Simulating the Contributions of Local and Regional Sources to fine PM in megacities

Dissertation
Submitted to
Department of Chemical Engineering
of
University of Patras

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In Partial Fulfillment of the Requirements for the
Master thesis
in Chemical Engineering

University of Patras
June, 2013
To my parents, Argyris and Georgia
Acknowledgments

This study took place in the laboratory of air quality studies of ICE-HT in Patras. First, I would like to thank my advisor, Dr. Spyros Pandis, for his expert guidance and most valuable support. Also I would like to thank my parents Argyris and Georgia and my aunt Maria because they were always there for me. I would never make it without the constant support and love of my family and my friends. I would also thank all the members of our group whom I’m enjoying working with and especially Thanasis Megaris, Dr. Benjamin Murphy and Dr. Christos Fountoukis for their scientific help which was very valuable for me.
Abstract

The Particulate Matter Source Apportionment Technology (PSAT) is used together with PMCAMx, a regional chemical transport model, to estimate how local emissions and pollutant transport affect primary and secondary particulate matter concentration levels in European megacities such as Paris, London and Po Valley. The case of Paris megacity was investigated in detail. During the summer and the winter period examined, only 13% of the PM$_{2.5}$ is due to local Paris emissions, with 36% due to mid range (within 500 km from the center of the Paris) sources and 51% resulting from long range transport (more than 500 km from the center of the Paris).

The local emissions contribution to elemental carbon (EC) is significant, with almost 60% of the EC originating from local sources during both summer and winter. Approximately 50% of the fresh primary organic aerosol (POA) originated from local sources and another 45% from areas 100-500 km from the receptor region during summer. Regional sources dominated the secondary PM components. More than 70% of the sulfate originated from SO$_2$ emitted more than 500 km away from the center of the Paris. Also more than 45% of secondary organic aerosol (SOA) was due to the oxidation of VOC precursors that were emitted 100-500 km from the center of the Paris. Long range sources are more important during winter because the photochemical activity is lower.

PSAT results for contributions of local and regional sources were also compared with observation-based estimates from field campaigns that took place during the MEGAPOLI project. PSAT predictions are in general consistent with these estimates OA and sulfate but PSAT predicts lower transported EC for both seasons.
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1. Introduction

Fine particles (PM\textsubscript{2.5}) can cause a variety of problems to human health, including premature death (Dockery et al., 1993; Kunzli et al., 2000; Klemm et al., 2000; Pope et al., 2002). PM\textsubscript{2.5} is also responsible for visibility reduction (Seinfeld and Pandis, 2006) and contributes to acid rain formation (Burtraw et al., 2007) and climate change by affecting the energy balance of our planet (Schwartz, 1996).

The ongoing urbanization over the past decade has led to an increasing number of Megacities around the world, now hosting more than half of the world’s population (UN 2007). These large urban centers are substantial sources of anthropogenic pollutants having adverse effects on human health, visibility and ecosystems (Seinfeld and Pandis, 2006). In order to improve air quality in those urban areas we need to quantify the fraction of the pollution originating from local and regional sources and to determine the response of the system to emission controls. Three-dimensional chemical transport models (CTMs) are well suited to help address these source receptor questions since they model all the necessary processes that impact air pollution concentrations and transport in the domain. Identifying the areas affecting the receptor is also a crucial issue.

A number of modeling approaches have been proposed and used in order to explain the role of local and regional sources in different areas. Three-dimensional Chemical Transport Models (CTMs) can simulate all relevant atmospheric processes, so they have been used in several different approaches. The simplest approach is the so called ‘zero-out analysis’ or the ‘brute-force method’ (Park et al., 2003; Knipping et al., 2006; Chin et al., 2007; Koo et al., 2009) which requires running the corresponding CTM multiple times by zeroing out the emissions of a specific source area or type. This is a computationally expensive method because it requires multiple simulations, one for each source area of interest. Another method is the direct decoupled method (DDM) (Dunker et al., 1981) which can provide local derivatives of contributions of all parameters (such as emissions or other parameters in the model). DDM calculates the sensitivity of the concentration levels to changes in emissions. As a result DDM cannot be applied in large scale perturbations (Dunker et al., 2002). Ying and Kleeman (2006) developed the source-oriented external mixture
(SOEM) approach which separates the species into different categories based on their source and tracks them separately throughout the model. In SOEM each secondary PM species is traced back to its precursors. For example the concentration of particulate sulfate is traced back to SO\(_2\) sources. Ying and Kleeman (2009) used SOEM to quantify transport distances in areas of California. Wagstrom et al. (2008) developed a computational efficient apportionment algorithm, the Particulate Source Apportionment Technology (PSAT) and used it for the first time in the Eastern United States (Wagstrom and Pandis, 2011) to estimate the contributions of emissions as a function of distance from the receptor for several urban and rural sites. PSAT is computationally efficient as it works in parallel with the main CTM without interfering with the CTM’s calculations. Koo et al. (2009) used PSAT to predict concentrations from different source regions and compared them with the brute force method’s results. They showed that DDM and PSAT can give similar results for pollutants that are related linearly with emissions but otherwise the results differ because of the nonlinearity of the chemistry of secondary species or other indirect effects.

In this study we will focus on the Megacity of Paris. Air quality of Paris has been investigated through different models such as CHIMERE (Zhang et al., 2013), PMCAMx (Fountoukis et al., 2013), POLYPHEMUS (Royer et al., 2011), H\(^2\)O (Couvidat et al., 2013) evaluated against measurement data. Sciare et al. (2010) compared SOA predictions of the regional CTM, CHIMERE using a single step oxidation SOA scheme (Pun et al., 2006) against observation-based estimates from the “EC-tracer” method (Turpin and Huntzicker, 1995; Strader et al., 1999; Cabada et al., 2004) at an urban site. Fountoukis et al. (2013) applied a fine grid nest over the Megacity of Paris with high resolution (4×4 km\(^2\)). The evaluation of the model against high time resolution (AMS) measurements of fine particulate matter of 3 sites was encouraging. Zhang et al. (2013) implemented the VBS approach into CHIMERE to simulate the behavior of organic aerosol and compared with measurements performed during the MEGAPOLI summer campaign. Beekman et al. (2013) used measurements inside the center of the Paris and the surrounding areas to estimate what fraction of pollution is local. The data were collected, during July 2009 and January to mid February 2010 as a part of the MEGAPOLI intensive field campaigns (Beekmann et al., 2013). The transported PM in Paris was calculated based on the
measurements in the appropriate upwind site. PM$_1$ concentration in Paris during summer was on average between 5.3 and 7.5 μg m$^{-3}$, but during winter was between 15.2 μg m$^{-3}$ and 18.5 μg m$^{-3}$. Beekman et al. (2013) also estimated that more than 70% of PM$_{2.5}$ was transported into Paris from areas far away from it. During more polluted periods (PM$_{2.5}$ > 40 μg m$^{-3}$ at the urban site), the regional contribution was even larger (on average 80%). 70% of the OA was found to be transported from regional sources both for summer and winter. Freutel et al. (2013) found that secondary species such as oxygenated OA, nitrates and ammonium during the summer MEGAPOLI campaign were quite similar for the three measurement sites in Paris, indicating the dominance of regional transport. Significant levels of secondary species were transported to Paris when the corresponding air masses originated from continental Europe. The dominance of the regional sources in Paris was also confirmed by Crippa et al. (2013) for the winter MEGAPOLI period.

The MEGAPOLI measurements provide a unique opportunity both to evaluate the PSAT predictions against the estimated regional contributions. In addition, PSAT can quantify how far from the receptor are the regional sources, providing additional insights. PSAT has been based on PMCAMx-2002, a CTM that assumes that primary OA is non-volatile and inert and simulated SOA formation using the Odum et al. (1996) 2-product approach. Recent developments including the semivolatile POA and the continuous aging of OA have not been considered in previous source-receptor analyses by PSAT or other algorithms.

In this work we first extend PSAT so that it can work with the VBS approach for OA. We then applied the extended PSAT in PMCAMx-2008 in the European domain focusing on Paris for the first time. This study describes the PSAT application to the megacity of Paris, as a characteristic case of a megacity, for two different seasons corresponding to the MEGAPOLI intensive campaigns.
1.1. Objectives and motivation

The overall objective of this research is to improve our understanding of the contributions of local and regional sources to air pollution in large urban areas. The knowledge of the impact of transported pollution into large urban areas is significant because we want to understand what fraction of pollution in a specific area is local or is transported from other areas. In such a way we can try to solve atmospheric pollution problems by applying emission reduction techniques to the corresponding areas. In an effort to achieve this we applied an apportionment algorithm such as PSAT in large urban areas. The new version of PSAT works together with the newest form of PMCAMx-2008 in order to improve the treatment of OA in PSAT. This version of the model treats both primary and secondary organic aerosol as semivolatile and chemically reactive. The description and information for the application of the main CTM (PMCAMx) and the apportionment algorithm (PSAT) are presented in section 2. The results and discussion of this work are presented in section 3 for the two different periods examined, in order to estimate the seasonal variation of the contributions from several sources in specific areas. First the results from summer are described, paying special attention to organic aerosol and how the receptor region can affect other areas or the opposite. The description of the behavior of the contributions during winter follows, and the comparison of the results of the two periods examined. In section 4, the results predicted by the model are compared to those calculated based on measurements during both periods examined in order to evaluate the performance of the model. Also the results of two additional simulations (for London and Po Valley) led to similar conclusions as those of Paris and are presented in the Appendix.
2. Model description

2.1 PMCAMx-2008

The model used in this study is PMCAMx-2008, a regional three-dimensional CTM. PMCAMx-2008 (Murphy and Pandis, 2009; Tsimpidi et al., 2010; Karydis et al., 2010, Fountoukis et al., 2011) 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 description of aerosol processes, three detailed aerosol modules are used. Aqueous-phase chemistry is simulated by the approach of Fahey and Pandis (2001). 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 gas-phase chemical mechanism used is based on the SAPRC99 mechanism (Carter, 2000; Environ, 2003), including 211 reactions of 56 gases and 18 radicals. The current SAPRC99 version uses five lumped alkanes, two olefins, two aromatics, isoprene, a lumped monoterpenic species, and a lumped sesquiterpenic species. The system of reaction rate equations solved using the chemical mechanism compiler (CMC) of Environ (2003). CMC solves the differential equations describing gas-phase chemistry using a hybrid approach: the equations of species with short lifetimes (i.e., radicals) are replaced by algebraic equations using the pseudo-steady state approximation, the equations of the species with intermediate lifetimes are solved using a second-order implicit Runge–Kutta method and finally the equations for the slow-reacting species are solved explicitly (Environ, 2003). Three options are available in PMCAMx 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 phase and the gas phase. At a given time-step the amount of each species transferred between the gas and the aerosol phase 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 which explicitly simulates the mass transfer 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 and chemically reactive. 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 types, “fresh” (unoxidized) POA, oxidized POA (OPOA) and any aged organic aerosol transported into the domain from the boundary conditions. SOA consists of organic aerosol of anthropogenic (ASOA) and biogenic (BSOA) origin. The SOA volatility basis-set approach (VBS) (Lane et al., 2008) 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 (Hildebrandt et al., 2009; Ng et al., 2006) have been used to update the SOA module in PMCAMx in order to include anthropogenic aerosol yields. 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 $4 \times 10^{-11}$ cm$^3$ molec$^{-1}$ s$^{-1}$ (Atkinson and Arey, 2003). Each reaction is assumed to decrease the volatility of the vapor species one order of magnitude or by a factor of 10.

PMCAMx-2008 was applied to a domain in Europe, covering a region of a 5400×5832 km$^2$, using 36x36 km grid resolution and 10 vertical layers extending up to 6 km. Also PMCAMx-2008 was set to perform simulations on a rotated polar stereographic map projection. 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. 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 was periodically re-initialized (every 3 days) to ensure accuracy in the corresponding fields that are used as inputs in PMCAMx-2008. 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 SAPRC99 chemical mechanism. Anthropogenic gas emissions that were used to develop the gridded fields include land emissions from the GEMS dataset (Visschedijk et al., 2007) as well as international shipping emissions. Anthropogenic particulate matter mass emissions of organic and elemental carbon are based on the Pan-European Carbonaceous Aerosol Inventory that has been developed as part of the MEGAPOLI activities. A variety of emission sources are identified in the two inventories, including industrial, domestic, agricultural and traffic. Three different datasets are combined in order to produce the biogenic gridded emissions for the model. Emissions from ecosystems are produced by MEGAN (Model of Emissions of Gases and Aerosols from Nature) (Guenther et al., 2006). MEGAN inputs include the leaf area index, the plant functional type and the emission factors while the weather data needed for MEGAN are provided from the WRF model. The sesquiterpene emissions have been set to 30% of the monoterpene emissions (Helmig et al., 2006) and the oxidation of the species is modeled based on the results of Griffin et al. (1999). Since sea surface covers a considerable portion of the domain, the marine aerosol emission model developed by O’Dowd et al. (2008) has been used to estimate mass fluxes for both accumulation and coarse mode including the organic aerosol fraction. Wind speed data from WRF and chlorophyll-a concentrations are the inputs needed for the marine aerosol model. Wildfire emissions were also included (Sofiev et al., 2008a; 2008b). The OA emissions in PMCAMx-2008 were distributed by volatility using the volatility distributions of Tsimpidi et al. (2010).

The model was applied for two periods, 1–30 July 2009 and 10 January–9 February 2010. Fountoukis et al. (2011) evaluated the PMCAMx-2008 performance for the European domain against ground measurements taken at 4 measurement stations over Europe and airborne measurements during May 2008. The model reproduced more than 87% of the hourly AMS measurements of PM$_1$ OA and more than 94% of the daily averaged OA concentrations within a factor of 2. Fountoukis et
al. (2013) investigated the role of grid nesting in concentrations in Paris megacity, by comparing the results of PMCAMx-2008 with 4x4 km grid resolution to those of higher resolution of 36x36 km for the summer and winter period of the MEGAPOLI campaign. Fountoukis et al. (2013) also evaluated the model against ground based measurements at the three ground measurement sites of Paris. For the site located at the center of the Paris (LHVP) the average predicted sulfate during summer was only 0.2 μg m\(^{-3}\) lower than the measured one and the predicted EC was less than 0.5 μg m\(^{-3}\) higher than the measured. Also for the suburbs of Paris (SIRTA site) during summer, the model predicts in excellent agreement with measurements the sulfate and OA components and it underestimates EC by less than 0.2 μg m\(^{-3}\).

### 2.2 PSAT description

The Particulate Source Apportionment Technology (PSAT) (Wagstrom et al., 2008) is an apportionment algorithm that can track different emission categories originating from different area sources or different sources types. Its main advantage is that it is computationally efficient, as it works in parallel with the main CTM without interfering with the CTM’s calculations. A diagram outlining the information flow in PSAT is shown in Fig. 1. PMCAMx-2008 communicates with the apportionment algorithm after each step of each process (e.g., gas phase chemistry, horizontal and vertical advection, etc.) by sending the corresponding concentrations of each species calculated by CTM’s modules to the apportionment algorithm. After each process step of PMCAMx, PSAT calculates the apportionment for each species and for each source. PSAT uses the apportionment of the upwind grid cell to apportion species after transport calculations instead of tracking the source-specific species separately:
\[ c_{_{A,i}}(t + \Delta t) = c_{_{A,i}}(t) + \Delta c_{\text{in}} \left( \frac{c^*_{_{A,i}}(t)}{c^*_{\text{A}}(t)} \right) - \Delta c_{\text{out}} \left( \frac{c_{_{A,i}}(t)}{c_{\text{A}}(t)} \right) \]  

(1)

where \( c_{_{A,i}}(t) \) is the concentration of species A from source i in a specific cell at the beginning of the corresponding time-step and \( c_{_{A,i}}(t + \Delta t) \) is the same quantity at the end of the time-step, \( \Delta c_{\text{in}} \) is the concentration transported into the grid cell, \( \Delta c_{\text{out}} \) is the concentration transported out of the grid cell, \( c^*_{_{A,i}} \) is the concentration of species A from source i in the upwind grid cell and \( c^*_{\text{A}} \) is the total concentration of species A from all sources in the upwind grid cell. Since operator splitting in PMCAMx treats advection in the east-west and north-south directions separately, there will be a separate upwind grid cell in each of the two directions. The apportionment of the newly formed secondary PM is calculated based on the apportionment of its precursor species. This means that the apportionment of each secondary PM species is calculated by the same equations as the apportionment of its gas phase precursor.

**Figure 1.** Information flow in PSAT for an example of two source classes.
PSAT uses different approximations in order to predict concentrations of species produced by gas phase chemistry, irreversible or reversible partitioning. For example, for the calculations of the concentrations resulting from gas phase chemistry if we consider the following reaction:

\[
A(g) + \text{oxidant} \rightarrow B(g) + \text{other products}
\]

PSAT uses the following equation (Eq. 2) to calculate the concentrations of species A and B after the gas phase chemistry step.

\[
c_{A,i}(t + \Delta t) = c_{A,i}(t) + \left[ c_A^T(t + \Delta t) - c_A^T(t) \right] \left[ \frac{c_{A,i}(t)}{c_A^T(t)} \right]
\]

where \( c_{A,i}(t + \Delta t) \) and \( c_{A,i}(t) \) are the concentrations of species A from a given source at the end and the beginning of the gas-phase chemistry time-step respectively and \( c_A^T(t + \Delta t) \), \( c_A^T(t) \) are the corresponding total concentrations of species A at the end and the beginning of the gas-phase chemistry time-step respectively. Molecules of species A regardless their source have the same probability of reacting; therefore during a time-step \( \Delta t \), the concentration of B produced from A originating from source i will be proportional to the total B produced during the corresponding time-step, \( c_B^T(t + \Delta t) \), \( c_B^T(t) \) and the fraction of A originating from source i, \( \frac{c_{A,i}(t)}{c_A^T(t)} \), at the beginning of the time step. As a result of this, the concentration of species B originating from each source after the gas-phase chemistry time-step will be given by:

\[
c_{B,i}(t + \Delta t) = c_{B,i}(t) + \left[ c_B^T(t + \Delta t) - c_B^T(t) \right] \left[ \frac{c_{A,i}(t)}{c_A^T(t)} \right]
\]

where \( c_{B,i}(t + \Delta t) \) and \( c_{B,i}(t) \) are the concentrations of species B from a specific source at the end and the beginning of the gas-phase chemistry time-step respectively, and \( c_B^T(t + \Delta t) \), \( c_B^T(t) \) are the corresponding total concentrations of species B from all sources. One assumption inherent in this approach is that each secondary species can
be linked to one precursor gas. Equations (2) and (3) are applied to the apportionment of H$_2$SO$_4$ (g) from SO$_2$, HNO$_3$ (g) from NOx and different condensable vapors from the corresponding VOC precursors.

In addition the apportionment of condensing non-volatile PM species, such as sulfate, after the partitioning calculations is similar to that described above for gas-phase species after gas-phase chemistry calculations. So, for the general condensation of a non-volatile gaseous species:

\[ B(g) \rightarrow C(p) \]

where \( C \) is the particulate form of \( B \) (e.g., sulfate and sulfuric acid). The apportionment of the precursor gas does not change due to the transfer of \( B \) to the particulate phase. The concentration of the remaining precursor gas species \( B \) from source \( i \) is given by:

\[
c_{B,i}(t + \Delta t) = c_{B,i}(t) + \left[ c_{B}^T(t + \Delta t) - c_{B}^T(t) \right] \left[ \frac{c_{B,i}(t)}{c_{B}^T(t)} \right]
\]

(4)

Similarly to the case of gas-phase chemistry, the concentration of the secondary particulate species \( C \) is then based on the apportionment of the precursor gas species and is given by:

\[
c_{C,i}(t + \Delta t) = c_{C,i}(t) + \left[ c_{C}^T(t + \Delta t) - c_{C}^T(t) \right] \left[ \frac{c_{B,i}(t)}{c_{B}^T(t)} \right]
\]

(5)

where \( c_{C,i}(t + \Delta t) \) and \( c_{C,i}(t) \) are the concentrations of species \( C \) from source \( i \) at the end and the beginning of the gas-phase chemistry time-step respectively, \( c_{C}^T(t + \Delta t) \) and \( c_{C}^T(t) \) are the corresponding total concentrations of species \( C \) from all sources.

PSAT uses a different approach to apportion semivolatile species, such as SOA, after partitioning calculations than for non-volatile species (e.g., sulfate) due to the simultaneous condensation and evaporation. Since this version of PMCAMx uses a thermodynamic equilibrium assumption for the partitioning calculations, only the net
amount transferred between the gas and particulate phase is known. We assume that because the characteristic time for equilibrium is much less than the time-step in the model, the apportionment in the two phases will be equal. This is equivalent to assuming that molecules of a compound from a given source will have the time to distribute themselves proportionally between the two phases. For a semi-volatile gas (B) condensing to form secondary aerosol (C):

\[
\text{B}(g) \longrightarrow \text{C}(p)
\]

the fractions of B and C originating from source i would be equal to each another and also equal to the apportionment of the sum of B and C before the partitioning calculations. The concentration of B and C attributed to source i after partitioning calculations are then given by:

\[
c_{B,i}(t + \Delta t) = c_{B}^{T}(t + \Delta t) \left[ \frac{c_{B,i}(t) + c_{C,i}(t)}{c_{B}^{T}(t) + c_{C}^{T}(t)} \right]
\]

(6)

\[
c_{C,i}(t + \Delta t) = c_{C}^{T}(t + \Delta t) \left[ \frac{c_{B,i}(t) + c_{C,i}(t)}{c_{B}^{T}(t) + c_{C}^{T}(t)} \right]
\]

(7)

Occasionally there is the case where two precursors will produce the same oxidation product. A generalized example of this is:

\[
\text{A}(g) + \text{oxidant} \longrightarrow \text{C}(g) + \text{other products}
\]

\[
\text{B}(g) + \text{oxidant} \longrightarrow \text{C}(g) + \text{other products}
\]

The apportionment of C can then be determined by weighting the apportionment of A and B by the corresponding reaction rates. The appropriate weighting factors would be equal to:

\[
a_{A} = \frac{r_{A\rightarrow C}}{r_{A\rightarrow C} + r_{B\rightarrow C}}
\]

(8)
\[ a_B = \frac{r_{B \rightarrow C}}{r_{A \rightarrow C} + r_{B \rightarrow C}} \tag{9} \]

where \( r_{A \rightarrow C} \) and \( r_{B \rightarrow C} \) are the rates of the corresponding reactions. The apportionment of \( C \) would then be based on the weighted combination of the apportionment of species A and B:

\[ c_{C,i}(t + \Delta t) = c_{C,i}(t) + [c_C^T(t + \Delta t) - c_C^T(t)] \left[ a_A \frac{c_{A,i}(t)}{c_A^T(t)} + a_B \frac{c_{B,i}(t)}{c_B^T(t)} \right] \tag{10} \]

We have extended the original PSAT algorithm of Wagstrom et al. (2008) to describe the OA based on the VBS approach (Donahue et al., 2006; Stanier et al., 2008; Shrivastava et al., 2008, Lane et al. 2008). Primary OA emissions are distributed into different classes of saturation concentrations (volatility bins). The corresponding gas-phase POA compounds can be oxidized by the hydroxyl radical leading to products of lower volatility. In the same way SOA is considered to be semivolatile and can also be oxidized further in the gas phase forming lower volatility products. PSAT keeps track of the sources of all OA components (fresh primary, oxidized primary, fresh and aged anthropogenic and biogenic secondary) using the same approach used for all semivolatile species. All OA species are distributed into different volatility bins regarding their saturation concentration and being tracked by PSAT as separate species. OA species are distributed between the gas and the particle phase according to Eq. (11) (Donahue et al., 2006):

\[ \xi_i = \left( 1 + \frac{C_i^*}{C_{OA}} \right)^{-1} \tag{11} \]

where \( \xi_i \) is the partitioning coefficient of compound i, \( C_i^* \) is the effective saturation concentration and \( C_{OA} \) is the total organic mass concentration. Each \( C_i^* \) corresponds to different volatility bin of complex mixtures of OA. Chemical aging reactions shift the organic mass from one order of magnitude of saturation concentration to another.
2.3 Definition of source regions within and around the Paris metropolitan area

We have chosen nine computational cells to describe the Paris metropolitan area (about 11,000 km$^2$, local Paris emissions). We have also defined areas covering distances of 100 km, 500 km, 1000 km and greater than 1000 km away from the center of the defined Paris metropolitan area (Fig. 2) for the calculation of the corresponding source contributions to PM levels.

PSAT also tracks the contributions to particle concentrations from initial conditions and boundary conditions. Concentrations resulting from emissions within Paris are considered as local. The sum of the concentrations resulting from emissions outside the Paris metropolitan area but within 100 km from the center of Paris plus the concentrations resulting from emissions between 100 and 500 km from Paris are considered as contribution of mid-range transport and those resulting from emissions more than 500 km away from Paris (including the effects of boundary conditions) are considered as long range transport. The long range contribution therefore includes also the emissions outside of the modeling domain.

![Figure 2](image)

**Figure 2.** Definition of different source areas around Paris indicating local Paris emissions (black area), 100 km from the center of the Paris (green area), 500 km from the center of the Paris (red area) and 1000 km (blue area) from the center of the Paris.
3. Results and Discussion

3.1 Summer

We will focus first on three representative major PM species: elemental carbon, sulfate, and secondary organic aerosol. Elemental carbon is non-reactive primary species, sulfate is secondary non-volatile, and SOA is a secondary semivolatile species.

Figure 3 depicts the diurnal pattern of EC, fresh POA, sulfate and SOA and the corresponding source areas. EC concentration peaks at 8 in the morning. The concentration of elemental carbon is on average 1 μg m⁻³. During the periods with the high concentrations the contribution of local transport is higher.

![Figure 3](image)

**Figure 3.** Average diurnal profiles of PM$_{2.5}$ components for summer period for: a) elemental carbon; b) fresh POA; c) sulfate; d) SOA.
The contribution of local sources for EC is on average 64% while the contributions of mid and long range transport are 30% and 6% respectively (Fig. 4). This behavior is characteristic of primary pollutants with significant urban sources (Wagstrom and Pandis, 2011). POA has almost the same behavior as EC with a morning peak at 7 in the morning, but with lower concentration level than EC (on average less than 0.5 \( \mu g \ m^{-3} \)).

The behavior of sulfate is quite different because it is a secondary species. The average concentration of sulfate is 1.5 \( \mu g \ m^{-3} \). The average contributions of local, mid range transport and long range transport to sulfate in Paris are 6%, 23% and 71% respectively (Fig. 4). This indicates that sulfate in Paris is mainly originating from areas more than 500 km away from the city. This is the result of the time required for its formation.

**Figure 4.** The percent contributions from each transport category during high and low particulate matter concentration days for summer period.
Similarly to sulfate, less than 10% of the SOA in Paris is the result of local sources. SOA consists of all the secondary compounds formed from reactions of evaporated POA, IVOCs and VOCs, SOA also include the boundary conditions of OA which are assumed to consist of 50% of biogenic SOA and another 50% of anthropogenic SOA. Paris has modest VOC emissions compared to its surroundings and also it takes enough time for the formation of SOA from freshly emitted VOCs. At the same time VOC emissions originated from Paris can be transported to other areas far from Paris and can be oxidized there, forming the semivolatile oxidation products which can be condensed to form SOA. Additionally mid and long range sources can affect the SOA concentration in Paris and these contributions in the center of the Paris are 45% and 48% respectively.

Figure 4 summarizes the average contribution from each source for clean and polluted days. Clean days are defined as the days with average concentrations of total PM$_{2.5}$ species in the lower quartile of the values predicted during this period. Polluted days are defined as the days with average concentrations of total PM$_{2.5}$ species in the upper quartile. During more polluted days 55% of the EC is emitted by local sources with another 37% coming from mid-range sources. On the other hand, during clean days these contributions of EC are on average 63% and 32% respectively. The contributions of different sources for sulfate and SOA do not change very much during cleaner days comparing to those of polluted days. For example for sulfate during more polluted days the contribution of mid-range sources increases slightly. SOA contribution from long-range sources is a little increased to 52% during more polluted days comparing to the average of all days concerned.

### 3.1.1 Organic Aerosol Sources

A little more than 50% of fresh POA in Paris is emitted from local sources according to PSAT, while another 45% is due to mid range transport and less than 5% coming from areas more than 500 km away (Fig. 5). The POA contributions are similar to those of the EC, but with a lower local contribution due to the evaporation of POA after emission.
Figure 5. Percent contributions from each transport category (local, mid-range and long-range) for different types of organic aerosol during the summer.

Secondary organic aerosol precursors emitted far from Paris are oxidized to form SOA which is then transported to the megacity. Almost 50% of anthropogenic SOA in Paris is predicted to be due to mid range transport and another 34% due to long range transport. The behavior of biogenic SOA is quite similar with outside sources contributing on average 83% (Fig. 5). Total organic aerosol behaves like SOA with local emissions contributing on average 11%, mid-range transport 43% and long range 46% (Fig. 5). Oxidized OA is predicted to dominate, contributing according to PMCAMx 85% of the OA in Paris during the summer.

As the volatility of organics gets higher the contribution of local sources is predicted to increase and the contributions of long range sources decreases (Fig. 6). Organics originating from local sources are in general less oxidized with higher volatilities, but organics which originate from long distances are heavily oxidized and
Figure 6. Predicted distribution of volatility of organics in vapor phase and particles for the three different source areas. The sum of the contributions for each volatility bin is 100%.

Thus of lower volatility. For the least volatile OA components in PMCAMx (effective saturation of $10^1 \mu g m^{-3}$), the contribution of local transport is on average 10% and the contribution of mid and long range transport is 62% and 28% respectively. On the other hand for the more volatile OA components (effective saturation of $10^4 \mu g m^{-3}$), the contribution of local sources is 42% and the contribution of mid range transport is on average 57%. These compounds are mostly in the gas phase.

3.1.2 Effects of Paris on other areas

PSAT has the ability to estimate the impacts of a specific source area, Paris in this application, on other areas and also the impacts of the other specified areas on the receptor region. In order to estimate how far from the source region, the plume of each species can travel, we have to use the appropriate quantitative metrics such as the Transport Distance. The TD (Eq. 12) is calculated as in Wagstrom et al. (2011)
and it is the distance between the center of emissions and the center of the plume of the predicted concentrations. By calculating the TD one can estimate how far the species can travel from their emission source area.

\[ TD = \sqrt{(X_{c,n} - X_{e,n})^2 + (Y_{c,n} - Y_{e,n})^2} \]  

(12)

where \( X_{c,n}, Y_{c,n}, X_{e,n}, Y_{e,n} \) are the coordinates of the centers of the concentrations and the emissions respectively. These coordinates of the centers \( (X_{c,n}, Y_{c,n}) \) \( (X_{e,n}, Y_{e,n}) \) are calculated based on equations (13) and (14) (Wagstrom et al., 2011):

\[ (X_{c,n}, Y_{c,n}) = \left( \frac{\sum X_i c_{i,n} + \sum X_i e_{i,n}}{\sum c_{i,n}}, \frac{\sum X_i c_{i,n} + \sum X_i e_{i,n}}{\sum c_{i,n}} \right) \]  

(13)

\[ (X_{e,n}, Y_{e,n}) = \left( \frac{\sum X_i e_{i,n} + \sum X_i e_{i,n}}{\sum e_{i,n}}, \frac{\sum X_i e_{i,n} + \sum X_i e_{i,n}}{\sum e_{i,n}} \right) \]  

(14)

where \( c_{i,n} \) are the concentrations, \( e_{i,n} \) are the corresponding emissions of cell i, n is the corresponding source area and \( X_i, Y_i \) are the coordinates of the cells of the corresponding concentrations and the emissions.

For the calculation of the TD of secondary species like sulfate and SOA the coordinates of the emission centers are calculated based on the emissions of their precursor gases, \( SO_2 \) and VOCs respectively. Figure 7 shows the temporal variation of the predicted TD (from precursors emitted from the center of the Paris) during summer period, for EC, sulfate and SOA. Some days the TDs are higher because strong winds can affect the motion of the plume. EC can travel on average 400 km from Paris and this TD is predicted to be lower than that of sulfate and SOA. The TDs of sulfate and especially of SOA are higher indicating that the centers of the concentrations of these species can exist far away from Paris and this is because it takes time for the chemistry to convert precursors to secondary aerosol. The TD of sulfate is on average 600 km and that of SOA 800 km.
Figure 7. Temporal variation of the transport distance for EC, sulfate and SOA for Paris emissions for summer period.

Figure 8. Predicted average ground concentrations (in μg m$^{-3}$) of PM$_{2.5}$, EC, sulfate and SOA for local Paris emissions a), b), c) respectively.
Although aerosol species can travel a lot distance far from their source region it is important to know if these species can significantly affect by their concentrations, the areas far from the source region. Figure 8 shows the impacts of local Paris emissions of EC, SO₂ and VOCs on PM in areas far from Paris. The impact of EC and SO₂ emissions, originating from Paris is significant to areas close to Paris, but Paris emissions do not have significant affect on other areas especially far from it.

### 3.2 Winter

Generally the behavior of all species during winter is quite similar to that during summer, despite their differences in concentration levels. Winter is generally characterized by higher emissions of EC and fresh POA and lower emissions of biogenic SOA precursors compared to summer (Table 1).

**Table 1.** Emission densities (in kg km⁻² for PM species and in kmoles km⁻² for gases) for each source area during summer and winter period.

<table>
<thead>
<tr>
<th>Source Area</th>
<th>EC (kg km⁻²)</th>
<th>Fresh POA (kg km⁻²)</th>
<th>Anthropogenic SOA precursors (kmoles km⁻²)</th>
<th>Biogenic SOA precursors (kmoles km⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>summer</td>
<td>winter</td>
<td>summer</td>
<td>winter</td>
</tr>
<tr>
<td><strong>Local</strong></td>
<td>9.73</td>
<td>12.6</td>
<td>5.61</td>
<td>13.38</td>
</tr>
<tr>
<td><strong>Mid range</strong></td>
<td>5.67</td>
<td>7.88</td>
<td>6.85</td>
<td>10.22</td>
</tr>
<tr>
<td><strong>Long range</strong></td>
<td>1.24</td>
<td>0.31</td>
<td>1.45</td>
<td>0.07</td>
</tr>
</tbody>
</table>
Figure 9. Average diurnal profiles of PM$_{2.5}$ components for winter period for: a) Elemental Carbon; b) fresh POA; c) sulfate, d) SOA.

During winter the average predicted concentration of EC in Paris was 2 $\mu$g m$^{-3}$, while during summer was 1 $\mu$g m$^{-3}$. Also the difference in concentrations between the two periods for fresh POA is significant with the predicted POA during winter being 1.5 $\mu$g m$^{-3}$ and during summer 0.2 $\mu$g m$^{-3}$. The predicted diurnal patterns of the concentrations and the corresponding source areas of EC, sulfate, fresh POA and SOA are shown in Fig. 9. The diurnal averaged profiles of EC and fresh POA are quite similar, predicting a morning peak and reveal that during the hours with the maximum concentration levels, the contribution of local emissions is higher. Also during winter the concentrations of secondary species such as sulfate and SOA are lower because of the slower photochemistry. The average predicted concentration of sulfate in Paris during winter was 1 $\mu$g m$^{-3}$ and during summer 1.5 $\mu$g m$^{-3}$, and the predicted concentration of SOA was 0.5 $\mu$g m$^{-3}$ and 1.5 $\mu$g m$^{-3}$ during winter and summer respectively. The diurnal profile of sulfate is almost flat showing again that the contribution of local emissions does not play an important role.
EC during winter is characterized by a little lower local Paris contributions and a little higher transport from mid range sources compared to summer (Fig. 10). The contribution of long range transport for sulfate is lower during winter due to lower regional sulfate levels. Due to wet deposition during winter the contributions of long range transport are lower, because PM components can not travel far distances as they are removed by rain.

The behavior of the contributions from each source area during clean and polluted days (Fig. 11) in general is similar to those of summer. In addition the contributions of different source areas to different types of organic aerosol during winter change compared to the summer. For example during winter the contribution of local sources to total OA is higher (Fig. 12) because the contribution of fresh-POA (which mostly originating from local sources) is higher compared to the summer.
Figure 11. The percent contributions from each transport category during high and low particulate matter concentration days during winter period.

Figure 12. The percent contributions from each transport category for different types of organic aerosol during winter period.
4. Comparison of PSAT Results and Observation-Based Estimates

Beekmann et al. (2013) performed a detailed analysis of measurement data collected inside and outside Paris, in order to determine the role of local and regional sources. They concluded that on an annual basis, 70% of PM$_{2.5}$ is transported into Paris from areas far away from it. PSAT estimated (as the average of two periods) that 80% is transported. Both the analysis of measurements and the PSAT predictions suggest that more than 80% of the sulfate is transported to Paris from other areas (Fig. 13). The two approaches are in excellent agreement during the winter, but PSAT predicts a lower contribution of local emissions during the summer. The discrepancy is of the order of 0.2 μg m$^{-3}$ and could be the result of underestimating the effect of local sources, as PMCAMx underpredicts the average sulfate in the center of the city by the same amount (Fountoukis et al., 2013) while it is not biased outside Paris.

![Figure 13. Comparison of predicted and measured contributions of local and regional sources.](image-url)
Also the local predicted contributions of OA are lower than those estimated by observations for both summer and winter. This underestimation of local sources (almost 0.2 \(\mu g\) m\(^{-3}\) for summer and winter) could be explained by the behavior of fresh POA. Both the measurement-based studies of Beekman et al. (2013) and Freutel et al. (2013) found that almost 62% of the OA in the center of Paris was HOA and cooking OA and 38% was oxygenated OA. The discrepancy between the measurements and the model can be explained by the cooking factor, which have not been considered in the emissions. Beekman et al. found that almost 40% of the OA was related with cooking and this is a part of OA that cannot be predicted by the model. On the other hand the local predicted contributions of EC are higher than the measured especially during summer but this is not so significant because the concentrations of EC are relatively low, so the discrepancies are almost 0.2 \(\mu g\) m\(^{-3}\) for both summer and winter. Generally the predictions of the model are in a good agreement with the results estimated based on measurements, especially for sulfate and OA.
5. Conclusions

In this study we implemented the PM source apportionment algorithm PSAT together with the volatility basis set framework for OA for the megacity of Paris. This new version of PSAT is used to quantify the contributions from selected source areas to Paris fine PM for two periods, a summer and a winter month. The specified areas are characterized as local, mid range and long range. The contribution of local sources was found to be around 60% for EC for both periods. On the other hand the concentrations of secondary PM components like sulfate and SOA were dominated by long range and mid range transport respectively. Long range transport was responsible for 71% of the sulfate during summer and 51% during winter. For SOA the contribution of mid range transport was 45% during summer and 17% during winter. During more polluted days the contribution of local emissions increased for all PM species.

PSAT predicted contributions of local EC are higher than those estimated by the observation-based method especially during summer (with local predicted being 64% and observation based 33%) indicating that the number of local emission sources of EC for Paris was estimated to be higher than the real. On the other hand the comparison between the predicted and the measured contributions of sulfate is encouraging with predicted transported being 94% during summer and 83% during winter and the measured 81% and 84% respectively. Also OA were found to be transported into Paris from regional sources, on average 89% during summer and 62% during winter and these results are relatively consistent with the measured values (80% and 55% respectively). The dominance of the contribution of regional sources for secondary species like sulfate and SOA for the center of the Paris is the result of the time required to convert precursors to PM species. The contribution of long range transport was found to increase as the particles are getting more oxidized.
6. Future work

In order to understand in detail the role of transported pollution from areas far from the receptor region, it is necessary to know how each emission source can affect the concentration of each pollutant. In order to do this, the splitting of the emission inventory into different types of emissions is needed (e.g. emissions from traffic, fires, biogenic sources, etc). Then the application of the new version of PSAT is essential in order to predict the impact of each specific source to the areas of interest. In such a way we can predict for example what fraction of organics originating from traffic, non-road transport, wildfires, or other biogenic sources, etc. This is very important because pollution originating from some emission sources, such as anthropogenic, can be reduced by the corresponding techniques. Also the impact of areas in specific areas of interest can be examined by separating the modeling domain in specific sub-domains and examine in detail what fraction of pollution is transported from one area to another.
7. References


Ying, Q., and Kleeman, M: Regional contributions to airborne particulate matter in central California during a severe pollution episode, Atmos. Environ., 43, 1218-1228, y, 2009.

Appendix

Figure A.1. The contributions from different source areas (local (within 36 km from Paris center), mid range (within 500 km from Paris center) and long range (everything else far from 500 km)) to PM$_{2.5}$ EC, sulfate and SOA concentrations in the center of Paris for the summer period.
Figure A.2. The contributions from different source areas (local (within 36 km from Paris center), mid range (within 500 km from Paris center) and long range (everything else far from 500 km)) to PM$_{2.5}$ EC, sulfate and SOA concentrations in the center of Paris for the winter period.
Figure A.3. The contributions from different source areas (local (within 36 km from Paris center), mid range (within 500 km from Paris center) and long range (everything else far from 500 km)) to PM$_{2.5}$ in the center of Paris for both summer and winter period.
Figure A.4. Average diurnal profiles and contributions from each source area of PM$_{2.5}$ for summer and winter period a), b) respectively for the center of the Paris.
Figure A.5. Predicted average ground concentrations (in μg m⁻³) of PM₂.₅ EC, sulfate and SOA for emissions coming from distances 500-1000 km from Paris a), b), c) respectively and boundary conditions d), e), f) during the summer period. The black dot indicates the Paris center.
Figure A.6. Predicted average ground concentrations (in $\mu g m^{-3}$) of PM$_{2.5}$ EC, sulfate and SOA for local Paris emissions a), b), c) respectively and emissions coming from distances 100-500 km from Paris d), e), f) during the winter period. The black dot indicates the Paris center.
Figure A.7. Predicted average ground concentrations (in μg m\(^{-3}\)) of PM\(_{2.5}\) EC, sulfate, and SOA for emissions coming from distances 500-1000 km from Paris a), b), c) respectively and boundary conditions d), e), f) during the winter period. The black dot indicates the Paris center.
Figure A.8. Predicted average ground concentrations (in $\mu$g m$^{-3}$) of PM$_{2.5}$ EC, sulfate, and SOA from London’s emissions a), b), c) respectively and for emissions coming from distances 100-200 km from London d), e), f) during the summer period. The black dot indicates the London center.
Figure A.9. Predicted average ground concentrations (in μg m$^{-3}$) of PM$_{2.5}$ EC and sulfate, from London’s emissions a), b) respectively and emissions coming from distances 100-200 km from London c), d) during the winter period. The black dot indicates the London center.
Figure A.10. The contributions from different source areas (local (within 36 km from London center), mid range (within 500 km from London center) and long range (everything else far from 500 km)) to PM$_{2.5}$ EC, sulfate and SOA concentrations in the center of London for the summer period.
Figure A.11 The contributions from different source areas (local (within 36 km from London center), mid range (within 500 km from London center) and long range (everything else far from 500 km)) to PM$_{2.5}$ EC, sulfate and SOA concentrations in the center of London for the winter period.
Figure A.12. Comparison of the contributions of each source area for summer and winter period for the center of London.

Figure A.13. The percent contributions from each transport category for different types of organic aerosol during summer and winter period for the center of London.
Figure A.14. Predicted average ground concentrations (in μg m⁻³) of PM\(_{2.5}\) EC, sulfate, and SOA from Po Valley’s emissions a), b), c) respectively and for emissions coming from distances 100-200 km from Po Valley d), e), f) during the summer period. The black dot indicates the Milan center.
Figure A.15. Predicted average ground concentrations (in $\mu g m^{-3}$) of PM$_{2.5}$ EC and sulfate, from PoValley’s emissions a), b) respectively and emissions coming from distances 100-200 km from PoValley c), d) during the winter period. The black dot indicates the Milan center.
Figure A.16. The contributions from different source areas (local (within 36 km from Po Valley), mid range (within 500 km from Po Valley) and long range (everything else far from 500 km)) to PM$_{2.5}$ EC, sulfate and SOA concentrations in Milan for the summer period.
Figure A.17. The contributions from different source areas (local (within 36 km from Po Valley), mid range (within 500 km from Po Valley) and long range (everything else far from 500 km)) to PM$_{2.5}$ EC, sulfate and SOA concentrations in Milan for the winter period.
Figure A.18. The percent contributions from each transport category for different types of organic aerosol during summer and winter period for Milan.