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A one-year comprehensive chemical characterisation of fine aerosol (PM$_{2.5}$) at urban, suburban and rural background sites in the region of Paris (France)

M. Bressi[1,2], J. Sciare[1], V. Ghersi[3], N. Bonnaire[1], J. B. Nicolas[1,2], J.-E. Petit[1], S. Moukhtar[3], A. Rosso[3], N. Mihalopoulos[4], and A. Féron[1]

[1]Laboratoire des Sciences du Climat et de l'Environnement, LSCE, CNRS-CEA-UVSQ, UMR8212, Gif-sur-Yvette, 91191, France
[2]French Environment and Energy Management Agency, ADEME, 20 avenue du Grésillé, BP90406 49004, Angers Cedex 01, France
[3]AIRPARIF, Surveillance de la Qualité de l'Air en Ile-de-France, Paris, 75004, France
[4]Environmental Chemical Processes Laboratory, ECPL, Heraklion, Voutes, Greece

Correspondence to: M. Bressi (michael.bressi@ensiacet.fr)

Abstract. Studies describing the chemical composition of fine aerosol (PM$_{2.5}$) in urban areas are often conducted for a few weeks only and at one sole site, giving thus a narrow view of their temporal and spatial characteristics. This paper presents a one-year (11 September 2009–10 September 2010) survey of the daily chemical composition of PM$_{2.5}$ in the region of Paris, which is the second most populated "Larger Urban Zone" in Europe. Five sampling sites representative of suburban (SUB), urban (URB), northeast (NER), northwest (NWR) and south (SOR) rural backgrounds were implemented. The major chemical components of PM$_{2.5}$ were determined including elemental carbon (EC), organic carbon (OC), and the major ions. OC was converted to organic matter (OM) using the chemical mass closure methodology, which leads to conversion factors of 1.95 for the SUB and URB sites, and 2.05 for the three rural ones. On average, gravimetrically determined PM$_{2.5}$ annual mass concentrations are 15.2, 14.8, 12.6, 11.7 and 10.8 µg m^{-3} for SUB, URB, NER, NWR and SOR sites, respectively. The chemical composition of fine aerosol is very homogeneous at the five sites and is composed of OM (38–47 %), nitrate (17–22 %), non-sea-salt sulfate (13–16 %), ammonium (10–12 %), EC (4–10 %), mineral dust (2–5 %) and sea salt (3–4 %). This chemical composition is in agreement with those reported in the literature for most European environ-

ments. On an annual scale, Paris (URB and SUB sites) exhibits its highest PM$_{2.5}$ concentrations during late autumn, winter and early spring (higher than 15 µg m^{-3} on average, from December to April), intermediates during late spring and early autumn (between 10 and 15 µg m^{-3} during May, June, September, October, and November) and the lowest during summer (below 10 µg m^{-3} during July and August). PM levels are mostly homogeneous on a regional scale, during the whole project (e.g. for URB plotted against NER sites: slope = 1.06, r^2 = 0.84, n = 330), suggesting the importance of mid- or long-range transport, and regional instead of local scale phenomena. During this one-year project, two thirds of the days exceeding the PM$_{2.5}$ 2015 EU annual limit value of 25 µg m^{-3} were due to continental import from countries located northeast, east of France. This result questions the efficiency of local, regional and even national abatement strategies during pollution episodes, pointing to the need for a wider collaborative work with the neighbouring countries on these topics. Nevertheless, emissions of local anthropogenic sources lead to higher levels at the URB and SUB sites compared to the others (e.g. 26 % higher on average at the URB than at the NWR site for PM$_{2.5}$, during the whole campaign), which can even be emphasised by specific meteorological conditions such as low boundary layer heights. OM and secondary inorganic species (nitrate,

non-sea-salt sulfate and ammonium, noted SIA) are mainly imported by mid- or long-range transport (e.g. for NWR plotted against URB sites: slope $= 0.79$, $r^2 = 0.72$, $n = 335$ for OM, and slope $= 0.91$, $r^2 = 0.89$, $n = 335$ for SIA) whereas EC is primarily locally emitted (e.g. for SOR plotted against URB sites: slope $= 0.27$; $r^2 = 0.03$; $n = 335$). This database will serve as a basis for investigating carbonaceous aerosols, metals as well as the main sources and geographical origins of PM in the region of Paris.

1   Introduction

Adverse health effects of aerosols and especially of fine particles (PM$_{2.5}$ i.e. particulate matter with aerodynamic diameter, AD, below 2.5 µm) have been widely demonstrated (Bernstein et al., 2004; Pope et al., 2004), especially in urban areas (Lawrence et al., 2007). Paris is highly concerned by these impacts as it is the second "Larger Urban Zone" in Europe with 11 million inhabitants, i.e. 18 % of the French population (Eurostat, 2011). A recent study (Aphekom, 2011) reported that a reduction of PM$_{2.5}$ concentrations in Paris (average 2004–2006: 16.4 µg m^{-3}; Airparif, 2012) towards the World Health Organization recommendation value (10 µg m^{-3}) would lead to a gain in life expectancy of 5.8 months for persons 30 years of age and older. In addition, epidemiologists and toxicologists suggest investigating chemical and physical characteristics of particles in order to better assess their toxicity (Schlesinger, 2007; Ramgolam et al., 2008).

Besides, climate effects of aerosols have been a subject of concern for more than 20 yr (WCP, 1983; Ramanathan et al., 1987). Whereas long-lived greenhouse gases and ozone contribute a positive radiative forcing (RF) of $+2.9$ (± 0.3) W m^{-2}, the combined aerosol direct and cloud albedo effect have a median RF of -1.3 W m^{-2} and a -2.2 to -0.5 W m^{-2} 90 % confidence range (Forster et al., 2007). To better estimate climate effects of aerosols, their chemical composition has to be exhaustively documented as each chemical component will play a specific role in the direct (i.e. the scattering and absorbance of solar and infrared radiation in the atmosphere) and indirect effects (i.e. the modification of the formation and precipitation efficiency of liquid water, ice and mixed-phase clouds) on climate (Forster et al., 2007; Isaksen et al., 2009).

Because of health and climate impacts of particles, limit values of PM$_{2.5}$ and PM$_{10}$ (particles with an AD below 10 µm) determined by the European Union (EU) became more stringent in recent years. As PM$_{2.5}$ represents 50–90 % of PM$_{10}$ mass in most European environments (Putaud et al., 2010), the conclusions drawn in this paper will also help to understand PM$_{10}$. Concerning PM$_{10}$, the actual EU daily limit value is 50 µg m^{-3} and not to be exceeded more than 35 days per year (European Directive 2008/50/EC). During

2010, this limit value has been exceeded from 42 to 176 days at seven traffic sites in the region of Paris, thus affecting 1.8 million inhabitants i.e. 16 % of the regional population (Airparif, 2012). In May 2011, France has even been summoned to the Court of Justice of the EU because of these PM$_{10}$ exceedances. Concerning PM$_{2.5}$, since 2007 annual levels have constantly been around 20 µg m^{-3} at an urban background (Airparif, 2012), which is under the 2015 EU annual limit value of 25 µg m^{-3}, but equal to the one planned for 2020. Therefore, there is a clear need to better understand the origin and chemical composition of PM over the region of Paris to tackle health, climate and legislative issues.

Studies describing the chemical composition of aerosols in the region of Paris are however scarce and were mostly conducted over short time periods (typically a few weeks), at only one sampling site (e.g. Hodzic et al., 2006; Favez et al., 2007; Gros et al., 2007; Sciare et al., 2010, 2011). Although they bring valuable information on the physical and chemical characteristics of PM in this region, they do not address their temporal and spatial evolution on a large scale. In particular, the seasonality of the chemical processes governing PM mass and chemical composition, as well as the annual evolution of the major emission sources are still poorly known.

To fill these gaps, a research project involving the Climate and Environmental Sciences Laboratory (LSCE) and the regional air quality network of Paris (AIRPARIF) has been implemented. This LSCE-AIRPARIF "Particles" project goes beyond the scope of this paper and its full description can be found in Ghersi et al. (2010) and Airparif and LSCE (2012). Briefly, its general strategy aims at documenting the daily chemical composition of PM$_{10}$ and PM$_{2.5}$ in different types of environments representative of urban, suburban, rural and traffic sites, during a one-year period (11 September 2009–10 September 2010). It should allow the identification of the major sources of PM as well as their geographical origins in order to implement effective abatement policies (Ghersi et al., 2012). In addition, a detailed study of carbonaceous aerosols has been performed and will help in better documenting its main sources (including traffic and domestic wood burning) and its atmospheric processing. Finally, a focus on metal concentrations will be made in order to describe their main primary sources, size distribution and temporality in the region of Paris. This "Particles" project will be helpful to put into perspective the recent intensive field campaigns performed within the European project MEGAPOLI (Megacities: emissions, urban, regional and Global Atmospheric POLlution and climate effects, and Integrated tools for assessment and mitigation), by providing a spatially and temporally extended view of the PM chemical composition in the entire region of Paris.

A focus will be made here on the daily chemical composition of fine aerosol determined during one-year at one urban, one suburban and three rural sites of the region of Paris. This paper aims at presenting this chemical dataset including a description and evaluation of measurement methods, and

a first analysis of its spatiotemporal variability. More precisely, Sect. 2 will describe (i) sampling sites, (ii) analytical techniques, (iii) chemical mass closure methodology and (iv) organic carbon to organic matter conversion factor's methodology. Section 3 will present (i) the representativeness of the studied period, (ii) first results regarding the chemical composition of $PM_{2.5}$, (iii) an evaluation of measurement methods and (iv) the adequate OC to OM conversion factor to use. Finally, Sect. 4 will discuss (i) the temporal variability of $PM_{2.5}$ with an emphasis on meteorological parameters that can explain daily and seasonal variations of specific chemical compounds; and (ii) the spatial variability of $PM_{2.5}$ and major chemical compounds hence giving an insight into their geographical origins (local versus regional or transboundary).

2 Material and methods

2.1 Sampling sites description

Six sampling sites were implemented, covering the region of Paris (see Fig. 1). These sites are part of the AIRPARIF Air Quality monitoring network, and are regarded as being representative of background conditions (Ghersi et al., 2010). They were categorised according to criteria proposed by the European Environment Agency (Larssen et al., 1999). The first site is an urban (URB) station located in the city centre of Paris (4th district, 48°50′56″ N, 02°21′55″ E, 20 m above ground level, a.g.l.). The second site is a near-city or suburban (SUB) station located at 10 km northeast of the URB station (48°52′54″ N, 02°30′23″ E, 5 m a.g.l.). The third, fourth and fifth sites are rural stations located respectively at ca. 65 km northeast (NER), 50 km northwest (NWR) and 60 km south (SOR) of the URB station (49°05′15″ N, 03°04′35″ E, 5 m a.g.l.; 49°03′48″ N, 01°51′59″ E, 5 m a.g.l. and 48°21′49″ N, 02°14′07″ E, 5 m a.g.l., respectively). A traffic (TR) station located at the ring road of Paris, at 9 km west of the UR station was also implemented (48°51′02″ N, 2°15′09″ E, 5 m a.g.l.). This last station will not be described here due to its specificity (traffic sources) whereas this paper aims at describing representative urban, suburban and rural backgrounds.

2.2 Aerosol sampling

Fine aerosol particles ($PM_{2.5}$) were collected at each site every day during 24 h (from 00:00 to 23:59 LT) during one year (from 11 September 2009 to 10 September 2010). Filter sampling was performed using two collocated Leckel low volume samplers (SEQ47/50) at each station running at $2.3\,\mathrm{m^3\,h^{-1}}$. One Leckel sampler was equipped with quartz filters (QMA, Whatman, 47 mm diameter) for carbon analyses, the second with Teflon filters (PTFE, Pall, 47 mm diameter, 2.0 µm porosity) for gravimetric and ion measurements. Before being sampled, QMA filters were baked at 480 °C

Fig. 1. Spatial distribution of the sampling sites in the region of Paris (Ile-de-France region). Source: Google Earth. Legend: SUB: SUBurban, URB: URBan, NER: North-East Rural, NWR: North-West Rural, SOR: SOuth Rural.

for 48 h and PTFE filters pre-weighed as reported in Sciare et al. (2003). Field blanks were taken every two weeks for PTFE filters, and every week for QMA filters. A total of 4040 filters have been collected including 2085 QMA and 1955 PTFE filters. Few samples have been discarded because of power failures, chemical analysis problems, etc. (Table S1) and represent ca. 5 % of QMA and 5 % of PTFE filters. Once sampled, filters were stored at −20 °C in a freezer prior to chemical analyses.

2.3 Chemical analyses

2.3.1 Gravimetry

In order to minimise the influence of water adsorption, loaded and unloaded PTFE filters were equilibrated for 48 h at ambient temperature and below 30 % relative humidity (RH) prior to being weighed (MacMurry, 2000; Sciare et al., 2005). PTFE filters were then weighed with a microbalance (Sartorius, MC21S) with 1 µg sensitivity. Filter weighing was repeated until having a difference between two weighs below 5 µg. The overall error is estimated to be 10 µg which represents 3 ± 2 % of loaded filters ($n = 1723$; all sites, one-year measurements, blank filters excluded). Aerosol masses (PM_{grav}) were deduced from the gravimetric measurements done before and after sampling. Field blanks taken on the field show an averaged PM_{grav} of 7 ± 11 µg ($n = 130$), which represents 2 ± 1 % of loaded filters ($n = 1723$), thus being below the overall microbalance error.

2.3.2 Ions

The following water-soluble major ions were analysed by Ion Chromatographs (IC): chloride, nitrate, sulfate, sodium, ammonium, potassium, magnesium and calcium. The analytical

protocol followed is thoroughly described by Sciare et al. (2008) and Guinot et al. (2007). Briefly, filter samples were extracted in 15 mL of Milli-Q water during 45 min in a sonic bath. To prevent bacteria activity, 50 µL of chloroform was added. Samples were then filtered using Acrodisc filters (Pall Gelman) with a porosity of 0.4 µm. Cations were analysed on a 2 mm diameter CS12 pre-column and column with an IC (Dionex, Model DX-600, USA), anions on a 2 mm diameter AS11 pre-column and column with an IC (Dionex, Model DX-600, USA). Both IC apparatus were equipped with a regent free system (automated eluent generation and self-regenerating suppression). Semi-annual laboratory IC inter-comparison studies were performed (accessible at http://qasac-americas.org/lis/summary/44) and showed errors of less than 5 % for every cited ion. Field blank measurement medians ($n = 130$) are 26, 29, 4, 9, 9, 4, 2 and 22 ppb for Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}, respectively, which represent 16, 2, 0, 5, 1, 3, 6 and 24 % of the medians of loaded filters ($n = 1723$), respectively. Blank corrections have only been performed for chloride and calcium ions by subtracting blank medians to the loaded filter values.

2.3.3   Carbon

Elemental carbon (EC) and organic carbon (OC) were determined by a thermal-optical method using a Sunset Laboratory Carbonaceous Analyser (Sunset Lab., OR, USA) and the EUSAAR_2 protocol (transmission method) defined by Cavalli et al. (2010). A detailed description concerning thermal-optical methods and the relevance of the protocol chosen can be found elsewhere (Chow et al., 1993; Schmid et al., 2001; Cavalli et al., 2010). The detection limit and the uncertainty given by the Sunset Company are estimated to be 0.2 µgC and 5 %, respectively, for EC and OC measurements. EC was not detected in field blanks (0.0 ± 0.1 µgC cm^{-2}, $n = 252$), and OC was found with an average value of 1.1 ± 0.5 µgC cm^{-2} ($n = 252$). On average, this field blank value represents 15 ± 7 % of sampled filter's OC concentrations ($n = 1723$). Blank corrections have been performed for OC concentrations by subtracting the blank average to the sampled filter values.

2.4   Chemical mass closure

Aerosol Chemical Mass Closure (CMC) consists in comparing the sum of the major aerosol chemical species (PM$_{chem}$) with gravimetric measurements (PM$_{grav}$). When achieved (i.e. when PM$_{chem}$ = PM$_{grav}$), CMC attests the consistency of chemical analyses, and confirms that all the major aerosol chemical species are taken into account. PM$_{chem}$ calculation is here expressed as:

$$[PM_{chem}] = [Sea\ Salt] + [Dust] + [Secondary\ Inorganic \quad (1)$$

$$Aerosols] + [Carbonaceous\ Matter]$$

Sea salt (ss-) concentrations are calculated from the six major ions accounting for more than 99 % of the mass of salts dissolved in seawater:

$$[Sea\ salt] = [Na^+] + [Cl^-] + [Mg^{2+}] \quad (2)$$

$$+ [ss - K^+] + [ss - Ca^{2+}] + [ss - SO_4^{2-}]$$

with $[ss\text{-}K^+] = 0.036 \cdot [Na^+]$; $[ss\text{-}Ca^{2+}] = 0.038 \cdot [Na^+]$ and $[ss\text{-}SO_4^{2-}] = 0.252 \cdot [Na^+]$

Typical seawater ion ratios based on the average seawater composition are taken from Seinfeld and Pandis (1998).

Different methods are used to calculate the mineral dust fraction in PM$_{2.5}$, and are based on its average elemental composition from specific sites, or on specific tracers (Pettijohn, 1975; Malm et al., 1994; Guieu et al., 2002). Recently, nss-calcium has been used to estimate mineral dust in aerosols because of its abundance (Putaud et al., 2004a; Sciare et al., 2005). We used the 15 % contribution of nss-calcium in mineral dust determined by Guinot et al. (2007) in Paris:

$$[Dust] = [nss - Ca^{2+}]/0.15 \quad (3)$$

This is in agreement with the ratio of 18 % reported by Putaud et al. (2004b) in Monte Cimone (Italy) during non-Saharan dust periods. The resulting proportion of dust in PM$_{2.5}$ during the whole campaign ranges from 2 to 5 % on average at the five sites (see Sect. 4.2.2). By changing this ratio by ± 3 %, the resulting proportion of dust in PM$_{2.5}$ remains very low at the five sites (3 to 6 % and 2 to 4 % of PM$_{2.5}$ with nss-Ca^{2+} to dust ratios of 12 and 18 %, respectively). In the frame of chemical mass closure, further investigation allowing the estimation of dust will thus not be conducted.

Secondary inorganic aerosols (SIA) are calculated as:

$$[Secondary\ Inorganic\ Aerosols] = [nss - SO_4^{2-}] \quad (4)$$

$$+ [NO_3^-] + [NH_4^+]$$

where $[nss\text{-}SO_4^{2-}] = [SO_4^{2-}] - [ss\text{-}SO_4^{2-}]$, "nss-" standing for "non-sea-salt".

Finally, carbonaceous matter can be expressed as:

$$[Carbonaceous\ Matter] = [EC] + [OM] \quad (5)$$

with $[OM] = f_{OC-OM} \cdot [OC]$.

The estimation of organic matter and more specifically of f_{OC-OM} will now be discussed.

2.5 Organic carbon to organic matter conversion factor

Organic matter (OM) is here inferred from filter OC measurements determined by the Sunset Laboratory analyser. The estimation of OM is of high complexity due to its varied chemical composition which changes according to location, season and time of the day (Turpin et al., 2000; Andrews et al., 2000). Turpin and Lim (2001) recommend the measurement of the average molecular weight per carbon weight in the location of interest; such measurements were not conducted in this study. In that case, they suggest the use of an OC to OM conversion factor (f_{OC-OM}) of 1.6 ± 0.2 for urban aerosols and 2.1 ± 0.2 for nonurban aerosols. These factors were widely used in recent peer reviewed publications (Terzi et al., 2010; Cheung et al., 2011; Rengarajan et al., 2011) despite their spatial and temporal dependencies. We decided to estimate f_{OC-OM} from our dataset by using a method adapted from Guinot et al. (2007) who used the chemical mass closure technique as a tool to assess f_{OC-OM} from OC measurements.

To infer f_{OC-OM}, we assumed that CMC is achieved ($PM_{grav} = PM_{chem}$), and used Eq. (1) to write the following equation:

$$f_{OC-OM} = 1/[OC] \cdot ([PM_{grav}] - ([Sea\ Salt] + [Dust] \quad (6)$$
$$+ [SIA] + [EC]))$$

This will allow us to find the "best guess" f_{OC-OM} value from our dataset. To simplify Eq. (6), a chemical fraction named "Remaining mass" (RM) has been defined in Eq. (7):

$$[Remaining\ Mass] = [PM_{grav}] - ([SeaSalt] + [Dust] \quad (7a)$$
$$+ [SIA] + [EC])$$

thus leading to:

$$[Remaining\ Mass] = f_{OC-OM} \cdot [OC] \quad (7b)$$

Two different methods were then used to estimate f_{OC-OM}. In the first method, RM concentrations are plotted against OC concentrations and f_{OC-OM} is the slope of the linear regression (Eq. 7). We decided to use a linear function without y-intercept because of the analytical form of this equation. In the second method, we numerically calculated f_{OC-OM} day-by-day from Eq. (6). Days with f_{OC-OM} higher than 3 and lower than 1 were considered as physically meaningless and were therefore excluded from the dataset. These days represent 6 to 14 % of the samples according to sites. Results will be discussed in Sect. 3.5.

2.6 Additional measurements

Meteorological parameters such as temperature, pressure, precipitation, wind speed and wind direction were provided by the French national meteorological service "Meteo-France" from measurements recorded at Montsouris (14th

district, $48°49'20''$ N, $02°20'18''$ E) located at about 5 km south of the URB station. Boundary Layer Height (BHL) is taken from simulations with the PSU/NCAR mesoscale model (MM5; Dudhia, 1993; Grell et al., 1994). In the vertical, 23 sigma layers extend up to 100 hPa. MM5 is forced by the final analyses from the Global Forecast System (GFS/FNL) operated daily by the American National Centers for Environmental Prediction (NCEP), using the grid nudging (grid FDDA) option implemented within MM5. The Medium Range Forecast scheme (MRFPBL) has been used to parameterize turbulence in the boundary layer (Troën and Mahrt, 1986). Air mass back trajectories were calculated using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Rolph, 2011).

3 Results

3.1 Representativeness of the campaign

The meteorological conditions and the PM level representativeness of the studied period were investigated and reported in Fig. S1. Air temperatures measured during our campaign were comparable to standard values determined by Meteo-France (calculated following Arguez and Vose, 2011), showing however lower values during winter (DJF, Fig. S1a). Levels of precipitation showed discrepancies in comparison with standard values (Fig. S1b). More specifically, September 2009 and April 2010 were particularly dry, unusual snow events occurred during January 2010 and heavy rains during July and August 2010. Paris is typically characterised by a dominance of south to southwest winds (ca. 35 %) and to a lesser extent north to northeast winds (ca. 20 %) (Fig. S1c). The studied period showed similar trends although a stronger contribution of the northeast sector was observed.

Finally, our yearly average $PM_{2.5}$ mass concentration of 18.4 µg m^{-3} was characteristic of a usual year (R&P Tapered Element Oscillating Microbalance – Filter Dynamic Measurement System, TEOM-FDMS, (Rupprecht and Patashnik Co., Inc.; Patashnik and Rupprecht, 1991) data corrected for semi-volatile materials at the urban site). It was lower than in 2007 (ca. −11 %), but higher than in 2008 (ca. +16 %, values calculated from TEOM-FDMS data measured at a similar urban site of the Airparif network).

3.2 Chemical composition of $PM_{2.5}$

Table 1 reports statistics on the chemical composition of $PM_{2.5}$ at the five sites, on the whole sample set. $PM_{2.5}$ levels range from 10.8 to 15.2 µg m^{-3} on average according to sites. Fine aerosols are primarily made of OC (2.1–3.2 µg m^{-3}), nitrate (2.2–2.9 µg m^{-3}), sulfate (1.8–2.1 µg m^{-3}) and ammonium (1.2–1.5 µg m^{-3}); and to a lesser extent of EC (0.4–1.4 µg m^{-3}) and minor ions (less than 0.2 µg m^{-3} for Cl$^-$, Na$^+$, K$^+$, Ca^{2+} and Mg^{2+}). Further discussion will be conducted in Sect. 4.

Table 1. Chemical composition (µg m^{-3}) of PM$_{2.5}$ at the five sites during the one-year period.

	SUBURBAN n = 348					URBAN n = 335					NORTH EAST RURAL n = 330					NORTH WEST RURAL n = 359					SOUTH RURAL n = 351				
	min	max	med	av	std	min	max	med	av	std	min	max	med	av	std	min	max	med	av	std	min	max	med	av	std
Mass	3.7	62.6	11.9	15.2	10.5	3.9	62.8	11.6	14.8	9.6	2.8	48.6	9.6	12.6	8.6	2.1	61.4	8.7	11.7	9.5	0.7	49.4	7.9	10.8	8.4
OC	0.5	19.8	2.5	3.2	2.5	0.6	12.7	2.6	3.0	1.7	0.4	13.1	2.2	2.9	2.2	0.2	12.8	1.6	2.2	1.9	0.3	10.6	1.7	2.1	1.5
NO$_3^-$	<LOQ	17.5	2.9	3.6	3.6	<LOQ	17.1	1.1	2.9	3.7	<LOQ	16.6	0.9	2.2	2.9	<LOQ	18.3	0.9	2.2	2.9	0.0	18.2	0.8	2.2	3.1
SO$_4^{2-}$	0.2	10.1	1.7	2.1	1.7	0.2	11.2	1.6	2.0	1.6	0.2	9.6	1.5	1.9	1.4	0.2	10.9	1.5	1.9	1.6	0.1	9.6	1.5	1.8	1.6
NH$_4^+$	0.1	8.1	0.8	1.5	1.6	0.0	9.0	0.7	1.4	1.6	0.1	7.2	0.7	1.2	1.3	0.1	8.0	0.7	1.2	1.3	0.0	7.9	0.7	1.2	1.4
EC	0.3	5.3	1.2	1.3	0.7	0.1	4.5	1.3	1.4	0.7	0.1	1.6	0.5	0.5	0.3	0.1	2.3	0.4	0.5	0.3	0.1	1.8	0.4	0.4	0.3
Cl$^-$	<LOQ	1.65	<LOQ	0.18	0.21	<LOQ	1.88	<LOQ	0.19	0.23	<LOQ	1.73	<LOQ	0.16	0.21	<LOQ	1.42	<LOQ	0.18	0.22	<LOQ	1.72	0.07	0.14	0.19
Na$^+$	<LOQ	1.08	0.11	0.16	0.15	<LOQ	1.19	0.11	0.18	0.17	<LOQ	1.22	0.09	0.14	0.14	<LOQ	0.94	0.11	0.16	0.15	<LOQ	1.01	0.08	0.13	0.13
K$^+$	<LOQ	0.74	0.08	0.13	0.12	<LOQ	0.73	0.07	0.12	0.17	<LOQ	1.59	0.07	0.12	0.13	<LOQ	0.72	0.06	0.11	0.12	<LOQ	0.61	0.06	0.10	0.10
Ca^{2+}	<LOQ	1.29	0.06	0.08	0.09	<LOQ	1.09	0.09	0.12	0.12	<LOQ	0.34	0.04	0.05	0.04	<LOQ	0.31	0.05	0.06	0.05	<LOQ	0.30	0.03	0.04	0.04
Mg^{2+}	<LOQ	0.18	0.02	0.03	0.02	<LOQ	0.16	0.02	0.03	0.02	<LOQ	0.16	0.02	0.02	0.02	<LOQ	0.13	0.02	0.03	0.02	<LOQ	0.15	0.01	0.02	0.02

Legend: LOQ: Limit of Quantification.

3.3 Comparison between filter and on-line determined masses

We investigated the atmospheric consistency of our PM$_{2.5}$ measurements, and attempted to estimate artefacts associated with filter sampling (Zhang and McMurry, 1987; Mc Dow and Huntzicker, 1990; Turpin et al., 2000). A conventional on-line automatic system (TEOM-FDMS) was running during the campaign at the urban station only and is used by Airparif since 2007 (Airparif, 2012). Gravimetric and TEOM-FDMS determined masses are compared in Figs. 2 and 3. TEOM-FDMS was running at 30 °C and was not corrected for semi-volatile materials (i.e. only the reference signal of the TEOM-FDMS was used here, without taking into account the SVM mass provided by the FDMS), in order to be as close as possible to our laboratory conditions. Very similar temporal variations are observed in Fig. 2 for both datasets for the whole duration of the campaign. TEOM-FDMS data plotted against gravimetric mass concentrations show a very good correlation ($r^2 = 0.94$, $n = 318$, Fig. 3). However, filter measurements exhibit mass concentrations about 6 % higher than the on-line method (slope ± 1 standard error = 0.938 ± 0.007). This can be related to temperature differences during filter sampling (ambient temperature) and TEOM-FDMS measurements (30 °C), leading in the latter case to a partial volatilization of semi-volatile materials. Absorption of volatile organic compounds (VOC) (Turpin et al., 1994, 2000) and/or water onto filters (Quinn and Coffman, 1998; Speer et al., 2003; Hueglin et al., 2005) could also enhance filter masses. In addition, taking into account semi-volatile materials in TEOM-FDMS measurements (i.e. adding the SVM mass provided by the FDMS to the reference signal of the TEOM-FDMS) leads to higher concentrations compared with the gravimetric method (18.4 versus 14.8 µg m^{-3}, respectively, on average at the URB site). The former method is regarded as an equivalent method to the EU reference method (EN 14907), whereas the latter does not fulfil EU requirements (by operating below 30 % RH instead of at 50 % RH). It should thus be borne in mind that our gravimetric method will underestimate PM$_{2.5}$ mass compared to EU reference methods by ca. 20 % on average.

3.4 Comparison between filters and on-line determined chemical components
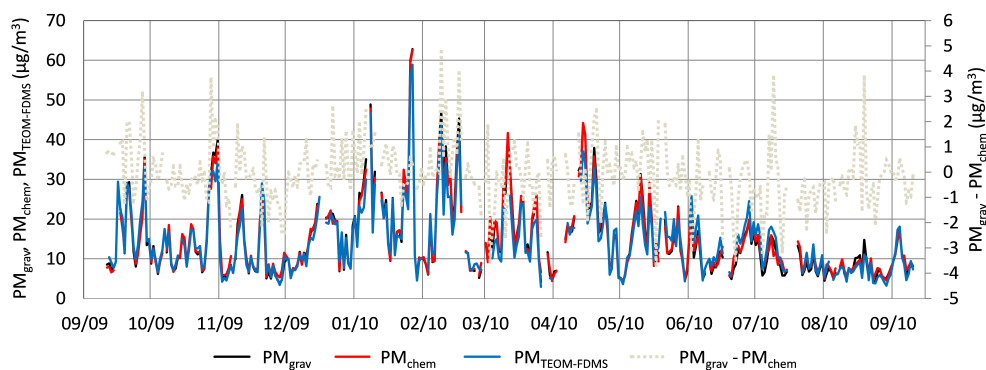
The chemical results obtained at the urban site were compared with real-time chemical analysers that were set in the Paris urban area (ca. 2 km south of the URB site) as part of the wintertime intensive field experiment of the European programme MEGAPOLI (15 January–15 February 2010). Such comparison may provide insights into the importance of positive and negative artefacts associated with our undenuded filter sampling of semi-volatile species (typically ammonium nitrate and organic aerosols).

Fig. 2. Gravimetric (PM_{grav}), chemically reconstructed (PM_{chem}), TEOM-FDMS ($PM_{TEOM\text{-}FDMS}$) and gravimetric minus chemically reconstructed ($PM_{grav} - PM_{chem}$) daily mass concentrations ($\mu g\,m^{-3}$) at the urban site from 11 September 2009 to 10 September 2010. Note: TEOM-FDMS measurements are conducted at 30 °C and do not take into account semi-volatile materials.
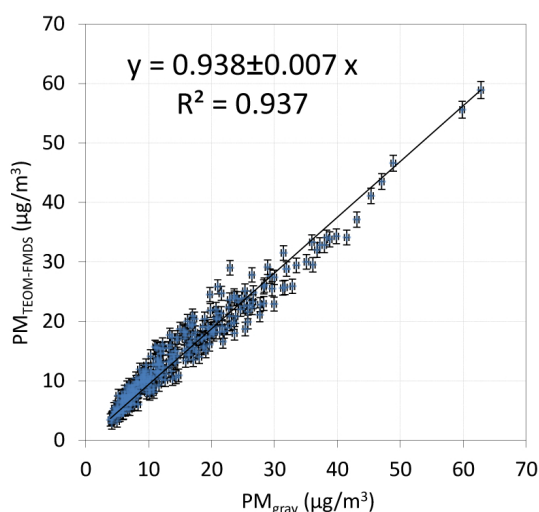
**Fig. 3.** Comparison between gravimetric (PM_{grav}) and TEOM-FDMS ($PM_{TEOM\text{-}FDMS}$) daily mass concentrations ($\mu g\,m^{-3}$) at the urban site from 11 September 2009 to 10 September 2010 ($n = 318$). Error bars represent uncertainties associated with PM_{grav} and $PM_{TEOM\text{-}FDMS}$ measurements. Note: TEOM-FDMS measurements are conducted at 30 °C and do not take into account semi-volatile materials. The slope is given ±1 standard error.

Concerning ion concentrations, filter measurements were compared for a period of 40 days (6 January–15 February 2010) with a Particle-Into-Liquid-Sampler (PILS; Orsini et al., 2003) coupled with two IC results. The PILS-IC instrument measures selected anions and cations (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) every 10 min in $PM_{2.5}$. Settings used here for the PILS-IC measurements are similar to those reported in Sciare et al. (2011) and will be presented elsewhere (Crippa et al., 2013). The liquid-based aerosol collection principle used in the PILS-IC avoids the positive and negative filter sampling artefacts usually associated with the collection of semi-volatile ammonium nitrate in $PM_{2.5}$. Un-

certainties of the PILS-IC measurements are typically within 20 % (Weber et al., 2003; Orsini et al., 2003; Hogrefe et al., 2004; Takegawa et al., 2005). They are compared with the filter sampling results in Fig. 4a for the three major ions (NH_4^+; NO_3^-, SO_4^{2-}). Very satisfactory results are obtained (r^2 ranging from 0.88 to 0.94) with slopes close to 1 (ranging from 0.91 to 1.15) and y-intercepts close to zero (ranging from -0.19 to $+0.56\,\mu g\,m^{-3}$), i.e. in the range of uncertainties given by the two techniques. One of the most important points is the absence of significant discrepancies concerning nitrate, which is a semi-volatile species exhibiting high concentrations during winter in Paris (Favez et al., 2007). Note that the comparison results obtained for the other ions (Cl^-, Na^+, Mg^{2+}) are also very satisfactory (r^2 ranging from 0.85 to 0.90) with slopes close to 1 (ranging from 1.11 to 1.19).

Filter sampling EC and OC concentrations were compared for a period of 70 days (6 January–15 March 2010) with semi-continuous hourly measurements of VOC denuded EC and OC concentrations in $PM_{2.5}$, obtained using an OCEC Sunset field instrument (Sunset Laboratory, Forest Grove, OR, USA; Bae et al., 2004). The default thermal programme (National Institute for Occupational Safety and Health, NIOSH; Birch and Cary, 1996) was used in this instrument. Measurement uncertainty given by the OCEC Sunset field instrument is poorly described in the literature and an estimate of 20 % was considered following Peltier et al. (2007). Comparisons between filter sampling and semi-continuous EC and OC measurements are performed in Fig. 4b and show a relatively good agreement (r^2 of 0.69 and 0.84) with slopes of 0.75 and 1.20, and y-intercepts of $+0.32$ and $+0.17\,\mu g\,m^{-3}$ for EC and OC, respectively. Slope differences may partly originate from the different thermal programs used, having a nearly 200 °C difference for the last temperature plateau under Helium (Cavalli et al., 2010). In order to test this assumption, a comparison was performed for Total Carbon (TC) measurements and showed a very
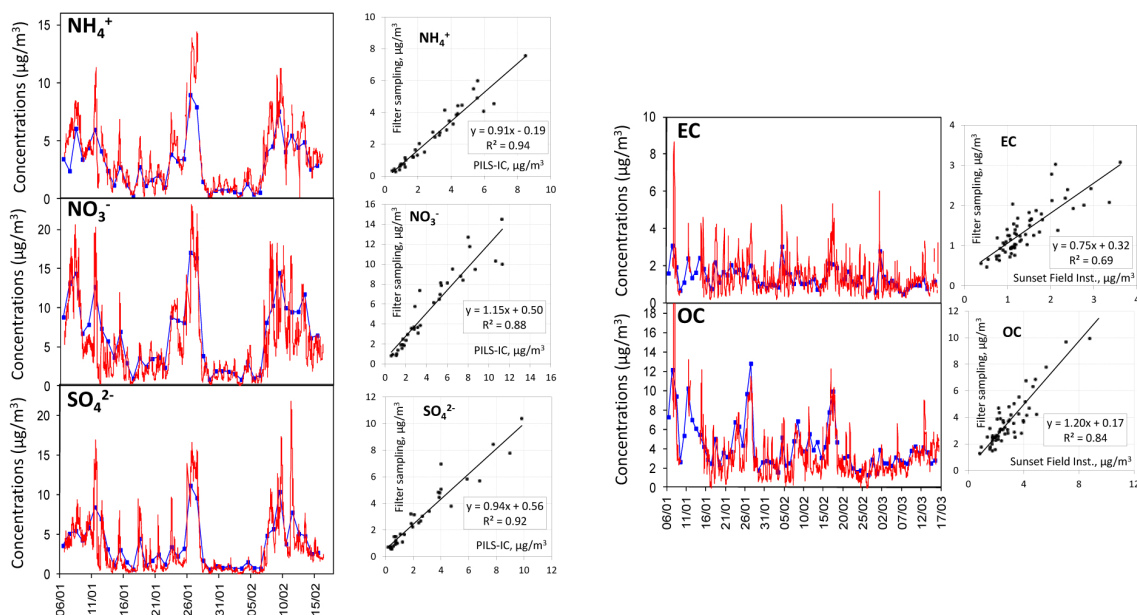
Fig. 4. Comparison between filter and on-line measurements for a 40-day period for the major ions (Fig. 4a), and for a 70 day period for carbonaceous matter (Fig. 4b).

good correlation ($r^2 = 0.87$) with a slope close to one (1.09) and a y-intercept close to zero ($+0.4 \, \mu g \, m^{-3}$).

3.5 OC to OM conversion factor

Results concerning the OC to OM conversion factor are reported in Table 2. Concerning the first method (linear regression), very good correlations between RM and OC concentrations were observed for the whole duration of the project, at every site (r^2 higher than 0.90, Fig. S2). This suggests that the unidentified chemical fraction RM is directly related to OC. In other terms, this confirms that all the major chemical components are taken into account in Eq. (1), and that the defined "Remaining Mass" fraction can be regarded as organic matter like. It should be noted that no significant amount of water is adsorbed onto filters because weighing is performed under dry conditions (RH below 30 %, Sect. 2.3.1). Conversion factors are slightly lower for the urban and suburban stations than for the rural ones (1.95, 1.98, 2.03, 2.08 and 2.12 for SUB, URB, NER, NWR and SOR, respectively). Organic matter is generally more oxidised in rural areas, leading to higher conversion factors (Turpin and Lim, 2001). The small discrepancy observed between the different types of environments in the region of Paris may be explained by the homogeneity of organic carbon concentrations, suggesting the importance of imported sources (see Sect. 4.2). Seasonal variations of f_{OC-OM} are illustrated in Fig. S3. This factor is relatively stable all along the year at the five sites, ranging between 1.8 and 2.2; different patterns are observed from one season to another according to sites, thus suggesting the absence of clear seasonal variations.

Very similar conclusions can be drawn concerning the second method (day-by-day calculation), which leads to slightly lower ($p < 0.005$ using the Welch's t test; Welch, 1947) conversion factors at SUB and URB than at the rural sites (1.96, 1.92, 2.08, 2.05 and 2.09 for SUB, URB, NER, NWR and SOR, respectively). High relative standard deviations are observed at every site, ranging from 15 to 20 %. This suggests that the organic matter chemical composition is strongly daily dependant, which can be related to the daily changing meteorological conditions (as air mass origins and air temperatures; see Sect. 4.1). No clear seasonal pattern (Fig. S3) is observed with this second method as well. Comparable f_{OC-OM} values are found with both methods in every environment, showing relative differences below 3 % for each site. The first method is however preferred as no days are excluded from the dataset and because of its more advanced mathematical approach.

We chose to apply an OC to OM conversion factor equal to 1.95 for the suburban and urban sites, and of 2.05 for the three rural sites, for the whole duration of the project. By choosing these factors, we wanted to give an insight of the general chemical properties of OM in the region, and to allow its comparison between sites. The chosen conversion factors set among the values suggested by Turpin and Lim (2001) of 1.6 ± 0.2 for urban areas and 2.1 ± 0.2 for non-urban areas, and Kiss et al. (2002) of 1.9–2.0 in a rural area. It is higher than the factors used in previous studies in the region of Paris by Guinot et al. (2007) of 1.8 and Favez et al. (2009) of 1.7 (this last factor was recalculated from water-soluble organic carbon and water-insoluble organic carbon contents), which can be related to differences

Table 2. Determination of the OC to OM conversion factor (f_{OC-OM}) at the five sites, from 11 September 2009 to 10 September 2010, using two analytical methods.

Methods	SUBURBAN		URBAN		NORTH EAST RURAL		NORTH WEST RURAL		SOUTH RURAL	
	1	2	1	2	1	2	1	2	1	2
n	348	326	335	307	330	297	359	309	351	306
f_{OC-OM}	1.95 ± 0.02	1.96 ± 0.33	1.98 ± 0.02	1.92 ± 0.33	2.03 ± 0.02	2.08 ± 0.34	2.08 ± 0.02	2.05 ± 0.38	2.12 ± 0.02	2.09 ± 0.38
r^2	0.94	–	0.90	–	0.94	–	0.92	–	0.90	–

Legend: Method 1: linear regression "$y = a \cdot x$" from Eq. (7). f_{OC-OM} is the slope of the linear regression. Standard deviation is calculated from the standard error of the slope. Method 2: day-by-day calculation from Eq. (6). Days with f_{OC-OM} higher than 3 and lower than 1 were excluded. f_{OC-OM} is the arithmetic mean.
n: number of samples.

in OC/EC separation methods (e.g. differences in thermo-optical protocols). It should also be mentioned that the relatively high conversion factors found in our study could be related to (i) possible aerosol water content – even at RH below 30 %, which is not taken into account in our mass closure calculation and (ii) possible errors from the applied functions defined for the calculation of sea salt and dust (see Putaud et al., 2010 for a quantification of these errors).

Gravimetric, chemically reconstructed and on-line determined PM$_{2.5}$ mass concentrations are compared in Fig. 2. Very good correlations are found between the three datasets, with r^2 of 0.98 and 0.94, and slopes of 1.00 and 1.05 for chemically reconstructed against gravimetric, and against TEOM-FDMS determined mass concentrations, respectively. This confirms the consistency of our measurements and the conversion factors chosen to estimate organic matter.

4 Discussion

Section 4.1 will describe the temporal variability of PM$_{2.5}$ mass and major chemical constituents, whereas Sect. 4.2 will focus on their spatial variability.

4.1 Temporal variability of PM$_{2.5}$

4.1.1 Daily temporal variability of fine aerosols

Daily temporal variability of fine aerosol chemical composition at the suburban site is reported in Fig. 5. Similar patterns are observed at the five stations (Fig. S4 and Sect. 4.2) making the conclusions drawn for this site relevant for the four others. Strong variability can be observed from one day to another, for PM mass and chemical composition. On the whole duration of the project PM$_{grav}$ is on average $15.2 \pm 10.5 \, \mu g \, m^{-3}$, and ranges from 3.7 to $62.6 \, \mu g \, m^{-3}$ (Table 1; unless otherwise stated all the figures mentioned in this Sect. 4.1 refer to the SUB site). Most pollution events occur during late autumn, winter and early spring (from December to April) and are associated with marked increases of secondary inorganic species (e.g. on 26 January 2010: PM$_{grav}$ and SIA concentrations are 58.7 and $32.1 \, \mu g \, m^{-3}$, respectively). Organic matter also significantly contributes to the enhancement of PM mass during pollution events (e.g.

more than 60 % of PM$_{grav}$ on 7 January 2010, with [PM$_{grav}$] $= 62.6 \, \mu g \, m^{-3}$), contrarily to sea salt, dust and EC. The strong daily variability of PM concentration and composition can be explained by the variations of source emission intensities, atmospheric processes (e.g. Healy et al., 2012) and meteorological parameters (e.g. Galindo et al., 2011; Martin et al., 2011; Georgoulias and Kourtidis, 2011). A focus will be made on the latter variable and especially on temperature, boundary layer height (BLH), precipitation and air mass origins. Although those meteorological parameters can be highly correlated, their individual influence will be highlighted during specific polluted and clean conditions.

4.1.2 Influence of meteorological parameters

Temperature modifies the emission of secondary PM precursors such as biogenic VOCs during summer (Fowler et al., 2009, and references therein), the formation of temperature inversion during winter (Stull, 1988) or the condensation of high saturation vapour pressure compounds such as nitric acid (Monks et al., 2009; Hueglin et al., 2005). In the city of Paris, low temperatures (daily average below 0 °C) often lead to high pollution events ([PM$_{grav}$] $> 40 \, \mu g \, m^{-3}$) mainly due to the increased contribution of SIA (Fig. 6). During winter (DJF) SIA concentrations exceed $10 \, \mu g \, m^{-3}$ during 35 days, contributing $50 \pm 9 \%$ of PM$_{grav}$ under temperatures of $-0.7 \pm 2.9 \,°C$ on average. SIA are thus a major cause of the high PM$_{2.5}$ concentrations observed in the region of Paris during cold events, hence asking for particular attention for the implementation of efficient abatement strategies. Whereas nitrate concentrations are enhanced during cold periods because of thermodynamic processes (Clegg et al., 1998), high nss-sulfate concentrations are certainly due to mid- or long-range transport episodes that are related to anticyclonic conditions, eastern air masses and low temperatures (see below and Sect. 4.2). (In the following, mid- or long-range transport will refer to transport from outside the region of Paris, the exact origin not being quantitatively assessed at the current state of analysis.) In fact, nss-sulfate is mostly produced from cloud processing over large scales rather than from local gas phase oxidation of SO$_2$ (Putaud et al., 2004a). Finally, nitrate and nss-sulfate are fully neutralized by ammonium ([NO$_3^-$] + 2[SO$_4^{2-}$] versus [NH$_4^+$] in
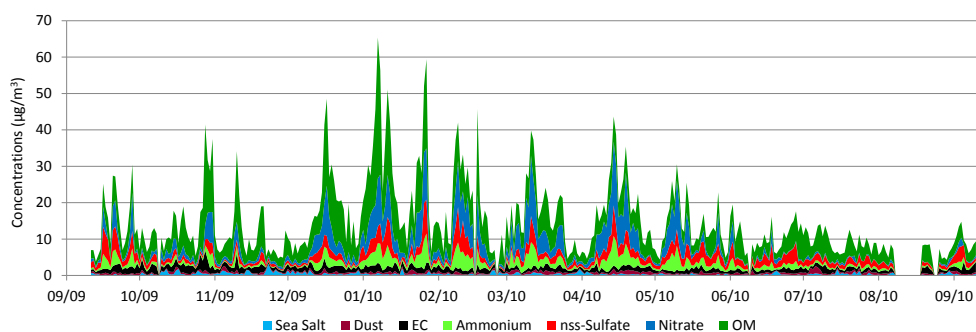
Fig. 5. Daily variation of fine aerosol chemical composition at the suburban site from 11 September 2009 to 10 September 2010.
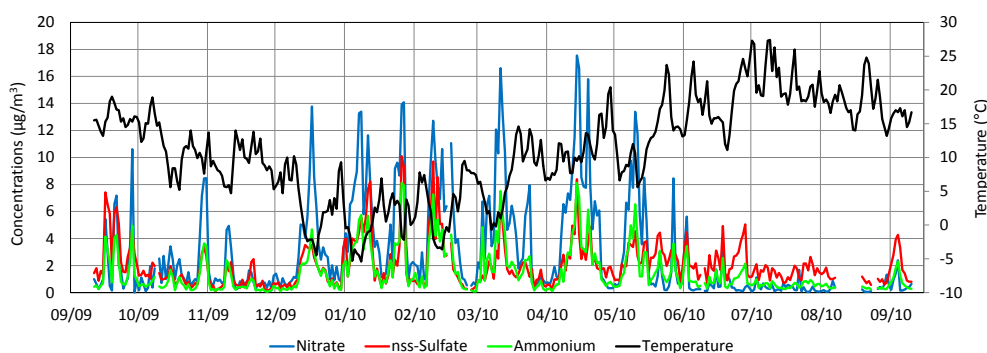
Fig. 6. Comparison between daily nitrate, nss-sulfate and ammonium concentrations ($\mu g\, m^{-3}$) and temperatures (°C) at the suburban site from 11 September 2009 to 10 September 2010.

mol m^{-3}: slope $= 0.96$; $r^2 = 0.96$, $n = 348$), which therefore follows the same pattern. Similar correlations between high atmospheric concentrations and low temperatures are also found for organic matter, which can be explained by strong biomass burning sources – related to domestic heating – in the region of Paris (Favez et al., 2009; Sciare et al., 2011; Healy et al., 2012) and probably to the condensation of semi-volatile organic species as observed in many European areas (Putaud et al., 2004a).

However, days exhibiting high SIA and PM concentrations cannot solely be explained by low temperatures (e.g. 14 April 2010, 10 May 2010, etc.), meteorological parameters such as precipitation and boundary layer height should be regarded as well (Fig. S5). BLH plays an important role in determining the transport, storage and dispersion of atmospheric pollutants (Salmond and McKendry, 2005) and is responsible for high PM daily variability in Paris during all the campaign. As an illustration, during two following days (31 October 2009 and 1 November 2009), PM$_{2.5}$ concentrations were reduced by a factor of 3.5 (37.7 and 10.6 $\mu g\, m^{-3}$, respectively) mainly due to the increase by a factor of 2.8 of the BLH (288 and 820 m, respectively). In addition, the wet removal by precipitation is known to be the most efficient atmospheric aerosol sink (Radke et al., 1980) and contribute to low concentration days ($< 10\,\mu g\, m^{-3}$) in Paris, especially from November to

April because of heavy rains (typically higher than 5 mm per day).

Finally, air mass origins can be a strong cause of PM daily variability because of the flat topography of the region, and the contrasted surrounding environments (marine versus continental areas). This is illustrated in Fig. S5 where two-days back trajectories were calculated every four hours for two typical types of air masses in the region, using HYSPLIT (Draxler and Rolph, 2011). Air masses originating from continental Europe (northeast to east of France) lead to high PM loadings and high contents of SIA, especially during winter, whereas air masses coming from marine sectors (west and north of France) bring much lower aerosol content. In fact, one of the highest PM pollution peaks of the campaign (26 January 2010, [PM$_{grav}$] $= 58.7\,\mu g\, m^{-3}$) is mainly due to mid- or long-range transport from continental Europe (concentrations ranging from 47.2 to 61.4 $\mu g\, m^{-3}$ at the other sites) and is predominantly made of SIA (50 % of [PM$_{grav}$]). (Mid- or long-range transport from continental Europe will be named continental transport or continental import later on.) Contrarily, under marine air masses that are poorly influenced by anthropogenic pollution, PM$_{2.5}$ concentrations are typically below 10 $\mu g\, m^{-3}$ (e.g. 6.5 and 8.6 $\mu g\, m^{-3}$ for 13 September 2009 and 25 October 2009, respectively). These conclusions, regarding the significant contribution of eastern mid- or long-range pollution in the region of Paris, are

in agreement with what Bessagnet et al. (2005), Sciare et al. (2010, 2011) and Healy et al. (2012) reported in short-term studies in this city in winter and spring. We attempted to quantify this phenomenon by focusing on days showing PM_{grav} concentrations higher than $25\,\mu g\,m^{-3}$, which is the $PM_{2.5}$ 2015 EU annual limit value and the $PM_{2.5}$ 24 h-mean World Health Organization Air Quality Guideline value. A total of 50 days fulfilled the aforementioned criterion on the whole duration of the campaign. Three categories were defined: days with air masses originating from the northeast to the east of France, days with BLH below 400 m (representing the 10th percentile of BLH values) and days that do not fit either of both above mentioned criteria. We found that 66 % of the polluted days can be attributed to continental import (among which 12 % show low BLH), 20 % exhibit low BLH with other air mass origins, and 14 % cannot be explained by the previous factors. Therefore, in Paris, two third of the days exceeding the 2015 EU annual $PM_{2.5}$ limit value are due to continental import from the northeast to the east of France, questioning the efficiency of local, regional and even national abatement strategies during pollution episodes, suggesting instead collaborative works with neighbouring countries on these topics. It should be added that French emissions can also impact surrounding areas as reported in Bessagnet et al. (2005), being significantly influential on Great Britain, Belgium, Germany, the Netherlands and Eastern Europe.

4.1.3 Monthly and seasonal variability of $PM_{2.5}$

Keeping in mind the high daily variability of PM mass and chemical composition, their monthly and seasonal trends have been studied (Figs. 7 and S6). On the annual scale, Paris (URB and SUB sites) exhibits its highest $PM_{2.5}$ concentrations during late autumn, winter and early spring (higher than $15\,\mu g\,m^{-3}$ on average, from December to April), intermediates during late spring and early autumn (between 10 and $15\,\mu g\,m^{-3}$ during May, June, September, October and November) and the lowest during summer (below $10\,\mu g\,m^{-3}$ during July and August). This pattern is mainly driven by OM and SIA concentrations that are the main components of fine aerosol (Fig. 7). Figure S6 shows that OM monthly mean concentrations significantly increase from autumn to winter (e.g. 2.5 times higher from November to January), slightly decrease from winter to early spring (e.g. -28% from February to April), and remain fairly constant until the end of the campaign ($4.0 \pm 0.7\,\mu g\,m^{-3}$ from June to September). During autumn and winter this pattern can be explained by stronger emissions of wood burning sources (Favez et al., 2009; Sciare et al., 2011, Sect. 4.2.3), whereas during spring and summer OM concentrations are likely related to biogenic emissions and secondary organic aerosol formations (Jacobson et al., 2000, and references therein). Nitrate concentrations are, on the other hand, on average significantly higher during winter and early spring months (JFMAM) than the rest of the year ($4.6 \pm 1.2\,\mu g\,m^{-3}$ and $1.1 \pm 0.8\,\mu g\,m^{-3}$,
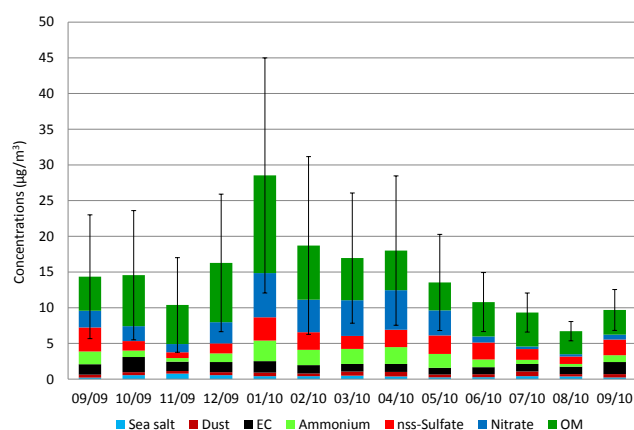

Fig. 7. Monthly mean concentrations ($\mu g\,m^{-3}$) of fine aerosol chemical composition at the suburban site from 11 September 2009 to 10 September 2010. Error bars represent the standard deviation ($\pm 1\sigma$) of fine aerosol mass concentrations.

respectively), partly because of thermodynamic conditions favouring the partitioning of this molecule into the particulate phase (Clegg et al., 1998). Non-sea-salt sulfate exhibits lower concentrations ($< 1.5\,\mu g\,m^{-3}$) during autumn (OND) and mid-summer (JA), because Paris is less exposed to continental advection during these months (Airparif and LSCE, 2012). Ammonium follows seasonal variations halfway between nss-sulfate and nitrate as it fully neutralizes both compounds. EC and mineral dust do not display any seasonal pattern with stable concentrations all along the year that are 1.3 ± 0.3 and $0.5 \pm 0.1\,\mu g\,m^{-3}$, respectively, on average and calculated from monthly means. Finally sea salt monthly variations are clearly related to wind directions, and show slightly higher concentrations during autumn (OND) as air masses coming from marine regions were prevalent (Airparif and LSCE, 2012).

4.2 Spatial variability of $PM_{2.5}$

4.2.1 $PM_{2.5}$ mass concentrations

Spatial variability of fine aerosol in the region of Paris will first be discussed by comparing atmospheric mass concentrations determined gravimetrically at the five sites (Fig. 8). PM concentrations are surprisingly very similar at the regional scale, during most of the one-year project. Very good correlations are found between urban and suburban sites ($r^2 = 0.94$, slope $= 0.99$, $n = 335$), good correlations are found between rural sites (e.g. for NWR plotted against SOR sites, $r^2 = 0.83$, slope $= 1.08$, $n = 351$) and, more surprisingly, between urban and rural sites (e.g. for URB plotted against NER sites, $r^2 = 0.84$, slope $= 1.06$, $n = 330$). Interestingly, when focusing on individual days a very high temporal variability is generally observed at the same time at the five sites. For instance, PM_{grav} levels range from 49.4 to $62.0\,\mu g\,m^{-3}$ on 27 January 2010, and from 3.9 to $5.9\,\mu g\,m^{-3}$ on 29 January 2010
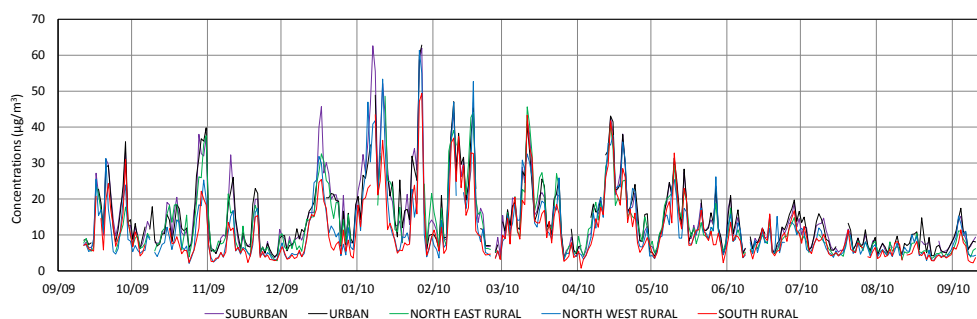
Fig. 8. Comparison between $PM_{2.5}$ daily mass concentrations (gravimetric measurements) at the five sites during the one-year period.

according to sites; therefore after only 2 days, PM levels have been reduced by a factor ranging from 10 to 14 according to sites. This suggests that, in the region of Paris, background $PM_{2.5}$ levels are mainly controlled by regional instead of local scale phenomena, which is in agreement with the above mentioned influences of mesoscale meteorological parameters and mid- or long-range transport (Sect. 4.1; Sciare et al., 2010).

Discrepancies between the different sites can however be noticed, with decreased concentrations when shifting from urban and suburban to rural sites, which is in agreement with most European environments (Querol et al., 2004; Van Dingenen et al., 2004; Putaud et al., 2004a). In fact, annual PM_{grav} mean concentrations are 15.2, 14.8, 12.6, 11.7 and $10.8\,\mu g\,m^{-3}$ for SUB, URB, NER, NWR and SOR sites, respectively (Table 1). Discrepancies between URB and SUB mean concentrations are not statistically significant ($p > 0.25$) and are due to differences between the sampling days discarded in each station (Table S1), whereas discrepancies between NER, NWR and SOR sites cannot be explained by the former argument. The same conclusions can be drawn when comparing datasets reconstructed by excluding at every site each day missing at one site minimum. In a general way, differences observed between $PM_{2.5}$ site's concentrations can mainly be attributed to local source emissions and chemical processes as it will be discussed later (Sects. 4.3.2 and 4.3.3). It is noteworthy that most pollution episodes that are related to variations of BLH show a very high concentration gradient between urban and rural sites (e.g. about 40 % higher at URB and SUB than at rural sites on 23 January 2010, with a BLH of 273 m) which can be related to enhanced effects of local emissions on atmospheric PM concentrations. To summarise, background $PM_{2.5}$ mass concentrations are most of the time homogeneous at the regional scale on the whole duration of the project; however urban and suburban sites show higher PM levels than the rural ones because of emissions of local anthropogenic sources that can be emphasised by meteorological conditions.

4.2.2 Annual average chemical composition of $PM_{2.5}$

The annual average chemical composition of fine aerosol is depicted in Fig. 9 and shows a very similar pattern at the five sites, confirming the homogeneous feature of fine aerosol at the regional scale. The major chemical component is organic matter, accounting for 38 to 47 % of PM_{grav} according to sites, and showing a slightly higher contribution at the NER station for reasons given later on (Sect. 4.2.3). It is followed by nitrate (17–22 %), nss-sulfate (13–16 %) and ammonium (10–12 %) i.e. secondary inorganic aerosols. The highest SIA contributions are found at two rural sites (NWR and SOR) and are due to lower influences of local anthropogenic sources compared to the other locations. This leads to higher proportions of SIA even though mass concentrations remain approximately the same at the regional scale (5.2 to $6.4\,\mu g\,m^{-3}$). EC has a $PM_{2.5}$ mass contribution of 4 to 10 %, and is about 3 times higher (in absolute concentrations) at URB and SUB than at rural sites because of its mainly local traffic source origin (Healy et al., 2012). Finally, dust and sea salts are minor components of fine aerosol in the region of Paris, representing 2 to 5 % and 3 to 4 % of its mass, respectively. The methodology developed to estimate the OC-OM conversion factor allows us to have a very small proportion of unaccounted mass (0 to 2 %). This overall chemical composition is consistent with what is found in other European environments (Putaud et al., 2010, and references therein), exhibiting very high proportions of carbonaceous and secondary inorganic aerosols.

4.2.3 Major chemical compounds of $PM_{2.5}$

A detailed discussion of the spatial variability of each major chemical compound will now be given from the highest to the lowest contributor to fine aerosol mass concentrations (see Figs. 10 and 11). To begin with, OM shows fairly homogeneous concentrations at the regional scale, on the whole duration of the project with good correlations between for example SUB and URB ($r^2 = 0.82$, slope $= 1.08$, $n = 335$), NWR and URB (0.72, 0.79, 335) or NWR and SOR sites (0.73, 1.05, 351) and slopes fairly close to 1. As for PM, comparable OM temporal variations are observed between sites,
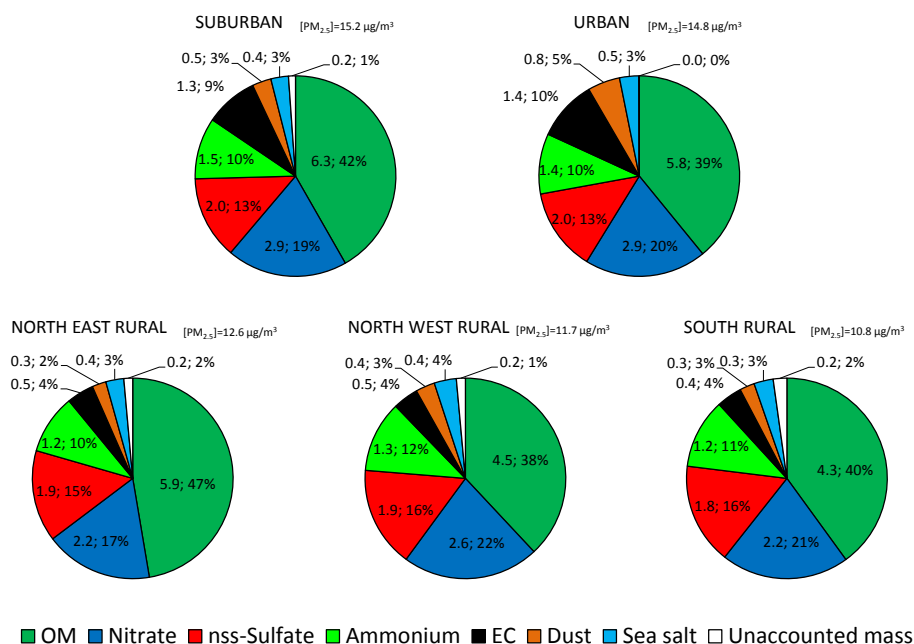
Fig. 9. Annual average chemical composition of $PM_{2.5}$ ($\mu g\,m^{-3}$; %) at the five sites from 11 September 2009 to 10 September 2010.
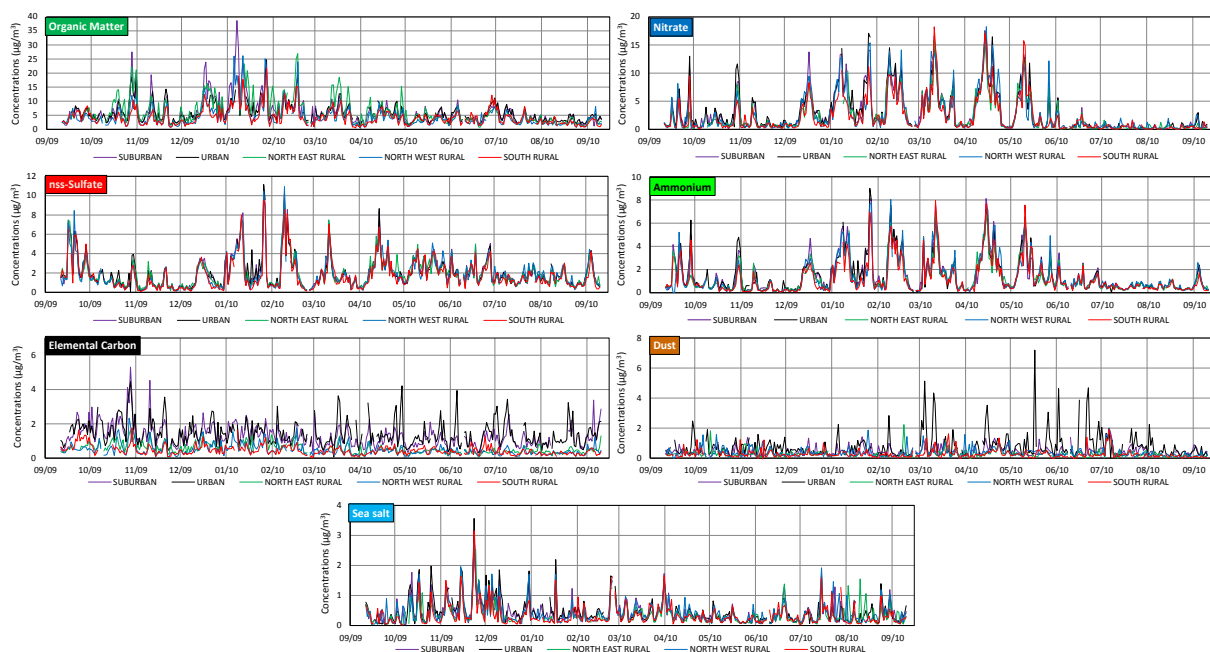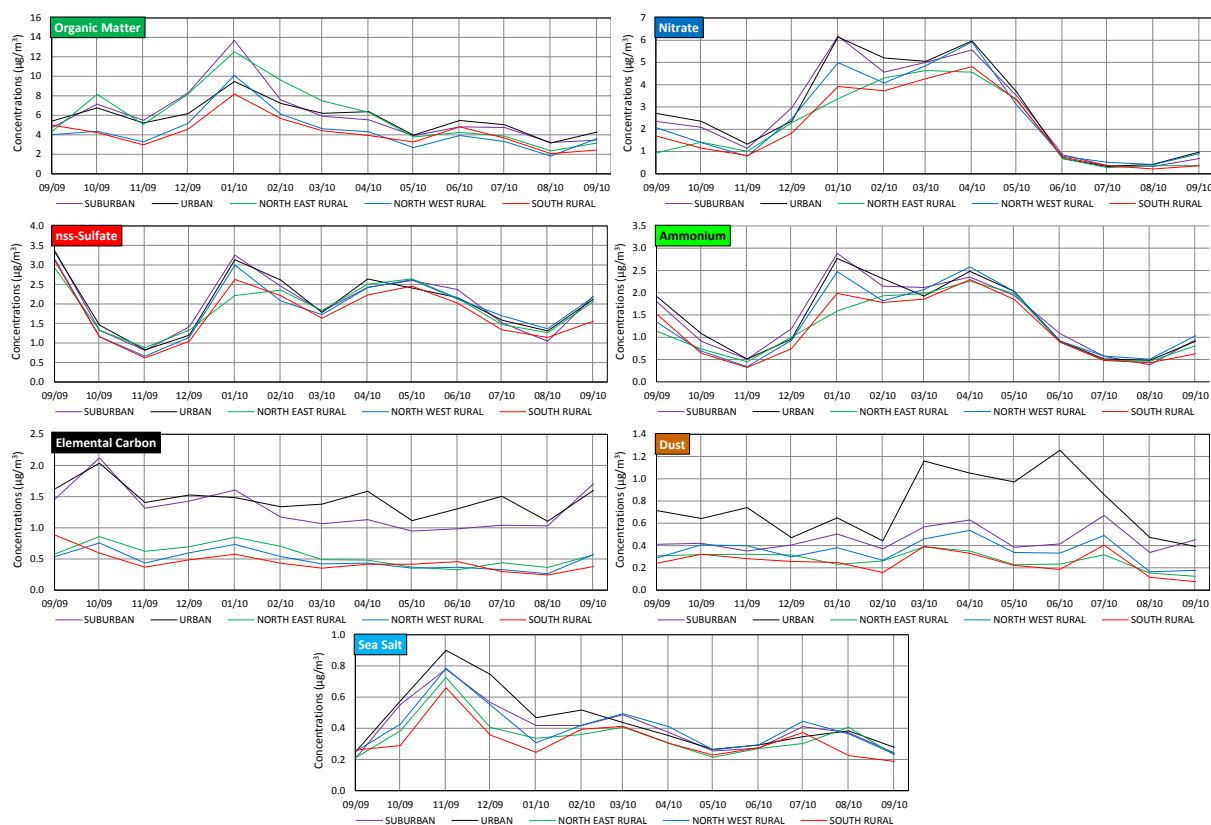

Fig. 10. Daily mass concentrations ($\mu g\,m^{-3}$) of the major chemical compounds of fine aerosol at the five sites from 11 September 2009 to 10 September 2010.

and very high levels can be followed by very low ones after only few days (e.g. on 27 and 29 January 2010, OM concentrations were 21.7–24.8 $\mu g\,m^{-3}$ and 1.0–3.2 $\mu g\,m^{-3}$ according to sites, respectively). This implies that a significant part of OM is either imported from outer regions of Paris, or spatially uniformly distributed over the region because

of similar primary emission sources. The latter argument is very unlikely because primary emission sources of OM, such as wood burning (WB) (Puxbaum et al., 2007, and references therein) and traffic (Thorpe and Harrison, 2008; Pio et al., 2011) are thought to be rather local and site-dependent. In fact concerning WB, good correlations between OM and

Fig. 11. Monthly mass concentrations (μg m^{-3}) of the major chemical compounds of fine aerosol at the five sites from 11 September 2009 to 10 September 2010.

levoglucosan (not shown here) at the NER site during cold days assert the presence of a local source, explaining higher OM concentrations at this site, and less satisfactory correlations with the other rural sites (e.g. for NER plotted against SOR sites, $r^2 = 0.55$, slope $= 1.46$, $n = 330$). Moreover, during low BLH days, clearly higher OM concentrations are found at URB, SUB and NER sites compared to NWR and SOR ones (e.g. 31 October 2009) that can be explained by the enhancement of local WB sources. It is however likely that a part of WB aerosols is also due to mid-range transport as suggested by the comparison of levoglucosan levels between sites and as reported for biomass burning (including WB) in other regions of the world (Niemi et al., 2005, 2009; Stohl et al., 2007; Mochida et al., 2010). It is worthwhile noting that given the large expected emissions associated with the Larger Urban Zone of Paris, it could reasonably be assumed that the OM spatial homogeneity observed in our study is the consequence of secondary formation processes of precursor emissions in the Paris region. The time needed for gas-to-particle conversion would explain the observed spatial variability of OM, which would be supported by the high observed fOC-OM values. Nevertheless, modelling and experimental studies conducted during the EU-MEGAPOLI summer and winter field campaigns by Crippa et al. (2013), Freu-

tel et al. (2013) and Zhang et al. (2013) do not support this assumption. Conversely, the aforementioned studies report that (i) OA is mostly controlled by mid- or long-range transport (Crippa et al., 2013), (ii) the influence of the Paris emission plume onto its surroundings is rather small for primary organic aerosols (Freutel et al., 2013) and (iii) the highest OA levels are due to the advection of SOA from outside Paris (Zhang et al., 2013). To conclude, in the region of Paris, OM is therefore mainly imported by mid- or long-range transport, although local sources such as traffic and wood burning also contribute to its atmospheric concentrations.

SIA including nitrate, nss-sulfate and ammonium also shows very good site-to-site covariations during this study (Figs. 10 and 11). As already mentioned in Sect. 4.1.2, SIA concentrations highly depend on air mass origins and temperatures, and are mainly due to transboundary mid- or long-range transport from countries located east of France (Bessagnet et al., 2005; Sciare et al., 2010, 2011). However, local emissions of precursor gases such as NO$_x$, NH$_3$ and SO$_2$ can partly explain the discrepancies observed between sites for nitrate and ammonium concentrations, and to a lower extent for nss-sulfate (Figs. 9, 10 and 11). In fact, when focusing again on the end of October (that was under low BLH conditions), nitrate shows a clear gradient exhibiting

its highest to lowest concentrations at URB, SUB, NER, NWR and SOR sites (11.6, 8.5, 8.0, 6.9, and 5.2 µg m^{-3}, respectively, the 31 October 2009). On the whole duration of the campaign, nitrate concentrations are 4, 11, 13 and 20 % higher at URB than at SUB, NWR, SOR and NER sites, respectively (values determined from the slope of the correlations between sites). This suggests a local production of ammonium nitrate that could be related to higher local traffic emissions of NO$_x$ at the URB and SUB sites (Alary et al., 1995; Frangi et al., 1996; Airparif, 2012), knowing that ammonia is in excess in the region of Paris (Hamaoui-Laguel, 2012). In addition, local chemical processes have been observed in this region by Healy et al. (2012) and could explain the differences observed between sites for specific days. For instance on 18 January 2010, a local thick fog was observed at the URB site and led to higher concentrations of SIA compared to the other sites (3 to 7 times higher according to sites) due to heterogeneous processing (Reid et al., 1998; Schaap et al., 2004). To summarise, SIA are mainly imported from countries located east of France, even if local sources and chemical processes could lead to discrepancies between sites on very specific days.

EC shows a completely different pattern, characteristic of a local source. A detailed discussion of EC sources and mixing state in Paris can be found in Healy et al. (2012). In this study, 88 % and 12 % of EC particle mass was apportioned to fossil fuel and biomass burning, respectively, and 79 % and 21 % to local emissions and continental transport, respectively, during a one-month winter period. In our study, no or poor correlations are found between rural sites (e.g. $r^2 = 0.01$, slope $= 0.76$, $n = 351$, for SOR plotted against NWR sites), URB and SUB sites ($r^2 = 0.45$, slope $= 0.84$, $n = 335$) or urban and rural sites (e.g. $r^2 = 0.03$, slope $= 0.27$, $n = 335$, for SOR plotted against URB sites) confirming the importance of local emissions. In addition, as clearly illustrated in Fig. 11, EC concentrations are significantly higher at URB and SUB sites (1.4 ± 0.7 and 1.3 ± 0.7 µg m^{-3} on average on the whole year, respectively) than at the rural ones (0.6 ± 0.3, 0.5 ± 0.3, 0.4 ± 0.3 µg m^{-3} on average at the NER, NWR and SOR sites, respectively) which is in agreement with its traffic origin. This can also be illustrated on specific days such as on 28 October 2009 which exhibits a very low BLH (182 m), the highest EC concentrations of the year at URB and SUB sites (5.3 and 4.5 µg m^{-3}, respectively) and comparatively low ones at the rural sites (1.6, 1.9 and 0.9 µg m^{-3} at NER, NWR and SOR sites, respectively).

The interpretation of the mineral dust dataset is complex because of the substantial uncertainties associated with the methodology chosen for its estimation, and because of the low contribution of this source in fine aerosol (Maenhaut and Cafmeyer, 1998; Gehrig et al., 2001; Putaud et al., 2004a, 2010). For these reasons, its spatial variability will not be discussed. Note however that the very high levels of dust estimated at the URB site during specific days (e.g. 7.2 µg m^{-3}

on 17 May 2010) are due to renovation of building façades located nearby.

Sea salt concentrations are, as expected, similar at the five sites most of the time (Figs. 10 and 11). The highest concentration is reached on 23 November 2009 (e.g. 3.6 µg m^{-3} at the URB site) and is associated with air masses coming from the Atlantic Ocean. At the exception of about 10 days exceeding 1.5 µg m^{-3} at the five sites, sea salt concentrations remained very low (< 1 µg m^{-3}) during the entire project.

5 Conclusion and perspectives

This study allowed the construction of a one-year database describing the daily chemical composition of fine aerosol (PM$_{2.5}$) in the region of Paris. It comprises EC, OC, Cl$^-$, NO$_3^-$, SO$_4^{2-}$, Na$^+$, NH$_4^+$, K$^+$, Mg^{2+}, and Ca^{2+} aerosol compositions at five sites being characteristic of urban, suburban and rural backgrounds. The chemical mass closure methodology was applied for the determination of the OC to OM conversion factor (f_{OC-OM}). Comparable f_{OC-OM} values were determined for the URB and SUB sites (1.95) and for the rural sites (2.05), which is consistent with the strong homogeneity of OC concentrations observed in the region and its aged (i.e. oxidised) nature. Although clear daily variations are observed, this factor does not show a significant seasonal dependence despite the expected temporality of organic aerosol sources (biogenic, wood burning, etc.) and atmospheric processes (e.g. photochemical ageing).

The temporal variability of PM$_{2.5}$ was investigated, showing a very strong daily variability at the five sites for PM mass and chemical compositions. The influence of specific meteorological parameters was highlighted: anticyclonic conditions, low temperatures, low BLH and mid- or long-range transport of air masses originating from the continental European sector lead to the highest pollution events of the year, whereas precipitations or western (oceanic) air masses lead to the lowest PM levels. On the annual scale, PM$_{2.5}$ concentrations in the city of Paris are (i) the highest during late autumn, winter and early spring, (ii) intermediates during late spring and early autumn and (iii) the lowest during summer. A seasonal dependence is observed for specific chemical species only (e.g. nitrate and OM) whereas others were rather stable along the year (e.g. EC and mineral dust).

The spatial variability of fine aerosol is very similar at the regional scale during most of the year, suggesting the substantial influence of mesoscale meteorological parameters and mid- or long-range transport. Nevertheless, emissions of local anthropogenic sources lead to higher levels at the URB and SUB sites. Organic aerosols are mainly imported by mid- or long-range transport, although local sources such as traffic and wood burning may also contribute to its atmospheric concentrations. Secondary inorganic aerosols are also mainly imported from continental European countries (east to northeast sectors), although local sources and chemical processes

(e.g. fog) can lead to discrepancies between sites on very specific days. EC is primarily locally emitted and associated with fossil fuel sources (predominantly traffic).

The very large quality controlled aerosol database presented here within the LSCE-AIRPARIF "Particles" project will allow the identification of the major sources of PM as well as their geographical origins, which are prerequisites to implement effective abatement policies. In conjunction with the use of specific tracers, this aerosol database will also help in better documenting primary and secondary sources as well as atmospheric processing of carbonaceous aerosols. Furthermore, this chemical database should help modellers to better understand the transport and transformation of aerosols in the region, or toxicologists to better assess the toxicity of individual chemical compounds, to mention only a few.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys.net/13/7825/2013/acp-13-7825-2013-supplement.pdf.

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