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MODELING OF ORGANIC AEROSOL WITH THE VOLATILITY-BASIS-SET APPROACH DURING THE MEGAPOLI SUMMER CAMPAIGN

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Abstract: An intensive campaign MEGAPOLI for air pollutant measurement (both airborne and ground-based) was launched in the Greater Paris Region in July, 2009. The main objective of this campaign was to quantify different sources of organic aerosols within a megacity and to better understand the interaction of secondary aerosol formation with the gas phase. In the frame of the modeling activity accompanying the campaign, the Volatility-Basis-Set approach is integrated into the regional transport-chemistry model CHIMERE to simulate the formation of secondary organic aerosol. Simulations with this scheme were performed during the MEGAPOLI summer campaign period, as well as simulation with classic two-product method. The results for a campaign day with large local pollution build-up show that with VBS approach, simulated OOA (oxygenated organic aerosol) resulted in a strong plume in the Paris region. The highest value in the plume reaches $10 \mu\text{g m}^{-3}$. The concentration of SOA simulated with two-product method is much less important. This difference shows the important impact of OPOA (oxidized primary organic aerosol) during local formation of OOA. In the downtown of Paris, the peak of OOA reaches about 70% of OA concentration, and an average of 50% of OA concentration is OPOA during this period. This indicates that the VBS approach offers the potential to improve the simulation of secondary organic aerosol in the CHIMERE model for a large European agglomeration.

Keywords: modeling, MEGAPOLI, Volatility-basis-Set, organic aerosol, oxygenated organic aerosol, secondary organic aerosol

INTRODUCTION

Organic aerosol (OA) is one of the main components of fine particulate matter (PM_{2.5}). It has negative impact on human health and also impacts climate. The formation of secondary organic aerosol (SOA) from semi-volatile VOC species (SVOC) is strongly underestimated by most of the current SOA formation schemes. Primary organic aerosol (POA) has long-time been considered in models as non-volatile species, but it has recently been pointed out that an important fraction of POA should evaporate when OA dilutes in air masses away from sources. In addition, a large amount of emissions of VOC of intermediate-volatility (IVOC) has not yet been considered in most of the simulations. Re-evaporated POA, IVOC and SVOC undergo gas phase oxidation which can render them less volatile and then leads to additional SOA formation (Robinson *et al.*, 2007). These features have been recently formalized and parameterized in a method named volatility-basis-set (VBS) approach (Robinson, 2007; Shrivastava *et al.*, 2008).

In the framework of the FP7 / EU project MEGAPOLI, an intensive campaign for air pollutant measurement (both airborne and ground-based) was launched in the Greater Paris Region in July, 2009. The major objective was to quantify different sources of OA within a megacity and to better understand the interaction of secondary aerosol formation with the gas phase. Several Aerodyne aerosol Mass Spectrometers (AMS) from different institutes were settled at 3 sites of the campaign (LHVP [2.36°E, 48.30°N], SIRTÀ [2.20°E, 48.7°N], GOLF [2.55°E, 48.93°N]). They provided preliminary data of daily concentration of organic aerosols and ions species.

In this work, the VBS approach has been integrated into the regional chemistry transport model CHIMERE, in order to improve simulations of primary and secondary aerosol formation within the Greater Paris Region. Several simulations have been performed for the summer MEGAPOLI campaign period with the traditional two-product method (Pun and Seigneur, 2006; Bessagnet, 2008) and the VBS module for POA and SOA formation. The simulation results from these two methods are compared to each other.

METHOD

Model Configuration

The model used in this work is the regional chemistry-transport model (CTM) CHIMERE (see <http://euler.lmd.polytechnique.fr/chimere>). CHIMERE is widely used for operational regional air quality forecast (Honoré *et al.* 2008; <http://www.prevoir.org>) and simulations in Europe (Bessagnet *et al.* 2004). The model has been applied for simulation of gas phase and particulate matter pollution in Europe.

In this work, we used CHIMERE v2008a, performing over 2 nested domains. A continental domain covers Europe with a resolution of 0.5° ($[35-57.5^\circ\text{N}; 10.5^\circ\text{W}-22.5^\circ\text{E}]$) and a regional domain covers the northern France with a resolution of 9 km (see figure 1). 8 hybrid-sigma vertical layers are used, extending to 500hPa, with the first layer at about 40m. Tropospheric photochemistry is represented using the reduced MELCHIOR chemical mechanism (Lattuati, 1997; Derognat, 2003) that includes 120 reactions and 44 prognostic gaseous species. For simulation

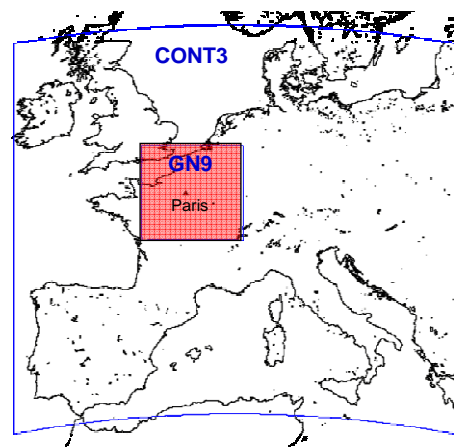


Figure 1. Simulation domain

of particulate phase, 8 bins of particulate sizes are used in the model. The thermodynamic mechanism of inorganic species (sulfate, nitrate and ammonium) is simulated with the ISORROPIA model (Nenes *et al.*, 1998). A classic two-product scheme (Pun and Seigneur 2006; Bessagnet, 2008) is used to model primary and secondary organic species from both anthropogenic and biogenic precursors in the standard version of CHIMERE. The surrogated species were selected by grouping products of particulate-phase species with similar properties. A detailed description of gas phase and particulate phase modeling can be found on the CHIMERE website: <http://euler.lmd.polytechnique.fr/chimere>.

Meteorological parameters are input to the CTM. Output 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 is used. 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. Used with VBS approach, anthropogenic emissions are calculated from EMEP annual totals (<http://www.ceip.at/emission-data-webdab/>) and scaled to hourly emissions applying temporal profiles provided by IER (Friedrich, 1997), and biogenic emissions are calculated using the MEGAN model data and parameterizations (Guenther *et al.*, 2006). Anthropogenic and biogenic emissions data provided by AIRPARIF are used for simulations with the two-product method.

CHIMERE simulations use boundary condition from monthly climatology of GOCART and LMD-INCA2 chemistry transport model.

Integration of Volatility-Basis-Set approach

In order to improve the results of simulated secondary organic aerosol (SOA) in urban regions, the Volatility-basis-Set approach (VBS) is integrated into CHIMERE. Robinson *et al.*, 2007 suggested that most of primary organic particulate is semi-volatile and should evaporate when OA dilutes in air masses away from sources. The evaporated part can oxidize to reproduce oxidized primary organic aerosol (OPOA) with lower volatility which can then recondense. OPOA and SOA are both grouped in a class OOA (oxygenated organic carbon) which can be derived from AMS measurements. A supplementary amount of emissions of intermediate volatile organic compounds (IVOC) with higher volatility should also be considered and was estimated as 1.5 times as those of primary organic aerosol (POA) (Shrivastava, 2008; Murphy and Pandis, 2009). This distribution, and other settings described in the following was used for the current work POA and IVOC emissions were redistributed into 9 classes with the saturation concentrations varying from 0.01 to $10^4 \mu\text{g m}^{-3}$ with a factor of ten between the adjacent bins. The reaction rate constant of SVOC and IVOC with [OH] is estimated as $4 \times 10^{-11} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ (Murphy *et al.*; 2009). The rate constant refers to a decrease of volatility by a factor of 10 due to oxidation. The mass weight of each species is 250g mol^{-1} . Each reaction increases the species mass of 7.5% to account for added oxygen (Shrivastava, 2008). The parameters used to simulate partitioning of POA emissions, ex: the saturation concentration C^* , the enthalpy and emission factors for each class of VOCs are presented in table 1. It has to point out, that settings displayed in Table 1 have been derived from only a limited number of chamber measurements and are affected by significant uncertainty.

Table1. Parameters used to simulate partitioning of POA and IVOC emissions in CHIMERE

	10^{-2}	10^{-1}	10^0	10^1	10^2	10^3	10^4	10^5	10^6
$C^* (\mu\text{g m}^{-3})$ at 298K									
$\Delta H_v (\text{kJ mol}^{-1})$	112	106	106	94	88	82	76	70	64
Emission factors	0.03	0.03	0.09	0.14	0.18	0.3	0.4	0.5	0.8

SIMULATION RESULTS

In this section, case studies of local formation of OOA during the MEGAPOLI summer campaign from simulations with both the classic two-product scheme and with VBS approach are presented. Oxygenated organic aerosols include “classical” secondary organic aerosols originating from anthropogenic and biogenic VOC’s and oxidized primary organic aerosols. In the two product scheme, only classical SOA is considered and contributes to OOA.

Local formation of OOA plume on July 4th and 5th

Local formation of secondary organic aerosol was detected by AMS in Paris downtown in the afternoon of July 4th. This day was characterized by very low wind speeds and build-up of large concentrations of organic aerosol from local emissions. Figure 3a illustrates a consecutive plume case of simulated with VBS approach. The formation of OOA occurred from 15h on July 4th. A plume began to form and was transported towards southeast. A peak value with more than $10 \mu\text{g m}^{-3}$ OOA appeared in the southeast of Paris. In Paris downtown the highest value occurred at 23h with more than $5 \mu\text{g m}^{-3}$. Later during the night, the plume was transported to the northeast and disappeared in the morning of July 5th. On the contrary, with the classic two-product method of SOA formation mechanism, less than $1 \mu\text{g m}^{-3}$ of SOA was produced on that day. Figure 3b displays the results from these simulations.

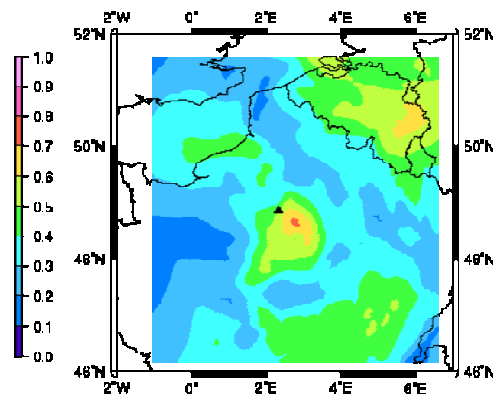


Figure 2. Mean fraction of OPOA(oxidized primary organic aerosol) among OA from 12h July 4th to 12h July 5th

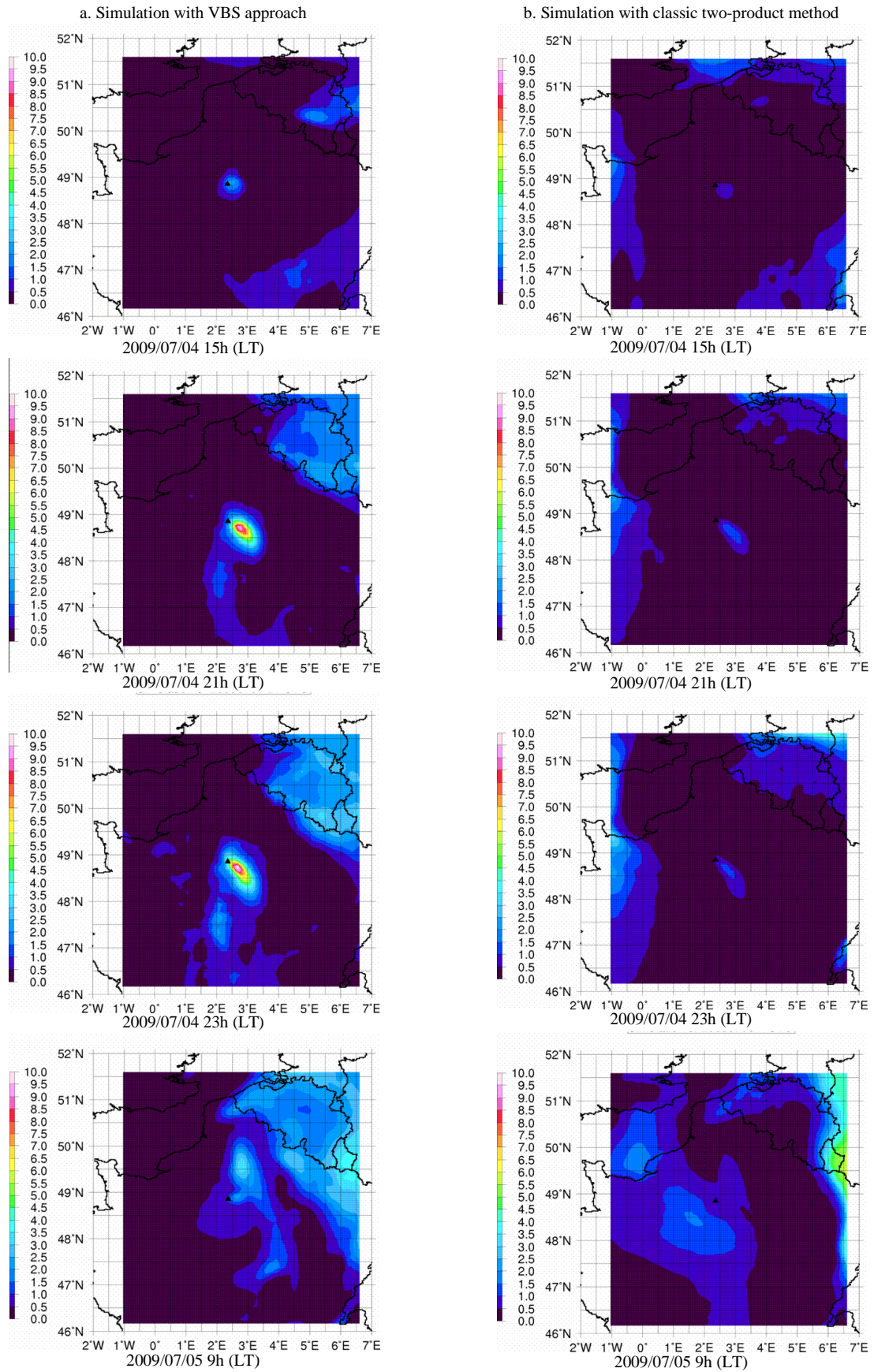


Figure 3. OOA plume with VBS approach (a) and SOA plume with two-product method in GN9 domain

Mean fraction OPOA/OA (from 12h July 4th to 12h July 5th) with VBS

Here, fraction of OPOA in OA concentration is analyzed. Figure 2 displays the mean value of the fraction of OPOA to OA concentration for the selected period. For this period, most of OA was OPOA, up to more than 70% forming locally. Thus, local emissions of POA and IVOC in large cities had an important import on the local formation of OPOA in this case.

Fraction of POA and OOA in OA at LHVP site

OOA was reported to be a main part of in OA from measurements in many megacities (Zhang *et al.* 2007) and from simulations (Murphy and Pandis, 2009) in recent studies. Figure 4 shows the temporal variation of OA and OOA (both OPOA and classic SOA) at the LHVP site within the Paris city. For this site, OA concentrations reached about $7\mu\text{g m}^{-3}$ and OOA concentrations reached $5\mu\text{g m}^{-3}$ for the peak during this period. On average, more than 45% of OA was contributed by OOA. OOA fraction reached 90% at 17h, July 4th and about 80% for the peak at 23h. Thus, not only in the plume, but also in the Paris urban area, OOA contributes a large fraction to OA.

CONCLUSION

Volatility-Basis-Set approach has been integrated into CHIMERE. Simulations with VBS approach were performed during the MEGAPOLI summer campaign, as well as simulation with classic two-product method. These two methods are compared during a period with local formation of OOA, from July 4th to July 5th. The results simulated with VBS approach showed an OOA plume produced in Paris region. The highest value in the plume reached about $10\mu\text{g m}^{-3}$. On the contrary, the results from the two-product method simulation showed much lower OA and OOA levels below $1\mu\text{g m}^{-3}$. This is due to the neglect of the formation of OPOA in the simulation, which can contribute to more than 70% of OA concentration in the plume. The next step of this work will now be to carefully compare these model results to the measurements that will become available from the MEGAPOLI campaign. These measurements will constitute an important benchmark to discern between the very different simulation results with the VBS and the two-product method.

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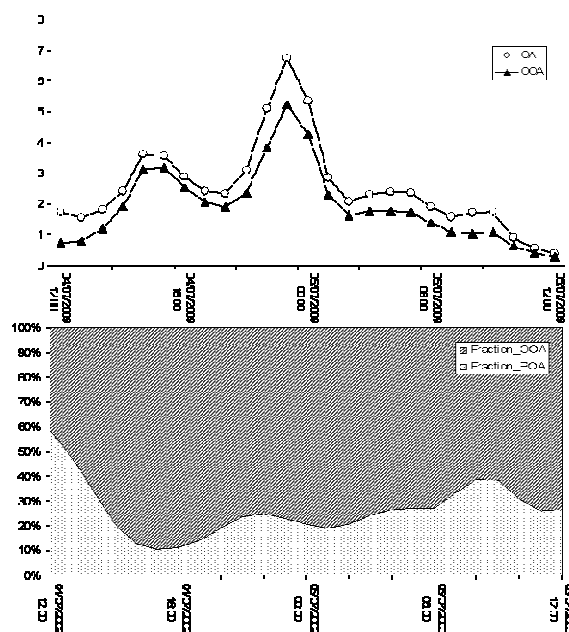


Figure 4. Temporal variation of simulated OA and OOA concentrations in $\mu\text{g m}^{-3}$ (above) and fraction of POA and OOA in OA (below)

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