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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

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 systemati-

cally 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 μg m⁻³ in average), simulated OA mass concentration
 is 2.0 μg m⁻³. For the autumn event, observed OA concentrations reached 2.6 μg m⁻³. The simulated concentrations reached only 0.6 μg m⁻³.

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 specifi-

- ¹⁵ cally 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 μ gm⁻³) and 18% (+0.4 μ gm⁻³), respectively for anthropogenic and biogenic VOCs. The dry deposition of gas-phase organic condensable vapours (OCVs)
- ²⁰ 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 μ gm⁻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 × 10⁻¹¹ to 4.0 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹, doubling the SOA yields for anthro-
- pogenic VOCs and finally doubling the SOA yields for biogenic VOCs results in an increase of the mean OA mass concentration by 56% (+1.1 µgm⁻³), 61% (+1.2 µgm⁻³) and 40% (+0.8 µgm⁻³), respectively. The consideration of both emission/dry deposi-



tion and SOA formation processes tests lead to a mean OA mass concentration of $10.7 \,\mu g \,m^{-3}$ 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 $2.4 \,\mu g \,m^{-3}$ is obtained by the model whereas a mass of $2.6 \,\mu g \,m^{-3}$ 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

 ²⁰ 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
 ²⁵ 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



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 sum-⁵ mer (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

- ¹⁰ 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
- ¹⁵ 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.

²⁵ 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



loss of process information (e.g. cloud/radiation feedbacks for example) because the physical and chemical processes usually occur on a time scale smaller than the time step of the meteorological model (Zhang, 2008). In "online" models where meteorological and chemical processes are solved simultaneously on the same grid, the errors in

vertical mass distribution are smaller than in "offline" models because the strong variability in vertical velocity is attributable to high frequency motions (periods less than 10 min) (Baklanov et al., 2014). Online models allow simulating complex aerosol-cloud-radiation feedbacks, solving physical and chemical processes on the same grid and at the same time, exclude numerical problems resulting from spatiotemporal interpolation of meteorological fields (Grell et al., 2004).

Currently, large gaps still remain between simulated and measured SOA concentrations: 3-D models tend to underestimate SOA concentrations both at regional and global scales and especially during summertime periods (Carlton et al., 2010; Knote et al., 2011; Yu et al., 2007). The models underestimate the SOA mass formed by

- ¹⁵ a factor ranging from 8 to 100 in both the boundary layer (Kleinman et al., 2008; Volkamer et al., 2006) and in the free troposphere (Heald et al., 2005). This underestimation is much more important in polluted areas (Heald et al., 2005; Hodzic et al., 2010; Volkamer et al., 2006) compared to remote areas located away from anthropogenic emission sources for which simulated SOA concentrations are closer to observations
- (Chen et al., 2009; Hodzic et al., 2009; Slowik et al., 2010). The most recent generation of models appear to be particularly challenged in regions where anthropogenic and biogenic emissions mix and have suggested that anthropogenic emissions enhance SOA formation from biogenic volatile organic compounds (Emanuelsson et al., 2013; Shilling et al., 2013). Carlton et al. (2010) estimate that approximately 50 % of the total biogenic SOA loading is from "anthropogenically controlled" biogenic SOA while
- total biogenic SOA loading is from "anthropogenically-controlled" biogenic SOA while Spracklen et al. (2011) come to an estimate of 70 %.

The uncertainties in 3-D models may be amplified by uncertainties in model inputs such as emissions but also by model treatments such as gas-phase mechanisms, aerosol treatments that involve simplifying hypothesis. For example as a result of the



complexity of volatile organic compounds (VOCs) identified in the atmosphere (Goldstein and Galbally, 2007), chemical species with similar characteristics (reactivity, functional groups, volatility, ...) are aggregated into one model species. This assumption can lead to potential errors in the chemical treatment of VOCs and thereby in SOA

formation. Also, SOA formation pathways are sketched in transport models using parameterizations such as the most recent one called Volatility Basis Set (VBS) approach (Donahue et al., 2006), which is based upon SOA yields and VOCs oxidation rates that have been evaluated in simulation chambers under controlled conditions (pressure and temperature, chemical concentrations, humidity, etc.) that are far from real atmospheric conditions (Hao et al., 2011). 10

In this study, the central objective will be the evaluation of such uncertainties using the WRF-CHEM model (Weather Research and Forecasting - Chemistry; Grell et al., 2005) to simulate SOA formation. Due to its versatility, WRF-Chem is attracting a large user and developer community worldwide (Baklanov et al., 2014). In Europe, it is being used for regional air quality studies (Ritter et al., 2013; Solazzo et al., 2012; Tuccella 15 et al., 2012), for the impact of emissions from megacities, and for the impact of biomass burning and biogenic emissions on elevated ozone levels during the 2007 European hot summer (Hodnebrog et al., 2012). WRF-Chem is continually developed, improved and additional options are being implemented such as parameterizations for SOA formation

(Ahmadov et al., 2012). 20

This paper will evaluate the ability of the WRF-CHEM model to reproduce the organic aerosol mass concentration originated from anthropogenic or/and biogenic emissions for two contrasted air masses. The model output will be compared to data available at the PUY station (France). For the first time, the detailed aerosol chemical composition

from AMS measurements combined with measurements of their gas phase precur-25 sors (both anthropogenic and biogenic VOCs) will allow evaluating the capacity of the WRF-Chem model to correctly simulate the concentrations levels observed at the site. This provides a unique opportunity to test remaining uncertain parameters involved in



the OA formation (emission/dry deposition vs. SOA formation processes) in the WRF-Chem model.

2 Modeling observed situations at the puy de Dôme (France)

2.1 Model set up

- ⁵ The model used in this study is the version 3.4.1 of the WRF-Chem model (Grell et al., 2005). WRF-Chem is an online model with state-of-the-art formulations of physical and chemical parameterizations and especially for the formation and aging of aerosols. The simulations last one week, which is the timescale of interest for simulating SOA formation episodes. Two nested domains are used as shown in Fig. S1. The coarse
- domain is located over Europe with a spatial resolution of 30 km and defined by 73 and 61 horizontal grid points respectively in the West–East and North–South directions. This domain is adapted to follow the origins of the air masses transported over the Atlantic Ocean, over the Mediterranean Sea or over continental area. The inner domain is located over France with a spatial resolution of 10 km and is defined by 130 and
- 97 horizontal grid points respectively in the West–East and North–South directions to focus on a region including mountains around the PUY measurement station. Vertical levels are used with enhanced resolution in the near-surface and planetary boundary layer. This allows the model to better represent the lower layers of the atmosphere and more specifically the variations of the boundary layer height where atmospheric pollutants are emitted.

The initial and boundary meteorological conditions come from ERA-Interim European reanalysis (Dee et al., 2011) provided by the European Centre for Medium-range Weather Forecast (ECMWF). They are available every 6 h with a horizontal resolution of 0.5°. The global model MOZART-4 (Emmons et al., 2010) provides initial and ²⁵ boundary conditions for concentrations of gaseous species and aerosol particles with a spatial resolution of 1.9° per 2.5° on 56 vertical levels and a temporal resolution of



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

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¹⁵ 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



RACM gas-phase mechanism and the MADE inorganic aerosol module to the Volatility Basis Set (Ahmadov et al., 2012; Donahue et al., 2006, 2009; Lane et al., 2008; Murphy and Pandis, 2009) for the SOA formation. MADE/VBS in WRF-Chem uses the modal approach with three log-normally distributed modes (Aïtken, accumulation and coarse mode). The aerosol species treated in MADE/VBS are the main inorganic ions (NH⁺₄, NO⁻₃, SO²⁻₄), elemental carbon (EC), organic matter (OM, primary and secondary OA), water, sea salt, and mineral dust.

Alkanes, alkenes, toluene, xylene, and cresol emitted by anthropogenic activities and isoprene, monoterpenes, and sesquiterpenes from biogenic sources are all oxidized by the hydroxyl radical HO[•], ozone O_3 or nitrate radicals NO_3^{\bullet} in the gas-phase mechanism. Once these species are oxidized, the VBS parameterization is used to partition the organic matter produced between gas and aerosol phases according to their volatility. Donahue et al. (2006) have suggested that the numerous organic compounds present in the atmosphere can be described by lumping the species with similar

- ¹⁵ volatilities in a decade of different volatilities bins established according to the saturation concentration (*C*^{*}): *C*^{*} is ranging from 0.01 and $1 \mu g m^{-3}$ for "Low Volatile Organic Compounds" (LVOCs) and between 10 and $1000 \mu g m^{-3}$ for "Semi Volatile Organic Compounds" (SVOCs). The "Intermediate Volatile Organic Compounds" (IVOCs) are characterized by saturation concentrations ranging from 1000 to 100 000 $\mu g m^{-3}$. The
- ²⁰ 1-D-VBS parameterization by Ahmadov et al. (2012) used in WRF-Chem, includes a four-bin volatility basis set with C^* ranging from 1 to 1000 µg m⁻³ at 298 K and are separated by one order of magnitude. In Ahmadov et al. (2012), the SOA yields are different for two regimes: high- and low-NO_x conditions. Under low-NO_x conditions, the peroxy radicals react preferentially with other peroxy radicals to form products that are
- ²⁵ characterised by lower volatilities and consequently higher SOA yields. Under high-NO_x conditions, the peroxy radicals react with NO to form other chemical products for which the SOA yields are lower. Moreover, the organic condensable vapours (OCVs), i.e. first generation VOCs oxidation products that condense on particles, may undergo a chemical aging by oxidizing with the hydroxyl radicals. According to the classification



of Donahue et al. (2006), OCVs represented in that 1-D-VBS parameterization correspond to LVOCs ($C^* = 1 \,\mu\text{gm}^{-3}$) and SVOCs ($10 \,\mu\text{gm}^{-3} < C^* < 1000 \,\mu\text{gm}^{-3}$). Among OCVs, only SVOCs are aging and the oxidation processes are modeled using a rate constant for the reaction of OCVs with HO[•] radicals equal to $1.0 \times 10^{-11} \,\text{cm}^3$ molecule⁻¹

- ⁵ s⁻¹. After each oxidation reaction, the volatility of the OCVs is reduced by one order of magnitude and the mass is increased by 7.5% to account for supplementary oxygen atoms. The 1-D-VBS scheme neglects fragmentation processes whereas in the real atmosphere, there might be an offset between functionalization (decreased volatility) and fragmentation (increased volatility) effects, especially for biogenic SOA (Donahue et al.,
- ¹⁰ 2011, 2012; Murphy et al., 2012). However, the 1-D-VBS approach still shows a better performance than a functionalization and fragmentation scheme (Murphy et al., 2012) which requires too many parameterizations (e.g. functionalization kernel and functionalization/fragmentation branching ratio) that are poorly constrained (Jo et al., 2013).
- The chemistry component of WRF-Chem adopts the radiative transfer TUV ¹⁵ (Madronich, 1992). The dry deposition of gas-phase species is parameterized according to Erisman et al. (1994) based on the resistance concept of Wesely (1989). For OCVs, the dry deposition velocity is assumed to be proportional to the deposition velocity of nitric acid (HNO₃) that is a very soluble gas (effective Henry's law: H^{*} = 2.69×10^{13} Matm⁻¹). The ratio between dry deposition velocities of OCVs and dry ²⁰ deposition of HNO₃ is determined through a factor (denoted by Ahmadov et al., 2012 as "depo_fact"), which is set to 0.25 due to the lack of observations available to constraint it. For aerosol particle species, dry deposition is calculated according to the Wesely approach (Wesely and Hicks, 2000).

2.3 Emissions

Anthropogenic emissions are taken from the MACCity inventory (MACC/CityZEN EU projects; Granier et al., 2011; Lamarque et al., 2010) available on the ECCAD database (Emissions of atmospheric Compounds and Compilation of Ancillary Data, see http://eccad.sedoo.fr/). Data are available with a spatial resolution of 0.5° per 0.5° and with



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 (SO₂), ammoniac (NH₃), nitrogen oxide (NO_x), 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, SO₂ or NH₃ are directly linked to the chemical species considered in the chemical mechanism. As it is assumed that the majority of NO_x is primarily emitted in the form of NO, NO_x emissions are assigned to NO. For emitted VOCs, they are not all in direct cor-

- ¹⁵ respondence 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[•] 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 Aïtken mode of the aerosol distribution and 80% to the accumulation mode as proposed by Ackermann et al. (1998).



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, α -pinene, β -pinene, etc.), oxygenated compounds (methanol, acetone, acetaldehyde, ethanol, formic acid, etc.), sesquiterpenes (α -farnescene, β -caryophyllene), and nitrogen oxide.

Biomass burning emissions are derived from the Fire Inventory from NCAR ver-¹⁰ sion 1.0 (FINNv1). As described by Wiedinmyer et al. (2011), global estimates of gas (CO₂, CO, CH₄, non-methane hydrocarbons NMHC, non-methane organic compounds NMOC, H₂, NO_x, NH₃, SO₂) and particle (OC, BC, PM_{2.5} and PM₁₀) 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.

15 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

- ²⁰ 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 cam-
- paigns 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



(NR-PM1), including sulphate, ammonium, nitrate, chloride and organic mass concentrations. The organic aerosol mass spectra were separated into different organic groups using Positive Matrix Factorisation (PMF) analysis using the procedures outlined in UIbrich et al. (2009). Details of this analysis is provided in Freney et al. (2011) for the EMEP campaigns from 2008 to 2010. To access the black carbon mass concentration, measurements are also performed using a Multi Angle Absorption Photometer (MAAP 5012). Aerosol measurements were performed behind a Whole Air Inlet (WAI) which upper 50% size-cut is 30 µm allowing to sample aerosols both under clear sky and cloudy conditions. Under cloudy conditions, cloud droplets are evaporated in the WAI so that the residual aerosols pass into the sampling probes. The cToF-AMS was not 10 connected to the WAI, and all cloudy periods were hence filtered out from the data set. In addition, VOCs species are measured at the PUY station since 2010 through active sampling on sorbent cartridges. Gaseous compounds are sampled through a Teflon sampling line on cartridge containing a mixture of Tenax TA 60-80 mesh (250 mg) and carbosievesIII (150 mg) at 100 mLmin⁻¹ during 3 h. This type of car-15

- tridges allows C4-C14 aromatic compounds, n-alkanes, monoterpenes and halogenated compounds to be sampled. The VOCs trapped by the cartridges are then analysed by a gas chromatograph–mass spectrometer system (GC/MS, Perkin Elmer) connected to an automatic thermal desorption. The cartridge is desorbed at 270 °C dur-
- ing 25 min at a flow rate of 40 mL min⁻¹ and reconcentrated in a second trap, at -10°C containing a mixture of Tenax TA and Carbosieve SIII. After the cryofocussing, the trap is rapidly heated to 300°C and the target compounds are flushed into the GC. The separating column is a 60 m × 0.25 mm × 0.25 µm Elite-5MS (5% phényl 95% PDMS) capillary column (Perkin Elmer).
- Detailed investigations of the chemical and microphysical properties of atmospheric aerosol particles were performed at the PUY research station in autumn (September and October 2008), winter (February and March 2009), and summer (June 2010) by Freney et al. (2011). In this paper, two particular episodes have been selected out of those observed periods of time to illustrate typical extremes that are encountered at the



top of the PUY: continental vs. Mediterranean air masses (i.e. polluted vs. remote air masses), for two seasons. Also, the case study period was chosen over days without any changes in the air mass origins so to be able to study the evolution of aerosol chemical composition within the same air mass. This was the case in autumn 2008 (from the 14 to the 18 September 2008) and in summer 2010 (from the 23 to the 26 June 2010).

3 Results

As discussed before, two air mass origins are studied with contrasting chemical composition between autumn 2008 and summer 2010. Prior to looking at organic aerosol evolution, it is important to verify that the WRF-Chem model correctly reproduces both the origin of air masses and the meteorological conditions. For these two situations, this is important to determine if the measurements at the PUY station are located in the boundary layer or are free from direct surface influences. Then, some OA gas phase precursor measurements were available, solely during 2010, and will be compared to WRF-Chem outputs. Finally, aerosol chemical composition observed at PUY will be simulated with the model.

3.1 Backward trajectories

In order to determine the origin of the air masses arriving at the top of the PUY, 48 h backward trajectories were computed using WRF-Chem every 6 h for the two episodes.

²⁰ Trajectories were classified according to their predominant transport direction prior to arriving at the PUY site following Freney et al. (2011) as either "Continental" (C), "Marine" (M), "Marine modified" (Mod), and "Mediterranean" (Med) (Fig. S2). For the summer case, as the air masses are all coming from the North sector and are classified as "Continental". For the autumn case, the backward trajectories exhibit two transport pathways over the whole period of time. On the 14 September 2008, air masses arriving



at the PUY are crossing the north-east of the France and Germany, and are characterized as "Continental". On the 18 September, the backward trajectories change to a southerly direction where they pass over the Mediterranean Sea and Spain. They are then described as "Mediterranean". These classifications are in agreement with those made by Freney et al. (2011) with the lagrangian model HYSPLIT widely used for atmospheric dispersion.

3.2 Boundary layer height

The puy de Dôme mountain can be either in the boundary layer (BL) or in the free troposphere/residual nocturnal layer. A recent study, based upon LIDAR measurements follows the seasonal variations of the boundary layer height (BLH) at the PUY station (Hervo et al., 2014). This study shows that the summit is mainly located in the free troposphere during winter and at night-time while in daytime summer it is merged into the BL. Further comparisons between the BLH retrieved from LIDAR profiles and the time series of BL tracers were conducted in Rose et al. (2014), indicating that there were little forced convection effects from the PLIX on the BL dynamics, likely due to

- ¹⁵ were little forced convection effects from the PUY on the BL dynamics, likely due to its relatively isolated pic topographic configuration. WRF-Chem model is able to reproduce the general diurnal evolution of the BLH observed by Hervo et al. (2014) as well as the seasonal variations between autumn and summer (Fig. 1). However, the very complex topography of the area around the puy de Dôme would require in WRF-Chem
- the use of a very fine vertical resolution (less than 1 m which is not practised in current transport-chemistry models). The height of the puy de Dôme summit is underestimated by the model since the surface elevation calculated by the model is 799 m (dotted black line) instead of 1465 m the real altitude of the puy de Dôme (full black line in Fig. 1). For this reason, according to the model, the summit would be always located in the
- BL independent of the season. Consequently, in the rest of the paper, results will be discussed at the real PUY height, where the WRF-Chem model correctly simulates the location of the summit with respect to the boundary layer.



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 obser-

vations (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_3) and carbon monoxide (CO)) and are presented in Table S3. For O_3 and

¹⁵ CO concentrations, in September 2008 as well as in June 2010, the model respects all criteria of acceptance. Since the O_3 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

- ²⁰ 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: α -pinene, β -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 in-²⁵ cludes α -pinene, β -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[•], ozone O_3 or nitrate radicals NO[•]₃ can lead



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 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 $_{5}$ 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 1,3,5trimethylbenzene. 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 HO[•] greater than 6.8×10^{-12} cm³ molecule⁻¹ 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.

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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.



3.5 Simulating aerosol particles

WRF-Chem model outputs are compared with in situ cToF-AMS aerosol measurements made at the PUY site for autumn 2008 (from the 14 to the 18 September) and summer 2010 (from the 23 to the 26 June 2010) (Freney et al., 2011).

Figure 4 shows the temporal evolution of sulphate (SO₄²⁻), nitrate (NO₃⁻), ammonium (NH₄⁺), chloride (CI⁻), black carbon (BC) and organics mass concentrations measured at the PUY station and simulated by the WRF-Chem model. The average mass concentration observed for the summer case (21.3 µg m⁻³) is significantly higher compared to autumn (7.2 µg m⁻³). Similar tendencies appear in simulations results but the model strongly underestimates the average total aerosol mass concentration (7.5 and 5.1 µg m⁻³ respectively for summer and autumn situations).

Based on the average aerosol mass concentrations for the two campaigns (autumn 2008 and summer 2010 respectively), organic species measured at the PUY station represent 2.7 and $12.5 \,\mu g m^{-3}$, sulphates 2.4 and $3.7 \,\mu g m^{-3}$, ammonium 1.3 and $2.7 \,\mu g m^{-3}$, nitrates 1.0 and $2 \,\mu g m^{-3}$ and black carbon 0.6 and $0.4 \,\mu g m^{-3}$ of the

and 2.7 μgm⁻³, nitrates 1.0 and 2 μgm⁻³ and black carbon 0.6 and 0.4 μgm⁻³ of the total particle mass concentration. The lowest mass concentrations are observed for non-refractive chloride particles: less than 0.01 and 0.1 μgm⁻³ respectively for autumn 2008 and summer 2010.

The average concentration levels of inorganic species modeled for the two campaigns (autumn 2008 and summer 2010, respectively) are fairly close to those observed: sulphates represent on average 2.6 and 3.0 μ gm⁻³, ammonium 1.1 and 1.4 μ gm⁻³, nitrates 0.6 and 0.8 μ gm⁻³ and black carbon 0.2 and 0.2 μ gm⁻³ of the total modeled particle mass concentration. For each inorganic aerosol species, mass concentrations and results of the statistical analyses are presented in Table S4. The agree-

ment between modeled and measured concentrations is not as good as the agreement with previous parameters (meteorological or chemical tracers). This is a result of the complexity of the processes involved in the formation and aging of the inorganic particles or of missing sources for primary compounds such as black carbon.



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 concentra-
- tion 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



26 June 2010 and from the 14 to the 18 September 2008). POA is the main OA component during both seasons since it contributes respectively 34 and 62 % to the total OA. The dominant secondary component of OA is ASOA for both cases, with a contribution of 57 % during June 2010 and 70 % during September 2008. During June 2010,

- ⁵ highest OA concentrations are simulated over a large area covering the northern part of France (over Paris agglomeration), Benelux and Northwestern Germany, while in southern Europe, and more particularly over Spain, lower concentrations are simulated ($\approx 1.5 \,\mu g \,m^{-3}$). During this period, a continental flux has been identified by air mass backward trajectory calculations: polluted air masses are transported from northern to
- southern Europe. POA and ASOA are important in northern part of Europe. BSOA is predominantly produced in the north of Spain and in Portugal. Zhang et al. (2013) studied the formation of organic aerosols in the Paris region during the summer campaign of MEGAPOLI using the CHIMERE model and the VBS approach, and reported similar patterns over Europe when northeasterly winds result in the advection of pollution from Benelux and Rhine-Ruhr region.

OA concentration levels simulated over Europe during autumn are lower compared to those simulated during summer. However, the peaks of OA mass concentrations calculated for 2010 over Paris and the Benelux area still remain in 2008 simulation but are mainly due to POA emissions.

For September 2008, ASOA mass concentrations are highest in the southwestern of France, eastern Spain and over the Mediterranean Sea. Backward trajectory calculations show that from 14 to 17 September a continental air mass crossed over Europe. On the 18 September 2008, the transport pathway of the air mass deviates from continental to Mediterranean origin. ASOA is produced from AVOCs emissions in the north

of Europe and is rapidly transported towards the south during the days characterized by a continental air mass origin. When the air mass origin deviates, pollutants are advected once again towards north; this can explain strongest ASOA mass concentrations located around the Mediterranean basin. As for the June 2010 period, BSOA mass concentrations are highest in the north of Spain, probably linked to the emis-



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 μg m⁻³ (13% of the total aerosol mass concentration) and 2.0 μg 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.



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±13% and SV-OOA: 34±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

- ¹⁵ 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.
- ²⁰ 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 Tg yr⁻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



rates than isoprene or monoterpenes, they may contribute significantly to SOA formation because they are very reactive and have high aerosol yields (Lane et al., 2008). Light and temperature are known to be the most important environmental factors controlling BVOCs emissions from plants, but little is known about their interdependen-

- ⁵ cies especially for BVOCs other than isoprene that are very numerous. For example, monoterpene and sesquiterpene emissions from *Quercuscoccifera* exhibit interacting responses to light and temperature (Staudt and Lhoutellier, 2011). Regarding anthropogenic emissions, several studies mention that the inventories traditionally used in the models are too static, e.g. with low time and space resolution (Menut et al., 2012;
- ¹⁰ Mues et al., 2012; Skjøth et al., 2011). Generally the emissions are redistributed over the model grid. Then, temporal profiles defined per activity sector are applied on each grid point of the model domain in order to determine the emission rate value. However, emission intensity varies according to the activity type, the area, the emitted species and their emission processes but as well as by the meteorological conditions (e.g.
- ¹⁵ temperature and relative humidity) (Mues et al., 2014). De Meij et al. (2006) showed that emissions with a seasonal temporal resolution are sufficient to correctly simulate the particulate organic matter and the black-carbon whereas emissions with weekly or daily temporal resolution are required to accurately represent NO_x, NH₃, and particulate nitrate. Moreover, some anthropogenic emission sources such as the emissions
- linked to the cooking activity are not taken into account in the European emission inventories even if they are recognized as an important organic aerosol source in North America (Ham and Kleeman, 2011; Schauer et al., 2002) and in Europe (Mohr et al., 2012; von der Weiden-Reinmüller et al., 2014; Zhang et al., 2013). Likewise, emissions of primary biological aerosol particles are not often considered in the inventories
 whereas they contribute to the particulate organic matter (Heald and Spracklen, 2009;
 - Winiwarter et al., 2009).

OA concentrations are often underestimated in global and regional chemical transport models (Dzepina et al., 2009; O'Donnell et al., 2011; Volkamer et al., 2006) where multi-step oxidation of semi-volatile compounds is not explicitly described (Athana-



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 bud-
- ¹⁵ get 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,
- ²⁰ 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

²⁵ under specific conditions (temperature, relative humidity, 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[•]. Bergström et al. (2012) used the VBS framework
⁵ 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 × 10⁻¹² to 4.0 × 10⁻¹¹ cm³ molecule⁻¹ 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 (HNO₃), 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
- ²⁰ 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 Matm⁻¹) and oxidation products that are treated using a Henry's law constant of 10⁵ Matm⁻¹. They
- ²⁵ 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.



All the uncertainties just mentioned above are critical to accurately simulate SOA formation. We use the summer 2010 experiment, where high-time resolution measurements were available for both aerosol and gas-phase species in order to evaluate a series of sensitivity tests to improve the modeled OA concentrations.

5 4.2 Sensitivity tests

To attempt to explain the observed discrepancies between measured and modeled organic aerosol mass concentrations, a series of sensitivity tests have been pursued. A number of parameters identified as sources of uncertainties are modified. Emissions and dry deposition of gas phase precursors of SOA have been tested together with parameters controlling the SOA formation (yields and oxidation rates of OCVs). Sensitivity studies are performed for each parameter individually, then by all parameters combined (emissions/dry deposition and SOA formation parameters), and finally by integrating all changes, allowing a synergy to develop among them. Table 2 presents the statistical parameters computed for the baseline simulation, for all these individual sensitivity tests and for the combined ones.

4.2.1 Individual tests on emissions, dry deposition and SOA formation parameters

As shown before in Sect. 3.4, in summer 2010, BVOCs concentrations are underestimated by the WRF-Chem model (API, LIM) compared to the VOCs measured at the ²⁰ PUY by at least a factor 2. The first test performed with the model is then to double the BVOCs emissions.

For the baseline simulation, the WRF-Chem model strongly underestimates the average OA mass concentration observed at the PUY station with a fractional bias of 1.4; the random errors (NMSE, VG) are out of the acceptance range recommended

²⁵ by Chang and Hanna (2004) and no value is within a factor of 2 of observations (Table 2). Multiplying the BVOC emissions by 2 leads to an improvement in the OA mass



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.

15

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

- ²⁰ 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 10⁵ and 10¹⁰ Matm⁻¹ 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
- ²⁵ 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 HNO₃ (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.



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

- ⁵ by HO[•], 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 (HO[•], O₃, NO[•]₃). Experiments in large environmental chambers covering a large temperature range are particularly suited to derive param-
- eterisations 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 µgm⁻³ (obtained with Murphy and Pandis, 2009, yields) to 1.7 µgm⁻³ with Farina et al. (2010) yields. In our case, to favour
- Pandis, 2009, yields) to 1.7 µgm⁻² 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%),

²⁵ 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 HO[•] and undergo further oxidation processes. An oxidation rate of 1.0×10^{-11} cm³ molecule⁻¹ s⁻¹ is used to implement these reactions within the gaseous chemical mechanism. As mentioned above, Bergström et al. (2012) recommended the



use of an oxidation rate of 4.0×10^{-11} cm³ molecule⁻¹ 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).

- ⁵ 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
- ¹⁰ 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.

15 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 $10.8 \,\mu g m^{-3}$ that is close to the observed value of $12.5 \,\mu g m^{-3}$ (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 (OA = $8.6 \,\mu g m^{-3}$) is more efficient at obtaining an accurate representation of measured OA concentrations than modifying emissions/dry deposition (OA = $3.1 \,\mu g m^{-3}$).



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

6 (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 $\approx 0.4 \,\mu g m^{-3}$ 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 1.0×10^{-11} to 4.0×10^{-11} cm³ molecule⁻¹ 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 1.0×10^{-11} to 4.0×10^{-11} cm³ molecule⁻¹ s⁻¹ of anthropogenic OCVs

- ²⁰ 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 $1.5 \,\mu g m^{-3}$ (+51%) and from 0.6 to $0.7 \,\mu g m^{-3}$ (+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



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

- ²⁰ reduces ASOA formation. These supplementary BVOCs likely consume HO[•] 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
- ²⁵ 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.



4.2.4 Comparisons between the two contrasted air masses (2010 vs. 2008)

Finally, it can be summarized that for the particular 2010 event, characterized by very high levels of OA mass concentrations, the model underestimates the observations. Available VOCs concentrations in 2010 at the PUY station are exploited to highlight
a strong underestimation of AVOCs that could explain part of the discrepancy between model and observations for SOA. This discrepancy has been also discussed as possibly due to a lack in the knowledge of key parameters in the SOA formation process. For the 2008 situation, the model was in better agreement with observations with a small underestimation in the SOA mass concentrations. If the same tests as those for the 2010 situation are applied, one notices that modifying the SOA yields and the rate constant for aging OCVs is enough to retrieve the levels observed in the SOA mass

- concentration as shown in Fig. 6b. This shows that increases in the oxidation rates are an important parameter to be considered when modeling OA concentrations, regardless of the meteorological conditions. However, applying all effects to the 2008 case results in a significant over-estimation of the average OA mass concentration by the
 - model (4.1 μ gm⁻³ modeled against 2.6 μ gm⁻³ observed) (Fig. 6b).

In 2010, it is likely that POA could have been emitted in the north eastern part of Europe (as seen in Fig. 5) and that the WRF-Chem model does not simulate correctly their aging during their transport from these source areas. Fountoukis et al. (2014) also

- ²⁰ mentioned possible wildfire emissions in certain areas such as Russia and southern Europe that could contribute up to 95 % to the POA and that are not taken into account in our model. In the WRF-Chem model, primary organic aerosols from biomass burning emissions are directly attributed to the POA component of organic aerosols. For the summer event when all effects are considered, POA contributes to 3 % of the total OA
- ²⁵ mass concentration. The results of the constrained ME-2 analysis provided by Crippa et al. (2014) for OA data from the PUY station show that both HOA and BBOA generally contribute to less than 10% of the total OA. So, emission sources of POA used with



the WRF-Chem model are probably underestimated. This could also explain the great discrepancy found between AVOCs simulated and measured at the PUY station.

5 Conclusions

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This paper presents a comparison between WRF-Chem outputs and AMS measurements performed at the PUY station for two one week period in summer 2010 and autumn 2008. A particular emphasis is made on decreasing the observed differences between modeled and measured OA concentrations. During the summer case, several measurements of VOC precursors of SOA were available allowing us to perform a detailed examination of the sources of the measured SOA and provided us with a unique
opportunity to target individual parameters implicated in the SOA formation and aging with a 10 km model resolution. In addition to this, we were able to test the robustness of both emission/dry deposition processes, and how they affect the formation of SOA.

The model globally underestimates the levels of OA concentrations, especially for the summer event where unexpected high concentrations were observed ($12.5 \,\mu g m^{-3}$). In the summer 2010 event, the calculated VOCs concentrations were much below those

observed, especially for AVOCs such as alkanes and aromatic compounds.

The present study provides details on spatial and temporal redistribution of both anthropogenic and biogenic organic aerosol. Contrary to many modeling studies considering that biogenic SOA dominate OA fraction (Fountoukis et al., 2014; Langmann

- et al., 2014), the baseline simulation with WRF-Chem showed the opposite with anthropogenic SOA contributing to 50 and 36% whereas the biogenic SOA contributing only to 32 and 17% to the total SOA, respectively for the summer 2010 and the autumn 2008 events; the remaining fraction being composed of primary OA. During the 2010 summer period, AVOCs were much higher than biogenic ones and rather support the
- ²⁵ importance of an anthropogenic component of OA over biogenic one. However, modifying the oxidation rate of both anthropogenic and biogenic OCVs in the model increases the biogenic contribution to OA so that it becomes the main component of SOA.



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 1.1×10^{-11} to 4.0×10^{-11} cm³ molecule⁻¹ s⁻¹ and doubling the SOA yields of both anthropogenic and biogenic SOA precursors leads to an increase in the OA mass concentration of $6.6 \,\mu gm^{-3}$ whereas when only emission/dry deposition changes are taken into account, the increase is only $1.1 \,\mu gm^{-3}$. 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.

¹⁰ The Supplement related to this article is available online at doi:10.5194/acpd-15-13395-2015-supplement.

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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	Yonsel University
Long-wave radiation	Rapid Radiation Transfer Model
Microphysics	Morrison
Cumulus paramotorization	Groll-Dovonvi
oundus parameterization	Cieli-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 FB < 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	0.2	0.4	1.0	1.2	1.4
All effects	0.1	0.2	1.0	1.1	1.2





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





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





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].







Figure 4. Temporal evolution of the aerosol mass concentrations (μ gm⁻³) measured at the PUY station (left) and simulated by the WRF-Chem model (right) for autumn 2008 (top) and summer 2010 (bottom).



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





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).

