained by partial dissociation of these ($pK_a < 4$) in particles of the accumulation mode or smaller. This explains K_p overestimates. The model performed better for acids with $pK_a > 4$ (all other markers, except PhA) (Table S6). Considering the good model predictions for 4-NPh (RSME = 0.9, 68%), the poor model performance for the isomer 2NPh (K_p underestimated, RSME = 2.2, only 2% of K_p values predicted within one order of magnitude), might be explained by the intramolecular H-bonding between adjacent nitro and hydroxy groups (not seen with 4NPh); this is captured in the ppLFER calculations of K_{OA} for 2NPh, and it typically leads to low modelled K_p values (Shahpoury et al., 2018). However, the observed K_p can be influenced by processes other than thermodynamic partitioning, such as enhanced dissolution of 2NPh in the aqueous phase, which could outweigh the thermodynamic limitations, leading to higher observed K_p (Fig. S17).

We cannot expect that any choice of organic solvent would be a perfect model for the organic or even a mixed organic and inorganic phase in PM, whose major components are moderately polar or polar and multifunctional (HuLiS fraction), non-polar with high aliphatic fraction (fatty acids, paraffin), and contain water and electrolytes. As no diffusion constraint in bulk SOA can be expected under the ambient conditions of our site, a phase equilibrium of semi-volatile compounds between air and OA should be established (Ye et al., 2016). Like what has been found here for K_{oa} as the predictor, vapour pressure has been shown to fail to predict GPP of several classes of polar organics (e.g. methyltetrols, furandiones and phthalic acids) (Al-Naiema and Stone, 2017; Xie et al., 2014). However, an aqueous phase on the particle surface may constitute a diffusion limit. Also, the water content of the OA changes with ambient humidity (Ansari and Pandis, 2000). For solutes with significant water solubility, i.e., all SOA markers, and especially the carboxylic acids, relaxation to a transient

phase equilibrium, triggered by changes in humidity, may continue during the day. Correspondingly, electrolytes (metal ions, ammonium, sulfate and nitrate etc.) will be present to some extent in the mixed phase; molecular interactions with ionic solutes are not captured by the model used here. Moreover, any phase anisotropy may be transient as well: changing humidity may lead to phase separation of organic fractions (Ciobanu et al., 2009).

Overall, the GPP model based on equilibrium partitioning between a model organic phase (octanol) as surrogate for OA and air obviously neglects processes significant for several SOA markers, with most of these processes suppressing volatility from a mixed organic and aqueous condensed phase. Possible explanations are dissociation of the carboxylic acids, chelating of transition metal ions (Scheinhardt et al., 2013; Shahpoury et al., 2018) or non-equilibrium conditions due to high-frequency transient processes (such as diurnal temperature and hygroscopic growth changes).

4.3. SOA source apportionment

4.3.1. SOA tracer method

Fig. 4 shows the annual evolution of SOC sources estimated using the SOA tracer method. The highest SOC concentrations were observed in February, October and November (2014 and 2015) accounting for about 9, 20 and 15% of OC. Through the year, three different periods with different SOC characteristics can be highlighted: the first period, from November 2014 until end of March 2015 was mainly dominated by anthropogenic SOC from the photooxidation of phenolic and monoaromatic compounds, including a minor contribution from the SOC formed through the oxidation of naphthalene. All of these species are largely emitted by biomass burning (Baudic et al., 2016; Bruns et al., 2016; Iinuma et al., 2010; Nalin et al., 2016). Combustion of wood combustion for residential heating is a predominant source for PM and S/VOCs during the cold period in the Paris region (Bressi et al., 2014; Crippa et

al., 2013b; Languille et al., 2020; Petit et al., 2014; Srivastava et al., 2018a; Zhang et al., 2019). The stable meteorological conditions (low boundary layer height and low wind speed, Figs. S18 and S19) together with high S/VOC precursor concentrations from these emissions were favourable for the enhanced formation of anthropogenic SOA during this period. The second period, from April to the end of September, was mainly dominated by biogenic SOC from pinene oxidation. High pinene emissions are usually noticed during the warmer months (Guenther, 1997; Guenther et al., 2006; Tarvainen et al., 2005), together with high solar fluxes (Fig. S19) and oxidant concentrations (i.e. O₃ and OH) that could facilitate high biogenic SOC formation (Docherty et al., 2008; Feng et al., 2013; Kleindienst et al., 2007b; Lewandowski et al., 2008; Sheesley et al., 2004; Shrivastava et al., 2007; Zhang et al., 2009). In addition, increase in the biogenic emissions at SIRTAs has already been found to be linked with the seasonal temperature rise (Zhang et al., 2019). During the last period, from October to the end of December 2015, biogenic SOC (from pinene) still accounted for a significant fraction of the total SOC. However, anthropogenic SOC from monoaromatic VOCs and naphthalene oxidation contributed also significantly. Other biogenic SOC, from isoprene and β -caryophyllene oxidation, and anthropogenic SOC (phenolic compounds oxidation), showed low contributions to the total SOC mass. From October to mid-November (see SM, section 5), favourable meteorological conditions, including an increase of the relative humidity, low wind speed, low planetary boundary level height, low precipitation and “warm” weather (mean temperature of 11°C), induced low atmospheric vertical mixing and a stagnation of the pollutants over a long period, further favouring SOA formation. Additionally, the NO_x concentrations during this period was higher than the annual average probably due to larger primary pollutant emissions from the higher volumes of road traffic (Fig. S11). In fact, at low temperatures, reduction in biogenic emissions is usually observed, but prevalent anthropogenic emissions (high NO_x conditions) could enhance the formation of biogenic SOA

(at least from isoprene) as already shown previously (Claeys et al., 2004; Edney et al., 2005; Kroll et al., 2006; Surratt et al., 2010, 2006). Finally, in December 2015, the SOC composition/concentrations was different from the SOC composition/concentrations observed in November-December 2014. The discrepancies could be linked to differences in temperature, noticed during these periods, and in terms of anthropogenic activities (low levoglucosan concentrations for instance, Fig. 2) and meteorological conditions.

4.3.2. Comparison of SOA tracer method and PMF outputs

The SOA-tracer method has several limitations due to the use of laboratory developed mass fractions to estimate SOC mass from the individual class of precursors. Indeed, this method is probably not representative of all the atmospheric conditions, and only determined for a limited number of SOA markers (Srivastava et al., 2018a). As suggested by Srivastava et al., (2018a), the use of a combination of different SOC estimation methodologies to apportion the SOC concentrations is necessary to get a higher level of confidence in the results obtained. Here, we compared the SOA tracer method with the outputs of a PMF analysis. PMF resulted in the identification of five primary (primary traffic emissions, biomass burning, fungal spores, sea salt, and dust) and six secondary (sulfate-rich secondary aerosol, nitrate-rich secondary aerosol, biogenic SOA-1 (marine), biogenic SOA-2 (isoprene and pinene oxidation), anthropogenic SOA-1 (biomass burning and traffic SOA) and anthropogenic AOA-2 (biomass burning SOA)) sources. The total PM mass was dominated by secondary fractions which accounted for 51% on annual basis. More than 40% of SOA was composed of biogenic SOA (biogenic SOA-1 + biogenic SOA-2) with the highest contribution observed during summer and fall due to high biogenic activities. Anthropogenic SOA (anthropogenic SOA-1 + anthropogenic SOA-2) linked to combustion processes (biomass burning and traffic emissions) were significant in winter and spring periods and accounted for 32% of the total

SOA mass (Figs. S25 and S26). Details on PMF analysis and results are provided in the SM (section 9, Figs. S19-S21). The specific PMF SOC apportionment results are shown on Fig. S22.

Fig. 5 shows the comparison of the SOC concentrations estimated using both methods. Overall, total SOC concentrations evaluated by both methods were in good agreement through the year. Significant differences were only observed in spring (and notably March) and in summer (from May to August) with a systematic underestimation by the SOA tracer method (Fig. S29, poor correlations observed and slopes from 0.33 to 0.46). March was characterized by an intense PM pollution event ($PM_{10} > 50 \mu\text{g m}^{-3}$ for at least 3 consecutive days) over a three weeks period (Fig. S20). This type of event is typical of the late winter - early spring period in North-western Europe and is characterized by large contributions of secondary organic species such as ammonium nitrate (and in a lesser extent, ammonium sulfate too), long range air mass transportation and significant aging. Detailed discussions about the PM and OA sources of the March 2015 PM pollution event can be found elsewhere (Petit et al., 2017; Srivastava et al., 2019, 2018a). The additional SOC contribution in the PMF method (other SOC, Fig. 5) was apportioned based on the nitrate- and sulfate-rich factors (Srivastava et al., 2018a) (Fig. S24). Even with advanced source apportionment method, we failed to get any better description due to the lack of specific molecular markers for such aged SOA (Srivastava et al., 2019). Similarly, as no specific markers and/or $f_{SOA/SOC}$ have been reported in the literature for any other SOA classes, especially for organonitrates and organosulfates, the SOA tracer method underestimated the total SOC concentrations under such conditions. The inability of the SOA tracer method to predict SOC concentrations during high pollution episodes remains a major limitation of this method due to lack of existing SOA markers to estimate SOC mass from different precursors (e.g. alkanes, alkenes, mono and poly-aromatic

compounds...). This is further discussed in another paper in which several SOC apportionment methods are compared (Srivastava et al., 2020).

Into details, the anthropogenic SOC contribution for the SOA-tracer method accounted for the SOC formed from the oxidation of naphthalene, monoaromatic and phenolic compounds while two anthropogenic secondary fractions (ASOA-1 (biomass burning + traffic) and ASOA-2 (biomass burning) factors) were apportioned by the PMF model. A very good agreement was noticed ($r = 0.9$, slope = 0.94, $p < 0.05$, $n = 123$) thanks to the similar species used in both approaches and to the inclusion of methylnitrocatechols into the SOA-tracer method. These results show that the $f_{SOC/SOA}$ estimated for these compounds here from Iinuma et al., (2010) data seem suitable.

The biogenic SOC fraction resolved using the SOA-tracer method was the sum of the SOC formed from the oxidation of isoprene, pinene and caryophyllene while biogenic SOC from the PMF model accounted two biogenic secondary fractions from marine origin (dimethylsulfide oxidation, BSOA-1) and from the oxidation of isoprene/monoterpenes (BSOA-2) (Figs 4, 5, S24 and S28). Temporal profiles of biogenic SOC estimated using both approaches showed significant disagreement, especially in summer and fall. The biogenic SOA mass in summer included a large fraction of marine SOA only apportioned by the PMF. Again, as no specific f_{SOC} value has been determined for the DMS oxidation, this fraction could not be accounted using the SOA-tracer method, explaining the significant differences observed between both methods. In fall, the large overestimation by the SOA-tracer method was probably due to the $f_{SOA/SOC}$ from smog chamber experiments that may be different and not representative of the atmospheric conditions observed during this period (NO_x concentrations, humidity, etc).

5. Conclusions

Over this one-year study, we observed similar individual SOA marker concentrations in the Paris region than those reported worldwide even if some pattern discrepancies due to differences in precursor emissions were highlighted. Over the anthropogenic species, only the concentrations of nitroaromatic compounds showed a clear seasonal trend with higher concentrations in winter due to larger precursor emissions from biomass burning used for residential heating. For biogenic SOA markers, only isoprene SOA marker concentrations increased in the summer. We found that, except nitrophenols and nitroguaiacols, all SOA markers were mainly associated to the particulate phase. In addition, the evaluation of the SOA markers GPP suggested that apart from phase equilibrium between OA and air, partitioning seems determined by processes suppressing volatility from a mixed organic and aqueous phase. Finally, we showed a good agreement between both SOA source apportionment methodologies used (i.e., SOA-tracer method and PMF), except in summer and during a highly processed Springtime PM pollution event, when a systematic underestimation by the SOA-tracer method was observed. These discrepancies highlighted the limitations of the SOA-tracer method due to missing specific markers for aged SOA and the lack of SOA/SOC conversion fractions ($f_{SOA/SOC}$) for a biogenic source like marine SOA. In addition, the $f_{SOA/SOC}$ from smog chamber experiments are probably not representative of the various atmospheric conditions that can be encountered in ambient air (variable NO_x concentrations, humidity, etc...). As it could provide a reliable average SOC estimation, we suggest the use of the SOA-tracer method as a first approach to apportion SOA but, in order to get a higher level of confidence in the results obtained, it should be further compared to another SOA apportionment method (Srivastava et al., 2018a).

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Author contributions

A.A. and O.F. designed and led the study. G.M.L., D.S., L.Y.A and N.B. performed the chemical analyses. B.A.M.B., P.S. and G.L. evaluated gas/particle partitioning by modelling. G.M.L. A.A. and O.F supervised D.S. PhD work. A.A, F.C., B.B. and O.F. supervised G.M.L PhD work. G.M.L., D.S. and A.A interpreted the data, and wrote the manuscript, with inputs from all co-authors.

Appendix A.

Supplementary data: Supplementary data to this article can be found online.

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Credit author statement

A.A. and O.F. designed and led the study. G.M.L, D.S., L.Y.A and N.B. performed the chemical analyses. B.A.M.B., P.S. and G.L. evaluated gas/particle partitioning by modelling. G.M.L. A.A. and O.F supervised D.S. PhD work. A.A, F.C., B.B. and O.F. supervised G.M.L PhD work. G.M.L., D.S. and A.A interpreted the data, and wrote the manuscript, with inputs from all co-authors.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Fig. 1. Temporal variations of total (gaseous + particulate phases) concentrations of selected biogenic SOA markers at SIRTa (2015). Upper panel shows the temperature, central panels show the first (PnoA and PniA) and second generation (HGA and MBTCA) pinene SOA markers, and the lower panel shows isoprene SOA markers (tetrols and MGA). Tetrols is the sum of 2-methylerythritol (MET) and 2-methylthreitol (MTR).

Fig. 2. Temporal variations of total (gaseous + particulate phases) concentrations of selected anthropogenic SOA markers at SIRTa (2015). Upper panel shows the temperature, central panel shows PhA together with 1-nitropyrene (1-NP) (diesel emission marker) and lower panel shows DHOPA and 3M5NC together with levoglucosan (marker for primary biomass burning emissions).

Fig. 3. SOA marker particulate phase mass fractions (F_p) distributed by temperature bins. Bins were defined based on 3 temperature quartiles (7 and 15°C were respectively the 25th and the 75th temperature percentiles). Data <LOQ have been excluded (3% of the data). The boxplots are built using the 15th, the 25th, the 50th, the 75th and the 85th percentiles as respectively the lower whisker, the bottom, the middle and the top of the box and the upper whisker. The black dots show the outliers.

Fig. 4. Temporal evolution of the identified sources of SOC mass concentrations at SIRTa (2015) using the SOA tracer method.

Fig. 5. Comparison of the SOC concentrations estimated using PMF analysis and SOA tracer method. For SOA tracer method, anthropogenic SOC includes SOA from naphthalene, monoaromatic and phenolic compounds; biogenic SOC includes SOA from pinene, isoprene and β -caryophyllene. For PMF analysis, anthropogenic SOC includes ASOA-1 (biomass burning + traffic) and ASOA-2 (biomass burning) factors; biogenic SOC includes BSOA-A (marine) and BSOA-2 (monoterpenes + isoprene) factors. Other PMF SOC was apportioned based on the nitrate- and sulfate-rich factors.

Table 1. Total atmospheric concentrations (gaseous + particulate phases, ng m⁻³) of biogenic and anthropogenic SOA markers measured at SIRT A (France) from mid-November 2014 to mid-December 2015. Annual average and median values together with the average concentrations for the cold and warm periods, the minimum and the maximum observed values, are reported. The measured mean particulate mass fractions (F_p, in %) with the associated coefficients of variation are specified for the SOA markers. OC concentrations (μg m⁻³) are also reported.

Compounds	Abbreviation	Annual mean (min – max)	Annual median	Cold period ^a mean	Warm period ^a mean	F _p (%)	CV F _p ^d (%)
<i>Pinene</i>							
cis-Pinonic acid	PnoA	2.8 (0.1-11)	2.1	2.2	3.4	75	44
Pinic acid	PniA	0.8 (<0.1-7.8)	0.5	0.7	1.0	94	35
3-(2-Hydroxy-ethyl)-2,2-dimethylcyclobutane-carboxylic acid ^b	HCCA	0.9 (<0.1-5.2)	0.6	1.1	0.7	98	31
3-Methylbutane-1,2,3-tricarboxylic acid	MBTCA	1.0 (<0.1-10.3)	0.6	1.4	0.6	99	39
3-Hydroxyglutaric acid	HGA	2.2 (<0.1-16.4)	0.8	2.6	1.7	83	45
Terpenylic acid	TerA	0.3 (<0.1-4.7)	0.1	0.2	0.3	78	47
3-Hydroxy-4,4-dimethylglutaric acid ^c	HDGA	0.3 (<0.1-2.3)	0.2	0.3	0.3	86	38
3-Acetyl-pentanedioic acid ^c	APDA	2.6 (0.1-21.9)	1.3	2.8	2.4	82	43
3-Acetyl-hexanedioic acid ^c	AHDA	5.1 (<0.1-34.9)	2.8	4.3	6.2	97	30
3-Isopropylpentanedioic acid ^c	IPPA	0.3 (<0.1-1.7)	0.2	0.4	0.3	84	43
<i>Isoprene</i>							
α-Methylglyceric acid	MGA	0.5 (<0.1-3.3)	0.2	0.3	0.8	89	58
2-Methylthreitol	MTR	0.8 (<0.1-6.2)	0.5	0.6	1.0	93	37
2-Methylerythritol	MET	3.1 (<0.1-40.8)	1.0	0.7	6.0	72	53
<i>β-Caryophyllene</i>							
β-Caryophyllinic acid	CarA	1 (<0.1-21.9)	0.4	1.5	0.4	97	32
<i>Anthropogenic SOA acids</i>							
Succinic acid	SuA	8.3 (<0.1-53.3)	5.0	10.5	5.6	88	33
Phthalic acid	PhA	2.7 (<0.1-25.1)	1.5	3.5	1.7	60	61
2,3-Dihydroxy-4-oxopentanoic acid	DHOPA	1 (<0.1-9)	0.5	1.6	0.3	84	41
<i>Nitroaromatic compounds (NACs)</i>							
2-Nitrophenol	2NPh	52.7 (<0.1-1086.3)	0.6	96.8	0.4	27	80
4-Nitrophenol	4NPh	6.9 (<0.1-27.9)	5.3	8.6	5.0	7	79
2-Methyl-4-nitrophenol	2M4NPh	1.6 (<0.1-12.1)	1.1	2.4	0.7	9	47
4-Nitroguaiacol	4NG	7.9 (<0.1-98.1)	2.3	13.9	0.7	10	72
5-Nitroguaiacol	5NG	0.4 (<0.1-6.2)	0.1	0.6	0.1	80	53
4-Methyl-5-nitrocatechol	4M5NC	18.9 (0.1-321.0)	1.5	33.6	1.6	95	29
3-Methyl-6-nitrocatechol	3M6NC	4.2 (1.7-39.6)	2.7	5.4	2.7	99	28
3-Methyl-5-nitrocatechol	3M5NC	15.9 (0.1-263.8)	1.4	28.0	1.4	79	40
<i>Organic carbon</i>	OC	3.3 (0.6-11.8)	3.0	3.6	2.9	-	-

^a Cold and warm periods were defined as follows: cold period included October, November (2014 and 2015), December (2014 and 2015), January, February and March months, and warm periods included April, May, June, July, August and September months. Average temperatures during both periods were about 7.4 and 17°C, respectively. ^b Quantified using pinic acid as response factor. ^c Quantified by internal calibration using 3-hydroxyglutaric acid as response factor. ^d coefficient of variation = standard deviation/mean in %

Highlights

- One-year monitoring of 25 key SOA markers in the Paris region
- Seasonal/chemical differences with non-EU data due to source precursor contrasts
- SOA marker GPP measurements/modelling highlighting volatility suppressing processes
- Good agreement on annual scale between SOA-tracer and PMF SOA source apportionments
- Underestimation by the SOA tracer for aged SOA due to missing conversion factors

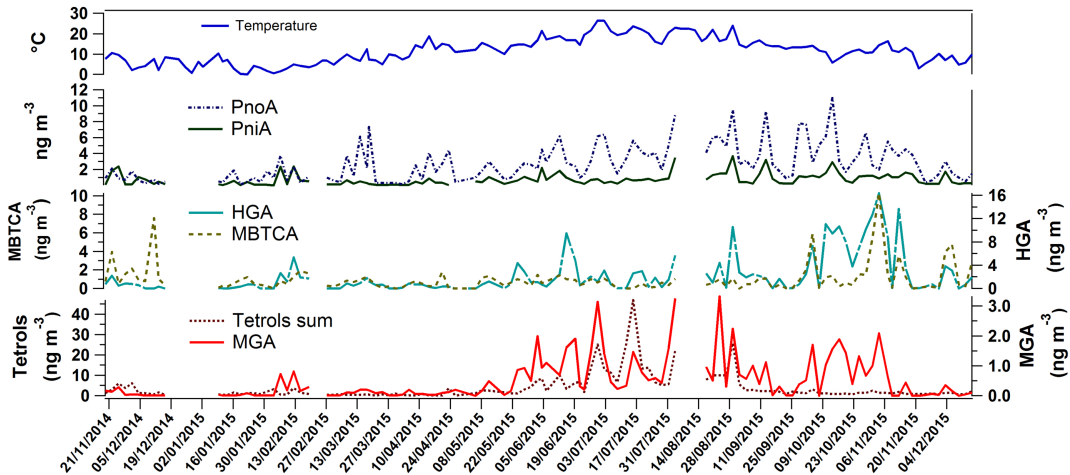


Figure 1

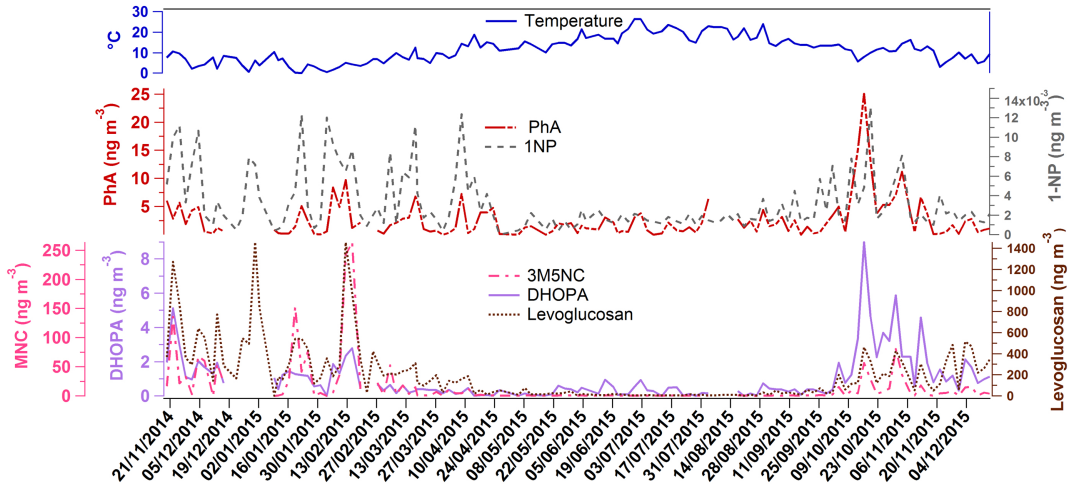


Figure 2

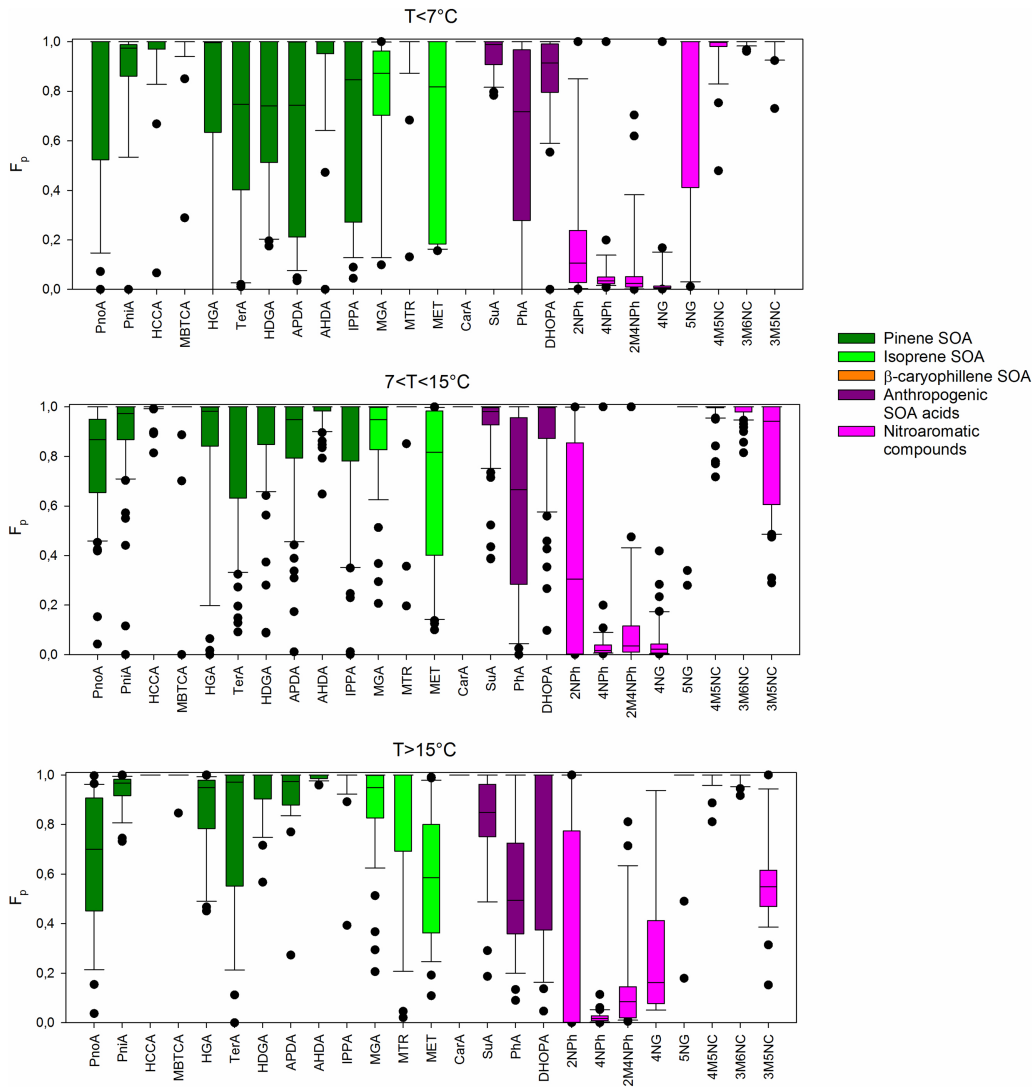


Figure 3

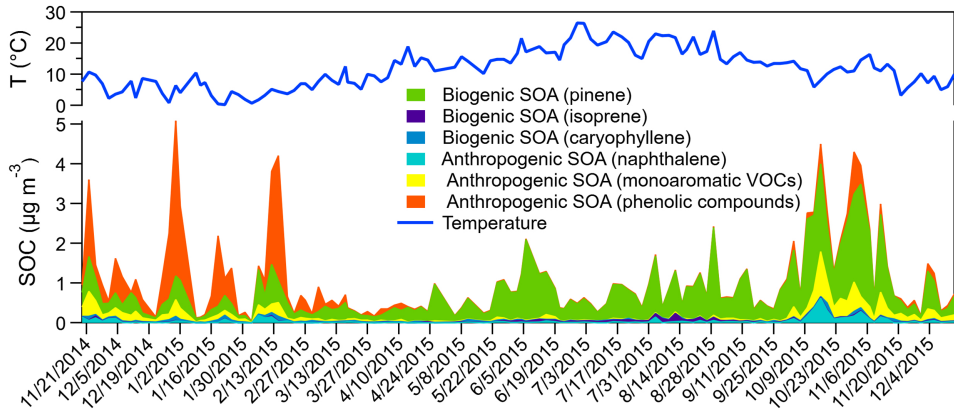


Figure 4

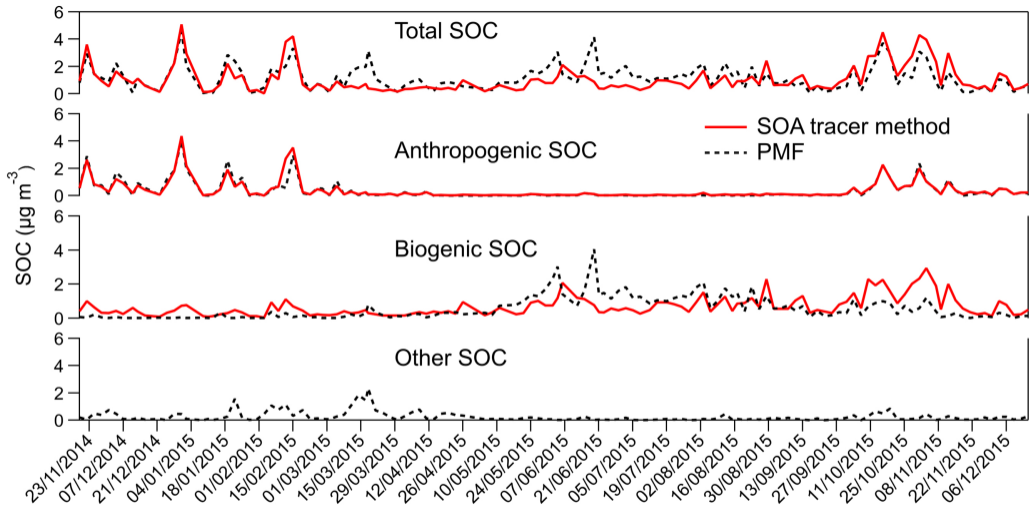


Figure 5