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Volatile and intermediate volatility organic compounds in suburban Paris: variability, origin and importance for SOA formation

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Abstract. Measurements of gaseous and particulate organic carbon were performed during the MEGAPOLI experiments, in July 2009 and January–February 2010, at the SIRTA observatory in suburban Paris. Measurements comprise primary and secondary volatile organic compounds (VOCs), of both anthropogenic and biogenic origins, including C_{12}–C_{16} n-alkanes of intermediate volatility (IVOCs), suspected to be efficient precursors of secondary organic aerosol (SOA). The time series of gaseous carbon are generally consistent with times series of particulate organic carbon at regional scale, and are clearly affected by meteorology and air mass origin. Concentration levels of anthropogenic VOCs in urban and suburban Paris were surprisingly low (2–963 ppt) compared to other megacities worldwide and to rural continental sites. Urban enhancement ratios of anthropogenic VOC pairs agree well between the urban and suburban Paris sites, showing the regional extent of anthropogenic sources of similar composition. Contrary to other primary anthropogenic VOCs (aromatics and alkanes), IVOCs showed lower concentrations in winter (< 5 ppt) compared to summer (13–27 ppt), which cannot be explained by the gas-particle partitioning theory. Higher concentrations of most oxygenated VOCs in winter (18–5984 ppt) suggest their dominant primary anthropogenic origin. The respective role of primary anthropogenic gaseous compounds in regional SOA formation was investigated by estimating the SOA mass concentration expected from the anthropogenic VOCs and IVOCs (I / VOCs) measured at SIRTA. From an integrated approach based on emission ratios and SOA yields, 38 % of the SOA measured at SIRTA is explained by the measured concentrations of I / VOCs, with a 2 % contribution by C_{12}–C_{16} n-alkane IVOCs. From the results of an alternative time-resolved approach, the average IVOC contribution to SOA formation is estimated to be 7 %, which is half of the average contribution of the traditional aromatic compounds (15 %). Both approaches, which are based on in situ observations

of particular I / VOCs, emphasize the importance of the intermediate volatility compounds in the SOA formation, and support previous results from chamber experiments and modeling studies. They also support the need to make systematic the IVOCs' speciated measurement during field campaigns.

1 Introduction

Since 1950, the number of people living in urban areas has steadily increased. According to the United Nations, the urban population has risen from 30 to 50 % of the world population within the last 50 years, and it will reach about 70 % by 2050 (United Nations, 2012). This intensive urbanization has led to the development of numerous megacities, defined as urban centers with at least 10 million inhabitants. If a high population density characterizes a megacity, they are also defined by their anthropogenic activities, which are not different from other urban centers but more intense; larger amounts of atmospheric pollutants are emitted in megacities. Among them, there are the volatile organic compounds (VOCs), the emissions of which are diverse and include both anthropogenic and biogenic sources. In urban areas like megacities, where industrialization and traffic are important (Molina and Molina, 2004), VOCs are mainly emitted by primary anthropogenic sources (Gros et al., 2007). Once emitted into the atmosphere, primary VOCs can be photolyzed or/and oxidized by atmospheric oxidants like the hydroxyl radical (OH), the nitrate radical (NO_3) or ozone (O_3), and then, other VOCs are produced (Atkinson and Arey, 2003). These newly produced VOCs or secondary VOCs, generally oxygenated (OVOC), can themselves undergo further reactions and produce different oxidants as by-products, including ozone (Jenkin and Hayman, 1999; Tanaka et al., 2003), whose adverse effects on climate and people are well-known (Heiden et al., 1999; Wildt et al., 2003; Filleul et al., 2006).

VOCs in megacities have been widely studied in the past. Their ambient concentrations have been commonly explored (Barletta et al., 2002; Khoder, 2007), but numerous studies mainly focused on traffic emissions (Baumbach et al., 1995; Colón et al., 2001; Barletta et al., 2002; Srivastava et al., 2005; Martins et al., 2007; Khillare et al., 2008; Majumdar et al., 2008). VOC emissions by other sources (solvent uses, gasoline evaporation, gas leakage, etc.) were also investigated, especially through source apportionment studies (Srivastava, 2004; Lanz et al., 2008; Bon et al., 2011; Gaimoz et al., 2011). As for biogenic VOCs, even though their emissions are not as strong in urban areas, their study remains of great importance in such areas, since they can contribute to the formation of secondary gaseous pollutants, including ozone (Chameides et al., 1988; Shao et al., 2000; Duan et al., 2008; Ran et al., 2011).

Oxidation of VOCs leads to the formation of other gaseous compounds. Also, organic aerosols (OA) can result from these reactions (Kanakidou et al., 2005; Hallquist et al., 2009). Just like VOCs, organic aerosols can be directly emitted into the atmosphere – they are then called primary organic aerosol particles (POA), or they can be formed from VOC precursors, whose oxidation products are partitioned between the particulate and the gaseous phases; they are then defined as secondary organic aerosol particles (SOA) (Odum et al., 1997; Kanakidou et al., 2005). In either of the two phases, some organic pollutants are known to be harmful to people, threatening their health (Magill, 1949; Dockery et al., 1993; Finkelstein et al., 2004; Kappos et al., 2004; Anderson, 2009). They also play a role in the climate change, impacting the visibility and earth's radiation balance (Park et al., 2003; Kanakidou et al., 2005).

Important uncertainties concerning the sources, formation and fate of the organic aerosol particles are still to be addressed. In order to fill gaps in the knowledge of aerosols, and especially of secondary aerosols, one needs to rely on chamber experiments, field measurements and modeling. Chamber experiments allowed for the study of SOA yields, resulting from the oxidation of individual VOCs. Several classes of species have been identified as important SOA precursors, in particular terpenes and aromatic compounds (Seinfeld and Pandis, 1998; Lee et al., 2006a; Ng et al., 2007a, b). Combined with these SOA yields, field measurements of both VOCs and organic aerosols have permitted the evaluation of the effective contribution of the measured VOCs to the observed SOA (de Gouw et al., 2005, 2008). Finally, predictive models have been developed from observations in the field and in the laboratory. In urban areas, estimations using these models often led to a large underestimation of observed SOA: de Gouw et al. (2008) explained only 37 % of the measured SOA in New England, USA, while Volkamer et al. (2006) underestimated observed SOA by a factor of 10 by using a gas-particle partitioning model. This discrepancy increased downwind of the sources, and a factor of up to 100 could be reached in remote areas (Heald et al., 2005). De Gouw et al. (2008) suggested a strong role of non-measured gaseous carbon, especially those of low volatility, as an explanation of this discrepancy. Indeed, until recently, biogenic VOCs were thought to be the main SOA precursors (Kanakidou et al., 2005). However, in urban areas, this assumption has since been refuted (Volkamer et al., 2006; Hodzic et al., 2010) and has been found true only in clean atmospheres, where the prediction of SOA formation appears to be accurate (Hodzic et al., 2009). Hodzic et al. (2010) recently improved the SOA prediction in urban areas by considering primary gaseous organic compounds of lower volatility, which could partition between the gas and the particulate phase (Robinson et al., 2007; Epstein et al., 2010; Zhang et al., 2013). Recently, laboratory studies as well as field measurements have indeed highlighted the importance of VOCs of lower volatility in the SOA formation in urban areas (Robinson et al., 2007; Coe, 2011; Li et al., 2013; Yuan et al., 2013) and downwind of a well-defined crude oil spill (de Gouw et

al., 2011), emphasizing the need to measure these species. Even though major progress has been made in the understanding of SOA formation and the role of the IVOCs, the studies rarely reproduce the conditions encountered in urban areas. Indeed, laboratory studies for the determination of the SOA yields only investigate SOA formed by the oxidation of a single IVOC precursor (Lim and Ziemann, 2005, 2009a, b; Chan et al., 2009; Presto et al., 2010). As for the in situ studies, they have only considered a single IVOC source (Robinson et al., 2007; de Gouw et al., 2011; Li et al., 2013).

In this context, the FP7 MEGAPOLI project (Megacities: Emissions, urban, regional and Global Atmospheric POLlution and climate effects, and Integrated tools for assessment and mitigation) aims to quantify sources of primary and secondary aerosols and the role of organic gas-phase precursors in and around a large metropolitan area, and to describe their evolution in the megacity plume. Two intensive field campaigns were conducted in the Greater Paris region during summer 2009 and winter 2010, during which simultaneous measurements of gaseous and particulate organic compounds were performed. A wide range of gaseous carbonaceous compounds, from C_1 to C_{16}, was measured at a suburban site of Paris (SIRTA), including important SOA precursors such as the C_6–C_8 aromatic compounds, monoterpenes and the C_{12}–C_{16} n-alkanes of intermediate volatility, which are rarely measured in an ambient atmosphere. Measurements of VOCs (C_2–C_6 and C_6–C_{10}) at an urban background site (LHVP) were also performed.

The first goal of this paper is to analyze the temporal and spatial variability and origin of gaseous organic carbon in suburban Paris. The respective role of chemical removal, primary and secondary emissions and meteorology is discussed (Sects. 3 and 4). The second goal of this paper is to estimate the respective contribution of the anthropogenic VOC precursors to the SOA formation in summertime, with a particular focus on the importance of the n-alkanes of intermediate volatility (Sect. 5). The method relies on two independent approaches: an integrated approach and a time-resolved approach.

2 Methods

2.1 Sampling sites

One summertime and one wintertime field campaign were conducted in Paris and its surrounding area in the frame of the EU-MEGAPOLI project. The first experiment took place during the whole month of July 2009; the second one started on 15 January 2010 and ended on 15 February 2010.

Measurements of the gaseous organic carbon were performed at two ground sites: SIRTA and LHVP, which are presented in Fig. 1. SIRTA, which stands for "Site Instrumental de Recherche par Télédétection Atmosphérique", is located in Palaiseau (48.713° N, 2.214° E; 156 m above sea
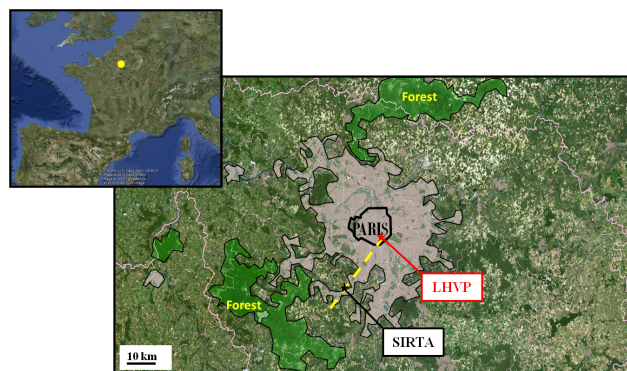

Figure 1. MEGAPOLI sampling sites (source: Google Earth).

level), 14 km southwest of Paris. This site, surrounded by fields, wooded areas, houses and industries, has been qualified as suburban (Haeffelin et al., 2005). LHVP ("Laboratoire d'Hygiène de la Ville de Paris", 48.829° N, 2.207° E; 62 m above sea level) is an urban background site located in the southern part of the French capital. The sampling site is located in a large public garden at approximately 150 m from a major street. Due to the low intensity of the surrounding traffic and from measurements, it has been qualified as representative of Paris background pollution (Favez et al., 2007; Sciare et al., 2010; Gros et al., 2011).

This article focuses on the gaseous and particulate organic carbon measured at SIRTA. Measurements performed at LHVP are used here to support the analysis of the organic carbon at SIRTA.

2.2 Measurements of organic carbon and ancillary data

The organic carbon was intensively measured at the two sites, in both the gaseous and particulate phases, using numerous offline and online instruments. All the instruments used in the present analysis and their performances are presented in Tables 1 and 2.

At SIRTA, gaseous organic carbon measurements included C_1–C_{16} organic compounds. These compounds can be classified according to their saturation concentration, C^*, which is an indicator of their volatility (Robinson et al., 2007; Epstein et al., 2010). Thus, given their C^*, C_{12}–C_{16} n-alkanes are of intermediate volatility, as they are characterized by $10^3 \, \mu g \, m^{-3} < C^* < 10^6 \, \mu g \, m^{-3}$, while all other measured compounds were volatile ($C^* > 10^6 \, \mu g \, m^{-3}$) (Robinson et al., 2007; de Gouw et al., 2011). It should be noted that, in this paper, the acronyms IVOCs and VOCs will be used to designate each family, while I / VOCs will include both of them. C_1–C_{16} organic compounds were collected by active sampling on sorbent cartridges, using a sampling module developed by TERA Environment – either a SASS (Smart Automatic Sampling System) in summer or an ACROSS (Automatic Clean ROom Sampling System) in winter (Detournay et al., 2011). Gaseous compounds were

Table 1. Offline measurements of the gaseous organic carbon during MEGAPOLI at SIRTA.

Column compounds	Column sorbent	Institution	Analysis	LOD (ppt)	Uncertainty (%)	Reference
Aromatics C_9–C_{16} alkanes C_9–C_{10} aldehydes Terpenes	Activated charcoal (carbotrap B + carbotrap C)	EMD/LISA	Adsorption/thermal desorption (ATD) + GC-FID	1–20	3–26	Detournay et al. (2011)
C_1–C_9 aldehydes Ketones	2,4-dinitrophenylhydrazine (DNPH)	EMD/LISA	Chemical desorption (acetonitrile) + HPLC/UV	10–60	11–37	Kleindienst et al. (1998) Bates et al. (2000) Dettmer and Engewald (2003)

LOD: limit of detection

Table 2. Online measurements of organic carbon and ancillary data during MEGAPOLI at SIRTA and LHVP.

Measurements	Site	Institution	Instrument	Time resolution (min)	LOD (ppt)	Uncertainty (%)	Reference
C_3–C_9 NMHCs	SIRTA	LISA	GC-FID AirmoVOC (Chromatotec®)	30	100	20	
C_2–C_6 NMHCs C_6–C_{10} NMHCs	LHVP	LSCE	2 GC-FIDs (Chromatotec®)	30	37–93	15–20	Gros et al. (2011)
CO	SIRTA	LSCE	GC (hot mercuric oxide detection)	15	1000	10	Gros et al. (1999)
NO	SIRTA	LISA	AC31M analyzer (Environnement S.A.)	1	500	5	
NO_2	SIRTA	LISA	NO_xTOy (MetAir)	1	500	5	Dommen et al. (2000) Michoud et al. (2012)
O_3	SIRTA	LISA	49C analyzer (Thermo Environment Instrument)	1	1000	5	
Meteorological parameters (T, RH, P, speed and direction of the wind)	SIRTA	LISA	Wind sensor and multiplate radiation shield (Young)	1	NA	NA	
Mixing layer depth	SIRTA	LMD	ALS450 Lidar	60	NA	NA	Haeffelin et al. (2012)
Non-refractory particulate matter (PM_1)	SIRTA	PSI	HR-ToF-AMS	5	NA	30–36	DeCarlo et al. (2006) Crippa et al. (2013a) Freutel et al. (2013a)

LOD: limit of detection.

sampled at approximately 4 m above ground level (a.g.l.), and then trapped into one of the two types of cartridges: a multi-sorbent cartridge, composed of carbopack C (200 mg) and carbopack B (200 mg) (carbotrap™ 202 from Perkin-Elmer®), and a Sep-Pak DNPH-Silica cartridge (Waters®). C_6–C_8 aromatic compounds, C_9–C_{16} *n*-alkanes, monoterpenes and C_6–C_{10} *n*-aldehydes were sampled during 3 hours at a flow rate of 200 mL min^{-1} on the multi-sorbent cartridges. Additional C_1 to C_9 OVOCs (oxygenated VOCs) were sampled onto the DNPH-cartridges, with a time resolution of 3 hours too but at a flow rate of 1.5 L min^{-1}. Prior to sampling, carbotrap™-filled cartridges were conditioned with purified air at 250 °C, at a flow rate of 10 mL min^{-1}, during 24 h. During the sampling, different ozone scrubbers were used in order to prevent any ozonolysis of the measured compounds: a KI ozone scrubber was installed upstream of the sampling onto DNPH cartridges, while a

MnO_2 ozone scrubber was used for the cartridges filled with carbotrap™. Besides, stainless-steel particle filters of 2 μm porosity (Swagelok®) were used to prevent any sampling of particles, which could block the sampling system. Cartridges were then analyzed by HPLC/UV (High-Performance Liquid Chromatography with Ultra Violet detection; for the DNPH cartridges) or by GC-FID (Gas Chromatography coupled to a Flame Ionization Detector; for the carbotrap™ filled cartridges) in the laboratory. The reproducibility of the analysis was checked by the daily analysis of a standard, leading to the plotting of a control chart for each compound, which allowed the reproducibility of the instruments to be checked.

At SIRTA, online measurements of C_3–C_9 NMHCs (nonmethane hydrocarbons) were also performed using an autosampling GC-FID, AirmoVOC (Chromatotec®). Two other auto-sampling GC-FIDs were installed at LHVP: ChromaTrap and AirmoBTX (both from Chromatotec®) for the

C_2–C_6 and the C_6–C_{10} NMHCs measurements, respectively. Details on the latter instruments can be found in Gros et al. (2011). Inlet lines of the instruments were located at 4 and 15 m a.g.l. at SIRTA and LHVP stations, respectively.

Carbon monoxide was measured at SIRTA by a Gas Chromatograph coupled to a Reduction Gas Analyzer (Trace Analytical, Menlo Park, CA, USA), following the method described by Gros et al. (1999). Calibration was performed with a 40 L aluminum cylinder CO standard gas (187 ± 20 ppb) in synthetic air, which was provided and calibrated by the Central Calibration Laboratories (CCL) of the National Oceanic and Atmospheric Administration (NOAA, Boulder, CO, USA) (Novelli et al., 1994). CO measurements were performed every 2.5 min, by alternating injection of a standard and of a sample (atmospheric air). Each sample was calibrated against the preceding standard and measurements were averaged every 15 min.

The chemical composition of submicron particulate organic carbon (PM_1) was investigated with a High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) at each site (Crippa et al., 2013a; Freutel et al., 2013a). A positive matrix factorization (PMF) analysis was used for the organic fraction of the particulate matter in order to identify the different components of the organic matter (OM) (Crippa et al., 2013a, b; Freutel et al., 2013a).

Complementary measurements of nitrogen oxide (NO) and nitrogen dioxide (NO_2), as well as of ozone (O_3) were performed at SIRTA. Temperature, wind speed and direction, relative humidity, solar radiation and pressure were measured by a weather station (see details in Table 2).

FLEXPART simulations were computed on a 3 h basis for the two campaigns. Based on a Lagrangian particle dispersion model, FLEXPART simulations provide information on the probable origin of particles and trace gases sampled at the receptor site by looking at the dispersion of air pollutants (Stohl et al., 2005).

3 Overview of the VOCs measurements

3.1 Seasonal variations of VOCs

Table 3 summarizes the means and the standard deviations of the concentrations of the VOCs measured at SIRTA during the summertime and wintertime MEGAPOLI campaigns and their properties. Data below the limit of detection (LOD) were replaced by LOD/2. It can be seen that the VOC mean concentrations exhibit high relative standard deviations, ranging from 50 to 100 %, caused by the high variability of the compounds during the two campaigns as a consequence of the changes in synoptic meteorology and air mass origin (Crippa et al., 2013a; Freutel et al., 2013a).

VOCs of anthropogenic origin, including aromatics and C_4–C_6 alkanes, have higher mixing ratios in winter. This difference can be explained by three factors (Boudries et al.,

1994; Cheng et al., 1997; Na and Kim, 2001; Swanson et al., 2003; Yang et al., 2005; Shirai et al., 2007): (i) a stronger temperature inversion in winter than in summer, leading to a mean daytime boundary layer 3 times shallower in winter than in summer at SIRTA (440 ± 220 m and 1340 ± 610 m, respectively, between 9 a.m. and 6 p.m.) (Filella and Peñuelas, 2006); (ii) lower OH radical concentrations in winter and thus less depletion by photochemistry (Michoud et al., 2012, 2014); and finally (iii) sources of different nature, composition and/or strengths. Different primary anthropogenic sources are known to be subject to the seasonal variations detailed in the last assumption, among these is the fuel evaporation. Indeed, seasonal modifications in the fuel formulation reduce the fraction of the light VOCs (butanes and pentanes) in summer to limit fuel evaporation (Borbon et al., 2003; Lee et al., 2006b; Gentner et al., 2009). Engine cold-start emissions also vary seasonally: they are enhanced in winter as a consequence of low temperatures, which results in the stronger emission of aromatic compounds in vehicular exhaust during winter (Heeb et al., 1999; Borbon et al., 2002; Hoque et al., 2008; Roukos et al., 2009). Finally, the cold weather in winter leads to an intensive use of domestic heating and thus to increased emissions of toluene, benzene or even butane (e.g., Borbon et al., 2002; Badol et al., 2008; Roukos et al., 2009).

Similarly, the light C_2–C_6 oxygenated VOCs (methylvinylketone (MVK) and methylethylketone (MEK) excluded) also have higher mixing ratios in winter, indicating that OVOC are dominated by primary anthropogenic emissions such as traffic (Grosjean et al., 2001; Legreid et al., 2007) or wood burning (Schauer et al., 2001; Gaeggeler et al., 2008). These observations contrast with previous studies that have found higher OVOC concentrations in summer at urban and suburban sites (Sin et al., 2001; Ho et al., 2002; Bakeas et al., 2003; Legreid et al., 2007; Wang, 2010) as a consequence of their enhanced photochemical secondary production in summer.

On the contrary, VOCs of biogenic origin (isoprene and pinenes) show higher levels in summer due to their temperature-dependent biogenic emissions. Isoprene emissions have the particularity to also be light dependent (Guenther et al., 1991). This is also observed for MVK for which isoprene is the precursor. Limonene and camphene exhibit different behaviors compared to other terpenes. Limonene, which does not vary seasonally, and camphene are still detected in winter. Measurements of monoterpenes (pinenes, camphene and limonene) in urban areas are not common, unlike for isoprene which is also known to be emitted by primary anthropogenic sources (Borbon et al., 2001). Monoterpene measurements are usually performed in remote areas, far from any anthropogenic influence (Kleindienst et al., 2007; Detournay et al., 2013). To our knowledge, only Yoshino et al. (2012) measured them individually in an urban area, Tokyo (Japan), during the two seasons. They found higher concentrations in winter than in summer for the

Table 3. Summer and winter mean concentrations, standard deviation (SD), percentage of values below limit of detection (% < LOD), rate constant with OH (kOH; when not indicated: Atkinson and Arey, 2003) and SOA yield formation (when not indicated: Seinfeld and Pandis, 1998) of the VOCs measured in suburban Paris (SIRTA).

| Compound	Summer (ppt)		Winter (ppt)		$10^{12} k_{OH}$ (298 K)	SOA Yield
	Mean	SD (% < LOD)	Mean	SD (% < LOD)	(cm^3 molecule^{-1} s^{-1})	(µg m^{-3} ppm^{-1})
i-Butane	250	140 (0)	460	282 (0)	2.12	0
n-Butane	377	393 (0)	963	588 (0)	2.3	0
i-Pentane	334	354 (11)	416	213 (0)	3.6	–
n-Pentane	193	138 (27)	nd	nd	3.8	0
Hexane	94	50 (66)	85	50 (13)	5.2	–
Nonane	14	13 (0)	18	13 (0)	9.7	425[d]
Decane	24	22 (11)	24	19 (0)	11	850[d]
Undecane	19	16 (1)	16	11 (0)	12.3	1726[d]
Dodecane	22	21 (0)	7	4(5)	13.2	258[e]; 1136[f]
Tridecane	13	12 (56)	2	1 (41)	15.1	754[e]; 2896[f]
Tetradecane	27	23 (0)	2	2 (63)	17.9 (312 K)	1152[e]; 3887[f]
Pentadecane	23	18 (0)	4	2 (8)	20.7 (312 K)	1416[e]; 4622[f]
Hexadecane	22	19 (6)	nd	nd	23.2 (312 K)	1750[e]; 5214[f]
Isoprene	357	280 (5)	69	39 (4)	100	64[g]
α-Pinene	48	45 (0)	20	52(25)	52.3	2338[h]
β-Pinene	10	6 (4)	nd	nd	74.3	1724[i]
Camphene	nd	nd	23	18 (1)	53	762
Limonene	16	16 (7)	15	19 (1)	164	3283[i]
Benzene	NA	NA	316	155 (0)	1.22	1181[j]; 898[j]
Toluene	207	179 (0)	321	216 (0)	5.63	1145[j]; 404[j]
Ethylbenzene	37	31 (0)	60	39 (0)	7	1145[j, k]; 404[j, k]
m,p-Xylene	80	76 (0)	150	109 (0)	23.1; 14.3	1578[j]; 276[j]
o-Xylene	40	31 (0)	53	39 (0)	13.6	1578[j, k]; 276[j, k]
Formaldehyde	1 607	1031 (0)	5984	1892 (0)	9.37	0
Acetaldehyde	621	283 (0)	1199	528 (0)	15	–
Acetone	1 344	480 (0)	1705	677 (0)	0.17	0
Glyoxal	47	23 (1)	158	119 (5)	11	0
Methylglyoxal	55	38 (15)	207	153 (9)	15	0
Propanal	85	42 (3)	247	125 (0)	20	–
Methylvinylketone (MVK)	290	273 (3)	54	108 (12)	20	–
Butenal	8	4 (100)	860	593 (1)	36.0[a]	–
Butan-2-one (MEK)	1639	1500 (0)	363	262 (6)	1.22	0
Methacrolein	60	63 (19)	121	178 (25)	29	–
i,n-Butanal	52	31 (24)	318	310 (3)	24–26	–
i-Pentanal	15	14 (85)	77	45 (26)	27	–
Benzaldehyde	26	16 (25)	638	301 (2)	12	–
Pentanal + o-tolualdehyde	29	12 (69)	84	60 (35)	28; 18	–
m,p-Tolualdehyde	8	4 (100)	25	22 (87)	17; 13	–
2,5-Dimethylbenzaldehyde	7.5	11 (93)	412	253 (6)	43.7[b]	–
Hexanal	54	50 (7)	31	27 (2)	30	–
Heptanal	67	68 (2)	46	26 (0)	30	–
Octanal	82	66 (2)	nd	nd	28.6[c]	–
Nonanal	58	45 (2)	18	14 (8)	30.0[c]	–
Decanal	39	22 (2)	nd	nd	31.4[c]	–

NA: not available; nd: not detected; [a]: Atkinson, 1986; [b]: Tse et al. (1997); [c]: Hellén et al. (2004); [d]: Lim and Ziemann (2009a); [e]: Presto et al. (2010), $C_{OA} = 2$ µg m^{-3}; [f]: Presto et al. (2010), $C_{OA} = 40$ µg m^{-3}; [g]: Kroll et al., 2006; [h]: Ng et al. (2007b); [i]: Lee et al. (2006a); [j]: Ng et al. (2007a); [k]: Odum et al. (1997). For the C_{12}–C_{16} n-alkanes and the aromatics, the first SOA yield values is the one determined under relevant atmospheric conditions to our study, the second one is the one determined under both high C_{OA} and high NO$_x$.

pinenes, with concentrations of β-pinene lower than those of α-pinene, which is in good agreement with our measurements. Camphene concentrations were equal to zero during the two seasons, while limonene concentrations were slightly more important in winter than in summer. Finally, our results, supported by those of Yoshino et al. (2012), suggest weaker sink processes in winter than in summer. Our results also imply a small anthropogenic source in urban/suburban areas of these compounds, in addition to their well-known biogenic origin. This latter assumption has been recently put forward by Hellén et al. (2012), who identified traffic and wood combustion as potential emission sources of VOCs formerly thought to be only of biogenic origin.

The C_{12}–C_{16} IVOCs alkanes have higher mixing ratios in summer than in winter, whereas the other compounds, the C_6–C_{10} aldehydes and the C_9–C_{11} n-alkanes, do not show any clear seasonality in their mixing ratios. The IVOCs alkanes, which can be emitted by traffic (Fraser et al., 1998; Schauer et al., 1999a, 2002), cooking activities (Schauer et al., 1999b) or biomass burning (Schauer et al., 2001), are more likely to be subject to their partitioning between the gas- and the particle-phase, which could explain the seasonal differences. Indeed, measurements and characterization of the chemical composition of ambient particles sampled in urban/suburban sites showed that IVOC n-alkanes were more abundant in the particle-phase in winter than in summer (Kadowaki, 1994; Bi et al., 2003; Guo et al., 2009). Estimation of the hexadecane partition coefficient K_p determined from Pankow theory (Pankow, 1994) show no significant difference between the summer and the winter campaigns (2.16×10^{-4} and 8.61×10^{-4}, respectively) (see the Supplement S1, for details of the K_p calculations). Changes in the emission sources are more likely the cause of their seasonal variations. Regarding the C_6–C_{10} n-aldehydes, to our knowledge, only Knobloch et al. (1997) and Cecinato et al. (2002) compared the seasonal measurements of all these compounds over an urban area. Both studies observed higher concentrations of C_6–C_{10} n-aldehydes in winter than in summer. Conversely, Dutta et al. (2010) found lower concentrations in winter than in summer for hexanal and nonanal. In our study, C_6–C_{10} n-aldehydes concentrations were higher in summer than in winter, suggesting their predominant secondary origin.

3.2 Temporal evolution of the particulate and gaseous organic compounds

PMF analyses performed on the particulate organic matter, measured using a HR-TOF-AMS, was used for the characterization of the particulate organic carbon at the SIRTA site (Freutel et al., 2013a). Two PMF components were determined: hydrocarbon-like organic aerosol (HOA) and oxygenated organic aerosol (OOA), respectively representing 40 and 60 % of the organic matter (OM) during the campaign. The first PMF component is associated with primary emis-
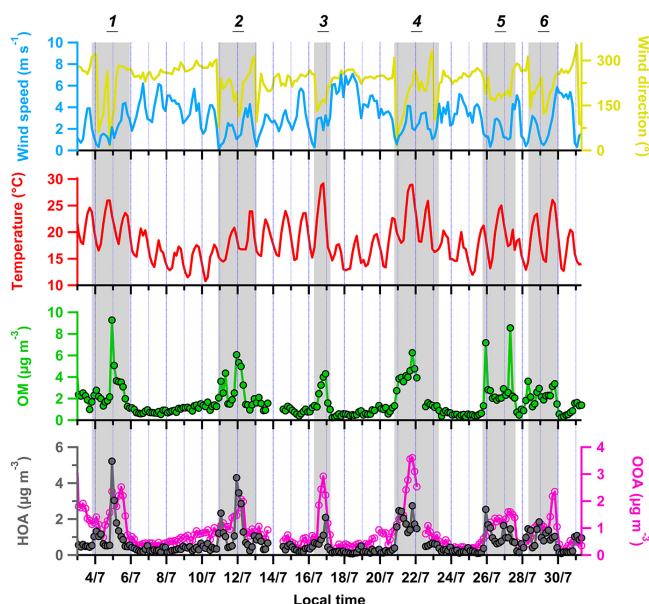

Figure 2. Time series of meteorological parameters (wind speed and direction, temperature), of the organic matter, and of the two PMF factors HOA and OOA in suburban Paris (SIRTA) in summer 2009. The grey-shaded areas highlight the "Atlantic Polluted" wind regimes associated with stagnant conditions and increased OOA.

sions, i.e., directly emitted organic aerosol (Zhang et al., 2005; Aiken et al., 2010; Hodzic et al., 2010). Here, HOA is assumed to represent the total primary organic aerosol, including aerosol emitted from traffic and cooking activities (Freutel et al., 2013a). Further PMF analyses (Crippa et al., 2013b) and single particle analysis (Freutel et al., 2013b) have actually separated the HOA component into the two different components HOA-traffic and cooking organic aerosol (COA). As for OOA, it represents more aged organic aerosol, and therefore is thought to be mainly representative of secondary organic aerosol. The OOA component has also been separated into two different factors based on the PMF analyses of Crippa et al. (2013b): semi-volatile OOA (SV-OOA) and low-volatile OOA (LV-OOA). SV-OOA is considered to be the freshest SOA, i.e., freshly formed, contrary to LV-OOA (Jimenez et al., 2009). During the MEGAPOLI summer experiment, SV-OOA and LV-OOA represent on average 56 and 44 % of OOA, respectively. The temporal evolution of the OM and of HOA and OOA PMF components at SIRTA is illustrated in Fig. 2. In addition, this figure depicts some meteorological parameters (wind speed and direction, temperature). Time series of a tracer of primary combustion sources (CO), anthropogenic and biogenic organic SOA precursors (toluene, tetradecane, pentadecane, α-pinene and isoprene), and of oxygenated VOCs (nonanal and acetaldehyde), which are known to have secondary sources, are presented in Fig. 3.

Cloudy conditions characterized the summertime campaign: between 3 and 31 July, only a few sunny
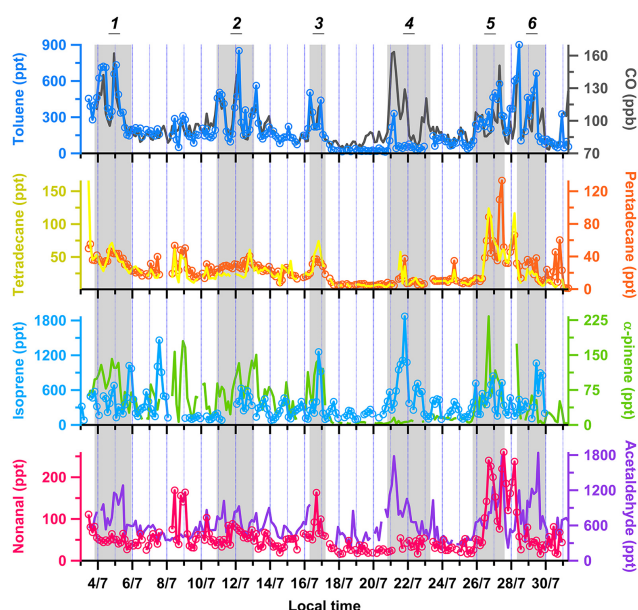
Figure 3. Summertime time series of carbon monoxide, toluene, tetradecane, pentadecane, isoprene, α-pinene, nonanal and acetaldehyde. The grey-shaded areas highlight the "Atlantic Polluted" wind regimes associated with stagnant conditions and increased OOA.

days were encountered and the average temperature was 18.3 ($\pm$ 3.8) °C. Southwesterly to westerly winds (215–285°) were dominant. They were associated with the highest wind speed ($0.3\,\mathrm{m\,s^{-1}}$ to $7.1\,\mathrm{m\,s^{-1}}$) and the lowest temperature: the average wind speed was 3.7 ($\pm$ 1.5) $\mathrm{m\,s^{-1}}$ associated with an average temperature of 16.8 ($\pm$ 3.0) °C (Fig. 2). Some periods under influence of southeasterly to southwesterly winds were also encountered. They were characterized by the lowest wind speed ($2.1\,\mathrm{m\,s^{-1}}$ on average, ranging from $0.1\,\mathrm{m\,s^{-1}}$ to $5.9\,\mathrm{m\,s^{-1}}$) and the highest temperature (from 13.2 °C to 29.2 °C, with an average value of 20.3 °C). This last type of air mass is distinguished in Figs. 2 and 3 by a grey-shaded area. These events under southeasterly/southwesterly influence, lasting 24 h up to 68 h, are also numbered from 1 to 6 in the following section.

Figure 2 indicates that 3 h averaged OM mass concentrations ranged from 0.2 to $9.3\,\mathrm{\mu g\,m^{-3}}$; about 33 % of the data were above the average value of $1.66\,\mathrm{\mu g\,m^{-3}}$. Like the gaseous compounds, the mass concentration of particulate organic matter is lower than in other megacities: concentrations of organic matter (PM$_1$) could reach up to $80\,\mathrm{\mu g\,m^{-3}}$ in March 2009 in Mexico City (Mexico) (Aiken et al., 2009) and $60\,\mathrm{\mu g\,m^{-3}}$ in summer 2008 in Beijing (China) (Zhang et al., 2011), respectively, and never less than $10\,\mathrm{\mu g\,m^{-3}}$. Moreover, in Europe, OM mass concentrations (PM$_1$) as low as those observed at SIRTA have been measured at the Jungfraujoch remote site (Switzerland), where summertime concentrations (August 2005) were ranging from about 0.5 to $3.5\,\mathrm{\mu g\,m^{-3}}$ (Cozic et al., 2008).

As shown by Freutel et al. (2013a), OM showed the lowest levels under a westerly wind regime, with an average mass concentration of $0.9\,\mathrm{\mu g\,m^{-3}}$. Under stagnant conditions, i.e., during events 1 to 6, OM mass concentrations clearly increased, as well as the HOA and OOA mass concentrations. An increase in the concentrations was also observed for the VOCs during these periods (Fig. 3), but it appeared to be variable from one event to another, from one gaseous compound to another. Indeed, during event 3, all the VOCs showed a notable increase in their concentrations, regardless of their emission sources. For the primary anthropogenic VOCs, such as toluene, the biogenic VOCs, like isoprene or α-pinene, and for acetaldehyde and other oxygenated VOCs, mean concentrations are about 1.5 times higher than the mean concentrations measured during the previous period influenced by westerly winds (13–16 July). An increase in the VOC concentrations was also observed during event 4. But, among all the SOA precursors, isoprene is the only one exhibiting a significant enhancement during the entire event; the other compounds, including primary anthropogenic I / VOCs, presented a sharp and short increase of their concentrations on 21 July. Remarkably, the increase in the isoprene concentrations was accompanied by a notable increase in the level of CO. CO is one of the primary anthropogenic emissions tracers, but it can also result from the photo-oxidation of VOCs, including those of biogenic origin (Gros et al., 2002; Kanakidou et al., 2005; de Gouw et al., 2008). Here, CO shows two increases on 21 July. The first increase occurs during morning hours with little dispersion, very low wind speed, with varying wind direction. Since CO correlates with toluene during this first increase, CO is predominantly of primary origin. The second increase is observed for the evening hours and is much more pronounced than those observed for the other primary anthropogenic VOCs. Hence, during event 4, CO might be of both primary and secondary origin. Besides, since it exhibits a substantial atmospheric lifetime of about a month (Parrish et al., 1998), long-range transport of CO cannot be discarded either. These assumptions are supported by the evening rise in the concentration of light OVOCs, such as acetaldehyde, propanal or MEK (not shown in Fig. 3) and, as it can be seen in Fig. 2, of the oxygenated PMF component of OM, OOA, or of ozone (not shown here) during the same event (end of 21 July).

Finally, the evolution of the VOCs is consistent with the air mass classification of Freutel et al. for the MEGAPOLI campaign period, which was carried out using the FLEXPART simulations (Stohl et al., 2005; Freutel et al., 2013a). Hence, for consistency purposes, the same terms qualifying the air masses, "Atlantic Clean" for plumes with high wind speed and low temperature and "Atlantic Polluted" when air masses are characterized by low wind speed and high temperature, will be used in the following section.

The different particulate and gaseous compounds appear to be strongly impacted by the origin of the air masses arriving at SIRTA during the MEGAPOLI summertime campaigns.

Table 4. Toluene and i-pentane mean concentrations in different cities worldwide.

Location	Period	Site	Toluene (ppb)	i-Pentane (ppb)	Reference
Beijing (China)	Sum. 2006	urban	19.44	17.70	Duan et al. (2008)
Karachi (Pakistan)	Win. 1998	urban	7.10	12.10	Barletta et al. (2002)
Tokyo (Japan)	Sum. 2007	urban	2.14	4.21	Yoshino et al. (2012)
	Win. 2007		10.10	2.87	
Mexico City (Mexico)	February 2002	urban	13.45	17.02	Velasco et al. (2007)
	and April–May 2003	rural	1.89	5.82	
Pasadena (suburb of Los Angeles, USA)	May–June 2010	suburban	0.58	1.56	CalNex framework
London	October 2006	urban	1.85	nm	Langford et al. (2010)
(United Kingdom)	2008	urban, K.	1.00	nm	von Schneidemesser et al. (2010)
Zürich (Switzerland)	Win. 2005/2006	urban, B.	1.25	nm	Legreid et al. (2007)
	Sum. 2005		1.43	nm	
Paris (France)	Sum. 2009	urban, B.	0.73	0.73	MEGAPOLI framework
	Win. 2010	(LHVP)	0.79	0.77	
Dunkerque (France)	2002–2003	urban, I.	1.06	0.94	Badol et al. (2008)
Donon (France)	1997–2006	rural	0.16	0.21	Sauvage et al. (2009)
Peyrusse-Vieille (France)	2000–2006	rural	0.11	0.14	Sauvage et al. (2009)
Tardière (France)	2002–2006	rural	0.27	0.21	Sauvage et al. (2009)
Paris (France)	Sum. 2009	suburban	0.20	0.33	This work
	Win. 2010	(SIRTA)	0.32	0.42	

Sum.: summer; Win.: winter; K.: kerbside; B.: background; I.: industrial; nm: not measured.

The pollutant concentrations were low or high as the air mass was characterized by either high or low wind speeds.

### 3.3 Concentration levels of VOCs: Paris vs. other areas

Table 4 compiles mean concentrations of toluene and i-pentane, two markers of vehicular exhaust and evaporation emission sources, measured at different locations, including megacities, European urban and suburban areas, and different areas in France. As VOC emissions are rapidly decreasing (Warneke et al., 2012), only observations performed within the last 15 years have been reported in Table 4. Mean concentrations of these VOCs observed at LHVP are also reported in Table 4. SIRTA exhibits the lowest VOC mean concentrations among all these data sets. Toluene mean concentrations in other megacities range from 0.58 to 19.44 ppb: the highest value, measured in summer at an urban site of Beijing (Duan et al., 2008), is a hundred times as high as the summertime toluene mean concentration at SIRTA (0.20 ppb). Higher i-pentane levels in other megacities are also observed. In winter, for instance, the i-pentane mean concentration at SIRTA (0.42 ppb) is 7 times lower than the minimum mean concentration which was measured in Tokyo (2.87 ppb) (Yoshino et al., 2012). At the suburban site of Paris, the only European megacity with more than 10 million inhabitants listed by the United Nations (United Nations, 2012), the concentrations of these two VOCs remain lower than at other urban/suburban sites in Europe (Legreid et al., 2007; Langford et al., 2010; von Schneidemesser et al., 2010). Even the French urban/urban background areas, including LHVP, have systematically higher VOC mean concentrations than SIRTA, by a factor of up to 15 (Badol et al., 2008; Gros et al., 2011). Finally, the mean concentrations of anthropogenic VOCs (aromatic and alkanes) at SIRTA are as low as those measured at French remote sites (Sauvage et al., 2009) from the EMEP network (European Monitoring and Evaluation Programme). The predominance of oceanic air masses with the highest wind speed arriving at SIRTA, both "Atlantic Clean" or "Atlantic Polluted", favors the dispersion of pollutants in the Paris region (Sect. 3.2).

4 Anthropogenic emissions of gaseous organic carbon present over suburban Paris

4.1 Method

The analysis of the correlations between pairs of trace gases is a first step towards the identification of the different processes governing the evolution of the compounds, including the emissions, while the effect of dilution is minimized (Roberts et al., 1984). The method relies on the hypothesis of absent or only little chemical loss processes of the compounds. Information on the emission sources is given by the quality of the linear regression fit (R^2) between VOC
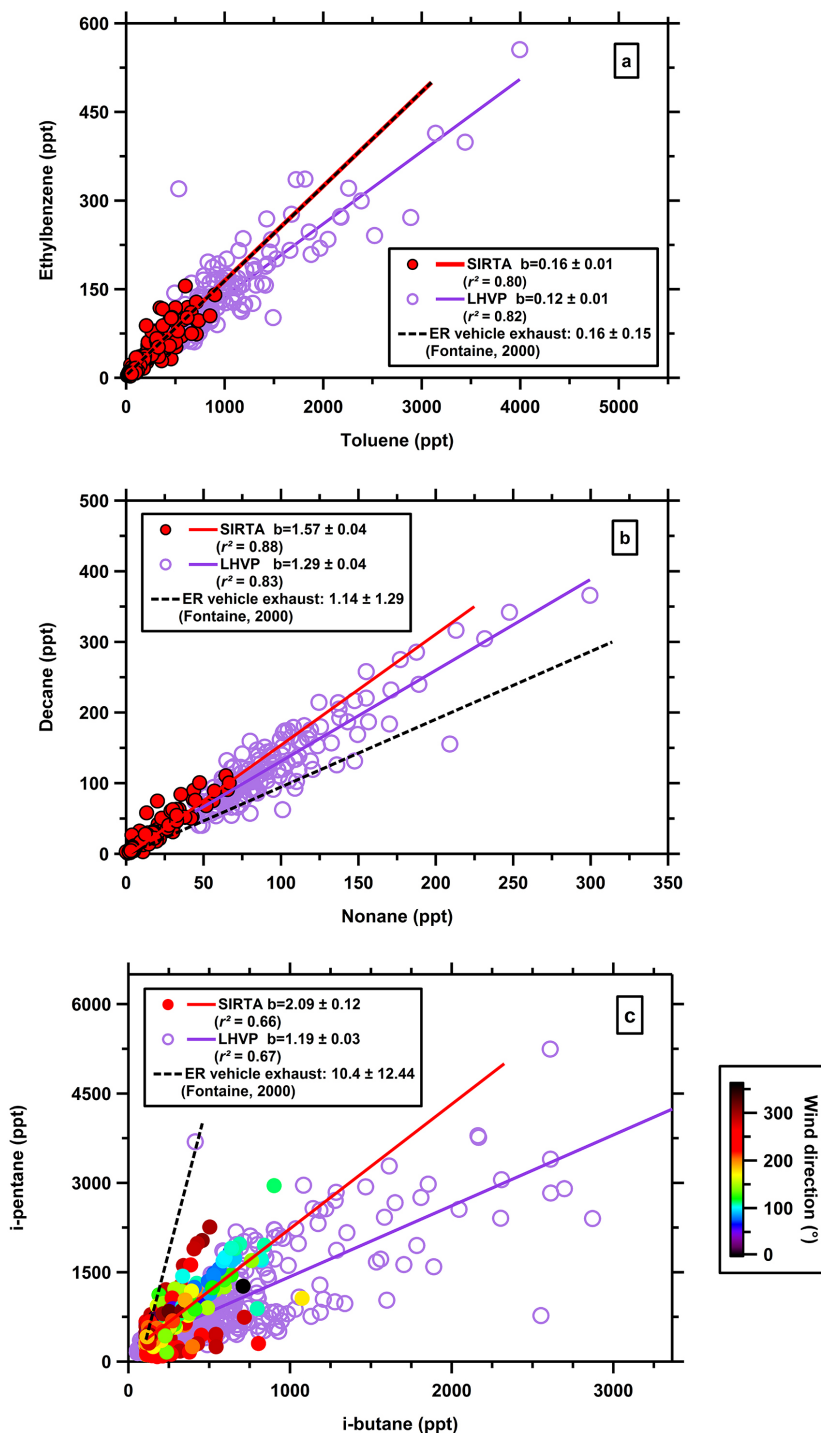
Figure 4. Scatterplots of ethylbenzene versus toluene **(a)**, decane versus nonane **(b)** and i-pentane versus i-butane **(c)** in suburban (SIRTA) and urban (LHVP) Paris in summer. The fit of correlation of i-pentane versus i-butane at SIRTA (Fig. 5c) does not take into account the upper and lower part of the envelope; SIRTA data are color-coded by the wind direction.

pairs with similar atmospheric lifetime and the value of the slope of the linear regression fit. On the one hand, common sources are highlighted by a tight correlation (R^2 value close to 1) (Parrish et al., 1998). On the other hand, the slope pro-

vides the value of the enhancement ratio (Borbon et al., 2003; Warneke et al., 2007). For each pair of VOCs, the enhancement ratio is defined as the enhancement of a VOC relatively to the second one, which is considered as a reference
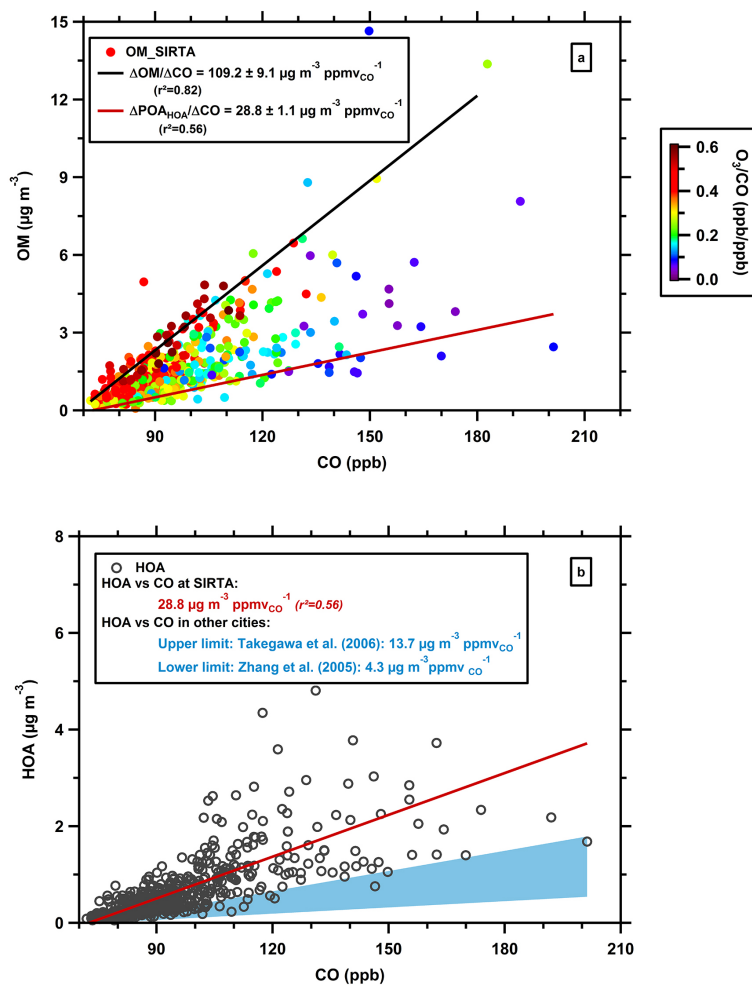
Figure 5. Scatterplots of OM versus CO **(a)** and scatterplots of HOA versus CO **(b)** in suburban Paris in summer 2009. OM, CO and HOA were averaged to 1 h.

compound (Hornbrook et al., 2011). Since most NMHCs in the Paris agglomeration are strongly impacted by vehicle exhaust emissions (Borbon et al., 2013), the enhancement ratios obtained at SIRTA are compared with the vehicle exhaust emission ratio derived from emission factors according to the method developed by Borbon et al. (2003). This will allow stating if observed enhancement ratios can be explained by traffic emissions alone. Briefly, emission factors (EF) of VOCs at the exhaust were determined in the late 1990s in France, from vehicles imitating mean urban driving conditions and using different types of fuels: diesel, gasoline with or without catalyst (Fontaine, 2000). The experimental conditions for the determination of the VOCs emission factors by Fontaine (2000) are detailed in the Supplement (Sect. S2); values of VOCs EF can be found in Borbon et al. (2003). In 2009–2010, the fleet of vehicles in Paris was composed of 60 % light-duty diesel vehicles and of 40 % gasoline light-duty vehicles equipped with catalytic convertors (CCFA, 2011). Emission ratios (ER) were then calcu-

lated following Eq. (1) defined by Borbon et al. (2003):

$$\mathrm{ER}_{\mathrm{VOC_1, VOC_2}} = \frac{\sum_j (\mathrm{EF}_{\mathrm{VOC_1, j}} \times f_j)}{\sum_j (\mathrm{EF}_{\mathrm{VOC_2, j}} \times f_j)}, \quad (1)$$

where $\mathrm{ER}_{\mathrm{VOC_1, VOC_2}}$ is the emission ratio of the given $\mathrm{VOC_1}$ with respect to $\mathrm{VOC_2}$ (in ppt ppt^{-1}), $\mathrm{EF}_{\mathrm{VOC}_i, j}$ the emission factor of the VOC_i for the engine type j (in mg km^{-1}) and f_j the fraction in % of the urban mileage running by the motor type j. The standard deviation of the ratios is determined from the standard deviations of the emission factors. As demonstrated in the Supplement (Sect. S3, Fig. S1), the ER determined from Fontaine's work (2000) are representative of northern mid-latitude urban areas.

4.2 Spatial variability: evidence of regional influences in suburban Paris

Summertime correlations of commonly measured VOCs with the same atmospheric lifetimes at SIRTA and LHVP

are illustrated in Fig. 4. As expected, the comparison of the scatterplots exhibits higher concentrations for anthropogenic VOCs in urban Paris than in suburban Paris as a result of the emission density and dilution. However, the shape and the slope of the scatterplots are fairly consistent between urban and suburban Paris in summer and in winter (not presented here).

Aromatic compounds and heavy alkanes show a narrow distribution with very good correlation ($R^2 > 0.80$, Fig. 4a and b). The emission enhancement ratios in urban and suburban Paris, given by the value of the linear regression fit slopes, agree well within $\pm 2\%$ and $\pm 18\%$ for aromatics and alkanes, respectively, regardless of the seasons and within the analytical uncertainties (Fig. 4a and b). The emission enhancement ratios determined during MEGAPOLI are also very close to the emission ratio (reported on Fig. 4) in vehicle exhaust determined from Eq. (1). These observations point to traffic emission as the dominant source of aromatics and alkanes $> C_5$ across the Paris basin in accordance with Borbon et al. (2013).

Scatterplots of light alkanes obtained at SIRTA and LHVP are overlaid (Fig. 4c), indicating that sources of the same composition affect their distribution at each site. These light alkanes are known to be emitted from common sources, i.e., vehicle fuel combustion and evaporation (Monod et al., 2001; So and Wang, 2004; Russo et al., 2010). However, the multi-shape distributions imply that sources with different iso-alkanes composition are driving their distribution in the Paris area. The scatterplot of SIRTA is color-coded as a function of the wind direction. When SIRTA is downwind of the 225–330° sector, enrichment in either i-pentane (upper part of the envelope) or i-butane (lower part of the envelope) is observed. Plumes arriving from the northwest at SIRTA flew over the Seine basin. In spring 2007, Gaimoz et al. (2011) also observed enrichment in i-butane concentrations in urban Paris when sampling oceanic air masses which had crossed this region. The Seine basin is an important industrialized area including different industries: chemistry, surface treatment and oil and gas production (iREP, 2012). When the upper and lower part of the envelope, which correspond to the data associated with the 225–330° wind sector, are not taken into account, a good correlation is obtained at SIRTA ($R^2 = 0.66$) with a slope of 2.09 (ppt ppt^{-1}) for the Paris wind sector. Contrary to the aromatic compounds and the heavy alkanes, the enhancement ratio of the light alkanes determined at SIRTA is very different from the vehicle exhaust emission ratio, namely by a factor of 4 to 5. This difference may indicate either a difference in gasoline composition or emission sources other than vehicular exhaust. This assumption is supported by the low wintertime i-pentane/i-butane ratio obtained at SIRTA from the VOCs' scatterplot (0.70, $R^2 = 0.65$ – not shown here).

Finally, the analysis of VOC/VOC correlations highlights the similar distribution of anthropogenic VOCs across the Greater Paris region, and so their common sources. This distribution is influenced by emissions from the whole Paris area as well as from the advection of industrial emissions along the Seine River for light alkanes. Thus, the SIRTA site is representative of regional anthropogenic footprint emissions. Similar conclusions were obtained from the observations of the particulate matter: the different organic and inorganic components of the PM1 particles exhibit the same trend at the different MEGAPOLI measuring sites (Crippa et al., 2013a; Freutel et al., 2013a).

5 Estimation of the contribution of I / VOCs to SOA formation in summer

Two different approaches can be used to quantify and qualify the contribution of VOC and IVOC precursors to the SOA formation: the integrated approach and the time-resolved approach. This chapter focuses on the description of these two approaches and a discussion of the obtained results.

5.1 Method

5.1.1 Estimation of the SOA from its gaseous precursors: the integrated approach

The method developed by de Gouw et al. (2005, 2008), the so-called integrated approach, is first applied to our data. This approach consists of the apportionment of $\Delta OM / \Delta CO$ enhancement into its primary component ($\Delta POA/\Delta CO$) and its secondary component ($\Delta SOA/\Delta CO$). $\Delta OM / \Delta CO$ is derived from the scatterplot of OM vs. CO. Experimentally, the $\Delta SOA/\Delta CO$ enhancement is the difference between $\Delta OM / \Delta CO$ and $\Delta POA/\Delta CO$, as illustrated by Eq. (2):

$$\left(\frac{\Delta SOA}{\Delta CO}\right)_{experimental} = \left(\frac{\Delta OM}{\Delta CO}\right) - \left(\frac{\Delta POA}{\Delta CO}\right). \quad (2)$$

In addition, a theoretical $\Delta SOA / \Delta CO$ enhancement is derived from the product of the VOC emission ratios to CO and the SOA yields of these VOCs, as described by Eq. (3):

$$\left(\frac{\Delta SOA}{\Delta CO}\right)_{theoretical} = \sum_i ER_i \times Y_{SOA,i}, \quad (3)$$

with ER_i and $Y_{SOA,i}$ the emission ratio and the SOA yield formation of the VOC$_i$, respectively. The comparison of these experimentally and theoretically derived SOA enhancements allows for the quantification of the effective contribution of the measured VOCs to the secondary formation of the aerosol particles. Based on the emission ratio, this approach considers that the amount of emitted I / VOC reacts entirely to form SOA. This approach leads then to an upper limit for the estimation of SOA formation from a gaseous precursor. Since CO is used as a primary anthropogenic tracer, the estimation of the SOA formation can be established by only considering VOCs of primary anthropogenic origin. Here, the measured n-alkanes of intermediate volatility, measured at SIRTA, will be included for the first time.

5.1.2 Estimation of the SOA from its gaseous precursors: the time-resolved approach

A second method, the so-called time-resolved approach adapted from Sjostedt et al. (2011), is applied to the data. Like the first approach, the aim of the time-resolved approach is to quantify the contribution of the different anthropogenic SOA precursors. However, unlike the first approach, the chemical atmospheric removal of the SOA precursors is considered, rather than their emission ratio. In this approach, it is assumed that the I / VOCs are removed from the atmosphere only by reaction with the hydroxyl radical. Their reaction with ozone or the nitrate radical is slow enough (Atkinson and Arey, 2003) to be neglected in SOA formation, even though the SOA yields from their reaction with NO_3 can be much higher, as observed for isoprene and the monoterpenes (Fry et al., 2009, 2011).

Thus, in this approach, the I / VOCs are assumed to follow a pseudo first-order kinetic reaction, such as

$$-\frac{d\,[\mathrm{VOC}_i]}{dt} = k_{\mathrm{VOC}_i}\,[\mathrm{VOC}_i]\,[\mathrm{OH}], \quad (4)$$

with k_{VOC_i} the rate constant of VOC_i with the OH radical (cm^3 molecule^{-1} s^{-1}), [OH] the concentration of the hydroxyl radical (molecule cm^{-3}), and $[\mathrm{VOC}_i]$ the concentration of a given VOC. The initial concentration of a given VOC, $[\mathrm{VOC}_i]_{t=0}$, is then retrieved from Eq. (4), such as in Eq. (5):

$$[\mathrm{VOC}_i]_{t=0} = [\mathrm{VOC}_i]_{\mathrm{SIRTA},t} \times \left(e^{k_{\mathrm{VOC}_i} \times [\mathrm{OH}] \times \Delta t}\right), \quad (5)$$

where $[\mathrm{VOC}_i]_{\mathrm{SIRTA},t}$ is the VOC_i concentration measured at SIRTA (ppt) and Δt the time elapsed since the emission. The removal of a gaseous compound, $\Delta[\mathrm{VOC}_i]$, is therefore estimated from Eq. (7):

$$\Delta[\mathrm{VOC}_i] = [\mathrm{VOC}_i]_{t=0} - [\mathrm{VOC}_i]_{SIRTA,t} \quad (6)$$

$$\Delta[\mathrm{VOC}_i] = [\mathrm{VOC}_i]_{\mathrm{SIRTA},t} \times \left(e^{\left(k_{\mathrm{VOC}_i} \times [\mathrm{OH} \times \Delta t]\right)} - 1\right). \quad (7)$$

Finally, for a given I / VOC, the result obtained in Eq. (7) is multiplied by the SOA yield (Table 3), resulting in the amount of SOA produced by the given I / VOC at time t. The total SOA mass concentration estimated on a temporal basis is obtained by adding the amount of SOA produced by all the VOCs, as expressed by Eq. (8):

$$\mathrm{SOA}_{\mathrm{estimated}} = \sum_i \Delta\mathrm{VOC}_i \times Y_{\mathrm{SOA},i}. \quad (8)$$

5.1.3 Assumptions in the different approaches

Both estimations of the SOA amount formed from the oxidation of I / VOCs rely on different assumptions that are discussed in the following section. Additional details on the assumptions can be found in the Supplement (Sect. S4).

1. *The SOA yields.* The SOA yields used here (provided in Table 3) are the most recent ones determined in chamber experiments, and the most relevant to the MEGAPOLI campaign conditions. SOA yields are known to be highly influenced by the experimental conditions in the chamber, especially by the NO_x concentrations and the organic mass concentrations (C_{OA}) (Hildebrandt et al., 2009; Presto et al., 2010; Aumont et al., 2012; Tkacik et al., 2012). At SIRTA, on average, $C_{\mathrm{OA}} = 1.8\,\mu g\,m^{-3}$ and the NO_x concentration is 6.9 ± 4.8 ppb. These environmental conditions correspond to low-C_{OA} and low-NO_x conditions, regarding chamber experiments. While chamber experiment conditions under which SOA yields are determined are quite variable, they never meet both the low-NO_x and low-C_{OA} criteria. SOA yields of the aromatic compounds were either determined at low-NO_x or high-NO_x (Ng et al., 2007a) conditions but always at high $C_{\mathrm{OA}} = 40\,\mu g\,m^{-3}$ (see the Supplement, Sect. S4 for details). Conversely SOA yields of the volatile and C_{13}–C_{16} intermediate volatile n-alkanes were determined at high or low C_{OA} but always under high-NO_x conditions (Lim and Ziemann, 2009a; Presto et al., 2010). Therefore, the SOA formation will be studied using two sets of SOA yields for the C_{12}–C_{16} n-alkanes and the aromatics, from the integrated approach only. The first SOA yield values reported in Table 3 are those determined under the most relevant atmospheric conditions for this study, i.e., low $C_{\mathrm{OA}} = 2\,\mu g\,m^{-3}$ (but high NO_x) for the IVOCs and low-NO_x (but high $C_{\mathrm{OA}} = 40\,\mu g\,m^{-3}$) for the aromatics. The second SOA yield values are those obtained from chamber experiments performed under similar C_{OA} and NO_x conditions, i.e., high NO_x and high $C_{\mathrm{OA}} = 40\,\mu g\,m^{-3}$. The second set of SOA yields will be used to compare the contribution to SOA formation of the C_{12}–C_{16} n-alkanes against the contribution of the whole VOC set. C_9–C_{11} n-alkanes SOA yields are those determined by Lim and Ziemann (2009a) under high NO_x and high C_{OA} ($400\,\mu g\,m^{-3} < C_{\mathrm{OA}} < 1600\,\mu g\,m^{-3}$) conditions. High-$NO_x$ SOA yields are much more important than low-NO_x SOA yields for the n-alkanes (Loza et al., 2014). Besides, the higher C_{OA} is, the higher the SOA yield is (Hildebrandt et al., 2009; Presto et al., 2010; Aumont et al., 2012; Tkacik et al., 2012).

2. *The VOC/CO emission ratios.* The ER to CO are the ones determined for the Paris area based on the LHVP ground site and airborne data by Borbon et al. (2013). While the SIRTA site was rarely downwind of the Paris plume, Borbon et al. (2013) and Boynard et al. (2014) showed that VOC/VOC ER were usually consistent between northern mid-latitude urban areas. However, the C_{11}–C_{16} alkanes were not measured at LHVP. For this reason, their emission ratios have been estimated from the ER determined at vehicle exhaust by Fontaine

(2000), as previous studies state that volatile alkanes and alkanes of intermediate volatility are mainly emitted from vehicle exhaust (Fraser et al., 1998; Schauer et al., 1999a). These ratios are not expected to have changed between 2000 and 2009 (see Fig. S2 in the Supplement).

3. $[OH] \times \Delta t$. The product of $[OH]$ and Δt is derived from the photochemical age. The photochemical age is an indicator of the photochemical processing induced by the hydroxyl radical, and so of the chemistry affecting the VOCs, from their emission to their measurement at the receptor site. It is based on the ratio of two VOCs, usually aromatic compounds (Nelson and Quigley, 1983; Roberts et al., 1984; Parrish et al., 1998; Monod et al., 2001; Warneke et al., 2007). m,p-Xylenes and ethylbenzene are the two VOCs used here in the calculation of the photochemical age. Besides, the photochemical age takes into account the ratios of VOC concentrations at the emission site and at the receptor site. Here, the LHVP VOCs concentration ratio is considered at $t = 0$, since ratios at LHVP are representative of urban emission ratios (Borbon et al., 2013). Finally, the product of $[OH]$ and Δt is calculated following Eq. (9):

$$[OH] \times \Delta t = \frac{1}{(k_{\text{m,p-xylenes}} - k_{\text{ethylbenzene}})}$$
$$\times \left[\ln \frac{[\text{m,p-xylenes}]}{[\text{ethylbenzene}]} \bigg|_{\text{LHVP},t=0} \right.$$
$$\left. - \ln \frac{[\text{m,p-xylenes}]}{[\text{ethylbenzene}]} \bigg|_{\text{SIRTA},t} \right], \qquad (9)$$

with $k_{\text{m,p-xylene}}$ and $k_{\text{ethylbenzene}}$ the rate constants with OH, as reported in Table 3, and $\left| [\text{m,p-xylenes}] / [\text{ethylbenzene}] \right|_{\text{LHVP},t=0}$ the m,p-xylenes/ethylbenzene ratio at time $t = 0$, i.e., the emission ratio of m,p-xylenes to ethylbenzene. In this calculation, $k_{\text{m,p-xylene}}$ is taken equal to $k_{\text{m-xylene}}$, the m-xylene/p-xylene ratio is equal to 2.23 (pptv pptv^{-1}) in urban areas (Monod et al., 2001).

4. *The use of an inert tracer for the normalization.* Equation (7) coupled to Eq. (9) considers that the compounds are in a constant volume from the emission source until the receptor, neglecting the dilution. To overcome the effect of dilution, de Gouw et al. (2009) had determined the VOC removal from the temporal evolution of the VOC/CO ratio; the removal relies then on the VOC emission ratio instead of a calculated initial concentration. However, here it was not possible to use CO as an inert tracer due to its levels close to background, estimated to be about 100 ppb at a remote European site (Balzani Lööv et al., 2008) (see Fig. 3). Besides, normalization to one of the C_4–C_5 alkanes, which exhibit

the longest atmospheric lifetime among all the VOCs measured during the MEGAPOLI summertime experiment (Table 3), was not feasible since they are emitted from diverse sources (Sect. 4.2). Finally, no normalization was applied at all.

Other simplifications are considered for the time-resolved approach: it is assumed that (i) no I / VOC is added to the plume between the emission site and the sampling site, which is described as an obvious simplification by de Gouw et al. (2009), (ii) SOA is produced instantaneously from the VOC reaction and (iii) is not subject to loss by deposition (Sjostedt et al., 2011).

5. *The biogenic VOC precursors.* Neither of the SOA estimation approaches included any biogenic SOA precursors. The integrated approach uses CO as an inert tracer, while the time-resolved approach relies on the ratio of anthropogenic VOCs to determine the photochemical age. Since biogenic VOCs have different emission sources than CO or anthropogenic VOCs, they cannot be taken into account in the SOA estimation in the integrated approach. Since they are very reactive, they cannot be estimated with the time varying approach (they would be completely lost). However, biogenic VOCs are known to be important SOA precursors (Lee et al., 2006a; Ng et al., 2007b). Their exclusion from the two approaches implies an expected underestimation of the theoretical SOA formation and will be discussed in Sect. 5.2.3.

6. *Gas-phase chemistry vs. heterogeneous chemistry.* Typically estimations only consider SOA formation under dry conditions. Nevertheless, aqueous-phase production is another possible pathway to SOA formation (Carlton et al., 2008; Ervens et al., 2011). Carlton et al. (2008) improved the agreement between observations and predictions of total mass concentrations and its variability, especially of organic aerosol in the regional air quality model, by taking into account SOA formed in the aqueous phase. Finally, the consideration of only gas-phase SOA formation in this study probably also likely leads to an underestimation of SOA formation.

To conclude, both approaches only consider the contribution of anthropogenic VOC precursors to SOA formation and homogeneous chemistry in the gas phase. As a consequence, one could expect an overall underestimation of SOA formation. Moreover, SOA yields determined in the conditions of chamber experiments are not perfectly representative of the real atmospheric conditions (high NO$_x$ and/or high C_{OA} loads). The discussion in Sect. 5 will be focused on the role of anthropogenic VOC classes to SOA formation and in particular the importance of IVOC compared to traditional aromatic precursors, when taking into account the most adapted SOA yields.

5.2 Results and discussions

5.2.1 Estimation of SOA from its gaseous precursors: the integrated approach

The first step in the integrated approach consists of determining the value of the $\Delta OM / \Delta CO$ enhancement ratio. Figure 5a shows the scatterplot of OM to CO averaged to 1 h at SIRTA. The data points have been color-coded by the O_3 / CO ratio, which is used here as a proxy of photochemical processing. This indicator considers CO as purely of primary origin. In our case, as discussed in Sect. 3.3, secondary CO might have been sampled at SIRTA on 21 July. However, this represents only 3 % of the summertime data set, allowing the O_3 / CO ratio to be used as a proxy of the photochemical processing. Hence, fresh air masses with low photochemical processing show the lowest level of ozone and the highest level of CO: the ratio O_3 / CO tends to zero. Processed air masses show the highest level of ozone and the lowest level of CO: the ratio O_3 / CO increases. The data with a higher photochemical processing tend to follow a steeper line (highest O_3 / CO ratio) than the points with a lower photochemical processing (lowest O_3 / CO ratio). Part of the OM scatter can therefore be explained by the secondary formation of organic matter. As a consequence, the value of the $\Delta OM / \Delta CO$ enhancement ratio is determined from the fit of the correlation of data with an O_3 / CO ratio higher than 0.5 (ppb ppb^{-1}), which corresponds to the upper limit of the scatterplot envelope, implying that a maximum OM enhancement is considered here. The $\Delta OM / \Delta CO$ enhancement observed at SIRTA in summer was

$$\left(\frac{\Delta OM}{\Delta CO} \right) = (109.2 \pm 9.1)\,\mu g\,m^{-3}\,ppmv^{-1}.$$

The POA emission ratio has been determined by plotting the HOA PMF component determined at SIRTA (Freutel et al., 2013a) versus CO, which is illustrated in Fig. 5b, both HOA and CO were averaged to 1 hour. At SIRTA, the fit of the correlation was

$$\left(\frac{\Delta POA_{HOA}}{\Delta CO} \right) = (28.8 \pm 1.1)\,\mu g\,m^{-3}\,ppmv^{-1}.$$

This value is consistent with the line describing the lower limit of the scatterplot envelope in Fig. 5a. However, this POA emission ratio is higher than all the values reported in the literature so far (Fig. 5b). The value obtained at SIRTA is at least two times higher than the ones observed in the American urban areas of Pittsburgh (Zhang et al., 2005), New England (de Gouw et al., 2008) and Mexico City (Aiken et al., 2009). The important use of diesel by light-duty cars in Europe, and more particularly in France, might explain the higher POA emission ratio determined at SIRTA: not only do diesel-fueled vehicles emit less CO than gasoline-fueled vehicles (Allan et al., 2010; Gentner et al., 2013), but the
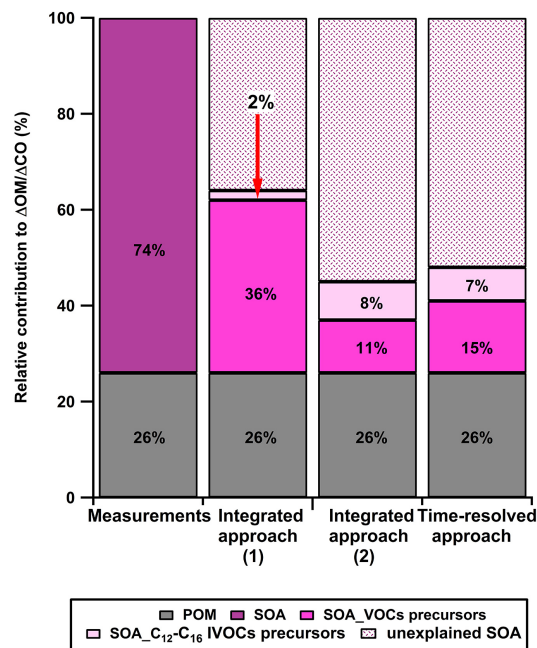
Figure 6. Comparison between the relative contribution to $\Delta OM / \Delta CO$ of measured SOA and SOA estimated from VOCs (SOA_VOCs precursors) and from the C_{12}–C_{16} IVOCs (SOA_IVOCs precursors), from integrated and time-resolved approaches in suburban Paris during summer 2009. SOA yields of atmospheric relevancy were used in the integrated approach (1); SOA yields determined under high NO_x and high C_{OA} were used in the integrated approach (2). Numbers in the bars correspond to the relative mass concentration (%) explained by each type of organic matter.

POA emission factor is 14 times more important from diesel-fueled vehicles (heavy-duty) than from gasoline-fueled cars (light-duty) (Dallmann et al., 2013). Also, some contributions from primary sources other than traffic to the HOA factor (e.g., cooking) could also potentially play a role (Crippa et al., 2013b; Freutel et al., 2013a, b).

Finally, the experimental value of the secondary OA increase is determined from Eq. (2) and found to be equal to

$$\left(\frac{\Delta SOA}{\Delta CO} \right)_{measured} = (109.2 - 28.8)\,\mu g\,m^{-3}\,ppmv^{-1}$$

$$\left(\frac{\Delta SOA}{\Delta CO} \right)_{measured} = 80.4\,\mu g\,m^{-3}\,ppmv^{-1}.$$

The theoretical SOA to CO enhancement is then obtained by summing the product of the SOA yield formation with the emission ratio of the individual VOCs relative to CO, including aromatic compounds, C_4–C_6 and C_9–C_{11} alkanes and the C_{12}–C_{16} alkanes of intermediate volatility (Eq. 3).

Illustrating the distribution of OM between its primary and its secondary components, Fig. 6 compares measured SOA and SOA estimated from I / VOCs measured at SIRTA during the MEGAPOLI summer campaign using SOA yields
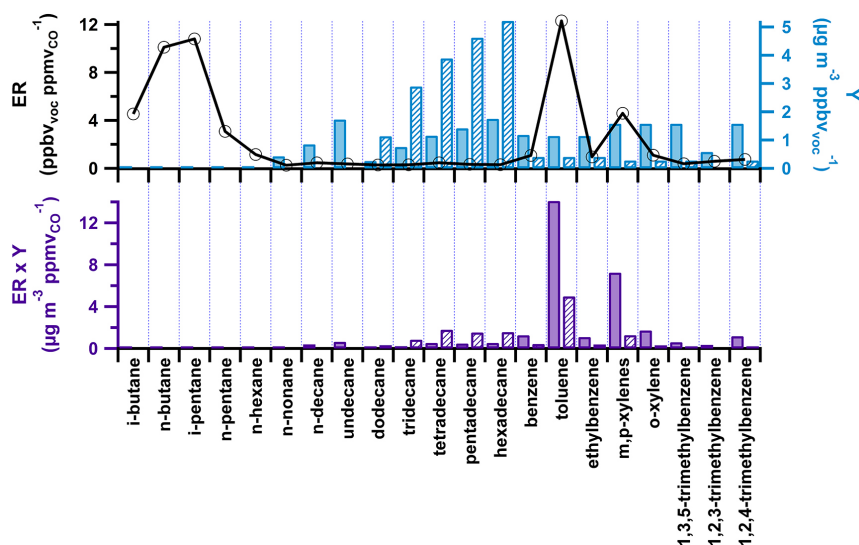
Figure 7. Emission ratios (ER) determined during the MEGAPOLI summer campaign and SOA yields (Y) of relevant VOC precursors (upper panel); products of emission ratios and SOA yields (lower panel). For the C_{12}–C_{16} IVOCs, the solid bars represent Y (and ER × Y) determined under the most relevant atmospheric conditions regarding the environmental conditions encountered at SIRTA during the MEGAPOLI summer campaign; the dashed bars represent Y (and ER × Y) determined under similar conditions ($C_{OA} = 40 \, \mu g \, m^{-3}$ and high NO_x).

determined under atmospheric-relevant conditions, i.e., low C_{OA} and high NO_x for the measured IVOCs and high C_{OA} and low NO_x for the aromatics, and under similar atmospheric conditions, i.e., high C_{OA} and high NO_x. As shown in Fig. 6, from SOA of atmospheric relevancy, the measured I / VOC precursors explain 38 % of the SOA measured at SIRTA: $28.6 \, \mu g \, m^{-3} \, ppmv^{-1}$ – i.e. 36 % of the measured SOA were explained by the traditional VOC precursors, which is consistent with the results of de Gouw et al. (2008) (who reported 37 %), and $1.8 \, \mu g \, m^{-3} \, ppmv^{-1}$, i.e., 2 % of the measured SOA, by the C_{12}–C_{16} n-alkane IVOCs. At SOA yields determined under similar environmental conditions ($C_{OA} = 40 \, \mu g \, m^{-3}$, high NO_x), the measured IVOCs explain $6.1 \, \mu g \, m^{-3} \, ppmv^{-1}$ – i.e. 8 % of the measured SOA, while the volatile compounds contribution to SOA formation drops to 11 % ($9.1 \, \mu g \, m^{-3} \, ppmv^{-1}$). Figure 7 reports the emission ratio of the gaseous compounds, their particulate yield(s) (determined under the most adapted environmental conditions regarding the conditions at SIRTA and under similar conditions for the IVOCs and the aromatic compounds), and the product of the two. It can be seen that light alkanes, which have the highest emissions, exhibit low to no SOA formation potential. Among all the VOCs, toluene and, to a lesser extent m,p-xylenes, exhibit high emission ratios, and the most important contribution to the SOA formation. For SOA yields representative of the atmospheric conditions encountered at SIRTA during the summertime MEGAPOLI campaign, aromatic compounds dominate SOA formation. The C_{13}–C_{16} n-alkanes exhibit SOA yields as high as some aromatics, but their contribution to SOA formation remains low because of their ER, which is a factor of 40 lower than the aromatics ER.

When considering the SOA determined under similar conditions, the IVOCs particulate yields are high enough to counterbalance their low emission ratios. Besides, the aromatic compounds that SOA yields are lower under high-NO_x conditions, reducing then their contribution to SOA formation. Under similar conditions, the n-alkane IVOCs up to C_{16} appear to contribute significantly to the SOA formation as much as the commonly measured aromatic compounds (benzene, ethylbenzene and o-xylene).

5.2.2 Estimation of SOA from its gaseous precursors: the time-resolved approach

The temporal evolution of the estimated SOA from the time-resolved approach (Eqs. 7, 8 and 9), by using VOCs or I / VOCs (sum of VOCs and C_{12}–C_{16} n-alkane IVOCs), is illustrated in Fig. 8 with the temporal evolution of the OOA PMF component. For this approach, SOA has been estimated by using only SOA yields of atmospheric relevance. Weak consistency is observed between the temporal evolution of measured SOA and the one estimated only from the traditional VOCs, explaining 15 % of SOA. The SOA events are barely noticeable in the latter case: the estimated SOA is as high between 13 and 16 July and between 16 and 17 July, while this latter period is an SOA event according to the measurements. When the IVOCs are taken into account, the estimation of SOA mass is improved: they explain 7 % of the measured SOA. However, the consistency between measured and estimated SOA remains weak when the IVOCs are taken into account, especially when SIRTA receives "Atlantic Polluted" air masses. Event 4 is characterized by an important underestimation of the SOA mass concentration from both
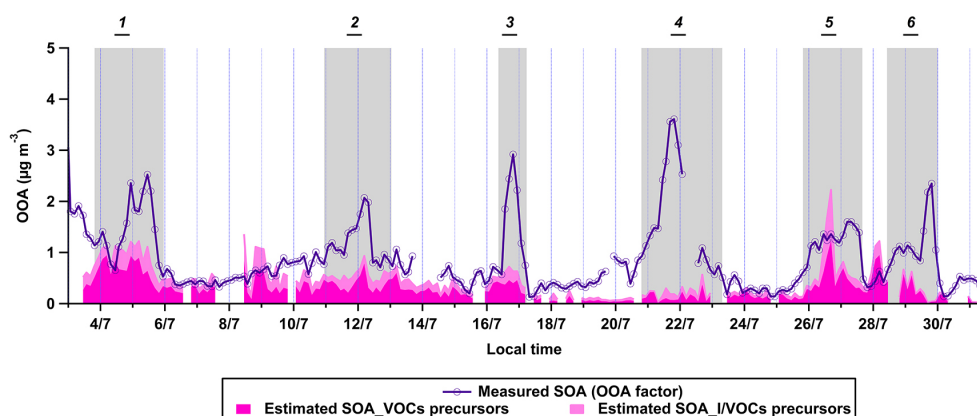
Figure 8. Temporal evolution of the OOA, or SOA, concentrations ($\mu g\,m^{-3}$) (1) observed at SIRTA, (2) estimated from the VOCs and (3) from the I / VOCs (i.e., VOCs+C_{12}–C_{16} IVOCs) measured at SIRTA using atmospheric-relevant SOA yields. The grey-shaded areas highlight the "Atlantic Polluted" wind regimes associated with stagnant conditions and increased OOA.

VOCs and C_{12}–C_{16} n-alkane IVOCs. During this latter event, the air mass passed over Spain and the Landes Forest (Freutel et al., 2013a; Zhang et al., 2013), where biogenic precursor compounds are strongly emitted. Thus, one can hypothesize that biogenic SOA could have been transported from the southwest of France to the SIRTA site, but this biogenic fraction is not taken into account by the time-resolved approach. A noticeable overestimation of the SOA mass is observed during event 5, due to high IVOCs' mixing ratios (Fig. 3). The hexadecane mixing ratio can reach up to 126 ppt, which is 6 times more than its mean mixing ratio (22 ± 19 ppt, Table 3) and only a third of the toluene mixing ratio in the same sample (344 ppt). Hence, since the SOA yield formation of hexadecane is at least equal to those of toluene (Ng et al., 2007a; Presto et al., 2010), the SOA estimation is mainly driven by the measured IVOCs, especially hexadecane, during event 5. Therefore, contribution of the measured IVOCs can overtake the aromatics contribution to SOA formation.

When SIRTA is influenced by "Atlantic Clean" air masses, some overestimation of the SOA mass concentration can be observed, such as between July 8th and 10th. Besides these overestimations, the SIRTA site appears to be characterized by local SOA formation under the influence of "Atlantic Clean" air masses. During these periods, the SOA estimations appear to be of the same order as the SOA observations.

Estimated SOA from VOCs and IVOCs from the time-resolved approach are reported in Fig. 6. When compared to the results of the integrated approach, overall estimated SOA from VOCs and/or IVOCs is lower from the time-resolved approach than from the integrated approach using atmospheric-relevant SOA yields. This difference results from the amount of precursor taken into account for the estimation (Sects. 5.2.1 and 5.2.2). The time-resolved approach considers only the precursor fraction that has reacted, while the integrated approach estimates SOA formation from the overall precursor's quantity.

5.2.3 Discussion

With both of the two approaches, the SOA estimation is significantly improved when the C_{12}–C_{16} n-alkane IVOCs are taken into account. When considering the estimations based on the SOA yields of atmospheric relevancy, 2 and 7 % improvement in the estimation of the formed SOA and of the SOA variability, respectively, are observed, when the IVOC alkanes are included in the estimation. IVOCs, especially n-alkanes, have been identified as important SOA precursors in past studies, whether they were chamber experiments (Lim and Ziemann, 2005, 2009a; Tkacik et al., 2012) or modeling (Jordan et al., 2008; Hodzic et al., 2010; Aumont et al., 2012; Pye and Pouliot, 2012). Our results confirm for the first time the important role of lower-volatility organic compounds in the SOA formation from their direct ambient measurements. However, when considering the integrated approach, $50\,\mu g\,m^{-3}\,ppmv^{-1}$, in other words, 62 % of the measured SOA, remain unexplained. Similar results were found by Freney et al. (2014). By implementing a similar integrated approach from OM and anthropogenic VOCs' airborne measurements performed in the Paris plume during the same MEGAPOLI summer experiment, Freney et al. (2014) explained 54 % of the SOA formation. When compared to the semi-volatile fraction of OOA, the SOA estimation (2014) from both Freney et al. and ourselves are consistent with SV-OOA, which represents 56 % of OOA; we both estimated the freshest OOA. When considering the time-resolved approach, important underestimations of SOA are observed, especially when the SIRTA receives "Atlantic Polluted" air masses. Part of the SOA measured in suburban Paris therefore remains unexplained. Following de Gouw et al. (2008) and various assumptions discussed in Sect. 5.1.3, possible explanations are uncertainties in the SOA yields, the exclusion of the biogenic compounds, significant unidentified mass in the C_{10}–C_{20} range, known as the unresolved

complex mixture (UCM) (Robinson et al., 2007), as well as other non-measured compounds of lower volatility $> C_{16}$. In this study, the exclusion of biogenic compounds certainly leads to an underestimation of the SOA formed. Indeed, simulations by Zhang et al. (2013) with the CHIMERE model, including the volatility basis set, have demonstrated that biogenic SOA has been transported to the Paris agglomeration from the south of France and Spain in "Atlantic Polluted" air masses. They estimated that 60 % of the SOA is of biogenic origin during these events. During the whole month of July, the Zhang et al. study estimates the contribution of biogenic VOCs, of anthropogenic VOCs and of the sum of IVOCs and semi-volatile organic compounds to SOA at SIRTA as respectively 47, 23 and 13 % (17 % being attributed to long-range-transported SOA from outside the European model domain). If all missing SOA is tentatively attributed to biogenic SOA and long-range-transported SOA, the corresponding values from our study, respectively, are 62–78, 36–15 and 2–7 % (integrated approach–time-resolved approach). Thus the modeling and our experimental results, with both their specific uncertainties, agree well.

However, our estimation of the IVOC part is still underestimated. Even though some IVOCs were taken into account here (C_{12}–C_{16} n-alkanes), numerous compounds of lower volatility, such as n-alkanes with more than 16 carbon atoms, cyclic alkanes or PAHs (polyaromatic hydrocarbons), were not measured, while they could contribute significantly to the SOA formation (Chan et al., 2009; Lim and Ziemann, 2009a; Yuan et al., 2013). Furthermore, these compounds are expected to be largely emitted by diesel cars (Schauer et al., 1999a; Chan et al., 2009; Gentner et al., 2012), which are widely used in France (CCFA, 2011). Measurements of more IVOCs and other compounds of lower volatility might improve the SOA estimation from the integrated approach. Hence, efforts should be made to make the IVOC measurements as systematic as the measurements of other compounds, like the aromatic VOCs (e.g., during field experiments).

6   Conclusions

Under the auspices of the MEGAPOLI project, measurements of gaseous organic carbon have been performed in the Paris megacity, resulting in a large and unique database (available at the French Ether database: http://ether.ipsl.jussieu.fr/megapoli/). Compounds of different sources and chemical and physical properties have been documented during a summer and a winter field campaign at SIRTA, a suburban site of the French megacity.

The first goal was to analyze the temporal and spatial variability and origin of gaseous organic carbon in suburban Paris. The analysis showed that

- The seasonal variation of anthropogenic VOCs is the one usually depicted in urban areas with higher winter-

time concentrations as a result of a combination of (i) a shallower boundary layer in winter than in summer, (ii) photochemistry processes less active in winter and (iii) emissions sources of different nature and/or intensity.

- The seasonal variation of C_{12}–C_{16} n-alkanes of intermediate volatility follows an opposite trend to traditional anthropogenic VOCs with lower concentrations in winter. The variation of these compounds mixing ratios probably results from a change in their emission sources (type, strength) than from the partition to the gas-phase to the particulate-phase of these lower volatility species.

- The seasonal variations of OVOCs shows a different behavior than usually observed with lower concentrations in summer, suggesting their dominant primary origin.

- The seasonal variation of α-pinene and isoprene, with higher concentrations in summer is typical of biogenic-emitted compounds. On the contrary, camphene and limonene exhibit higher concentrations in winter than in summer, suggesting weaker loss processes and/or additional anthropogenic emission sources to their biogenic ones.

The VOC levels at SIRTA are very low compared to other cities worldwide and are similar to the ones encountered in remote atmospheres. Like other atmospheric species in the whole Paris area, and organic aerosol in particular, meteorology and air mass origin strongly influence the variability of atmospheric species.

The second goal was to estimate the contribution of measured I / VOC precursors to SOA formation by implementing two independent approaches (integrated and time-resolved). Between 15 and 36 % of the SOA measured was explained by the measurements of the only volatile compounds (aromatics and C_9–C_{11} n-alkanes) from both approaches. The IVOCs (C_{12}–C_{16} n-alkanes) explain 2 to 7 % of the SOA formation. Finally, between 22 and 38 % of SOA observed at SIRTA was explained by observations. These values are consistent with the ones simulated with a chemistry-transport model, in which the volatility set basis has been implemented. They are also consistent with the results of a similar integrated approach using airborne measurements of organic compounds in the Paris area. From the time-resolved approach, the temporal estimation of the SOA formation indicated that the primary anthropogenic I / VOCs are greatly involved in the formation of the SOA background at SIRTA. But important discrepancies between the estimation and the observation remain during events of high SOA mass concentration. The estimations indicate that the SOA concentrations measured at SIRTA are not only strongly dependent (i) on the primary anthropogenic VOCs, which are widely measured around the world, but also (ii) on the IVOCs, since only five of them explain more than 10 % of the observed SOA,

(iii) on other compounds which were not included in the estimation because they were not measured or because they were not from primary anthropogenic sources, and finally (iv) on SOA transported over long distances for which the signature in gaseous precursors is lost. Thus, further investigations should be undertaken in order to take into account these compounds, either by developing their measurements (as for additional IVOCs), determining SOA yields in relevant atmospheric conditions or by including them in the estimations (as for biogenic SOA relying on specific tracers in both the gas and particle phase).

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