



Modeling organic  
aerosol composition  
at the puy de Dôme  
mountain

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# Modeling organic aerosol composition at the puy de Dôme mountain (France) for two contrasted air masses with the WRF-Chem model

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## Abstract

5 Simulations with the chemistry-transport model WRF-Chem are compared to aerosol measurements performed at the puy de Dôme station with a compact Time-of-Flight Aerosol Mass Spectrometer (cToF-AMS) for two episodes in autumn 2008 and in summer 2010. The WRF-Chem model is used with the Volatility Basis Set (VBS) approach dedicated to the formation of secondary organic aerosol (SOA). The model systematically underestimates the observed concentrations of organic aerosol (OA), with significant differences observed for the summer case. For this event, where high OA concentrations were observed ( $12.5 \mu\text{g m}^{-3}$  in average), simulated OA mass concentration is  $2.0 \mu\text{g m}^{-3}$ . For the autumn event, observed OA concentrations reached  $2.6 \mu\text{g m}^{-3}$ . The simulated concentrations reached only  $0.6 \mu\text{g m}^{-3}$ .

10 During the summer event, several gas-phase volatile organic compounds (VOCs) were measured and were used to test the robustness of both emission/dry deposition and SOA formation processes. The concentrations of VOCs, and more specifically the anthropogenic ones, calculated by the model are estimated to be much lower than the observed ones. Hence, the emissions of all SOA precursors are multiplied by 2 in the model: this induces an increase of the mean OA mass concentration of 25 % ( $+0.5 \mu\text{g m}^{-3}$ ) and 18 % ( $+0.4 \mu\text{g m}^{-3}$ ), respectively for anthropogenic and biogenic VOCs. The dry deposition of gas-phase organic condensable vapours (OCVs) is also critical to predict the SOA mass concentrations: dividing the deposition factor by 2 leads to an increase of OA mass by an additional 12 % ( $+0.2 \mu\text{g m}^{-3}$ ). However, these increases were not sufficient to explain the observed OA concentration, and the underestimation of the OA concentration levels seems to be principally related to a lack in the parameterization of SOA formation. Changing the oxidation rate of OCVs from  $1.0 \times 10^{-11}$  to  $4.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , doubling the SOA yields for anthropogenic VOCs and finally doubling the SOA yields for biogenic VOCs results in an increase of the mean OA mass concentration by 56 % ( $+1.1 \mu\text{g m}^{-3}$ ), 61 % ( $+1.2 \mu\text{g m}^{-3}$ ) and 40 % ( $+0.8 \mu\text{g m}^{-3}$ ), respectively. The consideration of both emission/dry deposi-

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tion and SOA formation processes tests lead to a mean OA mass concentration of  $10.7 \mu\text{g m}^{-3}$  for 2010, a value that is close to the observations. For 2008, modifying solely the oxidation rate of OCVs and the SOA yields is sufficient to reproduce the observed level of mean OA mass (a mass of  $2.4 \mu\text{g m}^{-3}$  is obtained by the model whereas a mass of  $2.6 \mu\text{g m}^{-3}$  was observed).

## 1 Introduction

In the atmosphere, aerosol particles play key roles on climate, air quality, and human health (IPCC, 2013). These particles are composed of a complex mixture of organic and inorganic species originating from both biogenic and anthropogenic sources. Particulate organic matter comes from primary organic aerosols (POA) directly emitted to the atmosphere. Secondary organic aerosols (SOA) are formed through chemical reactions that convert more volatile species into lower volatility products, which are then distributed in the particulate phase. Organic aerosols (OA) represent a large fraction (from 20 to 90 %) of the submicron particulate mass at both urban and remote locations (Zhang et al., 2007), and they are mainly composed of secondary organic aerosols (from 63 to 95 %; Ng et al., 2010b; Zhang et al., 2011). Despite the ubiquity of OA in the atmosphere, there are still large uncertainties in understanding the formation pathways of SOA (Kanakidou et al., 2005). Consequently, OA sources and physico-chemical transformations during their transport remain poorly represented in Chemistry-Transport Models (CTMs) (Hallquist et al., 2009; Volkamer et al., 2006).

Field measurements clearly demonstrate that the main sources of organic aerosols over the European continent in winter are the gaseous precursors and the primary particles emitted by the human activities (use of fossil fuels and biomass burning), whereas biogenic sources are predominant in summer (Gelencsér et al., 2007; Szidat et al., 2006). Analysis of organic aerosol mass spectra measured from an Aerosol Mass Spectrometer (AMS) allows the separation of the global organic aerosol into smaller groups of organic compounds such as hydrocarbon-like organic aerosol (HOA), tracer

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of primary emissions, and oxygenated organic aerosol (OOA) resulting from chemical transformations and gas-phase condensation (Aiken et al., 2008; Zhang et al., 2005). As HOA mainly results from the combustion sources, their contribution to the organic aerosol is important during winter, while the OOA fraction is predominant during summer (Lanz et al., 2010).

In the last decade, a large number of intensive field campaigns have been performed to characterize the inorganic and organic mass concentrations of the atmospheric aerosol, as well as the molecular composition of the organic particulate matter. Aircraft and ground-based measurements showed that aerosol species concentrations in the boundary layer are higher than those observed in the free troposphere. Some measurements also highlighted that mass contribution of organic aerosol to the total particulate matter is higher in the free troposphere than in the boundary layer (Crumeyrolle et al., 2013a, b; Heald et al., 2006; Murphy et al., 2006). The origin of air masses also determines the mass concentrations of the organic aerosols: high concentrations have been measured for air masses transported over polluted areas (Freney et al., 2011; Freutel et al., 2013). Even though these in situ observations provide information on the aerosol sources, as well as concentration levels, they are not numerous enough to describe the spatiotemporal size and chemical distribution of these particles (Kulmala et al., 2011; Zhang et al., 2007). Only very recently, the work of Crippa et al. (2014) offered, with measurements from 17 sites, including the puy de Dôme (PUY) station (France), an unprecedented overview of OA sources in Europe. However, even when widespread, observations are rather difficult to interpret in term of source identification/quantification and in term of chemical/physical processes responsible for the observed concentrations.

Chemistry-transport models allow linking the physical-chemical behaviour of gas phase species and particulate matter to their emission and transport (Baklanov et al., 2014; Kukkonen et al., 2012). Until recently, they were mainly implemented in “offline” configurations; i.e. meteorological fields are input parameters provided by an independent model. Decoupling meteorology and chemical processes can lead to a significant







6 h. The correspondence established by Emmons et al. (2010) between the MOZART-4 chemical species and several chemical mechanisms implemented in the WRF-Chem model such as RACM (Stockwell et al., 1997) is used to allocate the concentrations of 35 gaseous species and all particulate compounds defined by MOZART-4 to the WRF-Chem model species.

The WRF-Chem model includes several options for physical parameterizations and the main options adopted in this paper are listed in Table 1. These include: the Noah Land Surface Model (Chen and Dudhia, 2001), the Yonsei University planetary boundary layer scheme (Hong et al., 2006), the Grell-Devenyi cumulus parameterization (Grell and Dévényi, 2002), the Rapid Radiation Transfer Model long-wave radiation scheme (Mlawer et al., 1997), the Goddard shortwave radiation scheme (Chou et al., 1998) and the microphysical scheme of Morrison (Morrison et al., 2009). Chemical options used here are detailed in the next section.

## 2.2 Gas-phase mechanism and parameterization of SOA formation

The gas-phase chemical mechanism used is RACM (Stockwell et al., 1997), which includes 84 species and 252 reactions. This mechanism takes into account the oxidation of VOCs from both anthropogenic (alkanes, alkenes, ...) and biogenic (isoprene, monoterpenes and sesquiterpenes) sources. Initially, the RACM mechanism implemented in the WRF-Chem model did not include sesquiterpenes. To take into account the contribution of these VOCs to SOA production, the sesquiterpenes class was added within the RACM mechanism by Ahmadov et al. (2012) following the work of Papiez et al. (2009).

The WRF-Chem model commonly uses the aerosol module Modal Aerosol Dynamics Model for Europe (MADE; Ackermann et al., 1998) for the inorganic fraction coupled to the Secondary Organic Aerosol Model (SORGAM; Schell et al., 2001) for the organic fraction, which is based on a two-product approach (Odum et al., 1996). Since this parameterization tends to underestimate OA concentrations (McKeen et al., 2007), the WRF-Chem model has been recently updated by Ahmadov et al. (2012) by coupling the

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a monthly temporal resolution from 1990 to 2010, which allows the seasonal variations of gaseous species and aerosols emissions to be taken into account. MACCity provides emission fluxes for carbon monoxide (CO), sulfur dioxide (SO<sub>2</sub>), ammoniac (NH<sub>3</sub>), nitrogen oxide (NO<sub>x</sub>), Volatile Organic Compounds (VOCs), organic carbon (OC) and elemental carbon (EC).

Contrary to others European inventories such as EMEP (Vestreng et al., 2007) or TNO-MACC (Denier Van der Gon et al., 2011), MACCity better discriminates VOCs compounds and provides the emission rates of several VOCs like ethane, propane, and ethene. This facilitates the distribution of the 19 chemical species present in the emission inventory into the chemical species considered in the chemical mechanism RACM (Geiger et al., 2003; Stockwell et al., 1997). More precisely, some emitted species like CO, SO<sub>2</sub> or NH<sub>3</sub> are directly linked to the chemical species considered in the chemical mechanism. As it is assumed that the majority of NO<sub>x</sub> is primarily emitted in the form of NO, NO<sub>x</sub> emissions are assigned to NO. For emitted VOCs, they are not all in direct correspondence with those of the chemical mechanism. In this particular case, the VOCs emissions are disaggregated into model species following the aggregation procedure proposed by Middleton et al. (1990). This procedure is done in two steps. First, the emitted species are divided into 32 emission categories according to their reactivity towards the HO<sup>•</sup> radical, the magnitude of their emission rates and the similarities in their functional chemical groups. Second, these emission categories are further condensed into a smaller set of VOCs classes that directly correspond to those in a particular mechanism (here RACM). The partitioning ratios that redistribute emitted species into emission categories and aggregation factors used in this study are listed in Table S1.

For aerosol species, the emissions of organic carbon (OC) are converted into particulate organic matter (POA) multiplying the value by a conversion factor of 1.6 as proposed by Bessagnet et al. (2008). Then, 20 % of EC and POA emissions are allocated to the Aitken mode of the aerosol distribution and 80 % to the accumulation mode as proposed by Ackermann et al. (1998).

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Biogenic emissions are calculated online using MEGAN (Model of Emissions of Gases and Aerosols from Nature; Guenther et al., 2006) that uses a 1 km × 1 km resolution. Since isoprene emissions account for more than 50 % of VOCs emissions from vegetation (Wiedinmyer et al., 2004), MEGAN quantifies the net biogenic emissions of isoprene. It also estimates emissions of monoterpenes (myrcene, sabinene, limonene,  $\alpha$ -pinene,  $\beta$ -pinene, etc.), oxygenated compounds (methanol, acetone, acetaldehyde, ethanol, formic acid, etc.), sesquiterpenes ( $\alpha$ -farnescene,  $\beta$ -caryophyllene), and nitrogen oxide.

Biomass burning emissions are derived from the Fire Inventory from NCAR version 1.0 (FINNV1). As described by Wiedinmyer et al. (2011), global estimates of gas ( $\text{CO}_2$ , CO,  $\text{CH}_4$ , non-methane hydrocarbons NMHC, non-methane organic compounds NMOC,  $\text{H}_2$ ,  $\text{NO}_x$ ,  $\text{NH}_3$ ,  $\text{SO}_2$ ) and particle (OC, BC,  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$ ) emissions from open burning of biomass (wildfire, agricultural fires and prescribed burning) are provided with a daily temporal resolution and a spatial resolution close to 1 km.

### 2.4 Description of the sampling site and measurements

Measurements were conducted at the PUY research station located in the middle of France (45.46° N, 2.57° E) at 1465 m.a.s.l. This station is located either in the boundary layer or above depending on the time of the day and the season (Venzac et al., 2009). The station is equipped with a range of instruments measuring meteorological parameters, gas-phase species concentrations and aerosol physico-chemical properties. These instruments are regularly calibrated as part of the international networks to which the station belongs: the ACTRIS (Aerosols, Clouds, and Trace gases Research InfraStructure network) and GAW (Global Atmosphere Watch) networks. It also hosts intensive measurement campaigns such as the EMEP campaigns. During these campaigns supplementary instruments are deployed at the station. In particular, an Aerodyne compact Time of Flight Aerosol Mass Spectrometer (cToF-AMS) (Canagaratna et al., 2007; Drewnick et al., 2005) provides detailed information on the chemical composition and mass concentration of the non-refractory submicron particulate matter







### 3.3 Model statistical evaluation performance

In order to evaluate the WRF-Chem model performance, the simulation results for meteorological parameters (temperature, relative humidity and pressure) are compared with observations performed at the PUY station using several statistical performance measures recommended by Chang and Hanna (2004), which include the fractional bias (FB), the geometric mean bias (MG), the normalized mean square error (NMSE), the geometric variance (VG), and the fraction of predictions within a factor of two of observations (FAC2). Those statistical calculations are reported in the Supplement for more details. Computed statistics for meteorological parameters for autumn 2008 and summer 2010 are presented in Table S2. For the autumn case, pressure measurements were not available. The statistics for all meteorological parameters for both situations are well within the acceptable range.

Statistical analyses have also been performed for trace gases concentrations (i.e. ozone (O<sub>3</sub>) and carbon monoxide (CO)) and are presented in Table S3. For O<sub>3</sub> and CO concentrations, in September 2008 as well as in June 2010, the model respects all criteria of acceptance. Since the O<sub>3</sub> concentrations, as well as those of CO are well captured by the model, we can conclude that the WRF-Chem model is able to correctly simulate both the chemical reactivity and the transport.

### 3.4 Volatile organic compounds

A small number of biogenic (BVOCs) and anthropogenic (AVOCs) VOC species was measured during the 2010 experiment, at the PUY station. For the BVOCs, three monoterpene species are available:  $\alpha$ -pinene,  $\beta$ -pinene and limonene. These species represent from 10 up to 50% of the VOCs emissions from the vegetation (Guenther et al., 2000). They are taken into account in the model: API species in the model includes  $\alpha$ -pinene,  $\beta$ -pinene and other cyclic terpenes with one double bond and LIM species in the model groups together with d-limonene and other cyclic diene-terpenes. Their oxidation by the hydroxyl radical HO<sup>•</sup>, ozone O<sub>3</sub> or nitrate radicals NO<sub>3</sub><sup>•</sup> can lead

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to the formation of SOA (von Hessberg et al., 2009; Kristensen et al., 2014). The SOA yield of these VOC species is variable depending on their initial concentrations, the  $\text{NO}_x$  concentrations, the type of oxidants, the temperature, the relative humidity and the radiation (Lee et al., 2006). Typically, the SOA yields of these species are below 20 % but may reach 60 % for high concentrations of VOCs (Lane et al., 2008).

Measured AVOCs species included *n*-octane and *n*-nonane, benzene, toluene and ethylbenzene and *o*-; *m*-; *p*-xylenes, 2-; 3-; 4-ethyltoluene and 1,2,4-; 1,2,3- and 1,3,5-trimethylbenzene. Those species are emitted by industrial activity and traffic, and unfortunately are not represented in the model as individual species. Thereby, *n*-octane and *n*-nonane are included in the HC8 model species (alkanes, alcohols, ester and alkynes with  $\text{HO}^\bullet$  greater than  $6.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K and 1 atm); benzene, toluene and ethylbenzene are included in the TOL model species (toluene and less reactive aromatics) and finally *o*-; *m*-; *p*-xylenes, 2-; 3-; 4-ethyltoluene and 1,2,4-; 1,2,3- and 1,3,5-trimethylbenzene are included in the XYL model species (xylene and more reactive aromatics).

The temporal evolutions of pinenes and limonene concentrations simulated and observed are presented in Fig. 2. These comparisons show that the diurnal variation of these two species, with higher concentration levels during daytime than during nighttime, is well captured by the model. However, their concentration levels are underestimated by the model in average: by factors 2 and 10 respectively for pinenes and limonene.

The time evolutions of the AVOCs (alkanes, xylene and toluene) simulated and observed (Fig. 3) highlight a strongest underestimation of the concentration levels by the model compared to biogenic gaseous precursors of SOA. This underestimation of VOCs by the model is probably due to missing organic species in the emission inventories and to the misinterpretation of VOCs that are lumped in the emission inventories and in the model.



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For the autumn case, the WRF-Chem model overestimates the sulphate particles average mass concentrations observed at the PUY station over the whole period by 10 % whereas ammonium, nitrate, and black carbon average mass concentrations are underestimated by 20, 40, and 120 %. More precisely, the model does not respect any criteria except the random scatter acceptance ( $NMSE < 1.5$ ) for nitrate mass concentration. It is even worse for the black carbon concentration, for which the model does not respect any criteria.

For the summer case, the WRF-Chem model underestimates all aerosol species mass concentrations observed at the PUY station. Statistics for sulphate, ammonium and black carbon mass concentrations show smaller errors than for nitrate mass concentrations. Comparison between statistical results and acceptance criteria show that the model respects all criteria only for the sulphate mass concentration. For the autumn case, the model correctly reproduces the sulphate mass concentration observed at the PUY station; ammonium, nitrate and black carbon mass concentrations are quite well captured by the model. Statistical results are not shown for chloride, since concentration levels are too small.

For ammonium and nitrate, the model underestimation is probably due to some residual sources caused by agricultural activities that are not well considered in the model. The underestimation of the black carbon mass concentration is probably due to the anthropogenic emission inventory used in this study which is too coarse to correctly represent the local emissions of black carbon which is a primary particle, directly emitted into the atmosphere from fossil fuel and biomass combustion. The mass concentrations of organic aerosol mass are poorly reproduced by the model, especially for the 2010 situation, where the modeled organic aerosol mass concentration was 6 times lower than the measured values.

Before discussing this discrepancy at the PUY site, the spatial distribution of OA over Europe is presented. Figure 5 shows the simulated averaged ground-level concentrations of OA, distinguishing among primary OA (POA), anthropogenic SOA (ASOA) and biogenic SOA (BSOA) over the entire periods of interest (from the 23 to the



sions of BVOCs from nearby Landes forest and Pyrenees mountains but also from the northern Portugal characterized by broadleaf trees.

The seasonal global patterns obtained with WRF-Chem for summer 2010 and autumn 2008 situations are consistent with those drawn by Fountnoukis et al. (2014). At the PUY station (Fig. 4), the largest seasonal contrast observed appears for organic species with concentration levels clearly higher in summer than in autumn. The model underestimates the organic species mass concentrations as they are only  $0.6 \mu\text{g m}^{-3}$  (13 % of the total aerosol mass concentration) and  $2.0 \mu\text{g m}^{-3}$  (27 % of the total aerosol mass concentration) in the autumn and in the summer case respectively.

The underestimation of the organic aerosol concentrations is observed in most modeling studies (de Gouw, 2005; Heald et al., 2005; Hodzic et al., 2010; Jimenez et al., 2009). In particular, such discrepancies were already mentioned by Langmann et al. (2014) who have also used the measurements performed at the PUY site during the same 2010 period with the 3-D model REMOTE (Regional Model with Tracer Extension; Langmann, 2000; Langmann et al., 2008). In Langmann et al. (2013), SOA formation is represented by a new parameterization derived from the two-product approach (Odum et al., 1996). Langmann et al. (2014) found that the OA mass concentrations are in the range of the measurements by increasing the BVOCs emissions by a factor of 5 and considering that 10 % of the secondary organic compounds reach a saturation vapour pressure low enough to move into the next lower volatility category.

In connection to the underestimation of the organic aerosol concentration, the model underestimates VOC concentrations for both anthropogenic and biogenic contributions in 2010 (Sect. 3.4). In the following section, those discrepancies are analysed using the available measurements, and the uncertainties remaining in the SOA formation processes in the WRF-Chem model are discussed.

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## 4 Discussion

### 4.1 Uncertainties in OA formation

Some of these uncertainties were studied by Murphy and Pandis (2010) and Farina et al. (2010) by varying several parameters and processes that drive the atmospheric SOA formation. In our study, we concentrate on SOA formation since SOA contribute mainly to OA concentration measured at the PUY site. Indeed, the results of unconstrained PMF analysis on the total OA mass spectra measured during June 2010 at the PUY station identified two predominant factors (LV-OOA:  $66 \pm 13\%$  and SV-OOA:  $34 \pm 13\%$ ), typical for background rural sites (Freney et al., 2011). No primary HOA factor was identified. OOA (the sum of LV-OOA and SV-OOA) and HOA components are respectively considered as surrogates for SOA and POA (Ng et al., 2010a). Crippa et al. (2014) recently used a constrained PMF algorithm, ME-2, to re-analyse a number of datasets in which OA data from the PUY was included (autumn 2008 and spring 2009). After the reanalysis of the OA mass spectra and constraining a HOA factor, an LV-OOA ( $35 \pm 4\%$ ) and SV-OOA ( $55 \pm 18\%$ ) were identified as with the unconstrained PMF. However, in addition to these species, two less aged species, HOA and BBOA, contributing  $3.5 \pm 2.5\%$  and  $14 \pm 4\%$  respectively, were also identified. Although the constrained ME-2 analysis was not applied to the June 2010 dataset, it is likely that HOA would contribute  $< 10\%$  to the total organic aerosol.

Emission inventories for both biogenic and anthropogenic are uncertain. For instance, the estimation of isoprene biogenic emissions over Europe varies from a factor 3 up to a factor of 10 (Guenther et al., 2006; Smiatek and Bogacki, 2005). Zare et al. (2012) show that the annual emissions of isoprene over the Northern Hemisphere estimated by the MEGAN model for the year 2006 are  $526 \text{ Tgyr}^{-1}$ , 21 % higher than those provided by the GEIA model (Global Emissions Inventory Activity; Guenther et al., 1995). Monoterpenes and sesquiterpene emissions are often underestimated in models due to their strong reactivity and high aerosol yields (Griffin et al., 1999; Sakulyanontvittaya et al., 2008). Although sesquiterpenes have lower emission



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sopoulou et al., 2013). Simulation of OA concentrations have been based on the gas-particle partitioning of semi-volatile organics (Pankow, 1994) using three types of approach: two oxidation products (called the two-product approach) developed by Odum et al. (1996), the molecular approach (Couvidat et al., 2012; Pun et al., 2002), and the volatility basis set (VBS) approach (Donahue et al., 2006; Jimenez et al., 2009; Kroll and Seinfeld, 2008). The first method is derived from chamber observations (Chung and Seinfeld, 2002; Griffin et al., 1999) and largely underestimates ambient SOA since it does not account for chemical aging reactions. These reactions are important in the atmosphere because they can reduce volatility of organic compounds and increase SOA mass yields (Donahue et al., 2006; Jimenez et al., 2009; Kroll and Seinfeld, 2008). VBS has been developed to mitigate this lack of aging in the two-product approach. Several recent regional modeling studies are accounting for the semi-volatile nature and chemical aging of organic compounds both in the gas phase (OCVs) and/or in the aerosol phase demonstrating improvements in reproducing the organic aerosol budget and its chemical resolution (Ahmadov et al., 2012; Athanasopoulou et al., 2013; Bergström et al., 2012; Fountoukis et al., 2011, 2014; Hodzic et al., 2010; Murphy and Pandis, 2009; Shrivastava et al., 2011; Tsimpidi et al., 2010; Zhang et al., 2013). In VBS, the oxidation products are sorted into logarithmically spaced volatility bins that allow representing a wider range of organic compounds in the atmosphere. However, all these studies using recent OA parameterizations lack one or more potentially important processes such as the aging reactions, the semi volatile character of POA or the potential source of SOA from aqueous phase processes (Ervens et al., 2011).

In the SOA formation parameterizations, SOA yields are based on experiments conducted in atmospheric simulation chambers where several single VOCs are oxidized under specific conditions (temperature, relative humidity,  $\text{NO}_x$  concentrations, ...). The individual yields of each VOC are summed to model SOA from multiple species. However, due to the myriad of VOCs present in the atmosphere, it is not realistic to provide SOA yields for all these species through experimental studies and the extrapolation of



chamber-derived SOA yields to atmospheric conditions is an important source of error (Hao et al., 2011).

For the simulation of SOA aging processes using the VBS approach, it is generally assumed that OCVs react with HO<sup>•</sup>. Bergström et al. (2012) used the VBS framework in the EMEP model to study SOA formation over Europe. They found that the model results were in better agreement with all observations relative to the simulations without aging processes. They showed that the aging constant plays an important role because a high value leads to high mass concentrations of SOA, and *vice versa*. The aging constant of OCVs results in large differences in model results and can range from  $2.5 \times 10^{-12}$  to  $4.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Farina et al., 2010; Fountoukis et al., 2014; Lane et al., 2008; Murphy and Pandis, 2009, 2010).

To a lesser extent, in current chemistry-transport models, SOA concentrations are sensitive to the assumptions made on dry deposition of gas-phase SVOCs (Ahmadov et al., 2012) that are competing with uptake of gases to the organic particle phase. The effect of dry deposition of gas-phase OCVs on SOA concentrations is largely unconstrained since in many cases the deposition velocity of OCVs is proportional to the one of nitric acid (HNO<sub>3</sub>), which is very soluble. Bessagnet et al. (2010) found that neglecting dry deposition of semi-volatile organic compounds may lead to overestimations of SOA concentrations by as much as 50%. However, in their estimations they assign a solubility parameter to lumped oxidation products of aromatics and biogenic precursors, and are neglecting other important molecular properties (Hodzic et al., 2014; Lane et al., 2008; Robinson et al., 2007). Pye and Seinfeld (2010) distinguished between freshly emitted OCVs with a very low Henry's law constant ( $< 10 \text{ Matm}^{-1}$ ) and oxidation products that are treated using a Henry's law constant of  $10^5 \text{ Matm}^{-1}$ . They found that a considerable fraction is removed through the gas-phase. In a sensitivity study, they lowered the Henry's law constants for OCVs and showed that the global OA budget is sensitive to this parameter, but not conclusive to explain model bias against observations.

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concentration simulated. Although none of the acceptance criteria are reached by the model, both the median geometric mean (MG) and the random errors (NMSE, VG) are reduced in comparison with the baseline simulation (Table 2).

The comparisons between available measurements of VOCs from anthropogenic sources and simulation results have shown that the HC8, TOL, and XYL species are strongly underestimated by the model (Fig. 3). As observations are not available for the others AVOCs, it is difficult to determinate an accurate correction factor. So, it has been decided to increase the emissions of the AVOCs by a factor of 2, as has been done for the BVOCs emissions. This allows us to compare the contribution of anthropogenic vs. biogenic emissions to SOA formation.

Doubling the amount of AVOCs emissions leads to a slight increase in the average OA mass concentrations since the fractional bias is reduced from 1.4 to 1.3 (−10%) with smaller systematic (FB, MG) and non-systematic errors (NMSE, VG) (Table 2). However, still 0% of values are within a factor of two of the observations. So, for this situation, increasing the anthropogenic emissions results in an equivalent impact on OA formation than increasing the biogenic ones.

The next test performed with WRF-Chem consists in decreasing the deposition velocity of the OCVs since this parameter is very susceptible to the solubility of OCVs. Underestimation of organic aerosol mass with the model could also be attributed to too high dry deposition velocities of OCVs. Even if OCVs are known to be highly water soluble, not much is known about their effective Henry's law constants ( $H^*$ ) varying between  $10^5$  and  $10^{10}$  Matm<sup>−1</sup> as estimated by structure-activity relationships (SAR) of Raventos-Duran et al. (2010). Recently, based on this SAR, Knote et al. (2015) provided new deposition rates for each biogenic and anthropogenic volatility bins of OCVs that are more realistic but need further experimental validation. In the WRF-Chem model, a deposition factor is used as a fraction (25%) of those of HNO<sub>3</sub> (Ahmadov et al., 2012) that is a crude estimation for lumped organic species. Dividing this deposition factor by 2 slightly improves the model results. All statistics are better compared to the baseline simulation: the mean bias, and also the random errors are reduced.

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Similar impacts are found when doubling the emissions or reducing the deposition and are in agreement with Ahmadov et al. (2012) findings.

Two main parameters are driving the organic aerosol formation: the SOA yields defined in the VBS parameterization presented in Table S5 and the oxidation rate of OCVs by  $\text{HO}^\bullet$ , also referred as the aging of SOA. There have been a number of laboratory studies focusing on SOA yields, i.e. the mass of SOA produced per mass of reacted precursor. These mainly depend on the organic precursor molecules and on the oxidants initiating the degradation ( $\text{HO}^\bullet$ ,  $\text{O}_3$ ,  $\text{NO}_3^\bullet$ ). Experiments in large environmental chambers covering a large temperature range are particularly suited to derive parameterisations that are valid under real world conditions. However, formation of SOA in laboratory chambers may be substantially suppressed due to losses of SOA-forming vapours to chamber walls, which leads to underestimates of SOA in air-quality and climate models, especially in urban areas where anthropogenic SOA precursors dominate (Zhang et al., 2014).

In WRF-Chem model, SOA yields are taken from Murphy and Pandis (2009). Some other estimations exist such as in Farina et al. (2010) who used lower yields for the formation of SOA from AVOCs. So, we performed a sensitivity test using this latter set of SOA yields from Farina et al. (2010). As expected, the average organic aerosol mass concentration is reduced by 18%: from  $2.0 \mu\text{g m}^{-3}$  (obtained with Murphy and Pandis, 2009, yields) to  $1.7 \mu\text{g m}^{-3}$  with Farina et al. (2010) yields. In our case, to favour SOA formation and due to the uncertainties on SOA yields from VOCs, new tests are performed by increasing the yields of both AVOCs and BVOCs by a factor 2. When doubling the SOA yields of AVOCs, the fractional bias (FB) is reduced from 1.4 to 1.2 (meaning an underestimation of observations by the model by 120 instead of 140%), while it is only reduced from 1.4 to 1.3 by modifying the SOA yields of BVOCs (Table 2).

In the WRF-Chem model, the first generation VOC oxidation products may react with the hydroxyl radical  $\text{HO}^\bullet$  and undergo further oxidation processes. An oxidation rate of  $1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is used to implement these reactions within the gaseous chemical mechanism. As mentioned above, Bergström et al. (2012) recommended the

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use of an oxidation rate of  $4.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with the VBS approach which is the most widely used for semi/intermediate volatile organic compounds (S/IVOCs). So, we test this new oxidation rate and perform statistics again. The bias is reduced to 1.2 as in the test on SOA yields of AVOCs (Table 2).

Thus, our results show that the SOA yields of the VOCs and the oxidation rate of the first generation VOC oxidation products implemented in the WRF-Chem model are very sensitive parameters to represent the transfer of the VOCs to the particulate phase, as already suggested by Farina et al. (2010). The changes applied individually to the yields and the oxidation rate of OCVs allow to improve the representation of the OA by the model but are not sufficient to simulate the organic aerosol concentration levels observed at the PUY.

In summary, among all the performed tests on SOA formation, the last series of tests on SOA yields and oxidation rates of OCVs lead to model predictions in closer agreement with measurements than tests on emissions/dry deposition.

#### 4.2.2 All effects

Statistical results show good performance of the model when combining all effects with a small bias of 0.2 compared to 1.4 in the baseline simulation. Taking into account all contributions leads to an increased content of the OA concentration of around  $10.8 \mu\text{g m}^{-3}$  that is close to the observed value of  $12.5 \mu\text{g m}^{-3}$  (Table S6). This better performance in simulating OA formation is mostly due to the combination of tests on SOA yields and oxidation rate of OCVs. Results of the tests clearly show that the influence of SOA formation processes ( $\text{OA} = 8.6 \mu\text{g m}^{-3}$ ) is more efficient at obtaining an accurate representation of measured OA concentrations than modifying emissions/dry deposition ( $\text{OA} = 3.1 \mu\text{g m}^{-3}$ ).

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### 4.2.3 Partitioning of anthropogenic vs. biogenic SOA

The most recent generation of models appears to be particularly challenged in regions where anthropogenic and biogenic emissions mix and have suggested that anthropogenic emissions enhance SOA formation from BVOCs, though to varying degrees (Carlton et al., 2010; Spracklen et al., 2011). So, it is interesting to look at the partitioning of SOA among POA, ASOA and BSOA in the model.

Figure 6a presents results of all tests related to the mass concentration of OA observed and simulated at the PUY station averaged over the weekly episode of 2010. The spatially and temporally averaged POA concentrations, which are on average  $\approx 0.4 \mu\text{g m}^{-3}$  at the PUY station, are the same among all runs. Unlike POA, mean ASOA and BSOA concentrations vary significantly between the runs depending on the various settings. The difference between the various tests result in a more pronounced increase of BSOA compared to ASOA (Fig. 6a). Changing the oxidation rate of OCVs from  $1.0 \times 10^{-11}$  to  $4.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  favors more particularly BSOA formation whose average mass concentration is increased by 87 % whereas the ASOA average mass concentration increases by 56 % (Table S6).

In order to estimate the impact of aging processes from anthropogenic and biogenic OCVs separately, additional simulations were conducted by changing the oxidation rate of OCVs from  $1.0 \times 10^{-11}$  to  $4.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  of anthropogenic OCVs on the one hand and of biogenic OCVs on the other hand. As expected, the impact of modifying the oxidation rate of anthropogenic OCVs has a larger impact on the formation of ASOA than on the formation of BSOA: ASOA and BSOA average mass concentrations are respectively increased from 1.0 to  $1.5 \mu\text{g m}^{-3}$  (+51 %) and from 0.6 to  $0.7 \mu\text{g m}^{-3}$  (+5 %). The impact of the modification of the oxidation rate of biogenic OCVs on the BSOA average mass concentration is much more pronounced than the one due to the change of the oxidation rate of anthropogenic OCVs on the ASOA average mass concentration. Indeed, ASOA and BSOA average mass concentrations

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are respectively increased from 1.0 to 1.1  $\mu\text{g m}^{-3}$  (+5%) and from 0.6 to 1.2  $\mu\text{g m}^{-3}$  (+81%).

Matsui et al. (2014) have also studied separately the impact of the aging of anthropogenic and biogenic OCVs using the VBS approach over East Asia. In their study, the impact of aging processes of anthropogenic OCVs on BSOA concentrations is much more important than the one of biogenic OCVs on ASOA concentrations. This difference is attributed to the dominance of the anthropogenic sources over East Asia. Moreover, they showed that aging of anthropogenic OCVs is a determinant parameter controlling OA formation from both anthropogenic and biogenic sources. Indeed, they found that the aging of anthropogenic OCVs enhances considerably BSOA concentrations since large amounts of low-volatile organic compounds and ASOA are produced and contribute to a shift of the gas-particle partitioning ratio of the BSOA to the particulate phase. On the contrary, ASOA enhancement by aging processes of biogenic OCVs appeared to be very limited. In our study, the aging of anthropogenic OCVs does not seem to control OA formation since the enhancement of BSOA by aging processes of anthropogenic OCVs is close to 5%. The organic aerosol sampled at the remote PUY station is rather controlled by both anthropogenic and biogenic sources.

Even if the modifications applied to emissions/dry deposition has a lesser effect on OA formation (Table S6), it should be underlined that increasing BVOCs emissions reduces ASOA formation. These supplementary BVOCs likely consume  $\text{HO}^\bullet$  which is then no longer available to oxidize AVOCs (Carlton et al., 2010). Freney et al. (2011) found that organic aerosol particles measured at the PUY site during summer 2010 were likely linked to biogenic sources: the mass spectra of OOA (oxygenated organic aerosols) had spectral characteristics similar to SOA formed from chamber studies using alpha-pinene. This is not reproduced in the baseline 2010 simulation (Fig. 6a), but is reproduced in the simulation including modified oxidation rates of OCVs, SOA yields and increased emissions.

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This work shows that model underestimation seems to be mainly due to a lack in SOA formation processes. Indeed increasing the traditional aging rate of  $1.1 \times 10^{-11}$  to  $4.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and doubling the SOA yields of both anthropogenic and biogenic SOA precursors leads to an increase in the OA mass concentration of  $6.6 \mu\text{g m}^{-3}$  whereas when only emission/dry deposition changes are taken into account, the increase is only  $1.1 \mu\text{g m}^{-3}$ . These results highlight the importance of the aging processes of OCVs in the SOA formation. More measurements in the real atmosphere of both VOCs and OA mass concentrations are needed to constraint model parameterizations and emission inventories.

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**Table 1.** WRF-Chem model configuration (<http://www.wrf-model.org>).

Process	WRF-Chem option
Land-surface model	Noah Land Surface Model
Boundary layer scheme	Yonsei University
Long-wave radiation	Rapid Radiation Transfer Model
Short-wave radiation	Goddard
Microphysics	Morrison
Cumulus parameterization	Grell-Devenyi

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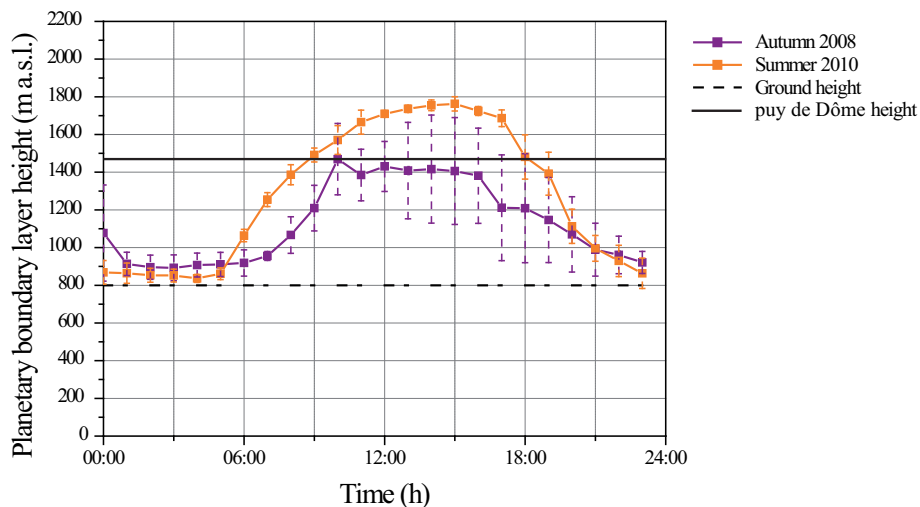


**Table 2.** Statistical results and comparison between statistical performance measures and criteria acceptance for organic aerosol mass concentrations for the baseline simulation and for sensitivity tests (individual and combined) for the summer 2010 period (bold font indicates good model performance).

Simulations	NMSE < 1.5	FB  FBI  < 0.3	FAC > 0.5	VG < 4	MG 0.7 < MG < 1.3
Baseline	4.5	1.4	0.0	27.7	6.1
BVOC emissions ×2	3.5	1.4	0.0	16.2	5.3
AVOC emissions ×2	3.2	1.3	0.0	13.0	4.9
Dry deposition factor/2	3.8	1.4	0.0	18.7	5.5
BSOA yields ×2	2.7	1.3	0.0	9.5	4.4
ASOA yields ×2	2.2	1.2	0.0	6.0	3.8
Oxidation rate of OCVs	2.3	1.2	0.0	6.6	3.9
Dry deposition and emissions	2.3	1.2	0.0	7.1	4.0
Oxidation rate of OCVs and SOA yields	<b>0.2</b>	0.4	<b>1.0</b>	<b>1.2</b>	1.4
All effects	<b>0.1</b>	<b>0.2</b>	<b>1.0</b>	<b>1.1</b>	<b>1.2</b>

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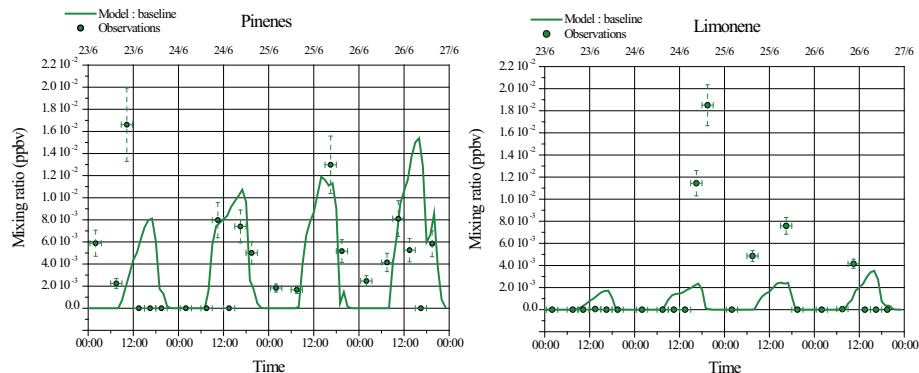


**Figure 1.** Boundary layer height simulated by the WRF-Chem model at the PUY station.



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**Figure 2.** Biogenic VOCs mixing ratios measured at the PUY station and calculated for the baseline simulation for summer 2010. Left: [ $\alpha$ -pinene +  $\beta$ -pinene] vs. [API model species]. Right: [limonene] vs. [LIM model species].

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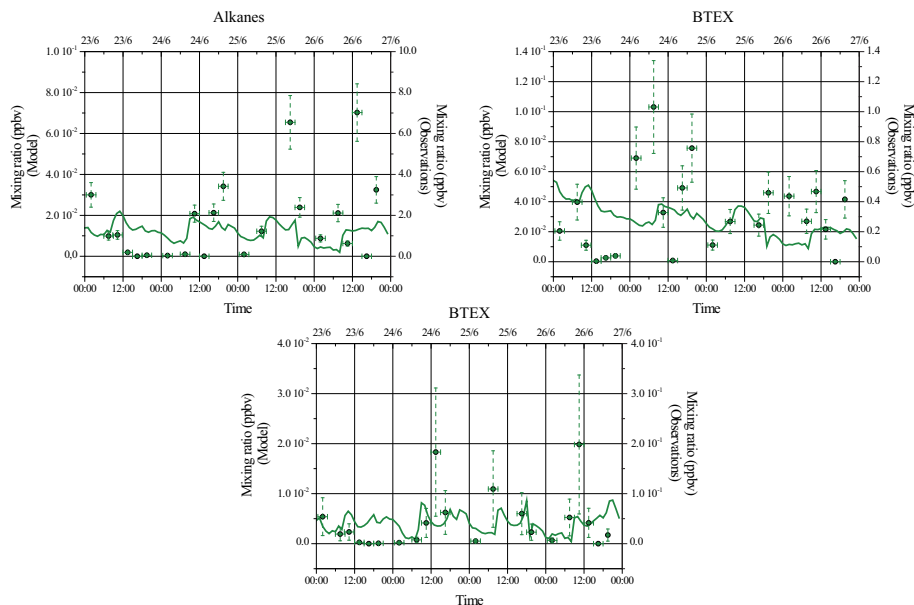
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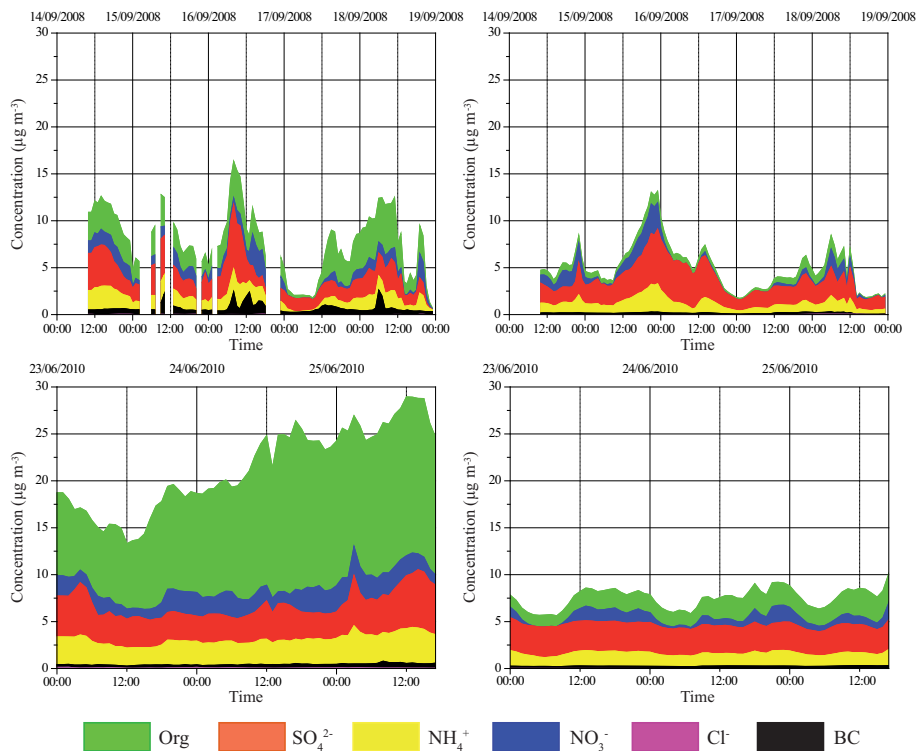
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**Figure 3.** Anthropogenic VOCs mixing ratios measured at the PUY station and calculated for the baseline simulation for summer 2010. Top-Left: [n-octane + n-nonane] vs. [HC8 model species]. Top-Right: [benzene, toluene + ethylbenzene] vs. [TOL model species]. Bottom: [o-; m-; p-xylenes, 2-, 3-, 4-ethyltoluene + 1,2,4-, 1,2,3-, 1,3,5-trimethylbenzene] vs. [XYL model species].

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**Figure 4.** Temporal evolution of the aerosol mass concentrations ( $\mu\text{g m}^{-3}$ ) measured at the PUY station (left) and simulated by the WRF-Chem model (right) for autumn 2008 (top) and summer 2010 (bottom).

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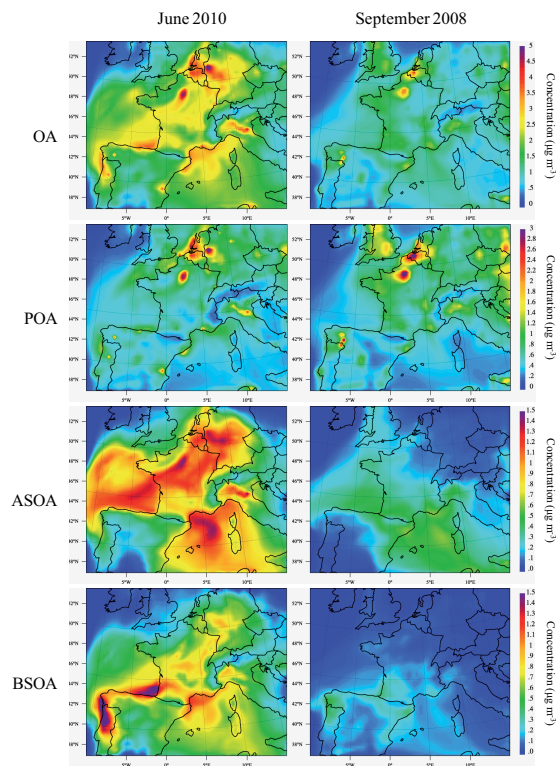
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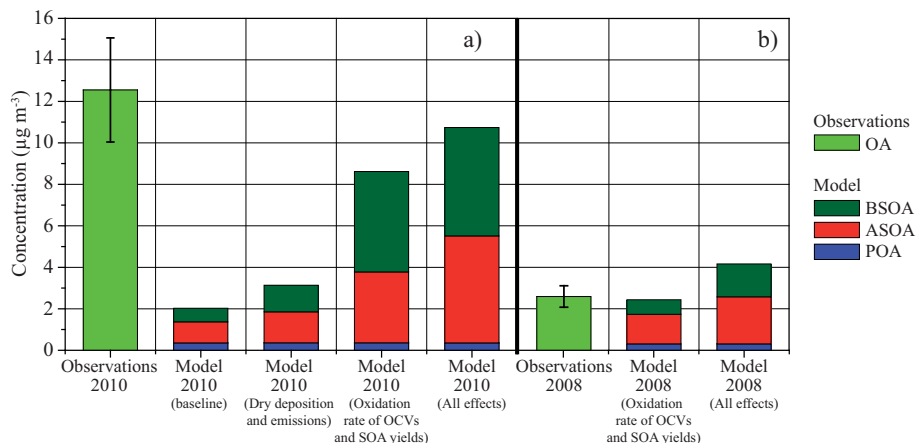


**Figure 5.** Averaged ground-level mass concentrations predictions for OA, POA, ASOA, BSOA over the model domain for September 2008 and June 2010 episodes.

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**Figure 6. (a)** Averaged OA mass concentration observed and simulated at the PUY in summer 2010 for the baseline simulation and for sensitivity tests (dry deposition/emissions, oxidation rate of OCVs/SOA yields, all effects cumulated). **(b)** The most significant tests for autumn 2008 are reported for comparison with summer 2010. Uncertainty in OA mass concentration measurements is estimated to 20 % (Bahreini et al., 2009; Middlebrook et al., 2011).