

# Chapter 8

## Regional Modeling of Aerosol Chemical Composition at the Puy de Dôme (France)

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**Abstract** Organic aerosols (OA) represent a large fraction (from 20 to 90 %) of the submicron particulate mass and it is mainly composed of secondary organic aerosols (SOA). Despite the ubiquity of OA in the atmosphere, there are still large uncertainties in understanding the formation pathways of SOA. Consequently, OA sources and physico-chemical transformations during their transport are poorly represented in chemistry-transport models and large gaps still remain between simulated and measured OA concentrations. The ability of the WRF-CHEM model to reproduce the organic aerosol mass concentration originated from anthropogenic or/and biogenic emissions is evaluated. From this perspective, simulations for two contrasted air masses are performed with WRF-Chem using the Volatility Basis Set (VBS) approach dedicated to the formation of SOA. Simulations results are compared to aerosol measurements performed at the puy de Dôme station with a compact Time-of-Flight Aerosol Mass Spectrometer for two episodes in autumn 2008 and in summer 2010. Moreover, measurements of both anthropogenic and biogenic VOCs are used to access the capacity of the WRF-Chem model to correctly simulate the concentrations levels of the gas precursors of the SOA.

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## 8.1 Introduction

In the atmosphere, aerosol particles play a key role on both climate change and human health due to their effect on air quality. These particles are made of a complex mixture of both organic and inorganic species emitted by several sources. Although the sources and the production mechanisms for inorganic species are now quite well understood, the characterization of the organic fraction is much more difficult to achieve. Chemistry-transport models developed to better understand the organic aerosol formation processes underestimate the organic aerosol concentrations both at regional and global scales and especially during summertime periods (Knote et al. 2011).

Remaining sources of uncertainties concern emissions but also dry deposition of SOA gas precursors together with parameters controlling the SOA formation (yields, oxidation rates of OCVs) used in the VBS approach.

## 8.2 Model Description

The model used in this study is the version 3.4.1 of the WRF-Chem model (Grell et al. 2005). The RACM chemical mechanism (Stockwell et al. 1997) is used with 84 species and 252 reactions among which the oxidation of VOCs from both anthropogenic and biogenic sources. This mechanism is coupled with the aerosol module MADE (Ackermann et al. 1998) for the inorganic fraction of aerosols and, since recently, with the VBS (Ahmadov et al. 2012) parameterization for the SOA formation. The aerosol species treated are the inorganic ions ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ), elemental carbon (EC), organic matter (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  $\text{HO}^\bullet$ ,  $\text{O}_3$  or nitrate radicals  $\text{NO}_3^\bullet$  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. The VBS parameterization includes a four-bin volatility basis set with saturation concentrations ( $C^*$ ) ranging from 1 to 1000  $\mu\text{g m}^{-3}$  at 298 K and separated by one order of magnitude. The SOA yields are different for two regimes (high- and low- $\text{NO}_x$  conditions) and 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  $\text{HO}^\bullet$  radicals.

Anthropogenic emissions are taken from the MACCity inventory (Lamarque et al. 2010). Data are available with a spatial resolution of  $0.5^\circ$  per  $0.5^\circ$  and with a monthly temporal resolution from 1990 to 2010. Biogenic emissions are calculated online using MEGAN (Guenther et al. 2006). MEGAN quantifies the net biogenic

isoprene emissions, estimates VOCs, nitrogen oxides emissions. Biomass burning emissions are derived from the Fire Inventory from NCAR version 1.0 (FINNv1) with a daily temporal resolution and a spatial resolution close to 1 km.

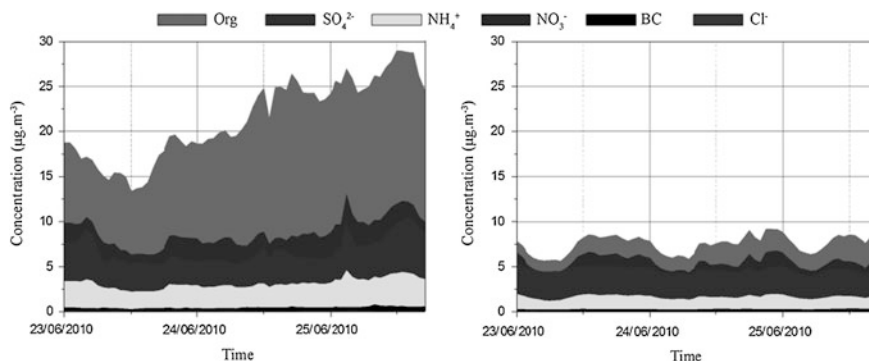
### 8.3 Simulating Aerosol Particles with the WRF-Chem Model

WRF-Chem model outputs are compared with in situ cToF-AMS aerosol measurements made at the puy de Dôme (PUY) station site during Autumn 2008 and Summer 2010 (Freney et al. 2011).

Figure 8.1 provides the temporal evolution of sulphate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ), ammonium ( $\text{NH}_4^+$ ), chlorine ( $\text{Cl}^-$ ), black carbon (BC) and organics mass concentrations measured at the PUY station and simulated by the WRF-Chem model for the summer event. The mass concentrations of inorganic species modeled are fairly close to those observed whereas the mass concentrations of organic aerosol are strongly underestimated by the model (Barbet et al. 2015).

For this particular 2010 event where unexpected high concentrations were observed ( $12.5 \mu\text{g m}^{-3}$ ), the model globally underestimates the levels of OA concentrations. VOCs concentrations calculated in the model were much below observed ones, especially for anthropogenic VOCs such as alkanes and aromatic compounds.

Several statistical performance measures recommended by Chang and Hanna (2004) have been applied to the baseline simulation, and to a series of sensitivity tests on emissions, dry deposition factor, SOA yields and oxidation rates of OCVs, taken individually, then combined and further all integrated (Table 8.1). Conclusions of those tests (only shown for the 2010 case but also valid for 2008



**Fig. 8.1** Temporal evolution of the aerosol mass concentrations measured at the puy de Dome station (*left*) and simulated by the WRF-Chem model (*right*) for Summer 2010

**Table 8.1** Statistical results compared with statistical performance measures and criteria acceptance for SOA mass concentrations for the baseline run and for sensitivity tests (individual and combined) for the summer 2010 period

Simulations	NMSE < 1.5	FB	FAC	VG	MG
		FB  < 0.3	>0.5	<4	0.7 < MG < 1.3
Baseline	4.5	1.4	0.0	27.7	6.1
BVOC emissions x2	3.5	1.4	0.0	16.2	5.3
AVOC emissions x2	3.2	1.3	0.0	13.0	4.9
Dry deposition/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
Oxydation 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
Oxydation rate of OCVs and SOA yields	<i>0.2</i>	0.4	<i>1.0</i>	<i>1.2</i>	<i>1.4</i>
All effects	<i>0.1</i>	<i>0.2</i>	<i>1.0</i>	<i>1.1</i>	<i>1.2</i>

*Italic values* indicate good model performance

situation) are that uncertainties on SOA formation and aging processes explained the major part of the discrepancies observed between modeled and measured SOA mass concentrations.

## References

- Ackermann IJ, Hass H, Memmesheimer M, Ebel A, Binkowski FS, Shankar U (1998) Modal aerosol dynamics model for Europe: development and first applications. *Atmos Environ* 32:2981–2999. doi:10.1016/S1352-2310(98)00006-5
- Ahmadvov R, McKeen SA, Robinson AL, Bahreini R, Middlebrook AM, de Gouw JA, Meagher J, Hsie E-Y, Edgerton E, Shaw S, Trainer M (2012) A volatility basis set model for summertime secondary organic aerosols over the eastern United States in 2006. *J Geophys Res* 117:D06301. doi:10.1029/2011JD016831
- Barbet C, Deguillaume L, Chaumerliac N, Leriche M, Freney E, Colomb A, Sellegri K, Patryl L, Armand P (2015) Evaluation of aerosol chemical composition simulations by the WRF-Chem model at the Puy de Dôme mountain (France). *AAQR*. doi:10.4209/aaqr.2015.05.0342
- Chang JC, Hanna SR (2004) Air quality model performance evaluation. *Meteorol Atmos Phys* 87:167–196. doi:10.1007/s00703-003-0070-7
- Freney EJ, Sellegri K, Canonaco F, Boulon J, Hervo M, Weigel R, Pichon JM, Colomb A, Prévôt ASH, Laj P (2011) Seasonal variations in aerosol particle composition at the puy de Dôme research station in France. *Atmos Chem Phys* 11:13047–13059. doi:10.5194/acp-11-13047-2011
- Grell GA, Peckham SE, Schmitz R, McKeen SA, Frost G, Skamarock WC, Eder B (2005) Fully coupled “online” chemistry within the WRF model. *Atmos Environ* 39:6957–6975. doi:10.1016/j.atmosenv.2005.04.027

- Guenther A, Karl T, Harley P, Wiedinmyer C, Palmer PI, Geron C (2006) Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). *Atmos Chem Phys* 6:3181–3210. doi:[10.5194/acp-6-3181-2006](https://doi.org/10.5194/acp-6-3181-2006)
- Knote C, Brunner D, Vogel H, Allan J, Asmi A, Äijälä M, Carbone S, van der Gon HD, Jimenez JL, Kiendler-Scharr A et al (2011) Towards an online-coupled chemistry-climate model: evaluation of trace gases and aerosols in COSMO-ART. *Geosci Model Dev* 4:1077–1102. doi:[10.5194/gmd-4-1077-2011](https://doi.org/10.5194/gmd-4-1077-2011)
- Lamarque J-F, Bond TC, Eyring V, Granier C, Heil A, Klimont Z, Lee D, Lioussé C, Mieville A, Owen B, Schultz MG et al (2010) Historical (1850–2000) gridded anthropogenic and biomass burning emissions of reactive gases and aerosols: methodology and application. *Atmos Chem Phys* 10:7017–7039. doi:[10.5194/acp-10-7017-2010](https://doi.org/10.5194/acp-10-7017-2010)
- Stockwell WR, Kirchner F, Kuhn M, Seinfeld S (1997) A new mechanism for regional atmospheric chemistry modeling. *J Geophys Res* 102:25847–25879. doi:199710.1029/97JD00849

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