

In-situ, satellite measurement and model evidence for a dominant regional contribution to fine particulate matter levels in the Paris Megacity

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Abstract

A detailed characterization of air quality in Paris (France), a megacity of more than 10 million inhabitants, during two one month intensive campaigns and from additional one year observations, revealed that about 70% of the fine particulate matter (PM) at urban background is transported on average into the megacity from upwind regions. This dominant influence of regional sources was confirmed by in-situ measurements during short intensive and longer term campaigns, aerosol optical depth (AOD) measurements from ENVISAT, and modeling results from PMCAMx and CHIMERE. While advection of sulfate is well documented for other megacities, there was surprisingly high contribution from long-range transport for both nitrate and organic aerosol. The origin of organic PM was investigated by a comprehensive analysis of aerosol mass spectrometer (AMS), radiocarbon and tracer measurements during two intensive campaigns. Primary fossil fuel combustion emissions contributed less than 20% in winter and 40% in summer to carbonaceous fine PM, unexpectedly little for a megacity. Cooking activities and, during winter, residential wood burning are the major primary organic PM sources. This analysis suggests that the major part of secondary organic aerosol is of modern origin, i.e. from biogenic precursors and from wood burning. Black carbon concentrations are on the lower end of values encountered in megacities worldwide, but still represent an issue for air quality. These comparatively low air pollution levels are due to a combination of low emissions per inhabitant, flat terrain, and a meteorology that is in general not conducive to local pollution build-up. This revised picture of a megacity only controlling part of its own average and peak PM levels has important implications for air pollution regulation policies.

1. Introduction

Megacities, defined as agglomerations with a population above 10 million inhabitants (Gurjar and Lelieveld, 2005) often concentrate in a small area a substantial part of a country's population, economic activities, and thus air pollutant emissions. Emitted primary and subsequently formed secondary gas or particulate phase pollutants cause substantial health problems especially in megacities with rapidly growing industry and low pollution control (e.g. Gurjar et al., 2010). The impact of local emissions on air quality in many of these megacities was shown to be large (e.g. Molina and Molina (2004) for a general overview; Hand et al. (2011) and Parrish et al. (2011) for Los Angeles; Molina et al. (2010) for Mexico City; Chan and Yao, 2008, for Chinese Megacities). In addition to the local contribution, levels of gaseous species and of fine particulate matter (fine PM, with an aerodynamic diameter below 2.5 μm , $\text{PM}_{2.5}$) are also affected by long-range transport from outside the cities. This important role of pollutant transport has been first shown for sulfate in New York City, a megacity located in a highly industrial belt in the North-Eastern US (Rahn and Lowenthal, 1985; Dutkiewicz et al., 2004; Quin et al., 2006). Indeed, as a secondary aerosol component, sulfate needs some time to be formed from SO_2 emissions by gaseous or aqueous phase oxidation pathways (Seinfeld and Pandis, 2006), important SO_2 emissions of industrial origin are often located outside of a megacity. For nitrate, another important secondary inorganic aerosol component, and for organic aerosol (OA, both of primary and secondary origin), only few explicit estimations of the local versus advected contributions to their burden in megacities are available. While for Chicago (with about 9.4 million inhabitants nearly a megacity) the advected part for both nitrate and OA is dominant (about 60% (Hand et al., 2011)), it is only minor for New York City (about 30 – 40%) (Lall and

Thurston, 2006; Hand et al., 2011). Important contributions to nitrate from advection were qualitatively estimated for London (Harrison et al., 2012).

Inorganic secondary particulate species are directly related to their precursor gases SO₂, NO_x and NH₃, with rather well known sources mostly related to fossil fuel burning (SO₂, NO_x) and agriculture (NH₃). By contrast, sources of organic aerosol are widespread (traffic, residential heating including wood burning, open biomass burning, cooking activities, secondary formation from biogenic as well as anthropogenic VOC precursors) and their relative contributions remain uncertain (Hallquist et al., 2009). Early source apportionment work on PM was based on the analysis of daily filter samples and analysis of correlations between organic aerosol and tracers for specific sources using different statistical methods (for a review of methods and results, see Viana et al. (2008)). In these earlier studies the secondary OA was often determined as the part of OA which could not be attributed to primary sources.

More recently, the combination of aerosol mass spectrometer (AMS) measurements (DeCarlo et al., 2006, Drewnick et al., 2005) and factor analysis techniques (e.g. positive matrix factorization, PMF, Paatero et al., 1994; Lanz et al., 2007; Ulbrich et al., 2009) has improved the high temporal resolution of source apportionment of primary and secondary OA (e.g., Jimenez et al., 2009; Zhang et al., 2011). Nevertheless, the biogenic versus anthropogenic origin of secondary aerosol in megacities and in megacity plumes is still an open question (Hallquist et al., 2009). The combination of radiocarbon (¹⁴C) measurements and AMS based source apportionment can provide valuable insights about the share of fossil and contemporary organic aerosol sources (Lanz et al., 2007; Minguillón et al., 2011; El-Haddad et al., 2013; Zotter et al., 2014). Despite this progress, sources of organic aerosol in megacities with respect to their local

versus advected and fossil versus contemporary contribution are still highly uncertain. Comprehensive data sets are needed to better quantify these sources.

Here, we report on measurements of air pollution by fine particles in the Paris agglomeration, a mid-latitude, post-industrial megacity with more than 10.84 million inhabitants (United Nations, 2015). We conducted two intensive field campaigns in the Greater Paris area during July 2009 and from mid-January to mid-February 2010 as part of the MEGAPOLI (Megacities: Emissions, urban, regional and Global Atmospheric POLLution and climate effects, and Integrated tools for assessment and mitigation) project (Butler, 2008; Baklanov et al., 2010). In addition, during one year (September 2009 – September 2010) daily PM_{2.5} chemical composition measurements were performed at one urban background and several rural sites during the PARTICULES project (Gherzi et al., 2010, Bressi et al., 2013 & 2014). Our major aim is to quantify the contribution of local versus advected sources of fine aerosol in a post-industrial megacity, with a special focus on organic aerosol sources. This will be addressed by combining observations from both the MEGAPOLI and PARTICULES campaigns, and considering also results from chemical transport modeling and satellite observations. The analysis of organic aerosol sources will be addressed by a synthesis of AMS, radiocarbon and tracer measurements. Finally, we will place results found for Paris in a larger context of particulate matter origin in other selected megacities.

2. Measurements and methods

In Section 2.1, we will present the sites and measurements used for this study during the MEGAPOLI and PARTICULES campaigns. The processing of the measurements will be described in Section 2.2. The analysis for attribution of local versus advected contributions is outlined in Section 2.3. Details of the combined use of ¹⁴C and AMS data are given in the

supplementary information Section S1. Additional data sets used in this study are described in the supplementary information: satellite data sets (AOD from the Advanced Along Track Scanning Radiometer (AATSR), NO₂ columns from the SCIAMACHY instrument, both on the ENVISAT platform) in Section S2, black carbon (BC) and elemental carbon (EC) observations from other megacities than Paris in Section S3, emission inventories in Section S4 and modeling simulations with the PMCAMx and the CHIMERE models in Section S5.

2.1 Sampling sites and strategy

MEGAPOLI summer and winter campaigns took place from 1 to 31 July 2009 and 15 January to 15 February 2010. The measurement design included 3 primary, and several secondary sites (Crippa et al., 2013a; Freutel et al., 2013), mobile platforms (Royer et al., 2011; von der Weiden-Reinmüller et al., 2014a), and an aircraft (Freney et al., 2014). Measurements at primary sites include gas phase pollutants, size-resolved chemical composition of fine PM, and aerosol physical properties. In this paper, we use in particular concurrent AMS and black carbon measurements derived either from a MAAP (Multi Angle Absorption Photometer ; Thermo) or an Aethalometer (Magee Scientific, model AE-31, USA) at the three primary sites. The urban background site (LHVP, Laboratoire d'Hygiène de la Ville de Paris) was located near the agglomeration center, in the 13th district of Paris. Two sub-urban background sites were located respectively at the south-western (SW) and north-eastern (NE) edges of the agglomeration at about 20 km from the city center (Figure 1): the SIRTA (Site Instrumental de Recherche par Télédétection Atmosphérique, Haefelin et al., 2005) site at Ecole Polytechnique, Palaiseau (later on referred to as SW suburban site), and the Golf Départemental de la Poudrerie site at Livry Gargan (NE suburban site). The sites are later on referred to as the SW and the NE suburban site, respectively). The sites are described in more details in Freutel et al. (2013) and Crippa et al.

(2013a). At the urban site, also filter sampling for ^{14}C analysis of PM_{10} aerosol was performed in order to distinguish between fossil and modern fuel origin (see Section S1 for a detailed method description). Briefly, in these samples TC (total carbon) was isolated for ^{14}C measurements using the THEODORE system (combustion in O_2 at 640°C for 12 min and subsequent cryo-trapping of the evolving CO_2 , see Szidat et al. (2004) for more details). ^{14}C was then measured with the accelerator mass spectrometry system MICADAS (Synal et al., 2007).

The French PARTICULES project (Gherzi et al., 2010; Bressi et al., 2013) was designed to identify the major sources of $\text{PM}_{2.5}$ in the city of Paris and document their geographical origin in order to better define effective local abatement strategies. A one-year survey of the daily $\text{PM}_{2.5}$ chemical composition (from 11 September 2009 to 10 September 2010) was performed at five background locations in the region of Paris (Figure 1): one urban background, one suburban background (not used in this study), and three rural background sites at about 70 km distance from the city center. Additional measurements (not used in this study) were performed at two traffic sites. Each site was equipped with two automated low-volume samplers (Leckel SEQ47/50) collecting 24-h $\text{PM}_{2.5}$ samples (from midnight to midnight) in order to determine the concentrations of $\text{PM}_{2.5}$, EC, OC, the major water-soluble inorganic ions, metals, and selected organic tracers such as levoglucosan (a marker for woodburning) as described in Bressi et al. (2013). From filter samples, total $\text{PM}_{2.5}$ mass was obtained from gravimetric measurements. Chloride, nitrate, sulfate, sodium, ammonium, potassium, magnesium and calcium concentrations were determined by Ion Chromatography (IC). Elemental carbon (EC) and organic carbon (OC) were determined by a thermal-optical method using a Sunset Laboratory Carbon Analyzer (Sunset Lab., OR, USA) and the EUSAAR 2 protocol defined by Cavalli et al. (2010).

2.2 Aerosol measurements processing

AMS measurements provide the chemical speciation (sulfate, nitrate, ammonium, chloride, and the organic fraction) of the non-refractory fraction of aerosols with a diameter below 1 μm (PM_{10}). The uncertainty in these measurements has been estimated at about 30% (Crippa et al., 2013a; Freutel et al., 2013). Positive matrix factorization (PMF) (Paatero et al., 1994; Lanz et al., 2007; Ulbrich et al., 2009) allows deconvolution of the OA mass spectra into several factors that can be assigned most of the time to specific OA sources. Error analysis for PMF output is performed by varying the algorithm parameters (seeds, f_{peak}). A relative uncertainty for different factors of usually several tens of percent has been obtained (Freutel et al., 2013). The PMF analysis was applied here to the AMS measurements at the three primary MEGAPOLI sites indicated in Figure 1. For the summer campaign a three factor solution comprising HOA (hydrocarbon-like organic aerosol), OOA (oxygenated organic aerosol) and COA (cooking related organic aerosol) was selected (Freutel et al., 2013). For the winter campaign a four factor solution with an additional BBOA (biomass-burning related organic aerosol) component was selected (Crippa et al., 2013a).

The combination of radiocarbon (^{14}C) analysis with PMF analysis of AMS measurements allows quantification of the fossil fuel and modern fractions of different OA sources (Minguillón et al., 2011; El Haddad et al., 2013; Zotter et al., 2014). All PMF factors (as obtained with a three factor analysis by Freutel et al. (2013)) are attributed *a priori* to fossil- or modern (non-fossil) fuel carbon. HOA, which largely originates from traffic, was assumed to be 100% fossil, thus neglecting the small biofuel contribution. COA and BBOA were assumed to be 100% non-fossil. Only for OOA this attribution is not possible *a priori*, but is obtained as a result of the combined

^{14}C /AMS-PMF analysis. For more detailed description of this analysis, see Section 1 of the supplementary information.

The measurement set-up, data processing, and the data sets obtained from the PARTICULES project are described in detail in Bressi et al. (2013). Chemical mass closure was successfully achieved at all sites leading to a large quality controlled aerosol dataset (Bressi et al., 2013).

2.3 Data processing for determining local versus advected contributions

The geographical origins of the various PM components measured during the PARTICULES campaign were determined assuming that the difference in PM chemical composition between the urban background site and the appropriate upwind rural site can be attributed to the emissions within the agglomeration (Lenschow et al., 2001). Backward trajectories calculated with the HYSPLIT model (Draxler and Hess, 1997) have been used to choose the convenient rural background site upwind of the agglomeration among the three sites located at the north-east, north-west and south of the agglomeration (as described in more details in Petetin et al. (2014)). Uncertainties in the annual advected fractions are below 5% (Petetin et al., 2014).

3. Aerosol origin: Regional or local?

3.1 Megapoli intensive campaign perspective

A first striking result is that PM₁ levels in the Paris agglomeration were much lower during the MEGAPOLI summer campaign in July 2009 than during the winter campaign (in January/February 2010): average PM₁ levels were between 5.3 and 7.5 $\mu\text{g m}^{-3}$ and between 15.2 and 18.5 $\mu\text{g m}^{-3}$ in summer and winter, respectively, at the three primary sites (Table S1 in

supplementary material; Freutel et al., 2013, Crippa et al., 2013a). This seasonal variation of PM_{10} is confirmed at the SW suburban site by two years long (June 2011 – June 2013) combined Q-ACSM (Quadropole Aerosol Chemical Speciation Monitor, Aerodyne, MA, USA) and Aethalometer measurements (Petit et al., 2015): Summer PM_{10} were on average $4.4 \mu\text{g}/\text{m}^3$ while winter reached on average $14.5 \mu\text{g}/\text{m}^3$. Also on a longer term perspective, PM levels in the Paris megacity appear moderate, when compared to the European background: average urban background $PM_{2.5}$ concentrations levels in and near Paris suburbs over the period 2007 – 2013 are about $18 \mu\text{g}/\text{m}^3$ (Petit, 2014). This value is similar to the median value of the annual $PM_{2.5}$ means of $17 \mu\text{g}/\text{m}^3$ derived from eight European rural background sites (Putaud et al., 2010). Nevertheless, Paris urban $PM_{2.5}$ background exceeds the WHO health guideline of $10 \mu\text{g}/\text{m}^3$ on an annual average; also for traffic sites European PM_{10} standards are exceeded. Average $PM_{2.5}$ levels in Paris rather close to European background suggest a strong regional contribution to the Paris background urban fine PM burden which needs to be confirmed by quantitative analysis presented here.

Firstly, time series have been analyzed (Crippa et al., 2013a; Freutel, et al., 2013). For all major aerosol components except black carbon, the average concentrations (Table S1 in the supplementary material) and their temporal variability are rather similar between the urban LHVP and the NE and SW suburban sites, located at the edge of Paris. This similarity implies indeed a major regionally controlled fine PM burden.

Second, we compared levels of different PM_{10} components and NO_x at the NE suburban site for air masses originating from (see Section S6 in the supplementary material): (1) the NE sector coming from Central Europe and (2) the SW sector and after passing over the Paris agglomeration before reaching the measurement site. Inorganic ions (sulfate, nitrate and

ammonium) and OA levels were substantially higher for air masses originating from the NE sector both during summer and winter (Figure 2). This increase is less apparent for OA in winter, because AMS measurements were not available during January 26 to 28 when heavily polluted air masses were transported to the agglomeration, and absent for BC and NO_x, both primary pollutants. Thus contrary to intuitive expectations, PM levels for most components are larger in air masses advected to the agglomeration (from NE) than in air masses (from SW) leaving Paris and having accumulated urban emissions while crossing the city.

3.2 One-year measurements perspective

The dominance of regional pollution for fine PM levels was additionally quantified by the analysis of the year-long measurements from the PARTICULES project. Using the appropriate upwind rural site (see Section 2.2, Figure 1) as background, we estimated that on an annual basis more than 70% of the urban PM_{2.5} was advected to Paris from outside (Figure 3). Results from this analysis are very similar for the summer (JJA) and winter (DJF) seasons (72% and 71%, respectively). During the polluted periods (PM_{2.5} > 40 µg m⁻³ at the urban site), especially during spring, the regional contribution can even be larger, around 90%. Thus the variability of fine PM levels in Paris background atmosphere is mostly controlled by advection from outside.

The three major fine aerosol species sulfate, nitrate and organic aerosol on average contributed at the urban background site 13%, 19% and 36%, respectively, to total PM_{2.5}. The predominance of advected aerosol compounds is observed as expected for sulfate (nearly 95% of total fine PM), but also for nitrate (nearly 80%) and for organic matter (about 70%). Such an important advected fraction of OA has to our knowledge not yet been shown before for a megacity. Possible reasons for this behavior will be discussed in Section 5.

3.3 Satellite observations

The homogeneous regional distribution of fine PM is also apparent from satellite AOD measurements, showing no significant gradient around Paris, in contrast to tropospheric NO₂ column measurements (derived from SCIAMACHY measurements on ENVISAT) which are clearly enhanced over the Paris agglomeration (Figure 4). This strong gradient in NO₂ is directly related to NO_x emissions in the Paris agglomeration and is enhanced due to its short lifetime of several hours during daytime and summer (Beirle et al., 2011).

Figure 4 also shows the AOD results obtained with the Advanced Along Track Scanning Radiometer (AATSR) instrument on ENVISAT (Veefkind et al., 1998) over Western Europe from March to October 2009. Around Paris (from 48.70° to 49.0° North and from 2.10° to 2.55° East) AOD has a value of around 0.15 ± 0.04 , while the average over Northern France (from 49° to 50° North and from 2° to 6° East) was 0.14 ± 0.04 . Thus, unlike NO₂, AOD is not affected by the Paris agglomeration. Therefore a megacity such as Paris does not significantly change the local AOD, which confirms results from surface observations of long-range transport dominance of the aerosol burden over the Paris area.

3.4 Modeling results

Results from Chemical Transport Model (CTM) simulations (for model descriptions, see Section S5 in the supplementary material) for the MEGAPOLI campaign and the year of PARTICULES measurements confirm the dominant advective contribution to PM levels over the Paris agglomeration. Simulations with the PMCAMx model show only a 15% and 25% local origin of fine PM during the summer and winter campaign periods, respectively (Figure 5). These values are about 10%, 20% and 10% for sulfate, nitrate and OA, respectively, during summer. For winter, the respective local contributions are more than 20%, 5% and 20% for the

same compounds (Figure 6). These values are obtained by comparing simulations with and without emissions from the Paris region. They are similar to those obtained by Skyllakou et al. (2014) for Paris using a specific tagging method imbedded in their PMCAMx model simulations, capable to discern the geographical origin of fine PM. Also simulations with the Polair3D/Polyphemus chemistry transport model (Sartelet et al., 2007) show a minor local contribution for OA (30-38%) for the Paris urban background during the MEGAPOLI summer campaign (Couvidat et al., 2013).

Year-round simulations with the CHIMERE model also show, consistently with the observation-based estimates, that around 65% of the fine PM_{2.5} over Paris is advected to the megacity from other areas (Petetin et al., 2014). For individual compounds larger errors of different sign occur, for instance the advected part of OA is underestimated by CHIMERE by about a factor of two, while nitrate is overestimated by a factor of 1.5. The strong underestimation of OA is most pronounced during wintertime and is thought to be related both to underestimated regional woodburning emissions and missing formation pathways in the model (Petetin et al. 2014). As a conclusion, CTM simulations are able to reproduce and confirm the general picture of a dominant advected fine PM burden over the Paris domain, although errors can occur for individual aerosol species.

4. Sources and origin of organic and inorganic aerosols

The MEGAPOLI campaign results also provide important insights into specific sources of carbonaceous PM (the sum of OA and BC), which represents on average almost 70% (summer) and 43% (winter) of PM₁ at the urban background site. Radiocarbon (¹⁴C) analysis clearly shows

a dominant non-fossil fraction of carbonaceous PM₁: $\sim 62\% \pm 8\%$ (uncertainty) during summer and $\sim 78\% \pm 14\%$ during winter (Figure 7). These values are much higher than those for other megacities reported in Hodzic et al. (2010), where contributions from non-fossil carbon are about 30 and 40%, respectively during summer and winter, for Tokyo, about 30% during summer for Los Angeles, about 30% during spring in Mexico City for days without significant contribution of wild-fires, and about 50% and 30% in summer and winter in Beijing, respectively. Thus sources of non-fossil carbon are much more important for Paris than for many other megacities.

Cooking-related OA (e.g. modern carbon) contributes to carbonaceous PM₁ up to 30% in summer and nearly 15% in winter. The high values at the urban site could be partly due to a large number of restaurants nearby, although the cooking source has also been identified at the SW suburban site (Crippa et al., 2013a) and in the Paris pollution plume (von der Weiden-Reinmüller et al., 2014a, 2014b). This finding for Paris is consistent with the importance of cooking contributions found in several other cities (London (Allan et al., 2010), Barcelona (Mohr et al., 2012), Beijing (Huang et al., 2010), New York City (Sun et al., 2011), and Toronto (Slowik et al., 2010)).

During summer, the PMF OOA factor, a proxy for secondary organic aerosol (SOA), accounted for nearly 40% of OA. Combined ¹⁴C/AMS-PMF analysis suggests that more than 90% of this OOA is of non-fossil origin with an uncertainty range between 60 and 100% (Figure 7). Secondary organic aerosol formation from non-fossil precursors is thus clearly the dominant source for SOA advected to the Paris megacity during summer. Modeling results using CHIMERE including the volatility basis set (description in Section S5) confirm the origin of SOA: more than 60% of SOA is of non-fossil and mostly biogenic origin, which is within, albeit at the lower end, of the experimentally derived range of values (see Figure 8). The simulations

indicate two transport patterns during high SOA periods in Paris: either transport from the north-east with SOA of mixed anthropogenic and biogenic origin, or transport from the south with predominantly biogenic SOA, from large biogenic VOC emissions over South-Western France and North-Eastern Spain (Zhang et al., 2013). Apparently, rapid SOA formation from anthropogenic VOC precursors as for example observed in Mexico City (e.g. Volkamer et al., 2006) is not strong and fast enough within the Paris agglomeration to compete with the imported biogenic SOA fraction. However, SOA within the Paris pollution plume at about 100 km downwind of the city is enriched with anthropogenic SOA after several hours of processing time, based on the analysis of aircraft data obtained during the summer campaign (Freney et al., 2014). It should also be noted that alternative PMF calculations of summer campaign AMS data slightly alter results. For instance, the five factor PMF analysis for the urban background site shows an additional factor related to biogenic marine emissions with high sulfur content and contributing a little more than 10% to summer PM₁ OA (Crippa et al., 2013b).

During winter, PMF analysis of AMS measurements directly attributes 12% of carbonaceous PM₁ to woodburning. A large fraction (44%) of carbonaceous PM₁ is attributed to OOA (Figure 7), similar to other megacities during winter (New York City and Tokyo (Zhang et al., 2007)). From the combined ¹⁴C/AMS-PMF analysis, at least about 80% of this fraction are estimated to be of non-fossil origin (Figure 7). This points to either strong contributions of aged organic aerosol from woodburning or of SOA formation from biogenic VOCs, even if in wintertime biogenic emissions are expected to be much lower than during summer. Estimated woodburning contributions to OA from the Aethalometer model (Sandradewi et al., 2008) and a tracer approach (using levoglucosan as a tracer for woodburning emission) for this period are also compatible with a part of the identified OOA fraction originating from wood-burning

emissions, within their large error bars (Crippa et al., 2013c). For instance Grieshop et al. (2009) and Heringa et al. (2011) showed that domestic wood burning emissions from logwood stoves form significant amounts of secondary organic aerosol. A question arises of the local versus regional origin of woodburning OA in the Paris agglomeration since the dominant OA fraction was assigned to advection from outside in Section 3.1. The regional origin of primary or secondary woodburning emissions is made evident by the strong correlation and similar levels of levoglucosan between the urban background and rural (south) Paris sites of the PARTICULES project ($R^2=0.83$, Figure 9). However, more work is required at a regional scale to better separate woodburning emissions from urban, suburban and rural areas. A large wood-burning contribution to OA (up to 60% during wintertime) was also found for the Grenoble agglomeration in the French Alps (~650,000 inhabitants) (Favez et al., 2010). In general, in Alpine valleys, woodburning contributions to OA around 50% were found (Herich et al., 2014). Crippa et al. (2014) showed that wood or biomass burning related organic aerosol concentrations were significant across Europe even in spring and autumn.

Fossil fuel EC and HOA contribute about 20% and 15%, respectively, of the carbonaceous PM_{10} in summer, and about 20% and 10%, respectively, in winter (Figure 7). According to emission inventories like those developed by MACC (Monitoring Atmospheric Composition and Climate, Pouliot et al., 2012) and EMEP (European Monitoring and Evaluation Program, Vestreng et al., 2007), the major contributor to this fossil fuel related fraction is traffic. Unlike biomass burning emissions, these contributions are expected to be dominated by local emissions within the agglomeration. This is confirmed for example by simulations with the PMCAMx model which attribute about 60% of EC to emissions within the agglomeration (during the MEGAPOLI summer campaign).

The secondary inorganic aerosol fraction, mostly associated with regional transport (>70%, see Section 3.2), represents about 30% of PM₁ during summer (19% sulfate, 6% nitrate and 7% ammonium) and more than 50% during winter (16% sulfate, 28% nitrate and 12% ammonium). Again, MACC and EMEP emission inventories (Pouliot et al., 2012; Vestreng et al., 2007) indicate that inorganic aerosol precursors SO₂, NO_x and NH₃ are mainly of anthropogenic origin. SO₂ is mostly emitted by industrial sources (including energy production) and shipping. NO_x emissions are dominated by transportation including shipping while NH₃ is mainly emitted by agriculture. Thus, unlike for organic aerosol with major non-fossil sources, transport and industry related fossil fuel combustion strongly contributes to fine inorganic PM. The dominant advected fraction of inorganic aerosol is explained by two factors: first, major source areas of its gaseous precursors are located outside the agglomeration (especially for SO₂ and NH₃), second the time necessary for oxidation of the precursors does not allow for efficient aerosol formation from emissions within the megacity (as for nitrate formation from NO_x emissions).

5. Comparison to other megacities

The strong regional control of fine PM in Paris is here compared to the situation in other megacities. We use BC as a tracer for the local megacity contribution to fine PM. A compilation of urban background BC and EC measurements in several megacities (Figure 10 and Table 1 in the supplementary material) shows that values for Paris (1.8 µg/m³) are at the lower end, within a cluster of megacities like Los Angeles, London, or New York City (1-2 µg m⁻³). Several American and Asian megacities have intermediate BC levels (Rio de Janeiro, Mexico City, Seoul, 3-5 µg m⁻³), while Asian megacities in fast developing countries (Beijing, Delhi, etc.) and Cairo display the largest values (> 6 µg m⁻³). Despite uncertainties due to different measurement

protocols (Bond et al., 2013; Petzold et al., 2013) and site representativeness (approximately a factor of two, Section S2), the general tendency towards lower values in post-industrial megacities is clear. Nevertheless, since BC and associated compounds like polycyclic aromatic hydrocarbons are known to have strong adverse health effects (e.g. Janssen et al., 2012), BC still represents an important air quality problem even for megacities with lower concentrations like the densely populated Paris agglomeration.

During specific pollution episodes, high PM concentrations can be encountered also in the Paris agglomeration. For instance, during March 2014 (during 10 days from 7 to 18 March), exceptionally high PM₁₀ concentrations exceeded pollution alert levels (daily average of 80 µg m⁻³ PM₁₀) on several occasions. During this episode, anticyclonic conditions led to regional PM accumulation over North-Western Europe. ACSM measurements at the SIRTA site showed a prevailing contribution of ammonium nitrate (~50% of PM₁) and ammonium sulfate (~15%) suggesting a strong advective impact from outside the agglomeration, in line with the results of our study (Sciare, 2014). In addition, low dispersive conditions during this period also favored additional local pollution build-up.

London is another European megacity with expected low average local contributions to PM levels. Indeed, the regional contribution for organic aerosol, nitrate and sulfate was found to dominate based on observations during the REPARTEE campaigns in autumns 2006 and 2007 (Harrison et al., 2012), although a quantitative assessment could not be made with the available data at only one central London site. These dominant regional and correspondingly smaller local emission contributions to urban background PM levels are reflected in recently revised emission inventories. For both the Paris and London agglomerations, bottom-up emission inventories using geographically specific information on activity and emission factors yield about a factor

three lower per capita emission values for BC and PM than for national averages (Timmermans et al., 2013), due to lower per capita fuel consumption for large cities with increased population density (Grimm et al., 2008), and possibly also due to lower emission factors.

In contrast, Mexico City is a good example of a megacity with larger local pollution impact. PMCAMx simulations for the MILAGRO campaign in March 2006 (Molina et al., 2010) indicated a much higher contribution of local emissions to fine PM for Mexico City (60% for $PM_{2.5}$, 60% for OA, 80% for nitrate, less than 10% for sulfate (Karydis et al., 2011)) than for Paris (Figures 5 and 6). Mexico City is surrounded by mountain ridges, leading to less favorable dispersion conditions with average summer wind speed of about 4 m s^{-1} during MILAGRO at about 300 m agl. (Fast et al., 2007) as compared to about 8 m s^{-1} in Paris during both the MEGAPOLI summer and winter campaign (from SODAR measurements at the SW suburban site at 200 m agl.). Also increased radiation intensity (enhancing the build-up of secondary pollutants already within the agglomeration), and higher per capita emissions than for Paris (consistent with larger BC values, Figure 10) contribute to this enhanced local pollution impact. These different conditions result in a local $PM_{2.5}$ contribution of about $1.4 \mu\text{g m}^{-3}$ per million inhabitants for Mexico City with 21 million inhabitants (United Nations, 2015) simulated during MILAGRO, but only $0.3 \mu\text{g m}^{-3}$ per million inhabitants for Paris (with 10.84 million inhabitants), observed on an annual average basis during PARTICULES. Thus, in terms of local versus advected contributions to PM, these two megacities might be two extremes.

6. Conclusions

Analysis of the MEGAPOLI and PARTICULES campaign observations, of satellite data, and of modeling results have allowed the quantification of the advected/regional versus local origin of particulate matter (PM) and especially carbonaceous aerosol in the Paris agglomeration. On average over one year, about 70% of the fine PM mass is transported into the megacity from upwind regions of France and continental Europe. Note that this number refers to urban background. For traffic sites, the local contribution would be larger. For organic aerosol (OA) and nitrate, also more than 70% of their urban background concentrations, respectively, are advected to Paris. For high PM periods, the advected fractions can be even larger. At a measurement site located at the NE edge of the agglomeration, the strong advective source caused higher PM levels for air masses originating in the NE sector (continental origin) than those originating in SW, but having crossed the agglomeration before arriving at the site. Satellite AOD measurements and chemistry-transport modeling simulations further confirm these results.

In contrast to other megacities, primary fossil fuel combustion emissions contribute little, less than about 20% in winter and less than 40% in summer, to carbonaceous fine PM. Instead, cooking activities and, during winter, residential woodburning are the major primary organic PM sources and contribute to non-fossil fuel aerosol. From combined ^{14}C and PMF analysis of AMS data, a mainly non-fossil fuel origin of secondary organic aerosol can be inferred both during summer and winter, either due to formation of secondary aerosol from biogenic VOC precursors or to processing of woodburning emissions.

Low BC/EC levels (in comparison to those at other megacities worldwide, and not precluding large episodic BC and PM levels) are consistent with relatively low emissions in a post-industrial megacity as Paris. Indeed, more efficient per capita energy use, and lower

emission factors than on national average contribute to these low emissions. Other post-industrial, mid-latitude, flat terrain megacities like New York City, London, and Tokyo probably show a similar type of behavior, while local sources are prevailing for megacities as Mexico City or Los Angeles affected by one or several factors as larger local emissions, dispersion limited by orography and larger radiation.

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Table 1 .

Origin of black and elemental carbon data and observation periods used in Figure 10, and megacity population in year 2015.

City	Observation Period	Reference	Population in 2015 (in 10 ⁶)
Bangkok	April 2008 – March 2008	Sahu et al. (2008)	9.27
Barcelona	January – December 2009	Reche et al. (2011)	5.26
Beijing	August 2004 Summer (July – August 2001; June – July 2002) Winter (December 2001 – January 2002 and December 2002); Spring (March 2003).	Gros et al. (2007) Dan et al. (2004)	20.38
Beijing (EC)	March 2005 - February 2006	Yang et al. (2011)	
Cairo	March - April 2005	Favez et al. (2008)	18.77
Chicago	January 2005 – December 2008	Hand et al. (2011)	8.75
Chongqing	March 2005 - February 2006	Yang et al. (2011)	13.33
Delhi	January 2006 - January 2007	Bano et al. (2011)	25.7
Guangzhou	December 2008 - February 2009	Yang et al. (2011)	12.46
Hyderabad	January – December 2003	Latha and Badarinath (2005)	8.94
Hong Kong	November 2000 - February 2001 and June to August 2001	Ho et al. (2006)	7.31
Istanbul	November 2007 - June 2009	Theodosi et al. (2010)	14.16
London	January – December 2009	Reche et al. (2011)	10.31
Los Angeles	January 2005 – December 2008	Hand et al. (2011)	12.31
Mexico City	March 2006	Aiken et al. (2010)	21.0
New York City	2006 – 2008	Rattigan et al. (2011)	18.99
Paris	September 2009 – September 2010	This study	10.84
Rio de Janeiro	June 2007 - August 2008	Miranda et al. (2012)	12.9
São Paulo	June 2007 - August 2008	Miranda et al. (2012)	21.07
Seoul	2003 – 2004	Kim et al. (2007)	9.77
Shanghai	March 1999 - May 2000	Ye et al. (2003)	23.74
Tokyo	2003 - 2005 2010	Kondo et al. (2012)	38.0

Figure captions

Fig. 1. Location of the sampling sites from the MEGAPOLI and PARTICULES projects in the Ile-de-France region. The grey zone stands for the urban area of the Paris agglomeration. The white circle shows the three rural background sites, all at about 70 km distance from the PARTICULES urban background site. The purple lines indicate administrative boundaries. Map source: Google Earth.

Fig. 2. PM₁ components ($\mu\text{g m}^{-3}$) and NO_x (ppb*10) at the NE suburban site for air masses arriving from SW (red bars) and NE sectors (blue bars); air masses originating from the SW sector sample emissions from Paris, those from the NE sector represent continental type air masses moving towards Paris: (a) for summer and (b) for winter.

Fig. 3. Local (hatched) and imported contributions to PM_{2.5} in Paris (PARTICULES urban background site) for the period September 2009 to September 2010, for different PM_{2.5} levels. An uncertainty range of $\pm 5\%$ (absolute value) is estimated for the local and imported PM_{2.5} contribution.

Fig. 4. AOD (aerosol optical depth) from the AATSR (Advanced Along Track Scanning Radiometer instrument) (a), tropospheric NO₂ columns from SCIAMACHY observations, both averaged over the period March–October 2009 (b). The black circle marks the Paris agglomeration. AOD values are only given over land areas (black over sea).

Fig. 5. Predicted relative decrease in PM_{2.5} levels when local emissions of the megacity are set to zero; calculated with the PMCAMx model for the summer (a) and winter (b) MEGAPOLI campaigns for the greater Paris region, and during the MILAGRO campaign (c) for Mexico City.

Domain widths: $5400 \times 5832 \text{ km}^2$ plus a subdomain of $216 \times 180 \text{ km}^2$ for Paris, $210 \times 210 \text{ km}^2$ for Mexico City.

Fig. 6. Simulated fractional decrease in $\text{PM}_{2.5}$ sulfate (a, b), nitrate (c, d), and organic aerosol (OA, e, f) levels for the summer (a, c, d) and winter (b, d, f) during the MEGAPOLI campaign period, when Paris agglomeration emissions are set to zero in the PMCAMx model.

Fig. 7. Combined analysis of AMS derived PM_1 OA fractions and elemental carbon with results from non-fossil and fossil fuel carbon ^{14}C analysis, for the summer (a) and the winter (b) campaign at the urban downtown site. The left columns for each season show the source apportionment from AMS and EC measurements, the right columns the fossil and non-fossil fractions of carbonaceous PM_1 . Combined, both columns allow the attribution of the individual aerosol types to fossil and non-fossil parts. EM denotes elemental carbon matter, BBOA biomass burning OA, COA cooking OA, OOA oxygenated OA, HOA hydrocarbon-like OA (associated with traffic). The dashed lines represent the combined uncertainties of the ^{14}C measurement and the splits between OC and EC, fossil and non-fossil EM and OOA and their variability as a fractional contribution to carbonaceous PM_1 . Note that for winter time, the fossil fuel EC and primary OA fractions identified from AMS-PMF analysis are somewhat larger than the total fossil fuel carbonaceous PM_1 from the ^{14}C analysis, but agree within their uncertainties.

Fig. 8. Contributions to secondary organic aerosol during the MEGAPOLI summer campaign period, simulated with the CHIMERE model: BGOA (background organic aerosol), BSOA (biogenic SOA), ASOA (anthropogenic SOA), OPOA (oxidized primary OA of anthropogenic origin). BSOA and BGOA are considered as of non-fossil, ASOA and OPOA as of fossil origin.

Fig. 9. Daily levoglucosan values observed during the PARTICULES project from September 2009 to September 2010 at the downtown urban and southern rural sites. The rural site is located far from direct sources. Levoglucosan is a tracer for wood burning emissions. The similar values at both sites ($R^2 = 0.83$, slope rural vs. downtown site 0.84) suggest a strong regional control of woodburning related organic aerosol.

Fig. 10. Concentrations of BC (black) and EC (grey) observed in megacities across the world. Note that Bangkok, Barcelona, Chicago, Chongqing Hyderabad and London have fewer inhabitants (Table 1) than the 10 million accepted as a limit for megacities. The uncertainty due to differences in the measurement methods and in the representativeness for urban background conditions is estimated to approximately 50% (Section S3 in the supplementary material). References for the studies used here are given in Table 1.

Figures

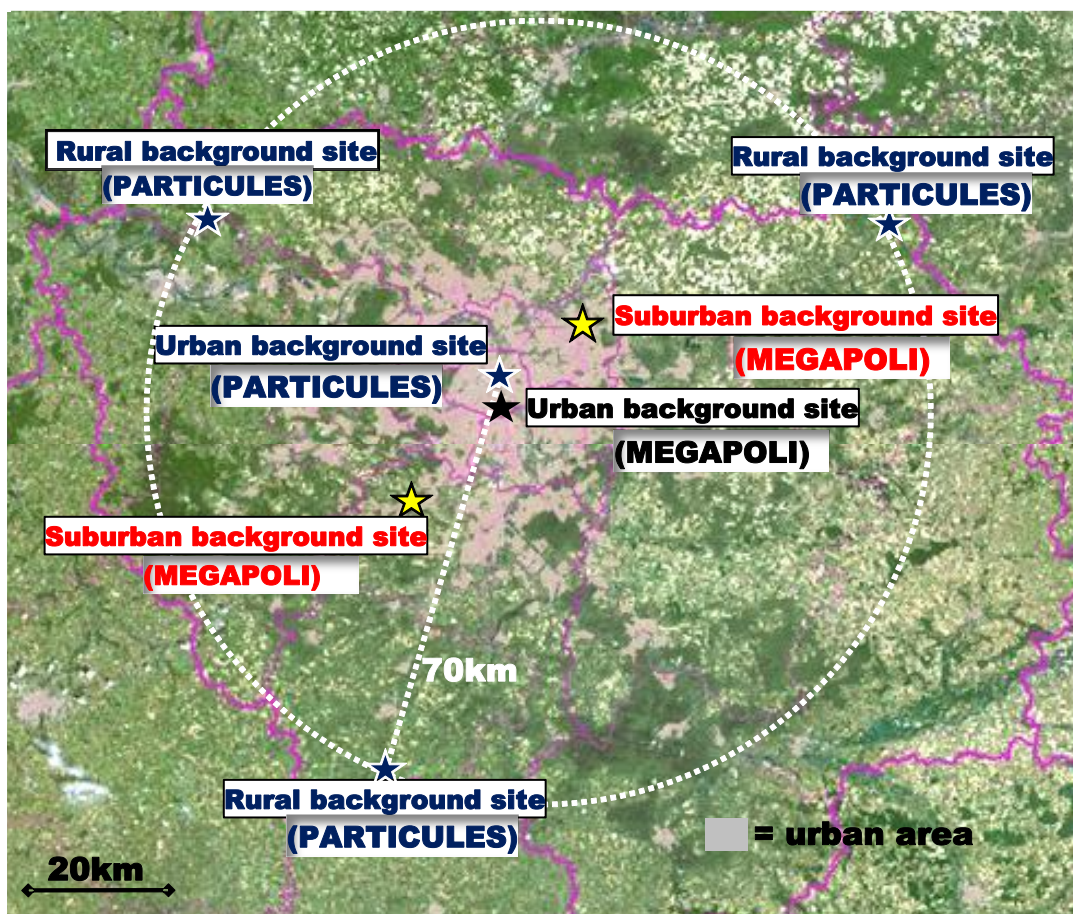


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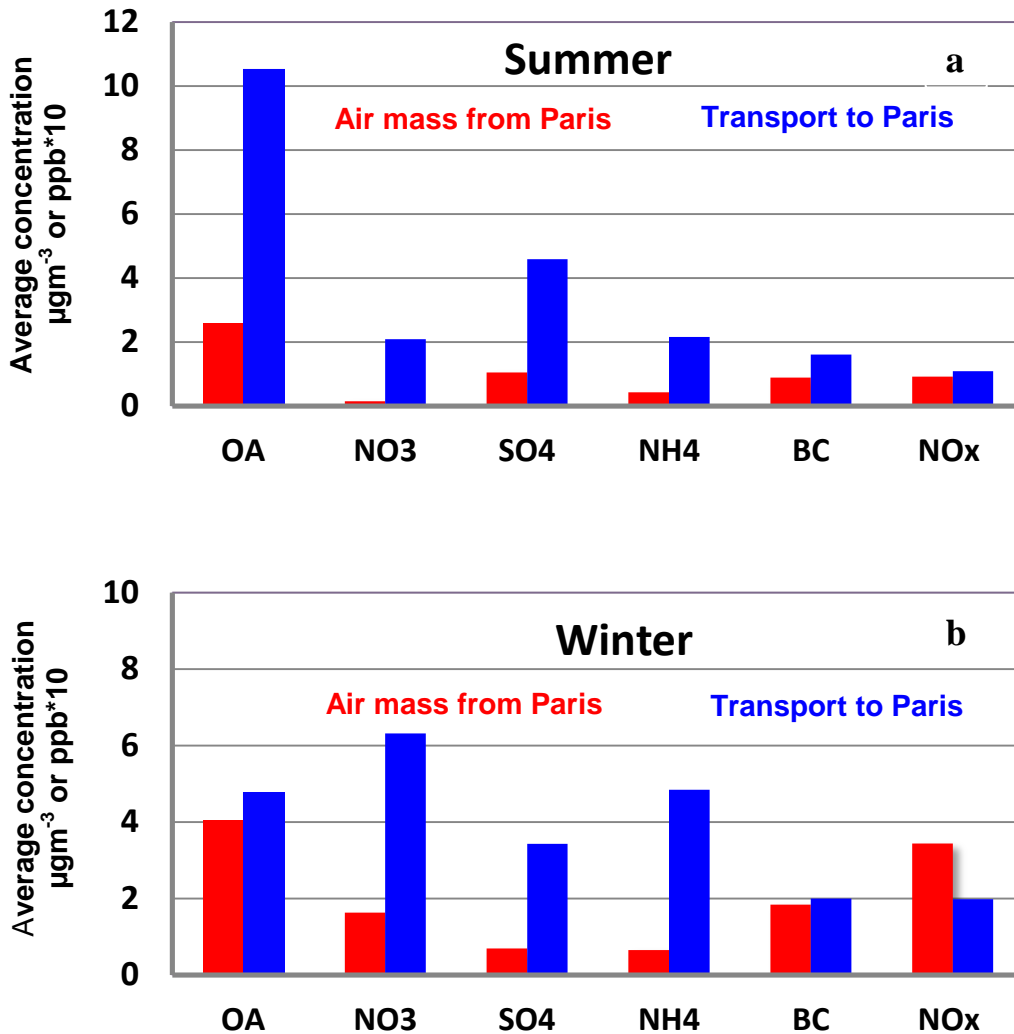


Fig. 2. PM₁ components ($\mu\text{g m}^{-3}$) and NO_x (ppb*10) at the NE suburban site for air masses arriving from SW (red bars) and NE sectors (blue bars); air masses originating from the SW sector sample emissions from Paris, those from the NE sector represent continental type air masses moving towards Paris: (a) for summer and (b) for winter.

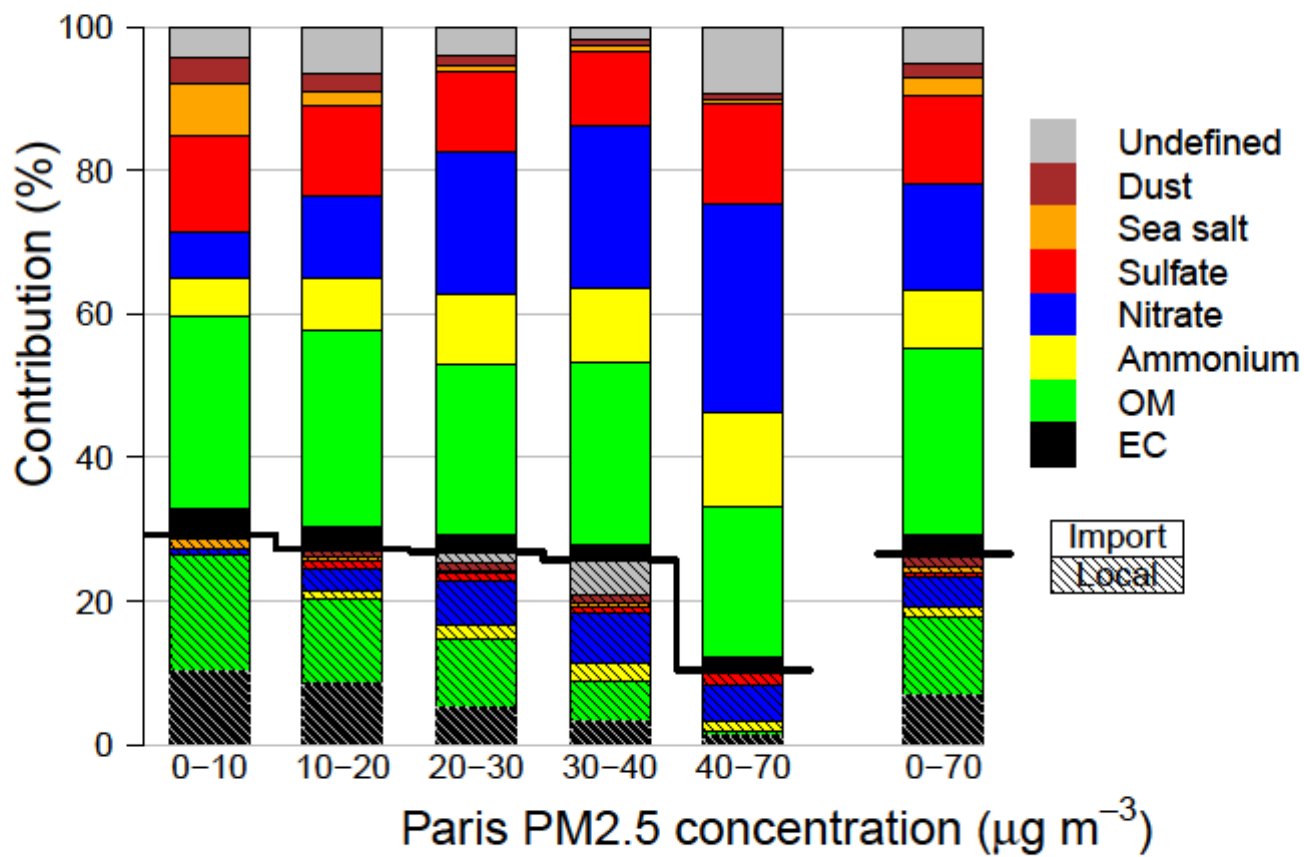


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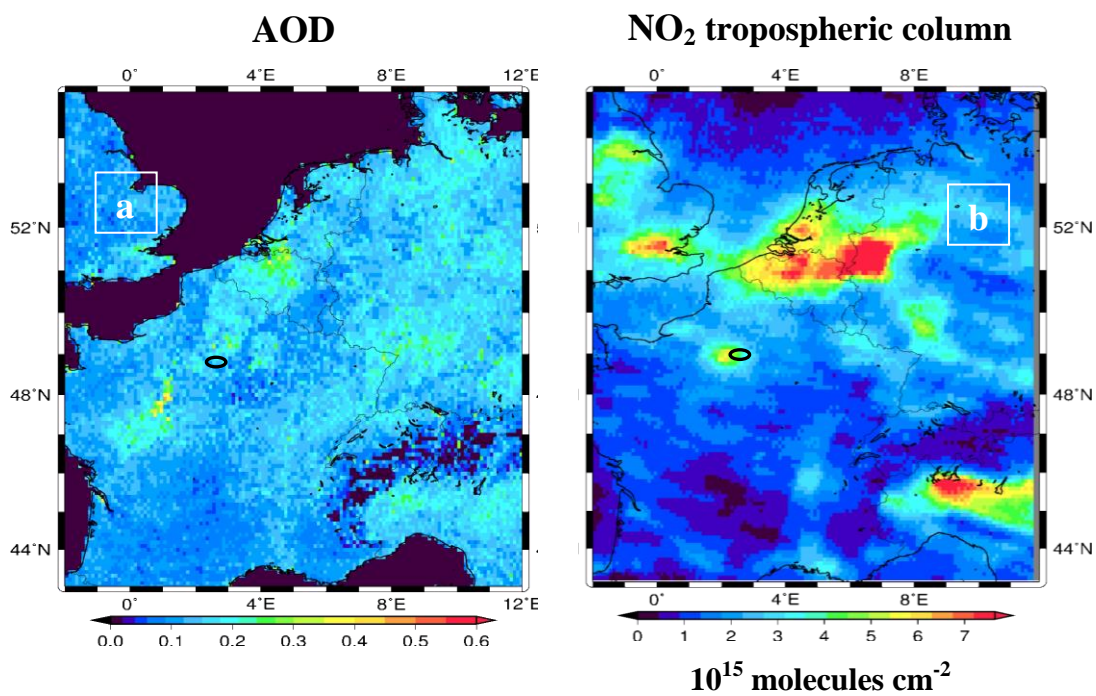


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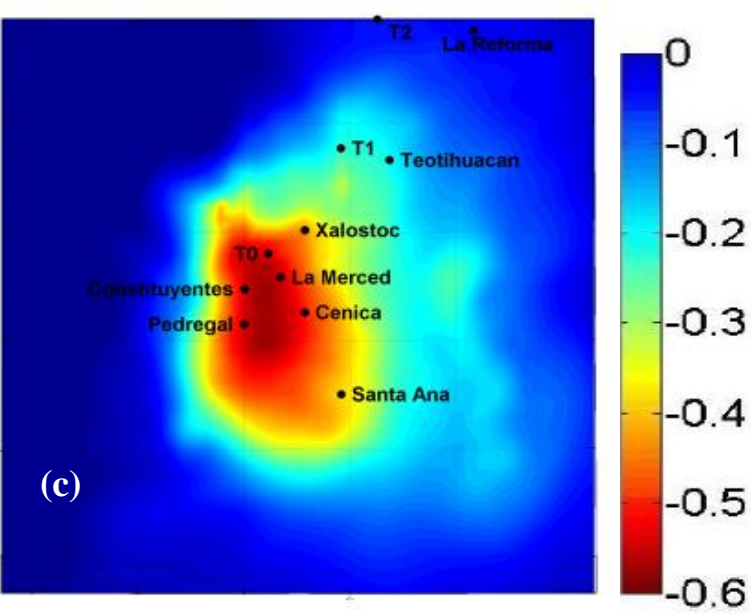
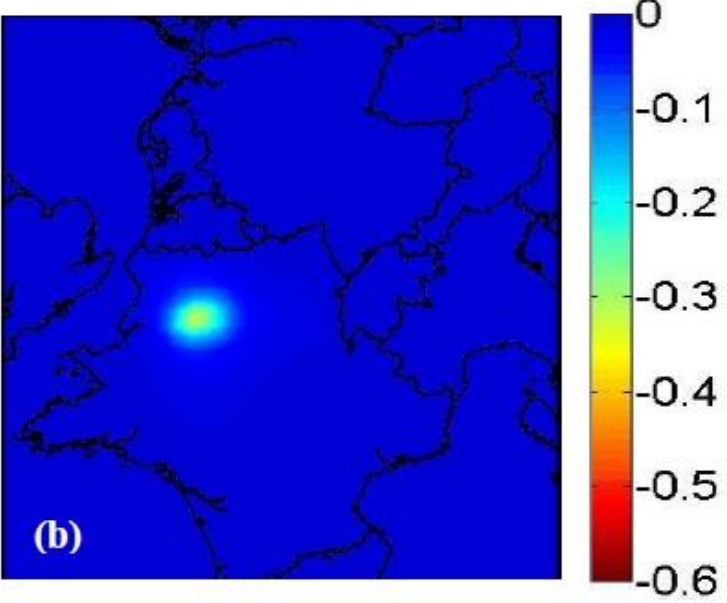
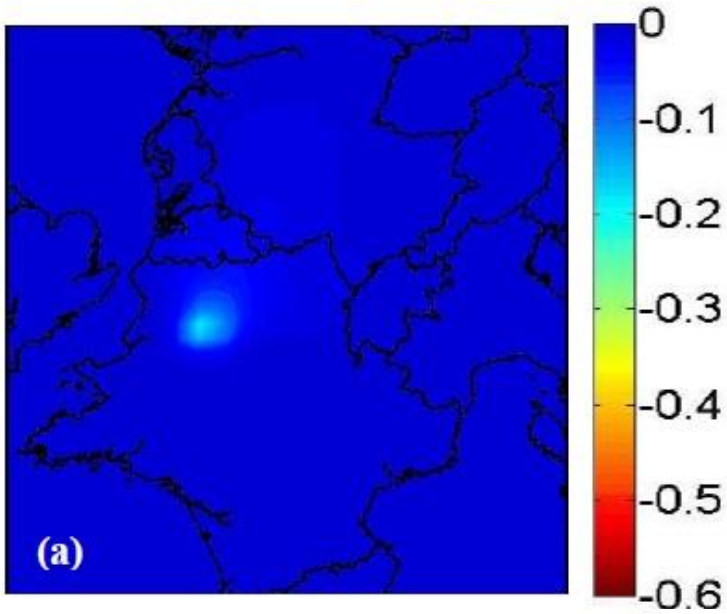


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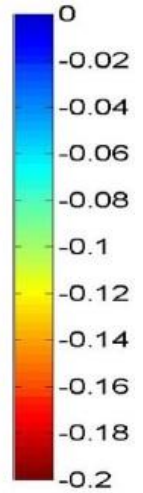
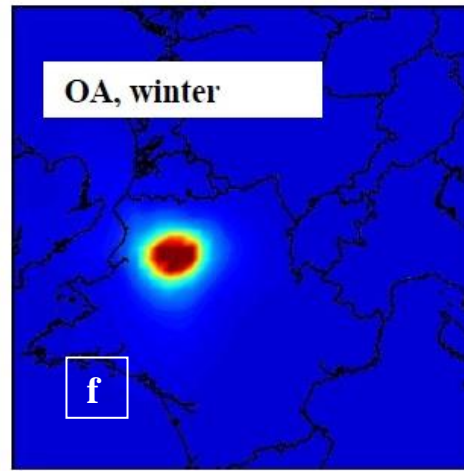
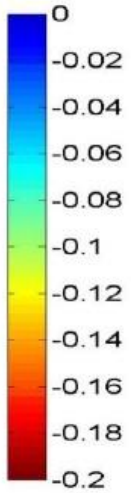
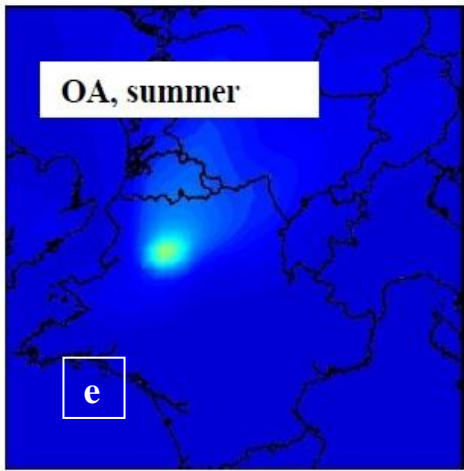
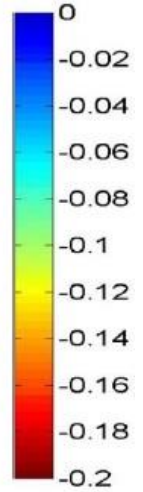
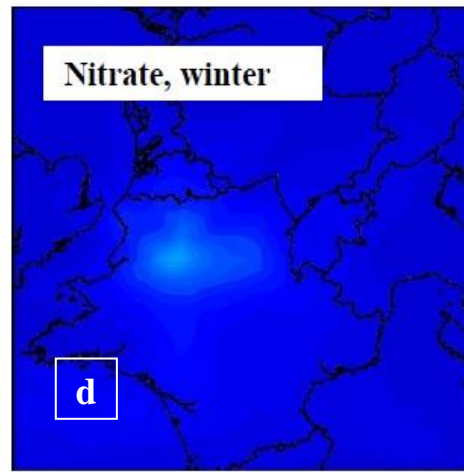
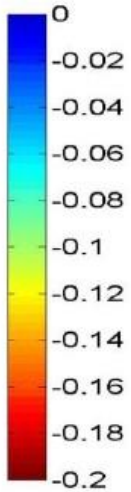
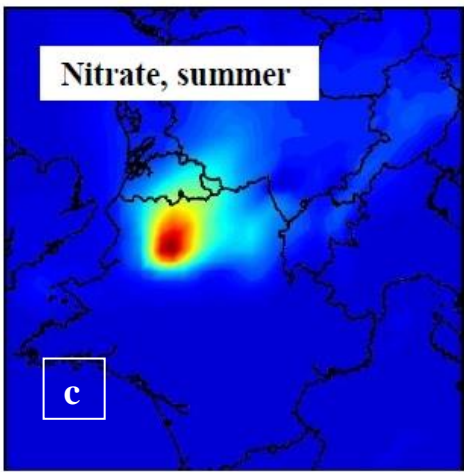
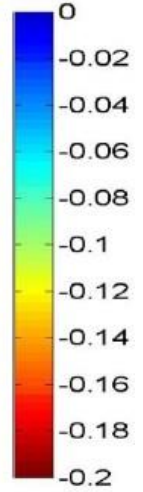
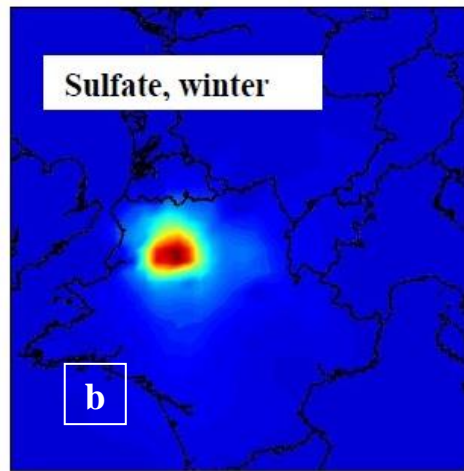
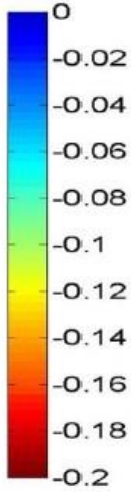
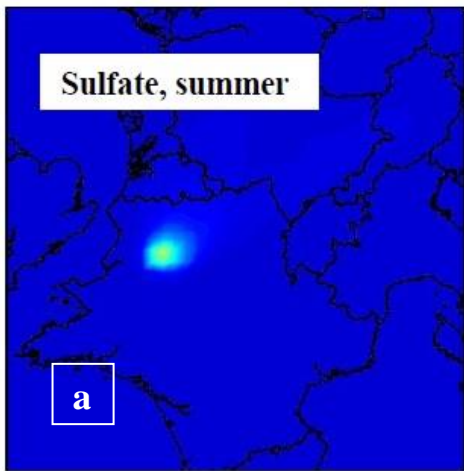


Fig. 6. Simulated fractional decrease in PM_{2.5} sulfate (a, b), nitrate (c, d), and organic aerosol (OA, e, f) levels for the summer (a, c, e) and winter (b,d, f) during the MEGAPOLI campaign period, when Paris agglomeration emissions are set to zero in the PMCAMx model.

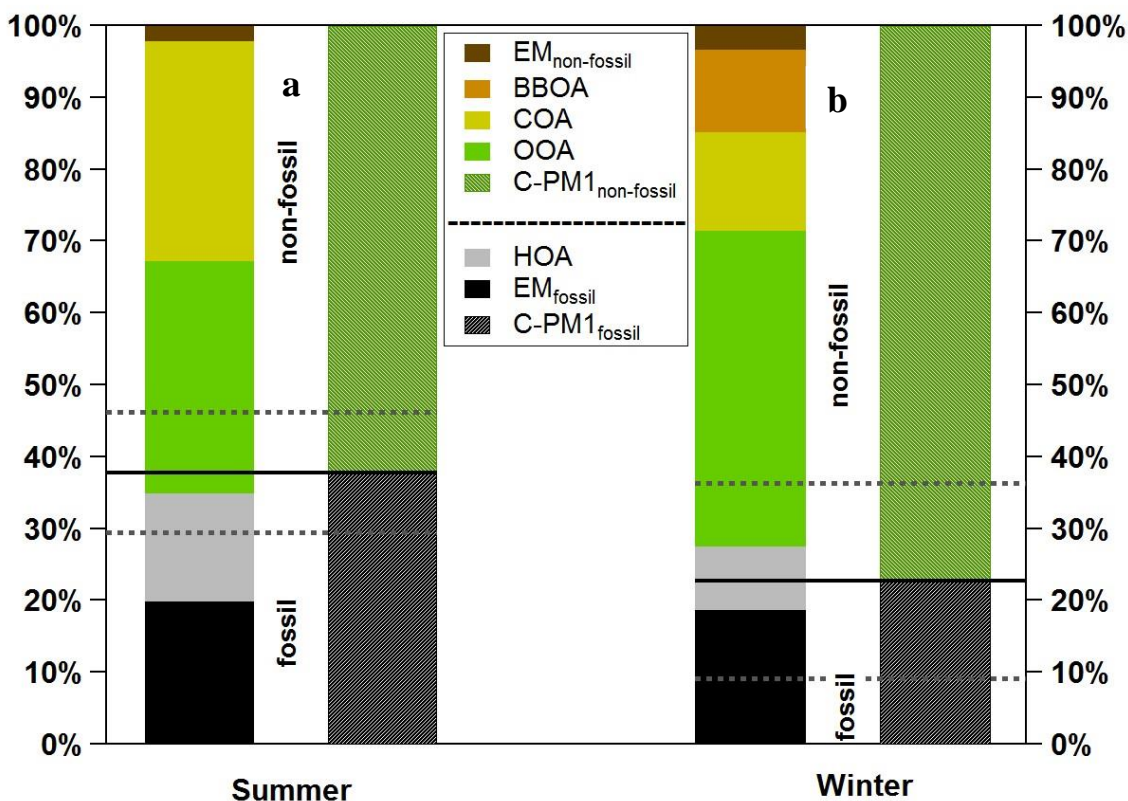


Fig. 7. Combined analysis of AMS derived PM₁ OA fractions and elemental carbon with results from non-fossil and fossil fuel carbon ¹⁴C analysis, for the summer (a) and the winter (b) campaign at the urban downtown site. The left columns for each season show the source apportionment from AMS and EC measurements, the right columns the fossil and non-fossil fractions of carbonaceous PM₁. Combined, both columns allow the attribution of the individual aerosol types to fossil and non-fossil parts. EM denotes elemental carbon matter, BBOA biomass burning OA, COA cooking OA, OOA oxygenated OA, HOA hydrocarbon-like OA (associated with traffic). The dashed lines represent the combined uncertainties of the ¹⁴C measurement and the splits between OC and EC, fossil and non-fossil EM and OOA and their variability as a fractional contribution to carbonaceous PM₁. Note that for winter time, the fossil fuel EC and primary OA fractions identified from AMS-PMF analysis are somewhat larger than the total fossil fuel carbonaceous PM₁ from the ¹⁴C analysis, but agree within their uncertainties.

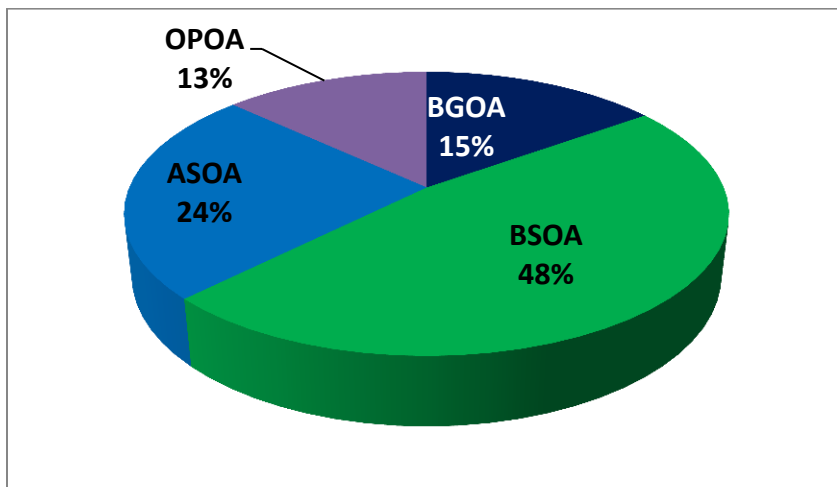


Fig. 8. Contributions to secondary organic aerosol during the MEGAPOLI summer campaign period, simulated with the CHIMERE model: BGOA (background organic aerosol), BSOA (biogenic SOA), ASOA (anthropogenic SOA), OPOA (oxidized primary OA of anthropogenic origin). BSOA and BGOA are considered as of non-fossil , ASOA and OPOA as of fossil origin.

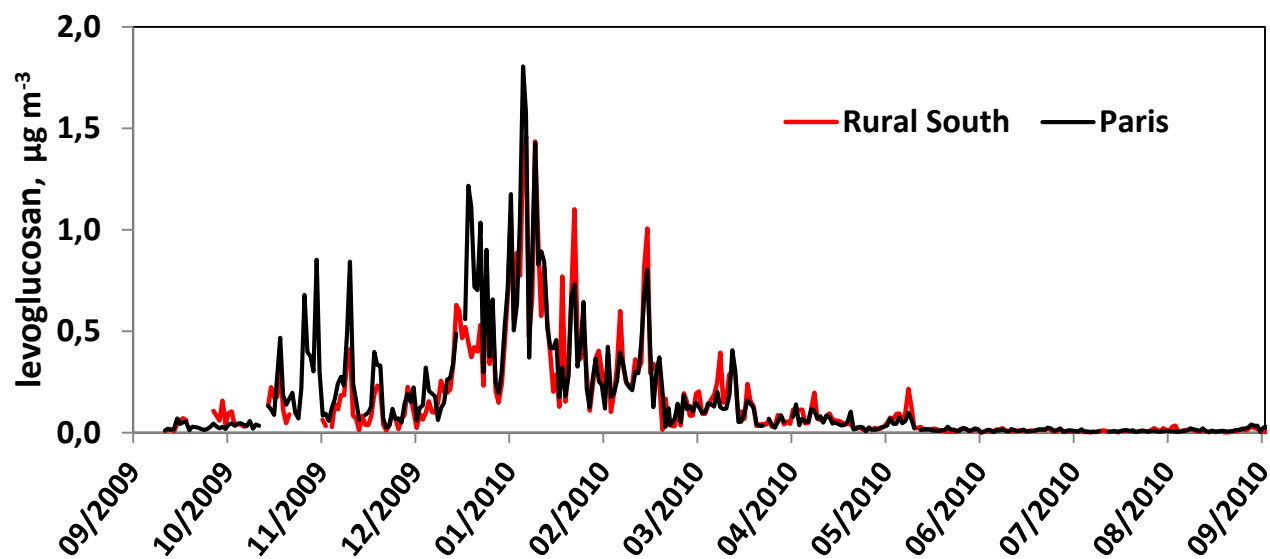


Fig. 9. Daily levoglucosan values observed during the PARTICULES project from September 2009 to September 2010 at the downtown urban and southern rural sites. The rural site is located far from direct sources. Levoglucosan is a tracer for wood burning emissions. The similar values at both sites ($R^2 = 0.83$, slope rural vs. downtown site 0.84) suggest a strong regional control of woodburning related organic aerosol.

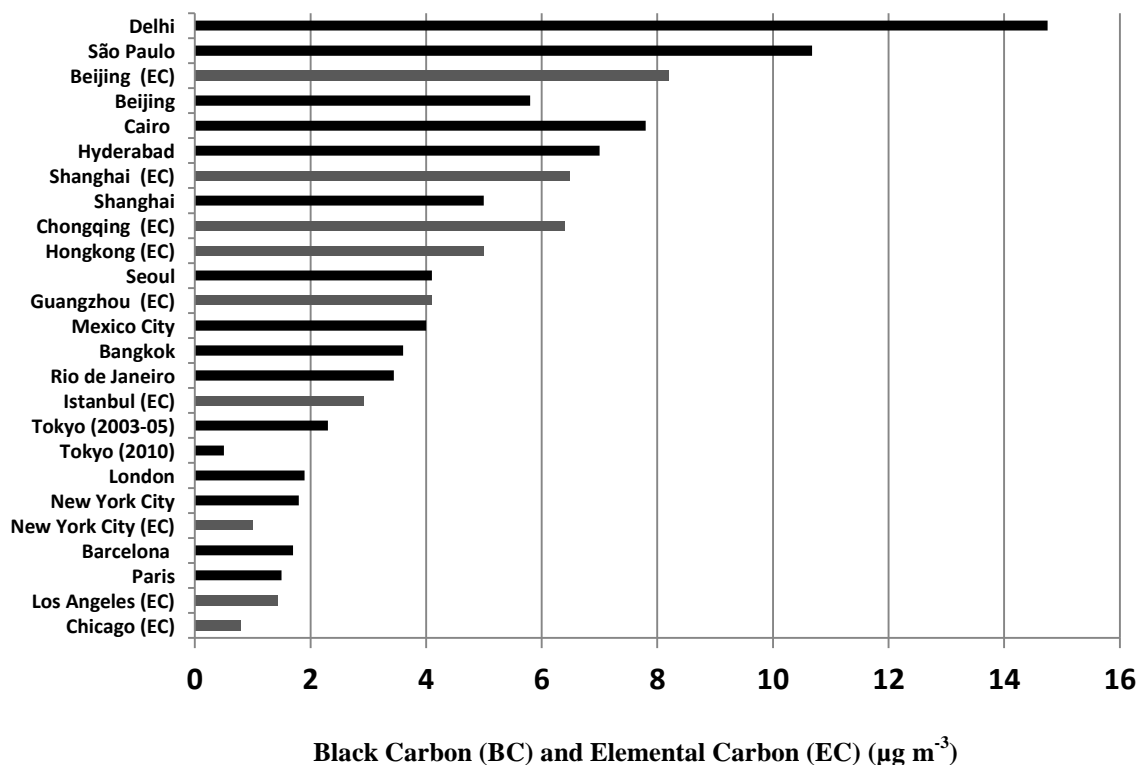


Fig. 10. Concentrations of BC (black) and EC (grey) observed in megacities across the world. Note that Bangkok, Barcelona, Chicago, Chongqing Hyderabad and London have fewer inhabitants (Table S2) than the 10 million accepted as a limit for megacities. The uncertainty due to differences in the measurement methods and in the representativeness for urban background conditions is estimated to approximately 50% (Section S3 in the supplementary material). References for the studies used here are given in Table S2.