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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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Supplementary Material

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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S1 Combined use of radiocarbon and AMS measurements for source apportionment

S1.1 Radiocarbon measurements

Analysis of the radioactive isotope ^{14}C is a unique tool for distinguishing fossil (F) and non-fossil (NF) sources of carbonaceous aerosol, as ^{14}C in fossil fuels is depleted whereas other emissions (e.g. biogenic emissions, biomass burning, etc.) have a contemporary ^{14}C level (Szidat, 2009a). Aerosol particles were collected on a 48 h basis at the urban downtown site onto pre-baked quartz fiber filters (Pallflex 2500QAT-UP) using a low volume sampler with a PM_1 inlet. The filters were stored after sampling at -18°C prior to the analysis. 8 summer and 13 winter samples were chosen for radiocarbon measurements of the total carbon (TC). The sample preparation was carried out using the THEODORE system and the procedure as described in Szidat et al., (2004). ^{14}C measurement was then performed using the accelerator mass spectrometry system MICADAS (Synal et al., 2007; Ruff et al., 2007) at the Institute of Ion Beam Physics at the Swiss Federal Institute of Technology (ETH) Zurich.

Elemental carbon (EC) and organic carbon (OC) concentrations were measured on the same filters using a thermo-optical OC/EC analyser (Model 4L equipped with a non-dispersive infrared (NDIR) detector, Sunset Laboratory Inc, USA) following the thermal-optical transmittance method (TOT) using the EUSAAR2 protocol (Cavalli et al., 2010).

S1.2 Apportionment of fossil and non-fossil contributions of the PMF factors

The PMF factors from primary emission sources were classified as fossil or non-fossil. HOA (hydrocarbon-like organic aerosol), which largely originates from traffic, was assumed to be 100% fossil, thus neglecting the small biofuel contribution. COA (cooking related organic aerosol) and BBOA (biomass burning organic aerosol) were assumed to be 100% non-fossil. The fossil and non-fossil fractions of the OOA (oxidized organic aerosol) factor ($f_{OOA,F}$ and $f_{OOA,NF}$, respectively) were estimated by combining all PMF factors with OC, EC, and radiocarbon measurements as discussed below.

The fossil and non-fossil contributions to EC were estimated as follows: for summer, EC was assumed to be 90.5% fossil, which represents an average for several urban European stations

covering a range from 84% to 97% as presented in Minguillón et al., (2011). For winter, EC was divided into EC_{NF} (mostly biomass burning) and EC_F (mostly traffic) using measurements from a 7-wavelength Aethalometer and a model based on optical absorption (Sandradewi et al., 2008a), where biomass burning and traffic exhibit different wavelength dependencies. To account for non-carbon elements (H, O…) in EC, an EM:EC ratio of 1.1 was assumed (Seinfeld and Pandis, 2006) (EM standing for elemental carbon matter). OC_F and OC_{NF} were then calculated by subtracting EC_F and EC_{NF} from TC_F and TC_{NF} measured with ^{14}C analysis.

The OOA factor was apportioned into fossil and non-fossil fractions using as inputs the PMF factor mass concentrations, OM:OC ratios estimated according to the method of Aiken et al. (2008), OC_F, and OC_{NF}. The iterative calculation proceeds as follows:

1. An initial guess for $f_{OOA,NF}$ is made.
2. Using this guess together with OC_F, OC_{NF}, and the PMF mass concentrations and OM:OC ratios, the fossil and non-fossil fractions of organic material are calculated (OM_F and OM_{NF}).
3. A new value for $f_{OOA,NF}$ is calculated using OM_F, OM_{NF}, and the non-OOA PMF factor mass concentrations. This new $f_{OOA,NF}$ is compared to the initial guess in step (1). The "guess" value is varied until the calculations in steps (1) and (3) agree, thus yielding a self-consistent solution.

Obtaining the total carbonaceous PM_1 (C-PM_1) apportionment requires combining the online AMS measurements with filter-based OC and EC measurements. As expected, discrepancies exist between the AMS and filter-based OC measurements. Sources of these discrepancies include differing size cuts, well-known filter sampling artifacts (adsorption of volatile gas phase organic compounds and evaporation of semi-volatile compounds), and uncertainties in the composition-dependent AMS collection efficiency. Therefore in Figure 7 the AMS OC is scaled to the filter-measured OC, because ^{14}C was measured on the filters.

S1.3 Uncertainty of the apportionment into fossil and non-fossil fraction

The dashes lines in Figure 7 denote the statistical significance of the estimates for OOA_F and OOA_{NF} across the entire sample period (8% for summer and 14% for winter, in terms of the C-PM_1 fraction). These lines incorporate estimates of (1) sample-to-sample variability (5% for summer and 11% for winter) and (2) measurement uncertainty (7% for summer and 8% for winter).

The total sample-to-sample variability (1) includes the sample-to-sample variability of the EM_F and EM_{NF} fractions which is 0.6% for winter and 0% for summer (because of the assumed constant fraction of EC_F) and the sample-to-sample variability of the OOA_F and OOA_{NF} fractions (5% and 11% for summer and winter, respectively).

The measurement uncertainty (2) includes uncertainties in the measurement of total ^{14}C (4% for summer and 3% for winter), fossil vs. non-fossil EM (4.4% for winter and 2.9% for summer), uncertainty of fossil vs. non-fossil OOA (4.2% and 5.7% for summer and winter respectively) introduced by the uncertainty in the EC/OC split (11%) which is included in the calculation, and uncertainty of the PMF solution (by varying the *fpeak*) on the OOA_F and OOA_{NF} fractions (1% for summer and winter). These uncertainties are discussed individually (now as relative uncertainties of the individual components) below.

The uncertainty of ^{14}C results includes the measurement error of the MICADAS, the uncertainty of a mass dependent blank correction and the correction for the bomb excess ^{14}C introduced into the atmosphere between 1950 and 1960 (Szidat, 2009a). The average uncertainty for the discrimination between fossil and non-fossil TC for all samples is 3.7 %.

The separation between EC and OC is method-dependent and the results can differ significantly from method to method. A 25% uncertainty of EC was assumed to account for possible differences due to different thermo-optical protocols (Schmid et al., 2001; Szidat et al., 2009b). Consequently, using this uncertainty and the measured EC/OC ratios an average OC uncertainty of 11% was derived.

Since EC accounts for about 30% of TC in summer and winter the discrimination between EC_F and EC_{NF} strongly affects the split between OC_F and $OC_{NF.}$ In summer, the whole 13% range (84% to 97%) of EC_F taken from several urban European stations (Minguillón et al., 2011) was considered as the uncertainty on the split between EC_F and $EC_{NF.}$ In winter, an uncertainty for the BC_{BB}/BC_{TR} ratio equal to 20% was considered (Sandradewi et al., 2008b).

The effect of the PMF solution uncertainty on the OOA_F and OOA_{NF} calculations was investigated by varying the PMF *fpeak* parameter (see section on aerosol mass spectrometer (AMS) measurements and positive matrix factorization (PMF)). This analysis provides a set of factors with potentially different absolute concentrations and OM:OC ratios that are approximately mathematically equivalent to the selected solution. However, the set of solutions obtained within the studied *fpeak* range produces less variability in the calculated fossil/non-

fossil OOA (3% for summer and 2% for winter) than does the variability of the individual samples (16% for summer and 25% for winter), because *fpeak*-induced changes in the factor mass concentrations are nearly cancelled by the corresponding changes in factor OM:OC ratios. The 11% uncertainty of the EC/OC split was included in the calculation of the OOA_F and OOA_{NF} fractions resulting in an additional uncertainty of 13% for the OOA split.

S2 Satellite data

S2.1 AOD measurements with the Advanced Along Track Scanning Radiometer (AATSR) instrument

The aerosol optical depth (AOD) was retrieved using radiances measured with the Advanced Along Track Scanning Radiometer (AATSR) on board the ENVIronmental SATellite (ENVISAT). The AATSR ground pixel resolution is 1x1 km^2 at nadir, but the retrievals are made for a resolution of 10×10 km^2. AATSR has two viewing angles, one near nadir and the other one at 55^o forward. For aerosol retrieval over land both views are used (Veefkind et al., 1998) after masking clouds in each of the views for individual pixels (Curier et al., 2009). The retrieval algorithm utilizes an *a priori* aerosol model consisting of a mixture of absorbing and non-absorbing models for fine particles and a mixture of sea salt and dust for coarse particles; during the retrieval the aerosol concentration as well as the ratios between fine and coarse mode are adjusted to fit the observations. In a post-processing step, the standard deviation of the AOD at 0.555 μm in the 10x10 km^2 box was used as a measure for the uniformity to account for both surface inhomogeneity and missed clouds, and pixels with a standard deviation above 0.1 were excluded. The results correlate well with ground-based AOD measurements from the AERONET network (Holben et al., 2001), with a correlation (R) of up to 0.8. The retrievals over sea are not shown here because there is an artifact due to the occurrence of sediment in the water in coastal regions which is not properly accounted for in the AATSR aerosol retrieval algorithm.

S2.2 Tropospheric NO_2 columns

The shown tropospheric columns are derived by applying a stratospheric correction based on SCIAMACHY limb measurements (Beirle et al., 2010), and a conversion of slant to vertical

column density based on an uniform relative tropospheric profile. Cloud-free satellite ground pixels (30×60 km^2) are gridded with 0.1° resolution and averaged for March-October 2009.

S3 Black carbon measurements in selected megacities

Observed black carbon (BC) and elemental carbon (EC) concentrations in several megacities were compiled in order to put levels observed in the Greater Paris area into a broader context (Fig. 10, Table S2). This type of comparison can give a qualitative picture, but is limited by several factors, among which are (i) different measurement techniques, (ii) different site characteristics, (iii) and different measurement periods.

To create a representative cross-section we compiled BC as well as EC concentrations. However, differences of a factor of two between different thermal, optical, and thermal/optical carbon analysis methods for EC and BC are common (Watson et al., 2005, Bond et al., 2013). Yet, differences between methods are not consistent among comparison studies. As the aim was to collect urban background data, data for curbsides were excluded. Nevertheless, for some of the results presented, the authors mention that the sites are highly traffic influenced (Miranda et al., 2012) and therefore the BC concentrations for São Paolo and Rio de Janeiro may be on the high side of values for an urban station within these cities.

The importance of the measurement technique is illustrated by the BC and EC data for New York City (Rattigan et al., 2011). Although BC and EC data were highly correlated, a pronounced seasonal BC/EC gradient was found with a summer ratio of about two, but only 1.2 during winter. For Beijing, data are taken from different studies (Dan et al., 2004; Gros et al., 2007; Yang et al., 2011) at different urban background sites, during different periods and with different measurement techniques. Still the range of BC levels is relatively small (5.5-8.2 μgm^{-3}). Hence, both the BC and EC data for New York City and Beijing in Figure 10 indicate that the uncertainty for each city is easily 30-50% but the pattern with relatively low concentrations in megacities with a relatively high technological development status (e.g. Paris, London, New York City, and Tokyo) appears as robust.

S4 Construction of bottom-up and down-scaled emission inventories

European countries are parties to the convention of long-range transboundary air pollution (LRTAP) and obliged to annually report their emission data. The aggregated emission database is

accessible through http://www.ceip.at/. To facilitate regional air quality modeling, an European wide gap filled, emission data base was constructed and spatially distributed on a 0.125° by 0.0625° longitude-latitude resolution (~7 x7 km²) grid (Pouliot et al., 2012). National source sector total emissions were broken down into contributions from approximately 200 source categories. Each source category was linked, when possible, to spatial distribution proxies such as population density, power plant capacity and location, road network and traffic intensity. Through this approach, national total emissions are down-scaled to a finer grid (Pouliot et al., 2012). From this, the total emissions within the administrative borders of large cities (London, Paris) can be estimated (down-scaling approach). The alternative, more accurate, determination of city emissions is a municipal scale "bottom-up" inventory, beginning from local data at municipal level or even from the specific object of the emission (e.g. a city road network with traffic counts). Using this information and proper emission factors, the *bottom-up* inventory quantifies emissions directly at local level. When comparing down-scaled and bottom-up emission estimates for European megacities, it was found that the PM city emissions are overestimated by a factor of 3-4 through the down-scaling approach (Timmermans et al., 2013). The major reason for the over-allocation of emissions in the city through downscaling is that population density is an important proxy for distributing the national emissions from several source sectors. Such a population-based downscaling fails to take local measures, like the London ban on solid fuels for residential heating, into account. Furthermore, energy use in cities is more efficient, with e.g., block heating for large apartment buildings and flats compared to individual houses in rural areas, and relatively small surface area per person in city houses. The result is that on a per capita basis, a megacity person emits less pollution than the average citizen. This has been shown previously for CO_2 emissions (Lobo et al., 2009) and as we show here for Paris and London, holds even stronger for other air pollutants. For modelling issues, a hybrid emission inventory especially prepared for the MEGAPOLI project was used, which integrates the bottom-up emissions inventories for several megacities including Paris (Timmermans et al., 2013) into the European emission data base (Pouliot et al., 2012).

S5 Chemistry transport modelling

S5.1 PMCAMx model

PMCAMx (Fountoukis et al., 2011 ; Karydis et al., 2011; Murphy et al., 2009; Tsimpidi et al., 2010, 2011) describes the processes of horizontal and vertical dispersion, wet and dry deposition, and gas-phase chemistry. The PMCAMx European modeling domain covers a 5400 × 5832 km² region in Europe with 36 × 36 km² grid resolution and 14 vertical layers. The model was set to run with coarse grid spacing (36 × 36 km²) over the wide European domain, while within the same run, a fine grid nest was applied over the greater Paris area with a higher resolution (4 × 4 km²). The Paris subdomain covers a total area of 216 × 180 km² with the city center placed centrally in the subdomain. PMCAMx was set to perform simulations on a rotated polar stereographic map projection. Application periods include a summer (1-30 July 2009) and a winter (10 January – 9 February 2010) period. For the Mexico City calculations, the modeling domain covers a 210×210 km region with 3×3 km grid resolution (Murphy et al., 2009).

S5.2 CHIMERE model

The CHIMERE model (Bessagnet et al., 2008; Hodzic et al., 2010; Menut et al., 2013) was used for simulations of a yearly period from September 2009 to September 2010 in a specific version (ESMERALDA plate-form) set-up by AirParif (Petetin et al., 2014). Emissions for Northern France are those from the plate-form, while European emissions are from EMEP (Vestreng et al., 2007). In addition, for the summer period (July 2009) of the MEGAPOLI campaign, the model was set-up in a specific configuration (Zhang et al., 2013) including the Volatility Basis Set approach for treatment of organic aerosol (Murphy et al., 2009), and using the emission inventory described in S4. Climatological background organic aerosol values (BGOA) were fixed at model boundaries (Seinfeld and Pandis, 2006) and are highly oxidized. Major aerosol compounds (BC, primary and secondary OA, ions) were in general simulated better than ± 30% as compared to observations from the MEGAPOLI summer and campaign (Zhang et al., 2013).

S6 Classification of air mass origin during the MEGAPOLI campaigns

Air mass origins at the Golf de la Poudrerie site at Livry Gargan during the MEGAPOLI campaigns were classified into a SW sector with marine origin and a NE sector with continental origin according to two criteria:

- Surface wind directions from the south-west sector (180° - 270°) or from the north-east sector (0° - 90°). Wind data were taken from measurements at the NE suburban site, because results from this classification were in particular applied to data obtained at this location.
- Results of dispersion model calculations on air mass origin. The Lagrangian Particle Dispersion Model FLEXPART (Stohl et al., 2005) was used in backward mode driven by meteorological data from the ECMWF model (1x1 degree global resolution, 0.18 x 0.18 degree nested resolution for Europe). For each 3 hour interval 60000 particles were released from a receptor location and followed backward in time for 20 days. Aerosol wet and dry deposition was also accounted for. Footprint emission sensitivities for aerosol tracers, proportional to the residence time of an air mass over a given grid cell in the lowest 100 m of the atmosphere, were used for the last 10 days before particle release. An air mass was classified as *marine*, if its residence time over Europe was less than one day, before the retro-plume crossed the Atlantic. It was considered as *continental*, if its residence time over Central Europe was at least two days.

Both criteria of SW surface wind sector plus a marine air mass origin or a NE surface wind sector plus a continental air mass origin had to be fulfilled simultaneously. During the summer campaign, 361 h were classified as SW/marine, and 43 h as NE/continental. During wintertime these numbers were 99 h and 138 h, respectively.

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Tables:

Table S1:

Speciation of average PM1 values at the three primary sites during the Megapoli summer and winter campaigns

Summer (µg/m3)	Urban site	NE suburban site	SW suburban site
Org	3.70	3.87	2.62
NO3	0.45	0.34	0.31
SO4	1.41	1.32	1.30
NH4	0.52	0.57	0.43
BC	1.37	1.14	0.67
Sum PM1	7.45	7.22	4.93

Winter (µg/m3)	Urban site	NE suburban	SW suburban
Org	6,02	4,58	6,08
NO3	4,74	4,35	5,17
NH4	2,00	2,02	2,51
SO4	2,63	2,17	2,94
BC	1,12	1,93	1,58
Sum PM1	16,72	15,17	18,47

Table S2.
Origin of black and elemental carbon data and observation periods used in Figure 10, and megacity population in year 2011.

City	Observation Period	Reference	Population in 2011 (in 10^6)
Bangkok	April 2008 – March 2008	Sahu et al. (2008)	8.4
Barcelona	January – December 2009	Reche et al. (2011)	5.6
Beijing	August 2004	Gros et al. (2007)	15.6
	Summer (July – August 2001; June – July 2002)		
	Winter (December 2001 – January 2002 and December 2002); Spring (March 2003).	Dan et al. (2004)	
Beijing (EC)	March 2005 - February 2006	Yang et al. (2011)	
Cairo	March - April 2005	Favez et al. (2008)	11.2
Chicago	January 2005 – December 2008	Hand et al. (2011)	9.7
Chongqing	March 2005 - February 2006	Yang et al. (2011)	9.9
Delhi	January 2006 - January 2007	Banoa et al. (2011)	22.7
Guangzhou	December 2008 - February 2009	Yang et al. (2011)	7.1
Hyderabad	January – December 2003	Latha and Badarinath (2005)	7.6
Hong Kong	November 2000 - February 2001 and June to August 2001	Ho et al. (2006)	7.1
Istanbul	November 2007 - June 2009	Theodosi et al. (2010)	11.2
London	January – December 2009	Reche et al. (2011)	9.0
Los Angeles	January 2005 – December 2008	Hand et al. (2011)	13.4
Mexico City	March 2006	Aiken et al. (2010)	20.4
New York City	2006 – 2008	Rattigan et al. (2011)	20.4
Paris	September 2009 – September 2010	This study	10.6
Rio de Janeiro	June 2007 - August 2008	Miranda et al. (2012)	12.0
São Paulo	June 2007 - August 2008	Miranda et al. (2012)	19.9
Seoul	2003 – 2004	Kim et al. (2007)	10.3
Shanghai	March 1999 - May 2000	Ye et al. (2003)	20.2
Tokyo	2003 - 2005 2010	Kondo et al. (2012)	37.2