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Evaluation of State-of-the-Art CTMs Using New Experimental Datasets
MEGAPOLI Deliverable D3.6

M. Beekmann, C. Fountoukis, Q.J. Zhang, S. N. Pandis
and the MEGAPOLI Campaign Team

Simulated CHIMERE urban OA plume on 16 July 2009 at 07 and 16 UTC
/OA mass concentrations are given in µg m⁻³/

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Main Author(s):
M. Beekmann (1), C. Fountoukis (2), Q.J. Zhang (1), S. N. Pandis (2)

(1) Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), Créteil, France
(2) Institute of Chemical Engineering and High Temperature Chemical Processes, Foundation for Research Technology Hellas (FORTH), Patra, Greece

Contributing Author(s):
-

Responsible institution(s):
Centre National de Recherche, Laboratoire Interuniversitaire des Systèmes Atmosphériques (CNRS-LISA)

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Abstract

Detailed observations obtained during the summer 2009 and winter 2010 MEGAPOLI campaign in and around the Paris agglomeration are used for the evaluation of two state-of-the-art chemical transport models (CHIMERE and PMCAMx). Aerosol and gas phase measurements obtained at three sub(urban) grand based sites and from research flights in the pollution plume during the MEGAPOLI campaigns are compared against the model predicted concentrations for the same periods. The simulation of organic aerosol is a major focus of this evaluation, given the inability of past modeling efforts to reproduce observations in polluted areas. Model predictions are compared against high time resolution (AMS) measurements of fine particulate matter from the three sites and from the aircraft.

PMCAMx-2008, a detailed three dimensional chemical transport model (CTM), is applied for the first time in the European domain to simulate the mass concentration and chemical composition of particulate matter (PM). The CHIMERE CTM has been largely used for pollution simulation and air quality forecast over Europe or European sub-domains. Both models have not yet been compared with detailed aerosol and gas phase measurement such as those obtained within the MEGAPOLI project. Both models include a state-of-the-art organic aerosol module which is based on the volatility basis set framework treating both primary and secondary organic components to be semi-volatile and photochemically reactive.

The comparison of the model predictions with the ground and aircraft measurements is encouraging. Models reproduce successfully the secondary organic aerosol (SOA) transport to the agglomeration, and its build-up within the Paris plume. This is clearly a positive result, given the difficulty for chemistry-transport models to correctly simulate SOA.
1. Introduction

Sulfate and organics are the major components of sub-micrometer particles (PM\textsubscript{1}) in most locations throughout the world. Organic particulate matter, originating from many different natural and anthropogenic sources and processes, is the least understood component of atmospheric aerosols. More than 50% of the atmospheric fine aerosol mass can be comprised of organic compounds at continental mid-latitudes and as high as 90% in tropical forested areas (Andreae and Crutzen, 1997; Roberts et al., 2001; Kanakidou et al., 2005). Organic aerosol (OA) is generally categorized into two types; primary organic aerosol (POA) which is injected into the atmosphere in the particulate phase and secondary organic aerosol (SOA) which is emitted as volatile organic compounds (VOCs) in the gas phase and then reacts and condenses in the particulate phase. In order to gain more insight into sources and processes of organic aerosol, quantification, characterization and speciation of organic aerosol is needed which was until recently hindered by analytical difficulties (Kanakidou et al., 2005). For instance, conventional techniques (e.g. GC-MS) can only be used for the speciation of a small fraction of the OA mass. Within the last decade, several new methods have emerged that can analyze and quantify the different types of OA present in ambient aerosol. Among several measurement techniques, the Aerosol Mass Spectrometer (AMS) is the most commonly used to measure the size-resolved mass concentration and corresponding total mass spectrum of organic aerosols with a time resolution of minutes (Jayne et al., 2000; Zhang et al., 2005a; Takegawa et al., 2005). Information about processes or sources contributing to the OA levels can be provided from the Positive Matrix Factorization (PMF) method (Paatero and Tapper, 1994; Paatero, 1997; Lanz et al., 2007, 2009; Ng et al., 2009) or the custom principal component analysis (Zhang et al., 2005b) of the AMS measurements. These methods allow a classification of the OA into two different types based on their different temporal and mass spectral signatures; the hydrocarbon-like organic aerosol (HOA) and the oxygenated organic aerosol (OOA) which together usually account for all the OA mass measured by the AMS (Zhang et al., 2005b). HOA correlates with fossil fuel fresh POA in urban areas while OOA correlates with secondary OA.

During the MEGAPOLI summer and winter campaigns, detailed aerosol and gaseous measurements have been obtained at three ground based sites located within the Paris greater area: LHVP within Paris (13 Arrondissement), SIRTA at the south-western edge of the agglomeration, and GOLF at its north-eastern edge (see MEGAPOLI Deliverable 3.1). In addition, aircraft measurements were taken in the Paris pollution plume during more than ten flights (see MEGAPOLI Deliverable 3.4).

These data are used for the evaluation of two state-of-the-art chemical transport models (CTMs), PMCAMx-2008 and CHIMERE. These models and their specific settings for this application are described in Chapter 2. Evaluation results are given in Section 3. PMCAMx-2008 is compared both to summer and winter campaign observations at ground based sites. CHIMERE is compared to summer campaign observations at the ground-based sites and aloft.
2. Model Description and Application

2.1 PMCAMx-2008

2.1.1 Model description

PMCAMx-2008 (Murphy and Pandis, 2009; Tsimpidi et al., 2010; Karydis et al., 2010) uses the framework of the CAMx air quality model (Environ, 2003) describing the processes of horizontal and vertical advection, horizontal and vertical dispersion, wet and dry deposition, and gas-phase chemistry. For the aerosol processes, three detailed aerosol modules are used. The approach of Fahey and Pandis (2001) is used for the simulation of aqueous-phase chemistry. The inorganic aerosol growth is described in Gaydos et al., (2003) and Koo et al., (2003), and the secondary organic aerosol (SOA) formation and growth in Koo et al. (2003). These aerosol modules use a sectional approach to dynamically track the size evolution of the aerosol mass across 10 size sections spanning from 40 nm to 40 μm. The aerosol species modeled include sulfate, nitrate, ammonium, sodium, chloride, potassium, calcium, magnesium, elemental carbon, primary and secondary organics. The chemical mechanism used in the gas-phase chemistry is based on the SAPRC99 mechanism (Carter, 2000; Environ, 2003). The mechanism includes 211 reactions of 56 gases and 18 radicals.

Three options are available in PMCAMx-2008 for the simulation of inorganic aerosol growth. The most computationally efficient approach is the bulk equilibrium approach, which assumes equilibrium between the bulk inorganic aerosol and gas phase. At a given time step the amount of each species transferred between the gas and aerosol phases is determined by applying the aerosol thermodynamic equilibrium model ISORROPIA (Nenes et al., 1998) and is then distributed over the aerosol size sections by using weighting factors for each size section based on their surface area (Pandis et al., 1993). The second approach (hybrid approach) assumes equilibrium for the fine particles (<1 μm) and solves the mass transfer differential equations for the coarse particles (Capaldo et al., 2000). The most accurate but computationally demanding method is the dynamic approach where mass transfer is simulated explicitly for all particles (Pilinis et al., 2000). In this work we use the bulk equilibrium approach since we are focusing on the model’s performance for fine particles. Based on the approach of Shrivastava et al. (2008), primary organic aerosol in PMCAMx-2008 is assumed to be semivolatile. Nine surrogate POA species are used, with effective saturation concentrations at 298 K ranging from 10^{-2} to 10^{6} μg m^{-3}. POA is simulated in the model in three two types, “fresh” (unoxidized) POA, and oxidized POA (OPOA) and any aged organic aerosol transported into the domain from the boundary conditions. For the intermediate VOC (IVOC) emissions we followed the approach of Tsimpidi et al. (2010) and Shrivastava et al. (2008), in which IVOC is in equilibrium with emitted particulate OA mass. Emission inventories do not include these compounds because of the difficulty in measuring mass in this volatility range (it is emitted and remains largely in the gas phase), and thus we add an additional 1.5 times the original POA mass emission rate to the intermediate volatility organic gas emission rate following several past studies (Robinson et al., 2007; Murphy and Pandis, 2009; Hodzic et al., 2010; Tsimpidi et al., 2010). In the gas phase, this mass can be oxidized by OH and may go to lower volatility and condense. SOA consists of organic aerosol of anthropogenic (aSOA) and biogenic (bSOA) origin. The SOA volatility basis-set approach (Lane et al., 2008a) used in the current version of the model includes four SOA species for each VOC with 4 volatility bins (1, 10, 100, 1000 μg m^{-3}). Laboratory results from recent smog-chamber experiments (Ng et al., 2006; Hildebrandt et al., 2009) have been used to update the SOA module in PMCAMx in order to include anthropogenic aerosol yields. The SOA module incorporates NOx-dependent SOA yields (Lane et al., 2008b) which are based on an assumed density of 1.5 g cm^{-3}. The model treats all organic species (primary and secondary) as chemically reactive.
Chemical aging through gas-phase oxidation of OA vapors is modeled using a gas-phase OH reaction with a rate constant of $k = 1 \times 10^{-11}$ cm$^3$ molec$^{-1}$ s$^{-1}$ for anthropogenic SOA and $k = 4 \times 10^{-11}$ cm$^3$ molec$^{-1}$ s$^{-1}$ for the primary OA (Atkinson and Arey, 2003). The base-case simulation does not age biogenic SOA (Ng et al., 2006; Presto et al., 2006; Lane et al., 2008b). Each reaction is assumed to decrease the volatility of the vapor material by a factor of 10.

### 2.1.2 Model application

The PMCAMx-2008 coarse grid modeling domain covers a 5400 × 5832 km$^2$ region in Europe with 36 × 36 km grid resolution and 14 vertical layers covering approximately 6 km. PMCAMx-2008 was set to perform simulations on a rotated polar stereographic map projection. The first three days of each simulation were excluded from the analysis to limit the effect of the initial conditions on the results. Concentrations of the major PM$_1$ species at the boundaries of the domain are shown in Table 1 (for the period of July 2009), representing background concentrations with each domain side having different boundary conditions. The boundary condition organic aerosol (BC-OA) is expected to consist of both SOA and oxidized POA. Here we assume that the BC-OA is all oxidized and half of it is biogenic OA and the other half oxidized primary OA (Kanakidou et al., 2005; Farina et al., 2010). All concentrations reported here are under ambient temperature and pressure conditions.

The necessary inputs to the model include horizontal wind components, vertical diffusivity, temperature, pressure, water vapor, clouds and rainfall. The meteorological model WRF (Weather Research and Forecasting; Skamarock et al., 2005) was used to create the above inputs. WRF was driven by static geographical data and dynamic meteorological data (near real-time and historical data generated by the Global Forecast System (1 x 1 deg)). 27 sigma-p layers up to 0.1 bars were used in the vertical dimension. Each layer of PMCAMx-2008 is aligned with the layers used in WRF. The WRF run for both periods was periodically re-initialized (every 3 days) to ensure accuracy in the corresponding fields that are used as inputs in PMCAMx-2008.

### Table 1: Aerosol concentrations (in μg m$^{-3}$) at the boundaries of the domain.

<table>
<thead>
<tr>
<th>Species</th>
<th>North</th>
<th>South</th>
<th>West</th>
<th>East</th>
</tr>
</thead>
<tbody>
<tr>
<td>OA</td>
<td>1</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>Sulfate</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Ammonium</td>
<td>0.37</td>
<td>0.37</td>
<td>0.37</td>
<td>0.37</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0.1</td>
<td>0.02</td>
<td>0.01</td>
<td>0.1</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.001</td>
<td>0.005</td>
<td>0.09</td>
<td>0.03</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.002</td>
<td>0.01</td>
<td>0.1</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Anthropogenic and biogenic hourly emission gridded fields were developed for the European domain for gases and primary particulate matter. Volatile organic compounds are split based on the SAPRC 99 chemical mechanism.

The model was run with coarse grid spacing over the wide regional (European) domain in which a spatial resolution of 36×36 km$^2$ was used, while within the same run, a fine grid nest was applied over the Megacity of Paris where high resolution (4×4 km$^2$) was used (Fig. 1). High resolution emissions were used for the fine grid nest simulation while for the meteorological input of the fine grid PMCAMx-2008 was set to interpolate the meteorological fields from the parent grid. The fine grid contains the same vertical resolution with the parent grid (14 vertical layers). The PMCAMx-2008 fine grid modeling domain covers a 216 × 180 km$^2$ region in Paris with the city center cen-
trally located in the domain.

Figure 1: Modeling domain of PMCAMx-2008 for Europe (36×36 km² grid resolution) and for the Paris greater area (4×4 km² grid resolution).

2.2 CHIMERE model description and set-up

The model used in this study is the Eulerian regional chemistry-transport model CHIMERE in its version V2008b (see http://euler.lmd.polytechnique.fr/chimere). The initial gas-phase only version of the model has been described in Schmidt et al. (2001) and Vautard et al. (2001), the aerosol part in Bessagnet et al. (2004 and 2008). The model has been largely applied for continental scale air quality forecast (Honoré et al., 2008; http://www.prevair.org), and simulations, including sensitivity studies, with respect to anthropogenic (Beekmann and Vautard, 2010) and biogenic emissions (Curci et al., 2009) and inverse emission modeling (Konовалov et al., 2006). The model has been extensively applied for simulating gas phase pollution levels over the Paris region (e.g. Deguil-laume et al., 2008), and on several occasions particulate matter (e.g. Bessagnet, 2005; Hodzic et al., 2006, Sciare et al., 2010).

In this work, we used CHIMERE with nested domains, a continental domain covering Europe (CONT3) with a resolution of 0.5° ([35–57.5°N; 10.5°W–22.5°E]) and a regional domain over Northern France (MEG3) covering all the flight patterns during this campaign (see MEGAPOLI Deliverable 3.4) with a resolution of 3 km (see Figure 2). 8 hybrid-sigma vertical layers are used, with the first layer at about 40 m, extending to 500 hPa.

Troposphere photochemistry is represented using the reduced MELCHIOR chemical mechanism (Lattuati, 1997; Derognat, 2003), including 120 reactions and 44 prognostic gaseous species. For simulation of the particulate phase, 8 bins of particulate sizes are used in the model from 0.04 to 10 µm. Condensation of semivolatile organic and inorganic gases is simulated with a coupled dynamic-thermodynamic scheme. The thermodynamic mechanism of inorganic species (sulfate, ni-
trate and ammonium) is interpolated from the tabulation calculated with the ISORROPIA model (Nenes et al., 1998).

![Figure 2: The two nested simulation domains, a continental domain CONT3 (in red) with a resolution of 0.5° and a Northern France domain MEG3 (in blue) with a resolution of 3 km.](image)

For the MEGAPOLI project, the VBS approach for SOA formation has been implemented in CHIMERE similar to work described in Hodzic et al. (2010). This scheme has already been described in Section 2.1 for the PMCAMx-2008 model. Here only specific settings in our application are described. The oxidation and aging of SVOC from evaporated POA is simulated with a kinetic reaction rate of OH of $4 \times 10^{-11}$ cm$^3$ molec$^{-1}$ s$^{-1}$ (Robinson et al., 2007). The oxidation of anthropogenic and biogenic VOCs and the aging of their semivolatile products are simulated according to Murphy and Pandis (2009) with yields corresponding to “low” NOx parameterization. Aging is included both for anthropogenic and biogenic VOC with a kinetic reaction rate of OH of $1 \times 10^{-11}$ cm$^3$ molec$^{-1}$ s$^{-1}$. Among others, numerical experiments with an explicit chemical mechanism coupled to a condensation scheme indicate that gas phase aging is important for SOA formation from α-pinene (Valorso et al., 2010). Sensitivity tests with different settings of the SOA formation scheme are described in the MEGAPOLI Deliverable 3.7.

Meteorological parameters are input for CTM with results from simulations with PSU/NCAR MM5 model (Dudhia, 1993) for the two nested domains with 45 km (European domain) and 15 km (North-West Europe) resolution. In the vertical, 23 vertical sigma layers extend up to 100hPa MM5 is forced by the 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.

Anthropogenic gas phase emissions are calculated from EMEP annual totals (http://www.ceip.at/emission-data-webdab), black carbon (BC) and primary organic aerosol (POA) are prescribed from the Laboratoire d’Aerologie data-base (Junkle and Louisse, 2008). These emissions are scaled to hourly emissions applying temporal profiles provided by IER (Friedrich, 1997). They are down-scaled to the high resolution grid over Northern France using an urban landuse fraction. Biogenic emissions are calculated using the MEGAN model data and parameterizations (Guenther et al., 2006).

CHIMERE simulations use boundary conditions from a monthly climatology simulated with the LMDz-INCA2 and LMDz-AERO general circulation model. The boundary condition for organic aerosol concentrations at the western model boundary (Atlantic) is set to 0.7 µg m$^{-3}$ according to
long-period measurements and climatologic analysis (*Seinfeld and Pandis, 2006*).
3. Evaluation Results

3.1 PMCAMx-2008

Figures 3 and 4 show the PMCAMx-2008 average ground-level concentrations for PM\textsubscript{1} total mass, organic aerosol, elemental carbon, sulfate, ammonium and nitrate over the two periods of simulation, respectively. Overall, during the summer period, OA is predicted to account for 25% of total PM\textsubscript{1} at ground level averaged over the entire (nested) domain, followed by nitrate (21%), sulfate (16%), ammonium (12%), and EC (6%). The remaining is crustal material, sea-salt and metal oxides. During the winter period the contribution of EC to total PM\textsubscript{1} increases to 15% while OA contributes almost the same as during the summer period, although its absolute concentrations increase by ~30% compared to the July 2009 period. Concentrations of ammonium, nitrate and sulfate are predicted to be lower during the January 2010 period, contributing 10, 11 and 8 %, respectively, to total PM\textsubscript{1} over the subdomain of the Paris area.

Figures 5 and 6 show time series of PM\textsubscript{1} OA concentrations (predicted vs. observed) at the LHVP, SIRTA and GOLF sites during the summer 2009 and winter 2010 campaigns in Paris. Model results include predictions from both the coarse and fine grid resolution. During summertime, in LHVP the average predicted concentration for total OA is 2.1 \(\mu\text{g m}^{-3}\) with the fine grid and 2.0 \(\mu\text{g m}^{-3}\) with the coarse grid compared to an AMS measured value of 3.5 \(\mu\text{g m}^{-3}\). In SIRTA the model captures the magnitude of the measured OA, predicting an average concentration of 1.8 and 1.9 \(\mu\text{g m}^{-3}\) with the fine and coarse grid, respectively, compared to an observed average OA concentration of 1.8 \(\mu\text{g m}^{-3}\). In GOLF, where concentrations are locally influenced by the nearby road traffic, the model under-predicts peak concentrations during some days. On average, the fine grid simulation predicts a concentration of 2.1 \(\mu\text{g m}^{-3}\) while the measured OA value was 2.5 \(\mu\text{g m}^{-3}\). During the winter period, concentrations of OA in Paris were higher than the summertime due to increased primary emissions from combustion processes. In the city center (LHVP site) the fine grid simulation predicts an average monthly value for OA of 4.0 \(\mu\text{g m}^{-3}\), considerably higher than the coarse grid simulation prediction (2.9 \(\mu\text{g m}^{-3}\)), and closer to the observed values. Contrary to the LHVP site, in the suburban site of SIRTA, the two simulations predict quite similar OA concentrations throughout the simulation period. At the GOLF site the 4x4 km simulation gives higher concentrations compared to the 36x36 km run, and closer to the measurements, although an under-prediction is seen as with the summertime period. The use of the fine grid resolution in the model run seems to be much more necessary during the winter rather than the summer period in reproducing OA levels in the city center. The 2 different horizontal grid resolutions produce almost identical sulfate concentrations at all sites during either the July or the January period. Figure 7 is an example of this behavior of the model, showing average diurnal profile of particulate sulfate at two sites during the summer period. Figure 8 shows time series of elemental carbon concentrations (predicted vs. observed) at LHVP during both periods. In July the model captures the magnitude of observed values reproducing the majority (90%) of the hourly average data points within a factor of 2. In winter, however, the model predicted levels of EC show an overestimation of the peak values of elemental carbon during the rush hours, which is more pronounced in the 4x4 km grid resolution, indicating possible errors in the emission rates. Overall the model performance against high time resolution measurements of OA, EC and sulfate from a highly polluted Megacity seems encouraging.
Figure 3: Ground-level concentration predictions of PMCAMx-2008 averaged over the entire simulation period (1-30 July 2009) for PM$_1$ (a) total mass, (b) total organic aerosol, (c) elemental carbon, (d) sulfate, (e) ammonium and (f) nitrate (in $\mu$g m$^{-3}$). Different scales are used.

Figure 4: Ground-level concentration predictions of PMCAMx-2008 averaged over the entire simulation period (January 10 – February 10, 2010) for PM$_1$ (a) total mass, (b) total organic aerosol, (c) elemental carbon, (d) sulfate, (e) ammonium and (f) nitrate (in $\mu$g m$^{-3}$). Different scales are used.
**Figure 5:** Comparison of PMCAMx-2008 model predictions with AMS measurements of PM$_1$ OA (in μg m$^{-3}$) taken at LHVP, SIRTA and GOLF during the summer 2009 campaign in Paris.
Figure 6: Comparison of PMCAMx-2008 model predictions with AMS measurements of PM$_1$ OA (in $\mu$g m$^{-3}$) taken at LHVP, SIRTA and GOLF during the winter 2010 campaign in Paris.
Figure 7: Average PMCAMx-2007 predicted diurnal profiles of PM$_1$ sulfate (in μg m$^{-3}$) in SIRTA and GOLF during the summer 2009 campaign in Paris. Model predictions are shown for high and low model resolution in the Paris area.

Figure 8: Comparison of PMCAMx-2008 model predictions with measurements of elemental carbon (in μg m$^{-3}$) taken at LHVP during the summer 2009 and winter 2010 campaign in Paris. Model predictions are shown for high (blue) and low (dashed black) model resolution in the Paris area.
3.2 CHIMERE

In the section, gas phase pollutants (NOx and O3) and particulate pollutants (black carbon (BC), sulfate (SO4\(^{2-}\)), nitrate (NO3\(^{-}\)), ammonium (NH4\(^{+}\)) and organic aerosols (OA) simulated with the CHIMERE model for the summer campaign are evaluated by comparisons with the measurements at 3 ground measurement sites GOLF, LHVP and SIRTA. Simulated OA is also compared to airborne gas phase and aerosol measurements. Common statistical measures as bias (relative bias to the mean concentration from both the measurements and the model (RB)), root mean square error (RMSE), relative RMSE) and correlation coefficient for particulates are presented in Table 2 for the summer campaign.

\[
RB = \frac{100}{n} \sum_{i=1}^{n} \left( \frac{V_{\text{mod}}^i - V_{\text{mes}}^i}{V_{\text{mod}}^i + V_{\text{mes}}^i} \right) 
\]

\[
RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (V_{\text{mod}}^i - V_{\text{mes}}^i)^2} 
\]

where \(n\) is the number of observations and, \(V_{\text{mod}}\) and \(V_{\text{mes}}\) are the modeled and measured values, respectively.

Table 2: Statics of model results comparing to measurements for BC, inorganic aerosols and organic aerosol in both PM1 and PM10 sections at GOLF, LHVP and SIRTA in summer.

<table>
<thead>
<tr>
<th>Statistic in summer 2009 (µg m(^{-3}))</th>
<th>PM1</th>
<th>PM10</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bias (RB)</td>
<td>RMSE (relative RMSE)</td>
</tr>
<tr>
<td><strong>GOLF</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BC</td>
<td>1.96 (92%)</td>
<td>2.90 (136%)</td>
</tr>
<tr>
<td>NO3</td>
<td>0.22 (50%)</td>
<td>0.95 (220.5%)</td>
</tr>
<tr>
<td>SO4</td>
<td>0.40 (29.6%)</td>
<td>1.06 (82.4%)</td>
</tr>
<tr>
<td>NH4</td>
<td>0.14 (22%)</td>
<td>0.54 (86.5%)</td>
</tr>
<tr>
<td>OA</td>
<td>-1.61 (-58.8%)</td>
<td>2.65 (96.8%)</td>
</tr>
<tr>
<td><strong>LHVP</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BC</td>
<td>1.98 (88.5%)</td>
<td>2.81 (125.5%)</td>
</tr>
<tr>
<td>NO3</td>
<td>0.02 (5.9%)</td>
<td>0.96 (231%)</td>
</tr>
<tr>
<td>SO4</td>
<td>0.26 (18.8%)</td>
<td>0.99 (70.9%)</td>
</tr>
<tr>
<td>NH4</td>
<td>0.19 (34%)</td>
<td>0.56 (101.6%)</td>
</tr>
<tr>
<td>OA</td>
<td>-1.36 (-52.2%)</td>
<td>2.20 (84.0%)</td>
</tr>
<tr>
<td><strong>SIRTA</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BC</td>
<td>-0.29 (58.3%)</td>
<td>0.67 (136.1%)</td>
</tr>
<tr>
<td>NO3</td>
<td>0.24 (79.4%)</td>
<td>0.64 (212%)</td>
</tr>
<tr>
<td>SO4</td>
<td>0.60 (51.7%)</td>
<td>1.07 (92.6%)</td>
</tr>
<tr>
<td>NH4</td>
<td>0.33 (70.5%)</td>
<td>0.48 (103.5%)</td>
</tr>
<tr>
<td>OA</td>
<td>-0.79 (-58.4%)</td>
<td>1.25 (92.1%)</td>
</tr>
</tbody>
</table>

3.2.1 Comparison for ground based sites

Figure 9 shows the daily variation of NOx, BC and O3 at GOLF, LHVP and SIRTA, respectively, during summer. The simulated and measured peaks of NOx occur at about 8 a.m., while ozone peaks in late afternoon due to important photochemical production in the afternoon in summer. NOx values are overestimated with a bias (RB) of 6.1 (44.7%), 2.7 (14.6%) and 1.7 ppb (20.7%) at GOLF, LHVP and SIRTA, respectively. The O3 concentrations vary between 15 to 40 ppb. It anticorrelates with NOx and the RB at these three sites are all within 10%.
The BC peaks are correlated with those of NOx, both pollutants being due to traffic emissions. The correlation coefficients between simulated and observed time series of BC at GOLF and LHVP are around 0.5 in summer. It is lower in SIRTA (~0.35). However, the daily variation of BC from simulation agrees well correlated with the measurements at SIRTA, but it is overestimated by a factor of two to three at GOLF and LHVP. This points to an overestimation in BC emissions in the urban area. Inorganic aerosols are often overestimated up to a factor of two for the nitrate concentrations in PM10 at LHVP. However, the correlation coefficients are often around 0.7-0.8 at these three sites, except for sulfate and ammonium at SIRTA where they are only 0.37 and 0.56, respectively. Simulated OA is slightly underestimated in the model by no more than 15% in PM10 in the summer (Fig. 10). Simulations captured almost all peaks for the summer campaign and the correlation coefficients are around 0.8. In particular the large OA peaks on July 16 and 21, due to long range transport of biogenic SOA (see MEGAPOLI Deliverable 3.5), are well captured, which is encouraging.

![Figure 9](image)

**Figure 9:** Daily variation of NOx (red, in ppb), BC (black, shadow is the range of PM1 to PM10 in µgm⁻³) and O₃ (blue, in ppb) from model (lines) and measurement (starred) at GOLF (left), LHVP (middle) and SIRTA (right) in July 2009. The x axis is in local time.

### 3.2.2 Simulations of the Paris urban plume

The pollutants emitted in the Paris agglomeration have a local impact, such as POA, BC and NOx, etc. In addition, they may also have regional and continental impact when they form secondary pollutants such as inorganic aerosols, O₃ and SOA during their transport away from the agglomeration. Fig. 11 gives a classical picture about ground surface OA concentration in the plume from Paris. On July 16th, a morning peak of OA was formed due to POA emissions and low boundary layer height and transported towards north-east. It disappeared at midday due to decrease of POA emissions and increase of PBL height. An OA plume is formed due to SOA production at 13h, in the north of Paris agglomeration and further transported towards north. The plume concentration reaches its highest values farther from Paris due to condensation of semivolatile VOC products formed by photochemical reactions in the afternoon. During evening and night northward transport and SOA formation continue. Therefore, although OA has a high value of about 13 µg m⁻³ in the morning in Paris related to local POA emissions, its highest value about (17 µg m⁻³) occurs during the early night at about 150 km north of the agglomeration, due to SOA build-up from anthropogenic VOC emissions in the Paris agglomeration and additional biogenic VOC showing enhanced emissions under the high temperatures prevailing in the afternoon of this day.

### 3.2.3 Comparison between airborne observations and simulations

AMS measurements from 8 flights are of good quality and are used for evaluation of the simulations. Here, as an example the flight N°30 on July 16 is analyzed. This day was cloudless with high temperature, and southerly winds. Large primary pollution peaks were observed in the urban area in
the morning, due to low winds. The Paris urban pollution plume was found from measurements and in simulations as heading towards north of France, with slight differences (about 15° in the plume direction) (Fig. 12). Enhanced BC and nitrate concentrations were observed within the plume both in the models and from measurements, with somewhat larger values in the simulations. Scaling nitrate with BC as a primary pollution tracer to take into account plume dilution (not shown), indicates a NO3 build-up when the plume is moving away from Paris. Background sulfate concentrations are slightly overestimated in simulations (2.5 instead of 2 µg m⁻³). The production of sulfate was underestimated within the plume in simulations (about 0.5 µg m⁻³ compared to 1 µg m⁻³ observed).

Simulated background OA concentrations are about 1 µg m⁻³ lower than the observations (2–3 instead of 3 – 4 µg m⁻³). Highest concentrations were measured when the aircraft returned to the airport on the northwest of Paris agglomeration. Enhanced plume values increments for OA are larger in simulations than observed (about 2–3 instead of 1–2 µg m⁻³). OA build-up in the plume was more closely analysed. OA (POA+SOA) is plotted against Ox (NO₂+O₃) (Fig. 13). Ox is used here as a tracer of photochemical activity. The idea is that under polluted conditions both SOA and Ox are related to the oxidation of VOC. The slope of OA vs. Ox thus should indicate the accuracy of the representation of SOA formation in the model. From PMF analysis of the AMS measurements (Deliverable 3.5), it appears that SOA related fractions are dominant with respect to POA. Thus in this analysis the more robust OA value is preferred to SOA. First, a good correlation of OA with Ox is observed both in simulations and observations (Fig. 13). The slope is 0.27 in the simulation compared to 0.13 in the observations. Thus the level of normalized SOA production in the Paris plume is thought to be correct within a factor of two. This is an encouraging result when considering the
**Figure 11:** Simulated CHIMERE urban OA plume on July 16 at different times of the day. Surface OA mass concentrations are given in $\mu$g m$^{-3}$.

**Figure 13:** OA/Ox ratio from measurements (black) and simulations CHIMERE (green) for the flight on July 16. The x-axis denotes Ox ($O_3$+NO$_2$) in ppb, the y-axis denotes OA in $\mu$g m$^{-3}$. 

\[
y = 0.13x + 3.0 \\
y = 0.27x + 12.2
\]
uncertainties of the SOA scheme of VBS approach, and when keeping in mind the traditional difficulty of models to simulate SOA formation.

Figure 12: Comparisons of OA, nitrate, sulfate, ammonium, BC from measurement (left, with suffix m) and from the simulation with CHIMERE (right, with suffix v) for the flight on July 16. All values are given in $\mu g m^{-3}$. 

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MEGAPOLI

Megacities: Emissions, urban, regional and Global Atmospheric POLLution and climate effects, and Integrated tools for assessment and mitigation

EC FP7 Collaborative Project

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Theme 6: Environment (including climate change)
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MEGAPOLI Project web-site

http://www.megapoli.info

MEGAPOLI Project Office

Danish Meteorological Institute (DMI)
Lyngbyvej 100, DK-2100
Copenhagen, Denmark
E-mail: alb@DMI.dk
Phone: +45-3915-7441
Fax: +45-3915-7400

MEGAPOLI Project Partners

- DMI - Danish Meteorological Institute (Denmark) - Contact Persons: Prof. Alexander Baklanov (coordinator), Dr. Alexander Mahura (manager)
- FORTH - Foundation for Research and Technology, Hellas and University of Patras (Greece) - Prof. Spyros Pandis (vice-coordinator)
- MPIC - Max Planck Institute for Chemistry (Germany) - Dr. Mark Lawrence (vice-coordinator)
- ARIANET Consulting (Italy) – Dr. Sandro Finardi
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- FMI - Finnish Meteorological Institute (Finland) – Prof. Jaakko Kukkonen
- JRC - Joint Research Center (Italy) – Dr. Stefano Galmarini
- ICTP - International Centre for Theoretical Physics (Italy) – Prof. Filippo Giorgi
- KCL - King’s College London (UK) – Prof. Sue Grimmond
- NERSC - Nansen Environmental and Remote Sensing Center (Norway) – Dr. Igor Esau
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- CUNI - Charles University Prague (Czech Republic) – Prof. Tomas Halenka
- IFT - Institute of Tropospheric Research (Germany) – Prof. Alfred Wiedensohler
- UCam - Centre for Atmospheric Science, University of Cambridge (UK) – Prof. John Pyle

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