

# **A new chemistry option in WRF/Chem v. 3.4 for the simulation of direct and indirect aerosol effects using VBS: evaluation against IMPACT-EUCAARI data**

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## Abstract

A parameterization for secondary organic aerosol (SOA) production based on the volatility basis set (VBS) approach has been coupled with microphysics and radiative schemes in the WRF/Chem model. The new chemistry option called “RACM/MADE/VBS/AQCHEM” was evaluated on a cloud resolving scale against ground-based and aircraft measurements collected during the IMPACT-EUCAARI campaign, and complemented with satellite data from MODIS. The day-to-day variability and the diurnal cycle of ozone ( $O_3$ ) and nitrogen oxides ( $NO_x$ ) at the surface are captured by the model. Surface aerosol mass concentrations of sulphate ( $SO_4$ ), nitrate ( $NO_3$ ), ammonium ( $NH_4$ ), and organic matter (OM) are simulated with correlations larger than 0.55. WRF/Chem captures the vertical profile of the aerosol mass concentration in both the planetary boundary layer (PBL) and free troposphere (FT) as a function of the synoptic condition, but the model does not capture the full range of the measured concentrations. Predicted OM concentration is at the lower end of the observed mass concentrations. The bias may be attributable to the missing aqueous chemistry processes of organic compounds and to uncertainties in meteorological fields. A key role could be played by assumptions on the VBS approach such as the SOA formation pathways, oxidation rate and dry deposition velocity of organic condensable vapours. Another source of error in simulating SOA are the uncertainties in the anthropogenic emissions of primary organic carbon. Aerosol particle number concentration (condensation nuclei, CN) is overestimated by a factor 1.4 and 1.7 within PBL and FT, respectively. Model bias is most likely attributable to the uncertainties of primary particle emissions (mostly in the PBL) and to the nucleation rate. Simulated cloud condensation nuclei (CCN) are also overestimated, but the bias is more contained with respect to that of CN. The CCN efficiency, which is a characterization of the ability of aerosol particles to nucleate cloud droplets, is underestimated by a factor of 1.5 and 3.8 in the PBL and FT, respectively. The comparison with MODIS data shows that the model overestimates the aerosol optical thickness (AOT). The domain averages (for one day) are  $0.38 \pm 0.12$  and  $0.42 \pm 0.10$  for MODIS and WRF/Chem data, respectively. Droplet effective radius ( $R_e$ ) in liquid phase clouds is underestimated by a factor of 1.5, cloud liquid water path (LWP) is overestimated by a factor 1.1-1.6. The consequence is the overestimation of average liquid cloud optical thickness (COT) from few percent up to 42%. Predicted cloud water path (CWP) in all phase displays a bias in the range +41-80%, whereas the bias of COT is about 15%. In sensitivity tests where we excluded SOA, the skills of the model in reproducing the observed patterns and average values of the microphysical and optical properties of liquid and all phase clouds decreases. Moreover, the run with SOA (NOSOAA) shows convective clouds with an enhanced content of liquid and frozen hydrometers, and stronger updrafts and downdrafts. Considering that the previous version of WRF/Chem coupled

1 with a modal aerosol module predicted very low SOA content (SORGAM mechanism) the new  
2 proposed option may lead to a better characterization of aerosol-cloud feedbacks.  
3

# 1 Introduction

It is well recognized that aerosol particles have a fundamental role in the climate system. They directly alter the budget of the radiation that reaches the Earth surface by scattering and absorbing the incoming sunlight (Haywood and Boucher, 2000), and they indirectly affect cloud properties and precipitation patterns, because they act as cloud condensation nuclei (CCN) (Rosenfeld et al., 2008; Lohmann and Feichter, 2005). Some aerosol species as black and brown carbon or mineral dust heat the atmosphere absorbing the solar radiation. The local warming may increase the atmospheric stability, leading to a decrease in cloud cover through the so called semi-direct effect (Hansen et al., 1997). The change in global median radiative forcing associated to anthropogenic aerosol particles since pre-industrial time is highly uncertain and it is estimated to be  $-0.9 \text{ W/m}^2$ , with uncertainty within a range from  $-1.9 \text{ W/m}^2$  to  $-0.1 \text{ W/m}^2$  (Boucher et al., 2013).

Experimental evidence of the influence of aerosols on cloud macrophysical and microphysical properties have been shown in several works (Klarke and Kapustin, 2010; Christensen and Stephen, 2011; Koren et al., 2011; Ten Hoeve et al., 2011; Li et al., 2012). Several modelling studies show that aerosol particles have a strong impact not only on the climatic spatial-temporal scale, but also at short range on the regional scale (Baklanov et al., 2013). At regional scale, online coupled mesoscale meteorology-chemistry models are useful tools to take into account aerosol feedback effects on both meteorology and atmospheric composition (Zhang et al., 2008; Baklanov et al., 2013). WRF/Chem, which is the model used in this study, is one of such models (Grell et al., 2005; Fast et al., 2006; Chapman et al., 2009). In this work we present and evaluate some developments of WRF/Chem for a better simulation of direct and indirect aerosol feedback.

The introduction of the aerosol-cloud-radiation feedback leads to non-linear chains and loops of interactions between meteorological and chemical processes that are inhomogeneous in space and time (Baklanov et al., 2013). Furthermore, the prediction of meteorological variables significantly improves when the direct and indirect aerosol effects are taken into account in numerical simulation. For example, Yang et al. (2011) found that the inclusion of aerosol feedback produces significant benefits in the simulated optical and microphysical properties of marine stratocumulus, and these improvements positively affect the simulation of the boundary layer structure and energy budget. Yu et al. (2013) reported an improvement of the simulation of shortwave and longwave cloud forcing when the aerosol feedback is added to the model.

Recent studies conducted with global models, predict an important contribution of secondary organic aerosol (SOA) to direct and indirect aerosol feedback. O'Donnell et al. (2011) calculated an annual mean direct and indirect shortwave forcing of  $-0.31 \text{ W/m}^2$  and  $+0.23 \text{ W/m}^2$ , respectively.

1 Biogenic SOA (BSOA) seems to play an important role on aerosol-cloud-radiation interaction.  
2 Scott et al. (2014) find that BSOA contribute for 4-21% to the global annual mean of CCN and 2-  
3 5% to global mean of cloud droplet concentration. They also attribute to BSOA a global mean  
4 indirect radiative forcing ranges from  $-0.77 \text{ W/m}^2$  to  $+0.01 \text{ W/m}^2$ .  
5 Previous studies over USA and Europe demonstrated that the “traditional” configuration of  
6 WRF/Chem (Grell et al., 2005) using the Secondary Organic Aerosol Model (SORGAM) (Shell et  
7 al., 2001), presents a negative bias of simulated  $\text{PM}_{2.5}$  mass, mostly attributable to a scarce  
8 production of SOA (Grell et al., 2005; McKeen et al. 2007; Tuccella et al., 2012). Therefore, an  
9 updated “chemistry option” with a more sophisticated treatment of SOA, fully coupled with  
10 radiative and microphysics modules, is highly desirable. In section 2 of this work, we describe the  
11 developments of WRF/Chem code carried out in order to simulate the direct and indirect effects  
12 with the new SOA parameterization (based on the Volatility Basis Set, VBS, approach) recently  
13 implemented in the model by Ahmadov et al. (2012). In section 3, we describe the measurements  
14 used to evaluate the model. In section 4, we evaluate the performance of the updated model through  
15 comparison with satellite data and with meteorological and chemical constituent measurements  
16 performed in the frame of the European Integrated project on Aerosol Cloud Climate and Air  
17 quality interaction (EUCAARI) (Kulmala et al., 2011). The aim of the section 5 is to address the  
18 two following questions: (1) Does the introduction of SOA particles interacting with radiation and  
19 cloud processes improve the numerical prediction of cloud fields? (2) What is the potential impact  
20 of SOA particles on cloud development? The final remarks are given in section 6.

21

## 2 WRF/Chem model

### 2.1 Description and upgrade

A pre-release of version 3.4 of Weather Research and Forecasting model with Chemistry model (WRF/Chem) (Grell et al., 2005) was used in this study. WRF/Chem is a community model that has many options for gas chemistry and aerosols. One of these has been updated in order to include a new chemistry option for simulation of direct and indirect effects with an updated parameterization for SOA production. The modifications introduced by Fast et al. (2006), Chapman et al. (2009), and Ahmadov et al. (2012) are the basis of our work. The technical details of the implementation are summarized in the Appendix A.

The gas-phase mechanism used is an updated version of the Regional Atmospheric Chemistry Mechanism (RACM) (Stockwell et al., 1997). The inorganic aerosols are treated with the Modal Aerosol Dynamics Model for Europe (MADE) (Ackermann et al., 1998). The updated parameterization for SOA production is based on the volatility basis set (VBS) approach (Ahmadov et al., 2012). MADE/VBS model has three log-normal modes: Aitken, accumulation and coarse. The species treated are the sulphate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ), ammonium ( $\text{NH}_4^+$ ), elemental carbon (EC), primary organic matter (POM), secondary organic aerosol (SOA, anthropogenic and biogenic), chloride (Cl), sodium (Na), unspiciated  $\text{PM}_{2.5}$  (that includes the fine fraction of sea-salt and soil dust), aerosol water, unspiciated coarse fraction of  $\text{PM}_{10}$ , soil dust and sea salt.

SOA parameterization implemented by Ahmadov et al. (2012) is based on a four bins volatility basis set, with saturation concentration of 1, 10, 100, and 1000  $\mu\text{g}/\text{m}^3$  at 300 K, respectively. VOCs are oxidized by reactions with hydroxyl radical (OH), ozone ( $\text{O}_3$ ), and nitrate radical ( $\text{NO}_3$ ). Oxidized VOCs are anthropogenic (alkanes, alkenes, toluene, xylene, and cresol) and biogenic (isoprene, monoterpenes, and sesquiterpenes). In each bin, organic mass is produced for two different regimes, high and low  $\text{NO}_x$ . In the former, organic peroxy radicals react with nitrogen oxide (NO), conversely in the latter organic peroxy radicals react with other organic peroxy radicals. The organic matter produced is partitioned into aerosol and gas phase assuming a pseudo-ideal partition. Organic condensation vapours (OCV) produced by the oxidation of VOCs may be oxidized by reacting with OH, consequently reducing the vapour pressure and shifting mass from high volatility bins to lower ones. The default oxidation rate (or aging factor) used in the model is  $1.0 \times 10^{-11} \text{ cm}^3/\text{molec.}/\text{s}$  for both anthropogenic and biogenic OCVs. The aging factor is one the key uncertainties in SOA formation in the VBS approach. Other two factors important factors of

1 uncertainty are those related to the SOA formation pathways and to the dry deposition velocity of  
2 OCVs. The latter is assumed to be 25% of the dry deposition velocity of nitric acid ( $\text{HNO}_3$ ).

3 The implementation of aerosol-cloud-radiation interaction within RACM/MADE/VBS follows the  
4 methods described by Fast et al. (2006) and Chapman et al. (2009). We modified the WRF/Chem  
5 code by preparing the inputs for the modules devoted to calculation of the aerosol optical properties  
6 and the aerosol activation, starting from the mass of each aerosol type as predicted by new  
7 chemistry package. In the approach of Fast et al. (2006), the three modes of the lognormal  
8 distribution are divided into 8 bins, and at each chemical constituent of the aerosol mass is  
9 associated a complex refractive index. The refractive index is calculated for each bin with a volume  
10 averaging. Mie theory is used to find the scattering and absorption efficiencies. Aerosol optical  
11 thickness (AOT), single scattering albedo and asymmetry parameter calculated with the optical  
12 package developed by Barnard et al. (2010), are used as input to the radiative scheme (Goddard and  
13 RRTMG). Aerosol direct effect on longwave radiation is included following Zhao et al. (2010).

14 Aerosol-clouds interaction is a complex problem that involves the activation and resuspension of  
15 the aerosol particles, aqueous chemistry and wet removal. Following Chapman et al. (2009),  
16 aerosols within cloud drops are treated as "cloud borne". Aerosols that do not activate as cloud  
17 droplets are treated as "interstitial". In WRF/Chem the activation process is based on the  
18 parameterization developed by Abdul-Razzak et al. (2000, 2002). The number and mass  
19 concentration of the activated aerosols are calculated for each mode. The activation of aerosols is  
20 based on a maximum supersaturation determined from a gaussian spectrum of updraft velocities and  
21 bulk hygroscopicity of each aerosol compound for all lognormal modes of particles. Bulk  
22 hygroscopicity is based on the volume weighted average of the hygroscopicity of each aerosol  
23 component. In addition to the activated aerosols at environmental conditions, the CCN spectrum is  
24 also determined, i.e. the aerosol particles acting as CCN at some given maximum supersaturations  
25 (0.02, 0.05, 0.1, 0.2, 0.5, and 1%) are calculated.

26 Within the dissipating clouds, the droplets evaporate and the cloud borne aerosols are resuspended  
27 to the interstitial state. Cloud borne aerosols and dissolved trace gases may be modified by aqueous  
28 chemistry. In this chemistry option, cloud chemistry is modelled using the scheme of Walcek and  
29 Taylor (1986). Wet deposition of trace gases and aerosols is treated in and below clouds. Within  
30 clouds the aerosols and trace gases dissolved in the water are collected by rain, graupel and snow.  
31 Below clouds the wet scavenging by precipitation is parameterized using the approach of Easter et  
32 al. (2004).

1 The simulation of the activation, resuspension and wet scavenging of the aerosol particles requires a  
2 prognostic treatment of the cloud droplets. The prognostic treatment of the clouds droplet takes into  
3 account the losses due to collision, coalescence, collection and evaporation, and the source due to  
4 nucleation. The Lin and Morrison microphysics schemes in WRF/Chem version 3.4 include the  
5 prognostic treatment of the cloud droplet number concentration. The source due to nucleation is  
6 parameterized following Ghan et al. (1997). Both microphysical schemes take into account the  
7 autoconversion of cloud drops to rain dependent on the cloud droplet number. Therefore, aerosol  
8 activation affects both the rain rate and the liquid water content. The droplet number concentration  
9 affects the calculation of the cloud droplet effective radius and cloud optical thickness (COT). The  
10 interaction of clouds with the incoming shortwave radiation is done by linking the microphysics to  
11 the radiation scheme. The reader should note that the contribution to SOA concentration by cloud  
12 chemistry is missing and the interaction of aerosol with ice nuclei is not taken into account in this  
13 version of the model.

## 14 **2.2 Model configuration**

15 The simulations were conducted over three 1-way nested domains centred on The Netherlands, as  
16 shown in Figure 1. The coarse domain (D1) has 30 km horizontal resolution, domain 2 (D2) 10 km,  
17 and domain 3 (D3) is cloud resolving at 2 km resolution. In our runs we used 67 vertical levels  
18 extending up to 50 hPa.

19 The main physical and chemical parameterizations used are listed in Table 1. The model setup is the  
20 same for all three domains, except that no cumulus parameterization is used for D3. Wet scavenging  
21 and cloud chemistry from both parameterized updraft and resolved clouds are taken into account in  
22 D1 and D2. However in these domains the sub-grid cloud processes involve only the interstitial  
23 aerosol, i.e. the aerosol-cloud coupling is not considered in convective parameterization. Therefore,  
24 the indirect effects are well resolved for domains with resolution less than 10 km in the version of  
25 WRF/Chem used in this work.

26 As mentioned in Section 2.1, two key uncertainties in SOA production are deposition velocity and  
27 aging factor of OCVs. The first is assumed to be 25% (this value is called “deposition factor” in  
28 WRF/Chem) of dry deposition velocity of  $\text{HNO}_3$ , the second is set to  $1.0 \times 10^{-11} \text{ cm}^3/\text{molec.}/\text{s}$ .  
29 Ahmadov et al. (2012) showed that reducing the aging factor of OCVs by 50%, daily average  
30 concentration of SOA decreases by 20%, and an increase of the dry deposition velocity of OCVs by  
31 a factor 4 the SOA concentration decreases by 50%. Deposition factor and aging are tunable  
32 parameters. After some sensitivity tests, we chose the default value for deposition factor and



1  $5.0 \times 10^{-11} \text{ cm}^3/\text{molec.}/\text{s}$  as aging of OCVs, because this combination minimizes the model bias with  
2 observations.

3 We simulated the period from 14 to 30 May 2008. We chose this period because aerosol and cloud  
4 state-of-art measurements were available to evaluate the model (see Section 3). Moreover, during  
5 this period anticyclonic and cyclonic meteorological conditions were observed which allows the  
6 evaluation of the model under varying conditions. The initial and boundary meteorological  
7 conditions for D1 are provided by the European Centre for Medium range Weather Forecast  
8 (ECMWF) analyses with a horizontal resolution of  $0.5^\circ$  every 6 hours. The chemical boundary  
9 conditions of D1 are taken from output of the global Model for Ozone and Related Chemical  
10 Tracers (MOZART) (Emmons et al., 2010). MOZART output has been converted to  
11 RACM/MADE/SOA-VBS species by using the “mozbc” interface that may be downloaded from  
12 the [www.acd.ucar.edu/wrf-chem](http://www.acd.ucar.edu/wrf-chem) website.

13 A series of 30-h simulations were performed on each day starting at 00 UTC, with the first 6 h  
14 discarded as model spin up for meteorology. Meteorology of D1 is reinitialized from global  
15 analysis, while initial and boundary meteorology conditions for D2 and D3 are taken from D1 and  
16 D2, respectively. For all three domains, the chemical initial state is restarted from previous run,  
17 while the chemical boundary conditions of D2 and D3 are taken from D1 and D2, respectively. The  
18 first 13 days of May 2008 are also simulated to spin-up the chemistry.

## 19 **2.3 Emissions**

20 Anthropogenic emissions data are taken from TNO 2007 inventory (Kuenen et al., 2014). TNO is a  
21 gridded European inventory with resolution of  $0.125^\circ \times 0.0625^\circ$ . It provides the anthropogenic  
22 emissions of  $\text{NO}_x$ , NMVOC,  $\text{NH}_3$ ,  $\text{SO}_2$ , CO, primary  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$ . EC and primary OC  
23 emissions are taken from a specific TNO database that is part of the EUCAARI project (Kulmala et  
24 al., 2011). These EC and OC emissions are size resolved, they are separated for particles less than 1  
25  $\mu\text{m}$ , particles in the range of 1–2.5  $\mu\text{m}$  and 2.5–10  $\mu\text{m}$ .

26 Horizontal and vertical interpolation, temporal disaggregation, NMVOC speciation, and  
27 aggregation of emissions into WRF/Chem species is done following Tuccella et al. (2012), with  
28 minor updates described in Curci et al. (2014a). In order to prevent spurious concentration of  
29 aerosol particles, the distribution of aerosol emissions into WRF/Chem modes is based on the low  
30 emission scenario of Elleman and Covert (2010). The 10% of the emitted aerosol mass is attributed  
31 to Aitken mode, and the 90% to the accumulation mode.

1 Biogenic emissions are calculated on line with Model of Emissions of Gases and Aerosols from  
2 Nature (MEGAN) (Guenther et al., 2006). Dust and sea salt emissions from soil and seawater are  
3 calculated on line in the simulations.  
4

### 3 Measurements

We evaluated model performances in D3 against ground and aircraft based data collected in May 2008 during the Intensive Cloud Aerosol Measurement Campaign (IMPACT) in the frame of the EUCAARI project (Kulmala et al., 2009). Model results were also evaluated against MODIS satellite data.

An overview of the synoptic conditions of May 2008 over Central Europe is given by Hamburger et al. (2011). The first 15 days of May are characterized by an anticyclonic block, while the period from 16 to 31 is dominated by westerly wind and passage of several fronts. The days from 17 to 20 May are referred as “scavenged background situation” (Mensah et al., 2012), because they are dominated by northerly wind from North Sea associated to a low aerosol mass loading, due to wet scavenging. The period starting from 23 May is dominated by long range transport of dust from Sahara desert (Roelofs et al., 2010; Begue et al., 2014).

#### 3.1 Ground based measurements

Meteorological and aerosol ground based measurements used in this study are collected in Cabauw (The Netherlands) at CESAR observatory Cabauw (Figure 1). CESAR observatory is a tower located at 51° 57'N, 4° 54' E, and -0.7 m a.s.l, at about 50 km south of Amsterdam. Measurements performed at CESAR observatory are typical of North-West Europe, and are representative of maritime and continental conditions depending on the wind direction (Mensah et al., 2012).

Standard meteorological variables are collected at 2 m, 10 m, 20 m, 40 m, 80 m, 140 m, and 200 m height. Besides, in this study we used the measurements of temperature and relative humidity profiles obtained with radiometer, and aerosol speciation from aerosol mass spectrometry (AMS) collected at 60 m (Mensah et al., 2012).

The model is also compared to ozone ( $O_3$ ), nitrogen oxide ( $NO_x$ ), nitric dioxide ( $NO_2$ ), nitric oxide ( $NO$ ), ammonia ( $NH_3$ ), nitric acid ( $HNO_3$ ), nitrous acid ( $HONO$ ), and sulphur dioxide ( $SO_2$ ) measurements issued by Cabauw Zijdeweg EMEP station (NL0011R).  $O_3$  is measured with an ultraviolet absorbing ozone instrument,  $NO_x$ ,  $NO$  and  $NO_2$  with a chemiluminescence monitor, and  $NH_3$ ,  $HNO_3$ ,  $HONO$  and  $SO_2$  with an online ion chromatograph.

Although Cabauw supersite provides very detailed measurements, it could not be enough to characterize the model performance near the surface. Therefore, WRF/Chem is also compared to daily  $PM_{10}$  data from 63 stations (10 rural, 25 suburban, and 28 urban) of AIRBASE network and to daily inorganic aerosol measurements issued at Bilthoven (NL0008R), Kollumerward (NL0009R),

1 Vredepeel (NL00010R), and De Zilk (NL00091R) EMEP stations.  $\text{SO}_4$  and  $\text{NH}_4$  measurements are  
2 also performed at all these sites while  $\text{NO}_3$  measurements are available only at De Zilk.

### 3 **3.2 Aircraft measurements**

4 During May 2008, the French ATR-42 research aircraft performed 22 research flights (RF). In this  
5 work we used 14 RF to evaluate the model. Their tracks are reported in Figure 1, while flight  
6 number, take-off and landing time are reported in Table S1. RF50, RF55, RF56, RF57, RF58, RF61  
7 and RF62 were conducted around Cabauw supersite, in order to study the origin and characteristic  
8 of air masses collected at Cabauw. Other RFs were aimed at the study of aerosol properties along a  
9 quasi-Lagrangian flight track, with west-east and north-south transects. ATR-42 was equipped with  
10 instrumentation suitable for aerosol-cloud interaction measurements. We used the measurements  
11 from a condensation particle counter (CPC), the CPC3010 with a cutoff size of 15 nm, a Cloud  
12 Condensation Nuclei Counter (CCNC) for CCN number concentration measurements, and an AMS.  
13 During the campaign a scanning mobility particle sizer (SMPS) was used to measure the number  
14 size distribution of aerosol particles with diameter in the range of 0.02-0.5  $\mu\text{m}$ , while the size  
15 distribution of aerosol particles larger than 100 nm was sampled with a passive cavity aerosol  
16 spectrometer probe (PCASP). SMPS and PCASP measurements were combined in order to  
17 calculate the  $\text{PM}_{2.5}$  concentration using an average aerosol density of  $1.7 \text{ g/m}^3$ . A more exhaustive  
18 and detailed description of the whole campaign and instrumentation is given by Crumeyrolle et al.  
19 (2013).

### 20 **3.3 Satellite measurements**

21 The model was also evaluated with MODIS-Aqua aerosol and cloud data. The Level 2 products  
22 used here are MYD04 and MYD06 collection 051 for aerosol and clouds, respectively. For ease of  
23 comparison with model output, both satellite and model data were regridded onto a common lat-lon  
24 regular grid. Model output is sampled at same time and location of each MODIS pixel, and then  
25 data are averaged in space and time over the same grid. In this study the horizontal spacing of the  
26 common grid is 4 km.

27

## 1    **4    Model evaluation**

2    Model results are compared to ground based and aircraft observations, as detailed in section 3. The  
3    statistical indices used are the Pearson's correlation coefficient ( $r$ ), mean bias (MB), normalized  
4    mean bias (NMB) and normalized mean gross error (NMGE). The indices are defined in the  
5    Appendix and reported in Table 2.

### 6    **4.1 Meteorology**

7    Figure 2 shows the observed and modelled time series of hourly vertical profiles of temperature and  
8    relative humidity at Cabauw supersite. WRF/Chem reproduces the day-to-day variation of  
9    temperature, before, after, and during the wet period. As shown by statistical indices (Table 2),  
10    within the first 200 m, the model reproduces the temperature with a correlation of 0.93-0.95 and a  
11    mean bias of about  $-0.5^{\circ}\text{C}$ . Looking at the free troposphere, we may realize that the model  
12    underestimates the height of the  $0^{\circ}\text{C}$  isotherm (the black line on Figure 2a) in the first days of  
13    simulation and during wet period by about 200-300 m (i.e., the model is colder than observed by 1-  
14     $1.5^{\circ}\text{C}$ ). Whereas immediately after the passage of the cold front, the temperature rise in the  
15    simulation is slower than the observed one. The model performances in simulating surface  
16    temperature are consistent with other European studies (e.g., Zhang et al., 2013a; Brunner et al.,  
17    2014). For example, Brunner et al. (2014) compared several meteorology-chemistry coupled models  
18    with annual simulations at continental scale, and found that on Central Europe the predicted surface  
19    temperature shows a correlation with observations in the range of 0.95-0.98, whereas the bias  
20    ranges from -1 to  $0.1^{\circ}\text{C}$ .

21    The model reproduces the vertical structure of relative humidity (Figure 2b) over the whole period,  
22    but it has the tendency to overestimate (underestimate) the higher (lower) observed values. This  
23    behaviour is more evident during scavenging days, when the relative humidity between 1000-2000  
24    m is overestimated on average by 40%, but sometimes up to 60%. Errors of this magnitude in  
25    simulating the vertical profile of RH were already found in previous works (Misenis and Zhang,  
26    2011; Luo and Yu, 2011). Nevertheless, the model correlation and mean bias are 0.84 and +3.4%  
27    below 1000 m of altitude, 0.50 and +13% in the range of 1000-2000 m, 0.78 and +6.4% between  
28    2000-3000 m. These values are comparable with those found by Fast et al. (2014) in the comparison  
29    of WRF/Chem simulations to aircraft data. They have shown correlations in the interval of 0.49-  
30    0.70, while the bias from -7 to +0.1%. Near the surface, the relative humidity is simulated with a  
31    correlation of 0.87-0.92 and a positive MB of 3-4% (+6-8%).

1 The biases of the temperature and relative humidity could be due to a misrepresentation of soil (and  
2 sea) temperature and soil moisture or by misrepresentation of the clouds and rain. These two  
3 problems are tightly coupled via land surface-atmosphere interaction. The errors in the simulation  
4 of surface moisture and energy budget influences the fluxes of latent heat and moisture in the  
5 atmosphere, affecting the local circulation, convective available potential energy (CAPE), cloud  
6 formation and rain pattern (Pielke, 2001; Holt et al., 2006). Moreover, WRF/Chem tends to fail  
7 simulating the thermodynamic variables near to coastline, because the uncertainties of land use data  
8 may play an important role (Misenis and Zhang, 2010). Initial and boundary meteorological  
9 conditions may also play an important role. Bao et al. (2005) demonstrated that meteorological  
10 prediction is sensitive to used input data. They showed that varying the inputs used as initial and  
11 boundary conditions, the mean daily model bias ranges from -2.71 to -0.65 K for the temperature  
12 and from -0.81 to 0.50 g/kg for vapour water content.

13 In Figure 3 we compare the time series of observed and predicted wind speed and direction at  
14 several heights of Cabauw Tower. WRF/Chem captures the diurnal trend of wind speed, but it  
15 overestimates the wind speed during night. Generally, we found the higher correlation at 10 and 200  
16 m (0.78 and 0.76 respectively) and higher NMB between 20 and 40 m (+30-40%). The wind  
17 direction is captured at all altitude levels of Cabauw tower, except of 18May when WRF/Chem  
18 does not reproduce some rapid variations most likely due to local effects. The simulation of wind  
19 direction tends to improve with height. Indeed, the correlation coefficient increases from 0.52 to  
20 0.73 at 10 and 200 m, respectively, and the MB decreases from 27° below 40m to 17° at 200 m. The  
21 performance in simulating the surface wind speed are consistent with those reported by Brunner et  
22 al. (2014) in Central Europe. They have shown a correlation for 10 m wind speed in the range of  
23 0.53-0.73 and a mean bias of 1-1.8 m/s. It is well recognized that WRF tends to overestimate the  
24 wind near the surface (e.g. Misenis and Zhang, 2010; Ngan et al., 2013; Brunner et al., 2014), but  
25 the bias of the simulated wind speed could be also explained with uncertainties in the large-scale  
26 pattern of analysis used as input. Bao et al. (2005) showed that varying the meteorological inputs,  
27 the mean daily model bias may range from -1.53 to -0.28 m/s and from -1.43 to 0.01 m/s for the u  
28 and v component of the wind, respectively.

## 29 **4.2 Surface gas phase and aerosol mass**

30 Figure 4 displays the comparison between the observed and modelled hourly time series and  
31 average diurnal cycles of O<sub>3</sub>, NO<sub>x</sub>, NO<sub>2</sub>, NO, NH<sub>3</sub>, HNO<sub>3</sub>, HONO and SO<sub>2</sub> near the surface.

1 WRF/Chem reproduces the day to day variations of  $O_3$ , capturing its decrease during scavenging  
2 period due to low photolysis rate caused by cloud presence, recovery in the following days, and a  
3 new decrease starting from 25 May. The average daily cycle is well reproduced with a morning  
4 minimum and an underestimated maximum in the afternoon. The model simulates the  $O_3$  with a  
5 correlation of 0.72 and systematic negative bias on average about  $3.4 \mu\text{g}/\text{m}^3$ . This bias is observed  
6 in the afternoon and the evening, and is most likely due to the titration in these hours caused by  
7 higher  $\text{NO}_x$  concentration than observed.

8 WRF/Chem simulates the  $\text{NO}_x$ ,  $\text{NO}$  and  $\text{NO}_2$  time series with a correlation of 0.70, 0.65, and 0.66  
9 respectively. The timing of  $\text{NO}_x$  daily cycle is reproduced. Indeed, the model captures the morning  
10 and evening peaks as well as diurnal minimum of  $\text{NO}_2$ . The mean bias of modelled  $\text{NO}_2$  is  $+1.25$   
11  $\mu\text{g}/\text{m}^3$  (+20%) and occurs in the afternoon and evening hours. Moreover WRF/Chem reproduces the  
12 morning peak and diurnal decrease of  $\text{NO}$ , but the daily cycle is affected by an average positive bias  
13 of  $0.28 \mu\text{g}/\text{m}^3$ , with the average morning maximum overestimated of about  $2 \mu\text{g}/\text{m}^3$  (+33%).

14 Ammonia is reproduced with a correlation of 0.43. WRF/Chem underestimates the  $\text{NH}_3$  during the  
15 scavenging days and from 28 to 31 May. The model captures the daily cycle shape of  $\text{NH}_3$   
16 concentration average, but the modelled  $\text{NH}_3$  concentrations are constantly underestimated. The  
17 negative mean bias over the whole period is on average about  $-4.75 \mu\text{g}/\text{m}^3$  (-28%). WRF/Chem  
18 reproduces the observed  $\text{HNO}_3$  with a poor correlation. The measured mean diurnal cycle is flat,  
19 conversely the model predicts a nocturnal minimum and diurnal maximum. The origin of model  
20 bias in simulating  $\text{NH}_3$  and  $\text{HNO}_3$  is discussed below, together with a discussion on inorganic  
21 aerosols.

22 The nitrous acid concentrations are not well captured by the model and are underestimated by 95%.  
23 This bias could be partly explained by the inefficiency of  $\text{NO}$  oxidation, the only important reaction  
24 known to form  $\text{HONO}$ . Lin et al. (2014), indeed, demonstrated that the major sources of  $\text{HONO}$  are  
25 some unknown reactions that consume nitrogen oxides and hydrogen oxide radicals.

26 The model reproduces the measured  $\text{SO}_2$  with a correlation of 0.48 and a positive bias of  $0.68$   
27  $\mu\text{g}/\text{m}^3$  (+90%). The overprediction is most likely attributable to anthropogenic emissions.  $\text{SO}_2$  is  
28 emitted mainly from isolated and elevated large point sources (Figure S1) that are immediately  
29 mixed in the model cell leading to overestimation outside of the local plume (Stern et al., 2008).  
30 This is demonstrated, for example, by the larger NMGE for  $\text{SO}_2$  than  $\text{NO}_x$  (116% and 45%,  
31 respectively).  $\text{NO}_x$  is emitted near the surface by traffic and domestic heating. Therefore,  $\text{NO}_x$   
32 emissions are subjected to a stronger temporal modulation than  $\text{SO}_2$  point sources.

1 The different uncertainties found for the involved species may depend on the choice of the chemical  
2 mechanism. Knote et al. (2014) compared several chemical mechanisms within a box model  
3 constrained by the same meteorological conditions and emissions, and found that the prediction of  
4 the O<sub>3</sub> diurnal cycle differs by less than 5% among the different mechanisms. Larger differences  
5 were found for other species. For example, the key radicals exhibit differences up to 40% for OH,  
6 25% for H<sub>2</sub>O<sub>2</sub> and 100% for NO<sub>3</sub> among the selected mechanisms.

7 Figure 5 shows the simulated and observed time series and diurnal cycle of aerosol sulphate, nitrate,  
8 ammonium, and organic matter, at CESAR observatory. WRF/Chem simulates the measured SO<sub>4</sub>,  
9 NO<sub>3</sub>, NH<sub>4</sub> with a correlation of 0.56, 0.68, and 0.66, respectively.

10 WRF/Chem captures the daily variations of SO<sub>4</sub> and its decrease during scavenging days. The shape  
11 of diurnal cycle is also reproduced, with the nighttime minimum and diurnal maximum. The mass  
12 concentration of SO<sub>4</sub> is overpredicted for the whole period with a mean bias of 1.04 µg/m<sup>3</sup> (+90%).  
13 The modelled SO<sub>4</sub> overestimation is directly attributable to SO<sub>2</sub> concentration overprediction.  
14 Another potential source of the surplus of simulated SO<sub>4</sub> is related to an excessive production  
15 within the clouds. Indeed, during scavenging days, the particulate sulphate is overestimated while  
16 the predicted SO<sub>2</sub> does not show a bias in respect to the measurements. The overestimation of SO<sub>4</sub>,  
17 moreover, explains in part the negative bias of predicted NH<sub>3</sub>. The excess of particle sulphate  
18 consumes too much ammonia (Meng et al., 1997)

19 NO<sub>3</sub> is reproduced with a positive bias of 1 µg/m<sup>3</sup> (+72%). Looking at diurnal cycle, the modelled  
20 nitrate is on average biased high in the daytime, with a peak in the afternoon. This maximum  
21 appears to be correlated with HNO<sub>3</sub> maximum. Really, the HNO<sub>3</sub> peak is caused by evaporation of  
22 particulate nitrate formed in the upper PBL (where the conditions of lower temperature and higher  
23 relative humidity are favourable to NO<sub>3</sub> formation), and mixed towards the surface by vertical  
24 mixing (Curci et al., 2014a; Aan de Brugh et al., 2012). Therefore, the unrealistic afternoon peak of  
25 modelled nitric acid should result from a too rapid relaxation of aerosol-gas partitioning to  
26 thermodynamic equilibrium (Aan de Brugh et al., 2012).

27 The behaviour of the simulated NH<sub>4</sub> is related to modelled trend of NO<sub>3</sub>. It is biased high by 0.66  
28 µg/m<sup>3</sup> (+66%). The NH<sub>4</sub> overestimation is related to NH<sub>3</sub> underprediction (Meng et al., 1997).

29 Similar performances are found in reproducing inorganic aerosols at other Dutch EMEP sites (see  
30 Section 3.1). Daily SO<sub>4</sub> is simulated with an average correlation (3 stations) of 0.66 and a positive  
31 bias of 35%. WRF/Chem simulates NH<sub>4</sub> with a correlation of 0.82 (4 stations) and a bias of +43%.  
32 Predicted daily NO<sub>3</sub> (measured at only one station) is overestimated by 15%.



1 Organic matter is reproduced with a correlation coefficient of 0.75. WRF/Chem reproduces the  
2 right concentration during dry period, the decrease in the wet days, and following recovery. The  
3 mean bias is negative by about  $0.4 \mu\text{g}/\text{m}^3$  and it is attributable to days from 23 to 26 May. The  
4 discussion about the origins of OM bias is given in section 4.3, where we will discuss the model  
5 evaluation with aircraft data.

6 The reader should consider that aerosol composition measurements performed with the AMS are  
7 representative of particles with diameter between roughly 100-700 nm, whereas the model is  
8 evaluated with aerosol concentration representative of  $\text{PM}_{2.5}$ . Therefore, a bias could be present in  
9 the comparison. This means that the bias found for inorganic aerosols could be smaller than that  
10 reported above, conversely the OM bias could be larger of that found.

11 The model evaluation performed so far is representative of few points in the domain and does not  
12 include other aerosol components like black carbon or primary PM. This could limit our  
13 understanding of the model behaviour. In order to overcome this shortcoming, WRF/Chem is also  
14 compared to daily  $\text{PM}_{10}$  measurements of AIRBASE network (Figure S2). The model captures the  
15 daily variations of  $\text{PM}_{10}$ , the  $\text{PM}_{10}$  decrease during scavenging days, the consequent recovery to  
16 reach back the background  $\text{PM}_{10}$  concentration and the  $\text{PM}_{10}$  enhancement during long-range  
17 transport period. Indeed, the correlations are of 0.72, 0.73, 0.75 in rural, suburban, and urban zones,  
18 respectively. Model bias at rural stations is important in the last days of May 2008, indeed in these  
19 days (28-30 May) it is about  $-15 \mu\text{g}/\text{m}^3$  (-30%). Conversely, at suburban and urban stations, the  
20 model presents a bias for the most part of the days of about  $3\text{-}4 \mu\text{g}/\text{m}^3$  (5-10%) that could partly  
21 explained by the missing source of resuspension due to traffic.

22 The results obtained here are statistically consistent with other modelling studies over Europe (e.g.,  
23 Lecœur and Seigneur, 2013; Zhang et al., 2013b; Balzarini et al., 2014). For example, the results of  
24 European annual simulations of Balzarini et al. (2014) exhibited a correlation of 0.48, 0.60 and 0.56  
25 for surface  $\text{SO}_4$ ,  $\text{NO}_3$  and  $\text{NH}_4$ , respectively. During EUCAARI campaign, Athanasopoulou et al.  
26 (2013) reported a mean correlation of surface OM with observations of 0.56 and a mean bias of  $-0.5$   
27  $\mu\text{g}/\text{m}^3$ , whereas Fountoukis et al. (2014) simulates the OM at Cabauw on May 2008 with a bias of  
28  $0.3 \mu\text{g}/\text{m}^3$ . Moreover, with regards to surface  $\text{PM}_{10}$ , our performances are comparable to those  
29 found for example by Im et al. (2014) over Europe with annual simulations in terms of correlation,  
30 but are higher in terms of bias. Comparing  $\text{PM}_{10}$  concentrations from several models, Im et al.  
31 (2014) found correlations of 0.18-0.86 and 0.07-0.82, and bias of about -40% and -50% for rural  
32 and urban sites, respectively. This improvement is most likely due to the very high resolution used

1 in this study with respect to the 23 km of Im et al. (2014), since the anthropogenic emissions  
2 inventory used is the same here and in Im et al. (2014) study.

### 3 **4.3 Aloft aerosol mass concentration**

4 The comparison of WRF/Chem to aircraft data is done interpolating the model output point by point  
5 along the flight track. Observed and modelled aircraft data are presented by using the box plots for  
6 planetary boundary layer (PBL) and free troposphere (FT) (see Figure 6). The height of the PBL  
7 was lower than 1600 m during the whole campaign (Crume rolle et al., 2013). Therefore, we  
8 considered for PBL and FT concentrations the data below and above 1600 m up to 3000-4000 m,  
9 respectively. This rough approximation of PBL height could affect the comparison of the model to  
10 data.

11 Figure 6 displays the observed and modelled box plots of the mass concentration of SO<sub>4</sub>, NO<sub>3</sub>, NH<sub>4</sub>,  
12 and OM for PBL and FT. Their mean value, standard deviation, relative mass fraction, and  
13 correlation coefficients, averaged over the whole period of interest, are reported in Table 3.

14 The average concentrations of inorganic aerosols show little absolute error (2-8%) with respect to  
15 the observations in the PBL, while the NO<sub>3</sub> and NH<sub>4</sub> mean concentration presents a bias of +14%  
16 and +20% (+0.3 and +0.2 µg/m<sup>3</sup>), respectively, in the FT. The mean OM mass is biased low by a  
17 factor 2 and 3 in the PBL and FT, respectively. The correlation coefficients of SO<sub>4</sub>, NO<sub>3</sub>, NH<sub>4</sub>, and  
18 OM are 0.39, 0.47, 0.43, 0.67 in the PBL and 0.23, 0.44, 0.42, 0.53 in the FT. These performances  
19 are comparable with those found with WRF/Chem (but with a different chemistry package) in  
20 California by Fast et al. (2014). They reported an absolute mean bias of about 0.01-0.2, 0.03-0.6,  
21 0.1-0.45, 0.2-0.57 µg/m<sup>3</sup> and a mean correlation of 0.42, 0.45, 0.44, and 0.72 for SO<sub>4</sub>, NO<sub>3</sub>, NH<sub>4</sub>,  
22 and OM, respectively.

23 Although the predicted aerosol mass of each species is within the range of the observed values for  
24 most of the flights used in this study (see Figure 4), the model does not capture the full range of the  
25 measured concentrations. This assertion is made quantitative by the standard deviations reported in  
26 Table 3. The predicted standard deviations for each species are lower than observed. In the PBL, the  
27 observed and modelled standard deviations differ by 4-10% for inorganic ions and 55% for OM. In  
28 the FT, the differences are higher than in the PBL. The model predicts standard deviations lower  
29 than 10-40% for inorganic particles and lower than 65% for organic matter with respect to the  
30 measurements.

31 For the purpose of this analysis, it is also interesting to explore how the model reproduces the  
32 relative fraction of aerosol mass species with altitude (see Table 3). WRF/Chem overpredicts the

1 relative fraction of the  $\text{SO}_4$  and  $\text{NO}_3$  by few percent in the PBL and about 10% in FT, while the  
2 relative mass of  $\text{NH}_4$  is overestimated by 3% along the whole profile. The relative amount of OM is  
3 underpredicted by about 20% in both PBL and FT. The decrease of relative amount of  $\text{NO}_3$  and  
4 increase of  $\text{SO}_4$  with altitude is captured by the model. The modelled relative mass of  $\text{NH}_4$  and OM  
5 is near constant with altitude as well as in the observations.

6 Looking at the individual flights, it is possible to note how the model captures the aerosol mass  
7 trend as a function of the synoptic frame in both the PBL and FT, during the dry period, scavenging  
8 days, and dust period characterized by southerly wind and passage of several fronts. The FT is a  
9 layer mainly affected by long range transport and cloud contamination. Therefore, the relative small  
10 bias in simulating aerosol inorganic mass in FT means that the model resolves quite correctly the  
11 large scale transport and processes related to clouds.

12 Nevertheless, it should be noted that  $\text{SO}_4$  is overestimated for 8 out of 14 RFs, while  $\text{NO}_3$  and  $\text{NH}_4$   
13 are underpredicted for 7-8 out of 14 RF. This  $\text{SO}_4$  overprediction is attributable to the  $\text{SO}_2$  excess  
14 and to a potential overproduction within the cloud chemistry scheme. The negative bias of  $\text{NO}_3$  and  
15  $\text{NH}_4$  could be explained by a low  $\text{NH}_3$  regime, that limits the formation of the ammonium-nitrate.

16 The simulated OM concentration is always at lower end of the observed variability. Several factors  
17 may explain this systematic bias. First of all, our simulations do not include the processing of  
18 organic compounds in aqueous chemistry. SOA may be produced in the clouds (Hallquist et al.,  
19 2009). Modelling studies suggest that the contribution of cloud chemistry to SOA budget is almost  
20 as much as the mass formed from the gas phase (Ervens et al., 2011). OM prediction is also affected  
21 by meteorological errors. Bei et al. (2012) found that the uncertainties in meteorological initial  
22 conditions have significant impact on the simulations of the peaks, horizontal distribution and  
23 temporal variation of SOA. The same authors demonstrated that the spread of the simulated peaks  
24 can reach up to  $4.0 \mu\text{g}/\text{m}^3$ . Other uncertainties may be related to the VBS formulation. SOA  
25 formation pathways is one these, indeed halving the SOA yields the concentration of SOA  
26 decreases by 30% (Ahmadov et al., 2012). Moreover, the assumption on the deposition velocity of  
27 the OCVs may play an important role in the uncertainties of SOA production. The OCV deposition  
28 velocity in the version of the VBS implemented in WRF/Chem by Ahmadov et al. (2012) is  
29 proportional to the deposition velocity of the  $\text{HNO}_3$ . The proportionality constant is a tunable  
30 parameter and in this work is set to the default value of 0.25. WRF/Chem prediction of SOA mass  
31 is very sensitive to the choice of the proportionality constant (Ahmadov et al., 2012). Previous  
32 studies have shown that SOA concentration is highly sensitive to the treatment of the deposition  
33 velocity of OCV (Bessagnet et al., 2010; Knote et al., 2014b). Finally we note that OM bias could

1 be partially explained by the uncertainties in the anthropogenic emissions (e.g. bias or spatial  
2 distribution) of primary organic carbon and in the factor 1.6 used to convert them to primary OM  
3 (POM) (Turpin and Lim, 2001). The reader should also consider that the uncertainties in POM  
4 simulation affect the SOA formation. Indeed, the partition between OCV and SOA used in VBS  
5 approach depends on the total OM (Equation 1 of Ahmadov et al., 2012), thus if POM is  
6 underpredicted the resulting SOA could be underestimated.

7 In order to have a more complete overview of the model skill in reproducing the upper air aerosol  
8 mass concentration, we compare also the observed and modelled  $PM_{2.5}$ . Figure 7 shows measured  
9 and predicted box plots of the  $PM_{2.5}$  concentration in PBL and FT. Modelled  $PM_{2.5}$  is in the range  
10 of the observed values within the PBL except during wet scavenging period when it is at the lower  
11 end of the observations. In FT conversely, predicted  $PM_{2.5}$  is at the lower end of the observed  
12 profiles for the most part of the flights. The comparison between modelled and observed  $PM_{2.5}$   
13 concentration within PBL and FT show good correlations (0.75 and 0.80, respectively).

14 Model correlation with observations is high, 0.75 and 0.80 in PBL and FT, respectively. The  
15 absolute mean bias is of  $-7 \mu g/m^3$  (30-35%) in both PBL and FT.

16 Although the box plot and statistical summary (Table 3) provide significant information on the  
17 model performances, the model skills in reproducing vertical profiles of aerosol properties need to  
18 be evaluated. Therefore, we also look at model vertical profiles along the flight tracks. As an  
19 example, we have chosen the 14 May 2008 (RF50) for two reasons: first, there is a relatively large  
20 contribution of OM, SOA (70-85% of OM), and CCN (see Figure 10), and second, it is a day of  
21 high pressure, thus the interpretation of the results is not complicated by cloud processes. Figure 8  
22 displays the comparison of modelled vertical profiles of  $PM_{2.5}$ ,  $SO_4$ ,  $NO_3$ ,  $NH_4$  and OM along the  
23 flight track and measurements. WRF/Chem captures several features present in the aircraft  
24 observations. Both observed and modelled  $PM_{2.5}$  exhibit a maximum in a layer between 500 and  
25 about 2000 m. Model predicts the inhomogeneity of chemical secondary species of  $PM_{2.5}$  displayed  
26 also in the observations:  $SO_4$  and OM concentrations are relatively homogeneous within the PBL,  
27 whereas  $NO_3$  and  $NH_4$  show enhanced concentrations in the upper levels of the PBL. For  
28 completeness, we note that primary  $PM_{2.5}$  components (not shown) have the maximum close to the  
29 surface (first 500 m) and are diluted throughout the PBL. These results are qualitatively similar to  
30 those found by Curci et al. (2015) above Milan (Italy).

#### 1    **4.4 Aloft aerosol particles**

2    The comparison of WRF/Chem output with aircraft measurements of the number concentration of  
3    condensation nuclei (CN) and of cloud condensation nuclei (CCN) at 0.2% of supersaturation is  
4    done by using the boxplots as for aerosol mass. In this case the modelled and measured data are  
5    smoothed by using a 10 seconds running mean.

6    Figure 9 reports the comparison of observed and modelled CN within PBL and FT. The measured  
7    and predicted average, standard deviation, and correlation of CN number over the whole period of  
8    our analysis are reported in Table 3.

9    The model resolves the decrease of a factor 5-6 of CN concentration between the PBL and the FT.  
10    The differences in simulated concentrations between land and sea (RF51 and 52) are also captured  
11    by the modelling system. Nevertheless, WRF/Chem overestimates, on average, the observed CN by  
12    a factor 1.4 within PBL and 1.7 within the FT. The bias is less pronounced above the sea during the  
13    (RF51 and RF52), where the anthropogenic sources are less important. Moreover, it should be noted  
14    that in some cases, for example during the RF56, 57 and 58, the predicted CN are completely  
15    outside the range of the observed values. In these cases the predicted CN are biased high by about a  
16    factor of 2-3. Predicted CN concentration shows a higher variability than measured, especially in  
17    the free troposphere where the difference of modelled standard deviation is biased high by 155%.  
18    Anyway, the modelled CN concentration correlates well with the observed one (0.40 and 0.74 in  
19    PBL and FT, respectively). These values are consistent with the 0.61 found by Luo and Yu (2011)  
20    studying the new particle formation and its contribution to CN with a version of WRF/Chem  
21    including an advanced aerosol microphysical model.

22    Figure 10 shows the comparison of observed and modelled CCN at 0.2% of supersaturation. The  
23    measured and predicted average and standard deviation of CCN are showed in Table 3. The bias of  
24    simulated  $CCN_{0.2}$  appears more contained with respect to CN prediction, especially in the free  
25    troposphere. Figure S3 shows the comparison of the modelled vertical profile of CCN along the  
26    flight track of 14 May and observed CCN aboard the ATR42. WRF/Chem predicts relatively  
27    homogeneous profile of CCN in the PBL also shown by observations.

28    The aerosol particles that mostly contribute to CCN number are those of accumulation and coarse  
29    modes, and accumulation and coarse mode particles are also the major contributor to  $PM_{2.5}$  mass  
30    concentrations. Since  $PM_{2.5}$  is underestimated and CCN overestimated, CCN bias cannot depend on  
31    model errors in  $PM_{2.5}$ . The major uncertainties in predicted CCN arise from aerosol nucleation rate  
32    and primary emissions (Lee et al., 2013). Direct emission of aerosol particles is the key factor for  
33    CCN production in the PBL and near particle sources (Spracklen et al., 2006), and account for 55%

1 of the total global production (Merikanto et al., 2009). On the other hand, nucleation and  
2 subsequent growth up to CCN size is an important mechanism of CCN formation in many parts of  
3 the atmosphere (Sotiropoulou et al., 2006). Using several nucleation parameterizations, Pierce and  
4 Adams (2009) showed that CCN on average varies by up to 12% within the PBL. At the same time,  
5 they also found that varying by a factor of 3 the primary emissions, the CCN mean changes by 40%  
6 in the PBL. On the basis of these argumentations and the correlation between predicted and  
7 observed CN being larger in the FT than in PBL (i.e. far from anthropogenic sources), we may  
8 speculate that the errors in the CCN prediction arise mainly from the uncertainties in the primary  
9 emissions of the aerosol particles and in their distribution in the lognormal modes.

10 The analysis of CCN efficiency reveals other interesting features in the model behaviour. The CCN  
11 efficiency is given by CCN/CN ratio and represents the ability of aerosol particles to nucleate cloud  
12 droplets (Andreae and Rosenfeld, 2008). CCN efficiency observed during the studied RFs is in the  
13 range of 0.02-0.33 for PBL and 0.18-0.41 in the FT, while the model predicts values of 0.03-0.17  
14 and 0.04-0.18 for PBL and FT, respectively. In other words, WRF/Chem underestimates the CCN  
15 efficiency by a factor of 1.5 and 3.8 within the PBL and FT, respectively. Moreover, the modelled  
16 CCN efficiency, contrary to the observation, shows almost the same range of values within the PBL  
17 and within the FT.

18 The so calculated and modelled CCN efficiencies could be underestimated. In general, the CCN  
19 efficiency should be computed with the aerosol population with size larger than the minimum  
20 activation diameter (Asmi et al., 2012). The latter depends on the aerosol type and ranges from  
21 about 50 to 125 nm. We calculated the observed CCN/CN ratio with the measurements of CPC  
22 3010 which gives the total number of particles larger than 15 nm, and modelled CCN fraction is  
23 calculated with total particle number given by the sum of the three modes of the lognormal  
24 distribution (Aitken, accumulation and coarse). In order to better characterize the relationship  
25 between CCN and corresponding aerosol population in the model, predicted CCN efficiency was  
26 also calculated with particles of the accumulation and coarse modes (the most favored particles to  
27 act as CCN) and it was qualitatively compared to observed efficiency during the IMPACT  
28 campaign computed with particles larger than 100 nm. Observed values of CCN efficiency are in  
29 the range of 0.28-0.4 and 0.38-0.6 in the PBL and FT (Crumeyroille et al., 2013), respectively. The  
30 simulated CCN fraction calculated with the particles of the accumulation and coarse modes, is  
31 always underestimated with respect to the observations, and it is in the range of 0.17-0.3 in PBL and  
32 0.23-0.36 in FT. The model deficiency in simulating the CCN/CN ratio could be attributable to the

1 uncertainties in geometrical diameter and bulk hygroscopicity of the lognormal modes, and updraft  
2 velocity that lead to error in the prediction of minimum activation diameter of each mode.

#### 3 **4.5 Comparison with MODIS data**

4 WRF/Chem output was also compared to aerosol optical thickness (AOT), cloud microphysical and  
5 optical properties retrieved by MODIS-Aqua.

6 Figure 11 shows the comparison between the AOT at 550 nm measured by MODIS and the  
7 corresponding AOT predicted by the model during the high pressure period on 14 May 2008.  
8 WRF/Chem reproduces the spatial distribution of observed AOT, such as the lowest values in the  
9 southern part of the domain or the highest values around Cabauw, but underestimates the strong  
10 gradient between eastern boundary and the centre of the domain. The model overestimates the  
11 regional mean of AOT, indeed the domain averages are  $0.38 \pm 0.12$  and  $0.42 \pm 0.10$  for MODIS and  
12 WRF/Chem data, respectively. Unfortunately, good coverage of the D3 domain by MODIS was  
13 achieved only on one day (14 May 2008), this does not allow us to have a general overview of  
14 model skill in predicting AOT. In general, model intercomparisons revealed that a large part of the  
15 uncertainties in simulating the AOT arises from the assumption on the mixing state. For example,  
16 AOT computed with external mixing is larger by 30-35% of that calculated with internal mixing  
17 assumption (Curci et al., 2014b). For typical atmospheric particle sizes and in the visible  
18 wavelength range, the AOT is then expected to be lower under internal mixing assumption (that is  
19 the assumption done in this work). Moreover, a 10% error in predicting AOT may be attributable to  
20 the choice of species density, refractive index, and hygroscopic growth factor (Curci et al., 2014b).

21 **As the WRF microphysics scheme accounts for aerosols only within liquid clouds**, comparison  
22 among predicted cloud optical and microphysical properties with MODIS data was done separately  
23 for liquid, excluding mixed clouds. Top liquid cloud effective radius ( $R_e$ ) was calculated from  
24 liquid water content (LWC) and cloud droplet number concentration predicted by WRF/Chem.  
25 Liquid water path (LWP) was calculated by vertically integrating liquid cloud mixing ratios (water  
26 and rain water), while liquid cloud optical thickness (COT) was estimated from LWC and  $R_e$ . Since  
27 MODIS L2 data provide the total cloud water path (CWP), combined effective radius for all cloud  
28 types and total (water and ice) cloud optical thickness (COT), the observed contribution to the  
29 liquid water cloud was separated by using the retrieved top cloud phase, i.e. were discarded mixed  
30 clouds.

31 The comparison between the predicted and observed  $R_e$ , LWP and liquid COT was done in the  
32 scavenging background and long-range transport periods in the days when MODIS cloudy pixel

1 coverage was larger than 60%. Figure 12 shows the comparison of the averaged values for 17-19  
2 May 2008 period (1P). The same comparison has been done on averaged values for 25-27 (2P) and  
3 28-30 May (3P) and are reported in the Supplement (Figures S4 and S5). WRF/Chem reproduces  
4 several features of the liquid cloud systems during 1P: the liquid cloud distribution, the maximum  
5 values of  $R_e$  close to the coast, maximum of LWP and liquid COT on the centre and at **North-East**  
6 of the domain. However, model results present a larger spatial extension of liquid water cloud  
7 highest values off the Dutch and Belgian coast not observed in the MODIS data. During 2P the  
8 structure of the cloud system is not completely reproduced by the model. Although  $R_e$  value  
9 magnitude is captured above the sea, WRF/Chem underestimates the cloud droplet dimension on  
10 the land. Therefore LWP and liquid COT structure on the sea is resolved by the model, whereas on  
11 the land they are too small compared to the observations. Finally, the model reproduces the average  
12 structure of the cloud system in 3P, but LWP and liquid COT are overestimated on the Western part  
13 of the domain.

14 As shown in Table 4,  $R_e$  values averaged over the entire domain is underestimated by the model by  
15 a factor of about 1.5 during all three periods of interest. LWP, values averaged over the entire  
16 domain, is also overestimated in all three cases by a factor of 1.1, 1.3 and 1.6 for 1P, 2P, and 3P,  
17 respectively. The  $R_e$  (LWP) underprediction (overestimation) may be due to the overestimation of  
18 droplet number concentration that stems from overestimation of CN. Another reason that could  
19 explain the positive bias of modelled LWP, is the inefficient autoconversion of cloud water to rain,  
20 typical of the Morrison microphysical scheme (Saide et al., 2012). The consequence of the negative  
21 (positive) of  $R_e$  (LWP) is the overestimation of average liquid COT by few percent for 1P and 3P,  
22 and 42% for 2P.

23 The biases found here are quite different from the WRF/Chem study by Yang et al. (2011) on the  
24 modelling of marine stratocumulus in Southeast Pacific. They have shown a bias of +30% in  
25 reproducing the COT, while LWP was underestimated by a factor 1.3. The reader should note that  
26 in Yang et al. (2011) the aerosol model adopted was different from the one used here and SOA  
27 formation was not included at all.

28 Figure 13 displays the distribution functions (DF) of  $R_e$ , LWP and liquid COT for 1P. The DF for  
29 2P and 3P are reported in the Supplement (Figure S6 and S7). In all three periods analysed, the  
30 model captures the frequency of large droplets ( $R_e > 18-20 \mu\text{m}$ ), underestimates the number of small  
31 droplets ( $8-10 < R_e < 18-20 \mu\text{m}$ ), and overestimates the frequency of very small cloud droplets ( $R_e < 8-10 \mu\text{m}$ ) by more 30%. Whereas DF of the observed  $R_e$  presents the maximum in the range of 8-13  $\mu\text{m}$ , modelled DF shows the maximum values in correspondence of the droplets with size less than



1 7-8  $\mu\text{m}$ . WRF/Chem captures the shape of the distribution functions of LWP and liquid COT, but  
2 underestimates the maximum and overestimates the higher and lower end of the distributions. Both  
3 variables show a variability higher than the observations. The predicted standard deviations (Table  
4 4) are about 2-3 and 1.5 times larger than those observed for LWP and liquid COT, respectively.  
5 This probably stems from the large variability in simulated CCN.

6 Now it is interesting to analyse the model behaviour in reproducing the total CWP and COT given  
7 by contribution of all cloud phases. Modelled CWP was calculated by vertically integrating all  
8 cloud mixing ratio (water, rainwater, ice, snow and graupel). Predicted COT is given by the  
9 contribution of the liquid water and ice. The contribution of the liquid water was calculated as  
10 described above for liquid water cloud. The contribution of ice phase to COT was calculated  
11 following Ebert and Curry (1992).

12 Figure 14 displays the comparison between observed and predicted CWP and COT in P1, whereas  
13 the same figures for P2 and P3 are reported in the Supplement (Figures S8 and S9). Although for all  
14 three cases, the model reproduces with good approximation the shape and localizations of the cloud  
15 systems, CWP and COT are systematically overestimated (except COT in P2). As shown in Table  
16 5, the predicted domain average of CWP presents, indeed, a bias of 62%, 41%, and 80% for P1, P2  
17 and P3, respectively, whereas the bias of COT is about 15% in P1 and P3.

18 At this point of the analysis, although the aerosol-cloud interaction is a very complex nonlinear  
19 process, we are able to relate the model error in aerosol particles to the uncertainties in cloud  
20 prediction. The overestimation of CN leads to overprediction of the CCN. Higher number of CCN  
21 means clouds with higher number of cloud droplets, higher water content, smaller droplets and  
22 clouds optically deeper.

23 In addition to the uncertainties in aerosol particle simulation, one typical source of error in the  
24 prediction of cloud fields, are the choices related to the model setup. For example Otkin and  
25 Greenwald (2008) found a strong sensitivity of cloud properties while evaluating the response of  
26 WRF model to the permutation of several PBL and cloud microphysical schemes. Moreover, the  
27 same authors have shown that the low level clouds are sensitive to PBL parameterization, whereas  
28 the upper level clouds are sensitive to both PBL and microphysics schemes.

29 One element that may affect the model-satellite comparison are the uncertainties associated to the  
30 retrieval. For example, in South-Pacific stratocumulus, MODIS overestimates the droplet effective  
31 radius by 13-20% with respect to concomitant in situ measurements (Painemal and Zuidema, 2011;  
32 King et al., 2013). The overestimation of COT by MODIS results in the overestimation of CWP  
33 (King et al., 2013). Henrich et al. (2010) have shown systematic differences between MODIS data

1 and in situ observations. Indeed, analysing a system of thin cumulus clouds during EUCAARI  
2 campaign, they also found that MODIS overestimates the droplet effective radius by a factor 2-3  
3 and COT is 2-3 times lower than in situ measurements.

4

## 1    **5    Impact of SOA particles on cloud prediction**

2    The last part of this study focused on the evaluation of the impact of SOA on the simulation of  
3    cloud fields. We performed sensitivity simulations during P1, P2 and P3 without the SOA  
4    (NOSOA), and compared them to the reference run (CTRL) discussed so far. NOSOA runs are  
5    carried out only in the higher resolution domain (D3). The simulations of all three periods are  
6    initialized at 00 UTC with the same meteorological and chemical input data used for CTRL, except  
7    chemical initial conditions that are restarted by previous NOSOA run. Each period is preceded by  
8    30 hours of simulation used as spin-up for D3 chemistry. The sensitivity simulation is performed  
9    zeroing the arrays pertaining to SOA. Thus, the SOA fields are not affected by incoming SOA from  
10    domain boundaries or by local production. We did not perform the sensitivity tests with SORGAM  
11    option because this model produces very little SOA mass concentrations (Grell et al., 2005;  
12    McKeen et al. 2007; Tuccella et al., 2012). Therefore, we may assume that simulations with  
13    SORGAM and without SOA (in VBS option) are roughly equivalent. The advantage of this  
14    assumption is that the model is forced with same initial meteorological conditions and boundary  
15    meteorological and chemical conditions of the CTRL simulation. The use of SORGAM would  
16    require to run the model on all three domains, leading to different results on D2 which is used to  
17    initialize D3. Finally, this would introduce dependencies on the D3 input data making the  
18    comparison not directly comparable to the CTRL run.

19    The comparisons of  $R_e$ , LWP and liquid COT simulated of CTRL and NOSOA runs with MODIS  
20    data are reported in Figures 12, S4 and S5. In general, the average spatial pattern of these three  
21    variables is captured better by CTRL simulation with respect to NOSOA run, especially in P1.  
22    Figures 13, S6 and S7 display the comparison between DFs of the cloud properties simulated by  
23    CTRL and NOSOA runs with those retrieved with MODIS observations. The domain averages for  
24    each variable are reported in Table 4. NOSOA runs show a domain averaged  $R_e$  larger than CTRL.  
25    DFs of the LWP are different between the runs, but it is not clear if there are improvements in  
26    CTRL with respect to NOSOA run. Only the domain averages allow to establish that LWP values  
27    predicted by CTRL run are closer to the observed means than NOSOA. The presence of SOA in the  
28    numerical prediction improves the DF of liquid COT with respect to NOSOA simulation in P1 and  
29    P3, whereas there are no differences during P2. NOSOA has 10% and 3% more optically thin liquid  
30    clouds (liquid COT<40) with respect to CTRL in P1 and P3, respectively.

31    Figures 14, S8 and S9 report the comparison of modelled CWP and COT of all cloud phases predict  
32    in CTRL and sensitivity runs with MODIS data. As well as for liquid phase, including SOA aerosol  
33    particles in the runs, the WRF/Chem skills to reproduce the observed pattern of observed CWP and

1 COT increase. As shown in Table 5, domain averaged CWP and COT are larger up to about 50% in  
2 CTRL with respect to NOSOA.

3 Now it is interesting to explore the impact of SOA on the vertical structure of the cloud fields. As  
4 example we chose the 17 May because around 6 UTC, a frontal system associated to a trough from  
5 North Sea crossed the Benelux area (Figure S10). In both runs, some isolated and shallow clouds  
6 form during the night. When the cold front reaches Benelux around 5-6 UTC, a low pressure centre  
7 forms (Figure S11). The winds rotate around the low pressure with speeds up to 14 m/s at 925 hPa  
8 height (Figure S12). A convective system develops around the vortex. Figure 15 shows the  
9 maximum radar reflectivity (maximum dBZ) at 6 UTC for CTRL simulation, and the difference of  
10 maximum dBZ between CTRL and NOSOA runs. In general, the echo is larger for run with SOA,  
11 i.e. the intensity of the storm is stronger in the CTRL run. Figures 16 and 17 show the vertical fields  
12 of PM<sub>2.5</sub> mass, vertical wind, liquid and frozen hydrometeor for both runs in the cross section A  
13 displayed in Figure 15. These differences between both simulations (CTRL-NOSOA) along the  
14 cross section A, are also displayed in Figures 16 and 17. The convection appears to be stronger in  
15 the control simulation, with a larger amount of hydrometeors and stronger updrafts and downdrafts.  
16 The larger differences in the simulated fields of vertical wind and hydrometeors occur in the same  
17 location where occurs the enhancement of PM<sub>2.5</sub> mass at cloud base (950-900 hPa), roughly at the  
18 distance of 5-15 and 40-90 km away of the origin of the cross section A (Figures 16 and 17). The  
19 results should be taken with caution because the aerosol-cloud interaction is treated only for liquid  
20 clouds, the interaction of aerosol with ice phase is still missing in the model. Although the aerosol-  
21 cloud interaction is a nonlinear process, it is possible to give an interpretation of the results with the  
22 conceptual model for cloud invigoration proposed by Rosenfeld et al. (2008). The larger number of  
23 CCN in CTRL may curb the autoconversion rate of droplets to raindrops, therefore the beginning of  
24 precipitation may be delayed with respect to NOSOA. This delay leads to a larger amount of  
25 condensed water that crosses the freezing level and forms ice hydrometeors. The freezing process  
26 warms the higher layers of the cloud through release of latent heat, whereas the melting process due  
27 to falling of ice cools the lower levels. This thermodynamic disequilibrium enhances the upward  
28 transport of heat. The enhanced conversion of CAPE to kinetic energy may yield the cloud  
29 invigoration found in the CTRL simulation.

## 6 Summary and conclusions

Secondary organic aerosol particles play an important role in the aerosol-cloud-radiation interaction because they contribute to the global budget of radiation and cloud condensation nuclei (CCN). The introduction of SOA particles in numerical simulations has the potential to reduce the uncertainties on the prediction of meteorological fields and air quality. To this aim, a parameterization for SOA production based on the recent VBS approach was coupled with microphysics and radiative schemes in the WRF/Chem community model.

The performance of the updated model at cloud resolving scale (2 km horizontal resolution) was evaluated using ground- and aircraft-based measurements collected during the IMPACT-EUCAARI campaign and the data from the MODIS satellite instrument. The study focuses on the Benelux area, around the supersite of Cabauw, from 14 to 30 May 2008. The analysed period was characterized by few days of high pressure (14-15 May), followed by a scavenged background situation (17-20 May), and finally by long range transport of Saharan dust with the passage of southerly fronts (23-31 May).

The model reproduces the variations of meteorological variables as a function of the synoptic frame. The model broadly captures the inter- and infra-diurnal variability of  $O_3$  and  $NO_x$  at the surface. The concentration of  $NH_3$  is underestimated. Concentrations of  $HNO_3$  and  $HONO$  is reproduced with poor correlation. Simulated  $SO_2$  shows a positive bias of +90%, probably due to overestimated point sources. Surface aerosol mass of  $SO_4$ ,  $NO_3$ ,  $NH_4$ , and OM is simulated with a correlation larger than 0.55. Their diurnal variations as a function of the synoptic frame are resolved by the model. The bias of simulated inorganic aerosol mass is explainable together with error of  $SO_2$ ,  $NH_3$ , and  $HNO_3$  in terms of anthropogenic emissions and the approximation to instantaneous thermodynamic equilibrium. The performances in reproducing the surface aerosol mass found here are comparable to other European studies where these variables are simulated with correlations range from 0.5-0.7 (e.g., Lecœur and Seigneur, 2013; Zhang et al., 2013b; Balzarini et al., 2014 for inorganic species; Athanasopoulou et al., 2013; Fountoukis et al. 2014; Li et al., 2013; Knote et al., 2011; for organic aerosols).

The analysis of aircraft data reveals that WRF/Chem captures the aerosol mass trend both in the PBL and the free troposphere (FT). The predicted aloft aerosol mass of each species is within the observed values range, but the model does not capture the full range of the measured concentrations: the modelled standard deviations of aerosol mass are lower than those observed. Nevertheless,  $SO_4$  ( $NO_3$  and  $NH_4$ ) mass is overpredicted (underpredicted) in more than half of the flights.  $SO_4$  bias is attributable to the  $SO_2$  excess and to a potential overproduction within the cloud

1 chemistry scheme. The negative bias of  $\text{NO}_3$  and  $\text{NH}_4$  could be explained by a low concentration of  
2  $\text{NH}_3$  that limits the formation of the ammonium-nitrate. The simulated OM concentration is at  
3 lower end of the observed mass. The bias is attributable to the missing aqueous chemistry processes  
4 of organic compounds, uncertainties in meteorological fields, to assumptions on the VBS approach  
5 such as the SOA formation pathways, oxidation rate and dry deposition velocity of organic  
6 condensable vapours. Another source of error in simulating SOA are the uncertainties in the  
7 anthropogenic emissions of primary organic carbon and in the factor (1.6) used to convert them to  
8 POM. In general, the statistical analysis reveals that the predicted average concentrations of  
9 inorganic aerosols show absolute error of 2-8% in the PBL, while the  $\text{NO}_3$  and  $\text{NH}_4$  are simulated  
10 with a bias of +14% and +20% (+0.3 and +0.2  $\mu\text{g}/\text{m}^3$ ), respectively, in the FT. The mean OM mass  
11 is underestimated by a factor 2 and 3 in the PBL and FT, respectively. These biases are similar to  
12 those reported by Fast et al. (2014) comparing WRF/Chem (but with a different chemistry package)  
13 to aircraft data performed over California. Indeed they found an absolute mean bias of about 0.01-  
14 0.2, 0.03-0.6, 0.1-0.45, 0.2-0.57  $\mu\text{g}/\text{m}^3$  for  $\text{SO}_4$ ,  $\text{NO}_3$ ,  $\text{NH}_4$ , and OM, respectively. However, we  
15 highlighted that the comparison of aerosol composition predicted by the model with AMS  
16 measurements could be affected by a bias because the model concentrations are representative of  
17  $\text{PM}_{2.5}$  particles and AMS collects aerosols with diameter only between 100-700 nm.

18 Condensation nuclei (CN) are overestimated by a factor of 1.4 and 1.7 in the PBL and FT,  
19 respectively. However, in some cases, the predicted CN are overestimated by a factor of 3.  
20 Predicted CN show higher variability than measurements. The model correlation with observed CN  
21 is 0.40 and 0.74 in PBL and FT, respectively. These values are consistent with the 0.61 below 10  
22 km of altitude found by Luo and Yu (2011) in the Eastern United States with WRF/Chem including  
23 an advanced aerosol microphysical model. Model biases in predicting CN are attributable in large  
24 part to the uncertainties of primary particle emissions (mostly in the PBL) and to the nucleation  
25 rate.

26 The bias of simulated CCN is more contained with respect to that of CN. The CCN efficiency  
27 (CCN/CN ratio) is underestimated by a factor of 1.5 and 3.8 in the PBL and FT, respectively. This  
28 could be due to a low number of particles in the accumulation and coarse mode or to uncertainties  
29 in the hygroscopicity of aerosol particles. CCN/CN ratio represents the ability of aerosol particles to  
30 nucleate in cloud droplets. Therefore, its misrepresentation may lead to issues in the simulation of  
31 cloud droplet number. In other words, the uncertainties in CCN efficiency is a general modelling  
32 problem that may prevent a correct representation of the amplitude of the aerosol-cloud interaction,  
33 i.e. the response of microphysical cloud properties to the variation of CCN **concentrations**. This

issue surely deserves and warrants further insight in the future, **studies on the sensitive of the CCNs to emission distribution in the lognormal modes, aerosol hygroscopicity and updraft velocity are desirable to improve the aerosol activation in the models.**

The bias of simulated CN affects the prediction of droplet effective radius ( $R_e$ ), aerosol optical thickness (AOT), cloud water path (CWP), and cloud optical thickness (COT). The comparison with MODIS data shows that the model overestimates the AOT. The AOT averaged over the entire domain on a single day are  $0.38 \pm 0.12$  and  $0.42 \pm 0.10$  for MODIS and WRF/Chem data, respectively. The domain averaged  $R_e$  of liquid cloud droplets is underestimated by a factor of 1.5 in all the periods examined in the main text. Modelled mean cloud liquid water path (LWP) is also overestimated by a factor 1.1-1.6. The consequence of the negative (positive) bias of  $R_e$  (LWP) is the overestimation of average liquid COT by few percent up to 42%. CWP and COT of all cloud phases are systematically in 2 out of 3 periods analysed. Predicted domain average of CWP presents a bias that ranges from 41-80%, whereas the bias of COT is about 15% in P1 and P3. The overprediction of CWP could be due to the overestimation of droplet number concentration that results from the overestimation of CN, and to inefficient autoconversion of cloud water to rain. The reader should note that the model error found here are different from the study conducted with WRF/Chem by Yang et al. (2011) on the modelling of marine stratocumulus in Southeast Pacific where SOA formation was not included in the simulations. Those authors reported a bias of +30% in reproducing the COT, while CWP was underestimated by a factor 1.3.

In summary, the model behaviour of this new chemistry option in WRF/Chem in simulating the relationship between aerosol and cloud fields may be summarized by this way. The overestimation of CN results in the overprediction of the CCN. Higher number of CCN leads to clouds with higher number of cloud droplets, higher water content, smaller droplets and clouds optically deeper.

As test application of the new chemistry option, we performed a sensitivity simulation where SOA mass concentration is set to zero. The aim was to answer two questions:

1. Does the introduction of SOA particles improve the numerical prediction of cloud fields?

The introduction of SOA in the numerical simulations improves the predicted spatial pattern of microphysical and optical properties of cloud in liquid and all phases. NOSOA runs show an average  $R_e$  larger than CTRL. The analysis of LWP distribution function does not reveal a clear difference between CTRL and NOSOA simulations during the examined periods, only the domain averages allow to establish that LWP values predicted by CTRL run are closer to the observed means than NOSOA. Conversely, including SOA in the numerical prediction improves the distribution function of liquid COT with respect to NOSOA in 2 out

of 3 cases. In these two cases, NOSOA has up to 10% more optically thin liquid clouds (COT<40) with respect to CTRL. Finally, with regards to CWP and COT (all phase), including SOA aerosol particles in the runs, the WRF/Chem improves to reproduce the observed pattern of observed CWP and COT.

2. What is the impact of SOA particles on cloud development?

The analysis was conducted on a convective system. The simulated radar reflectivity is larger for run with SOA, i.e. the intensity of the storm is stronger in the CTRL run. The CTRL simulation exhibits a larger amount of hydrometeors and stronger updrafts and downdrafts. The larger differences in the simulated fields of vertical wind and hydrometeors are associated to the larger differences of PM<sub>2.5</sub> mass located at the cloud base.

On the basis of the results discussed in this work, the option RACM/MADE/VBS coupled with cloud microphysics and radiation allows the WRF/Chem community to use a powerful tool for the study of the aerosol-cloud interactions, improved in terms of representation of the aerosol processes with respect to previous versions based on the RADM/MADE/SORGAM scheme.

For the future, there is still large space for improvements. For example, a more advanced treatment of deposition of organic condensable vapours is desirable. Moreover, the missing production of SOA in cloud is a gap that should also be filled. Finally, the extension of aerosol-cloud interaction to the ice-phase would lead to a complete representation of the aerosol indirect effects.



## 1    **Code availability**

2    The code updated, described, and evaluated here will be incorporated in the next available release  
3    of WRF/Chem. The users will be able to freely download the code from the WRF website  
4    ([http://www2.mmm.ucar.edu/wrf/users/download/get\\_source.html](http://www2.mmm.ucar.edu/wrf/users/download/get_source.html)). A general WRF/Chem user's  
5    guide is also available online (<http://ruc.noaa.gov/wrf/WG11/>).

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19

20

## 1 APPENDIX A: Technical details of coupling of VBS scheme with radiation and 2 microphysics schemes

3 The new chemistry option in namelist.input is *chem\_opt=44*. It works with both *Lin* and *Morrison*  
4 microphysics scheme, *Goddard* and *RRTM* shortwave scheme, and *RRTM* longwave  
5 parameterization. Coupling of new scheme for SOA production with microphysics and radiative  
6 processes requires several modifications to code:

- 7 1. The first step is to create a new chemistry option. The package *racm\_soa\_vbs\_aqchem\_kpp*  
8 (*chemopt==44*) has been added to */Registry/registry.chem* together to some new model  
9 variables for the cloud-borne organic aerosols, called, for example, *asoalcwi*, *asoalcwj* etc.
- 10 2. New chemistry package is a KPP option. Therefore, we created a new subdirectory in  
11 */chem/KPP/mechanisms/racm\_soa\_vbs\_aqchem* containing the files (\*.spc, \*.eqn, \*.kpp,  
12 and \*.def) where are defined the chemical model species and constants, chemical reactions  
13 in KPP format, model description, computer language, precision and integrator. The files are  
14 the same used in *racm\_soa\_vbs\_kpp* package (*chemopt==108*).
- 15 3. The last step is to update the subroutines in *chem* subdirectory. In order to call necessary  
16 subroutines, the modules that we modified are:
  - 17 • *chemics\_init.F*
  - 18 • *module\_input\_chem\_data.F*
  - 19 • *mechanism\_driver.F*
  - 20 • *cloudchem\_driver.F*
  - 21 • *module\_sorgam\_aqchem.F*
  - 22 • *module\_wetscav\_driver.F*
  - 23 • *module\_aerosols\_soa\_vbs.F*
  - 24 • *aerosol\_driver.F*
  - 25 • *dry\_dep\_driver.F*
  - 26 • *module\_mixactivate\_wrappers.F*
  - 27 • *emissions\_driver.F*
  - 28 • *module\_bioemi\_megan2.F*
  - 29 • *optical\_driver.F*
  - 30 • *module\_optical\_averaging.F*
  - 31 • *module\_ctrans\_grell.F*

## 1 APPENDIX B: Statistical indices used in the model evaluation

2 Let  $Obs_i$  and  $Mod_i$  be the observed and modeled values at time  $i$ , and  $N$  the number of  
3 observations.

- 4 • The Pearson's Correlation ( $r$ ):

$$5 \quad r = \frac{1}{N} \sum_{i=1}^N Z_i(Mod) \cdot Z_i(Obs)$$
$$6 \quad Z(X) = \frac{X - \langle X \rangle}{\sigma_X}$$

7 where  $X$  is a generic vector,  $Z(X)$  is its standard score, and  $\sigma_X$  is the standard deviation.

- 8 • Mean Bias:

$$9 \quad MB = \frac{1}{N} \left( \sum_{i=1}^N Mod_i - Obs_i \right)$$

- 10 • Normalized Mean Bias (NMB):

$$11 \quad NMB = \frac{1}{N} \sum_{i=1}^N \frac{Mod_i - Obs_i}{Obs_i} \times 100$$

- 12 • Normalized Mean Gross Error (NMGE):

$$13 \quad NMGE = \frac{1}{N} \sum_{i=1}^N \frac{|Mod_i - Obs_i|}{Obs_i} \times 100$$

14

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2 **TABLES**

3 Table 1. Physical and chemical parameterizations used in the simulation

Physical Processes	WRF/Chem parameterizations
Cloud Microphysics	Morrison
Cumulus Cloud	New Grell (D1 and D2)
Longwave radiation	RRTM
Shortwave radiation	RRTM
PBL	MYNN
Surface Layer	Monin-Obukov
Surface	Noah LSM
Gas-phase Chemistry	Modified RACM-ESRL
Aerosol Chemistry	MADE/SOA-VBS
Biogenic Emissions	MEGAN

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2 Table 2. Statistical indices of the comparison of WRF/Chem to observations of temperature (T),  
 3 relative humidity (RH), wind speed (WS), wind direction (WD), ozone (O<sub>3</sub>), nitrogen oxide (NO<sub>x</sub>),  
 4 nitric dioxide (NO<sub>2</sub>), nitric oxide (NO), ammonia (NH<sub>3</sub>), nitric acid (HNO<sub>3</sub>), nitrous acid (HONO),  
 5 sulphur dioxide (SO<sub>2</sub>), particle sulphate (SO<sub>4</sub>), particle nitrate (NO<sub>3</sub>), particle (ammonium), and  
 6 particle OM, collected at Cabauw tower.

Variable	R	MB	NMB	NMGE
T (°C) at 2m	0.93	-0.66	-5.46	10.65
T (°C) at 10m	0.93	-0.67	-5.24	9.31
T (°C) at 20m	0.94	-0.56	-4.15	8.16
T (°C) at 40m	0.94	-0.46	-3.24	7.21
T (°C) at 80m	0.95	-0.32	-2.10	5.97
T (°C) at 140m	0.95	-0.26	-1.51	5.92
T (°C) at 200m	0.95	-0.45	-2.79	6.66
RH (%) at 2m	0.87	3.17	6.42	11.23
RH (%) at 10m	0.89	4.44	8.36	11.48
RH (%) at 20m	0.91	3.04	6.33	10.50
RH (%) at 40m	0.92	2.99	6.40	10.51
RH (%) at 80m	0.73	-1.04	2.13	13.34
RH (%) at 140m	0.92	2.81	6.40	11.19
RH (%) at 200m	0.91	2.99	7.44	12.50
WS (m/s) at 10m	0.78	0.67	27.90	35.56
WS (m/s) at 20m	0.66	1.27	40.89	49.32
WS (m/s) at 40m	0.67	1.26	32.64	42.04
WS (m/s) at 60m	0.72	1.23	24.42	38.99
WS (m/s) at 140m	0.74	1.21	28.66	41.55
WS (m/s) at 200m	0.76	1.13	27.79	41.48
WD (deg) at 10m	0.52	27.32	43.31	43.31
WD (deg) at 20m	0.53	24.80	40.48	40.48



WD (deg) at 40m	0.60	23.59	40.34	40.34
WD (deg) at 80m	0.67	20.22	30.34	30.34
WD (deg) at 140m	0.71	19.21	32.01	32.01
WS (deg) at 200m	0.73	17.18	28.46	28.46
<hr/>				
O <sub>3</sub> (µg/m <sup>3</sup> )	0.72	-3.43	70.03	90.88
NO <sub>x</sub> (µg/m <sup>3</sup> )	0.70	0.43	19.76	44.77
NO (µg/m <sup>3</sup> )	0.65	0.28	116.08	167.59
NO <sub>2</sub> (µg/m <sup>3</sup> )	0.66	1.25	28.68	54.20
NH <sub>3</sub> (µg/m <sup>3</sup> )	0.43	-4.75	-27.72	42.94
HNO <sub>3</sub> (µg/m <sup>3</sup> )	0.21	-0.09	-1.22	108.65
HONO (µg/m <sup>3</sup> )	0.05	-0.56	-95.37	95.37
SO <sub>2</sub> (µg/m <sup>3</sup> )	0.48	0.68	90.20	116.33
<hr/>				
SO <sub>4</sub> (µg/m <sup>3</sup> )	0.56	1.04	92.2	95.4
NO <sub>3</sub> (µg/m <sup>3</sup> )	0.68	1.00	72.4	94.3
NH <sub>4</sub> (µg/m <sup>3</sup> )	0.74	0.66	63.0	67.3
OM (µg/m <sup>3</sup> )	0.75	-0.42	3.21	29.9

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2 Table 3. Observed and modelled mean values, standard deviations, and relative amount (expressed  
 3 as percentage) of aerosol species, number of aerosol particles, cloud condensation nuclei, over the  
 4 whole period of the aircraft campaign in boundary layer and free troposphere.

	Boundary Layer			Free Troposphere		
	Observation	WRF/Chem	r	Observation	WRF/Chem	r
SO <sub>4</sub> (µg/m <sup>3</sup> )	3.1±2.4 (19%)	3.2±2.1 (24%)	0.39	2.6±2.0 (29%)	2.5±1.2 (38%)	0.23
NO <sub>3</sub> (µg/m <sup>3</sup> )	4.5±5.4 (28%)	4.6±5.1 (34%)	0.47	1.3±3.0 (14%)	1.5±2.7 (23%)	0.44
NH <sub>4</sub> (µg/m <sup>3</sup> )	2.6±2.2 (16%)	2.4±2.1 (19%)	0.43	1.4±1.5 (16%)	1.2±1.2 (19%)	0.42
OM (µg/m <sup>3</sup> )	6.1±5.8 (37%)	3.0±2.6 (23%)	0.67	3.7±4.5 (41%)	1.3±1.4 (20%)	0.52
PM <sub>2.5</sub> (µg/m <sup>3</sup> )	23±13	16±10	0.75	19±17	12±9	0.80
CN (10 <sup>3</sup> #/cm <sup>3</sup> )	6.7±5.0	9.4±5.4	0.40	1.0±1.1	1.7±2.8	0.74
CCN (10 <sup>3</sup> #/cm <sup>3</sup> )	0.6±0.5	0.9±0.8	0.45	0.3±0.3	0.3±0.3	0.73

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2 Table 4. MODIS and modelled mean values and standard deviations of droplet effective radius at  
3 cloud top, liquid cloud water path and liquid cloud optical thickness, on 17-19, 25-27, and 28-30  
4 May 2008.

	R <sub>e</sub> (μm)			LWP (g/m2)			COT		
	MODIS	CTRL	NOSOA	MODIS	CTRL	NOSOA	MODIS	CTRL	NOSOA
17-19 May	10.2±3.5	7.5±3.5	8.5±4.3	230±343	242±343	208±352	32±22	33±33	21±24
25-27 May	13.7±3.7	9.1±4.4	9.8±4.9	200±166	256±502	273±480	22±19	23±30	21±27
28-30 May	10.7±3.9	8.4±4.1	7.8±3.6	141±128	224±327	243±447	19±14	27±27	24±30

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2 Table 5. MODIS and modelled mean values and standard deviations of cloud water path and cloud  
 3 optical thickness of clouds in all phases, on 17-19, 25-27, and 28-30 May 2008.

	CWP (g/m <sup>2</sup> )			COT		
	MODIS-Aqua	CTRL	NOSOA	MODIS-Aqua	CTRL	NOSOA
17-19 May	207±203	336±531	218±359	26±20	30±33	19±23
25-27 May	235±182	331±533	244±418	21±16	17±23	16±21
28-30 May	206±201	370±714	262±523	21±16	24±26	21±27

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## FIGURES

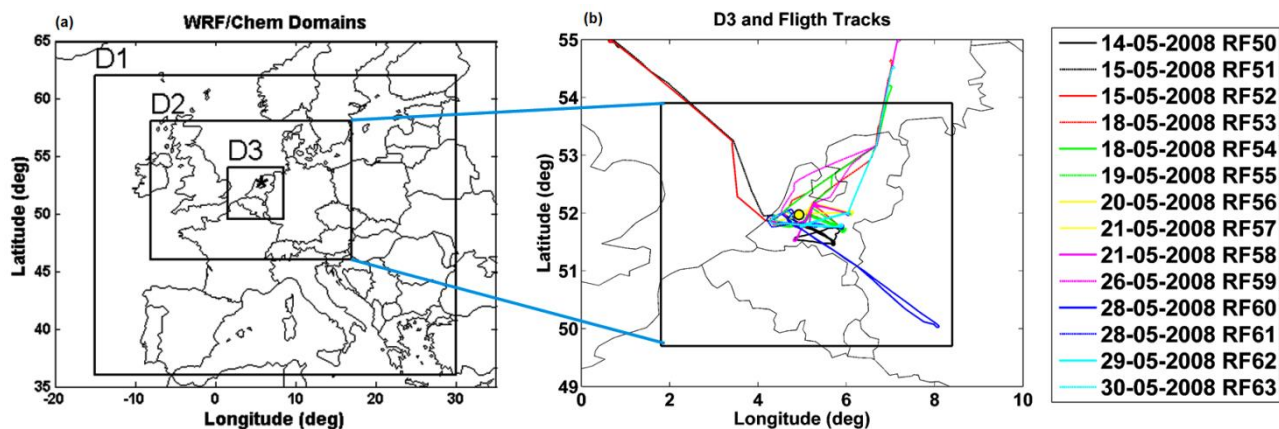


Figure 1. Panel (a) shows the three nested model domains used for simulations. D1 is 30 km resolution, D2 10 km, and D3 2 km. The black star indicates the Cabauw supersite. Panel (b) is a zoom of D3 and shows the track of every flights used in this study, yellow circle represents Cabauw supersite.

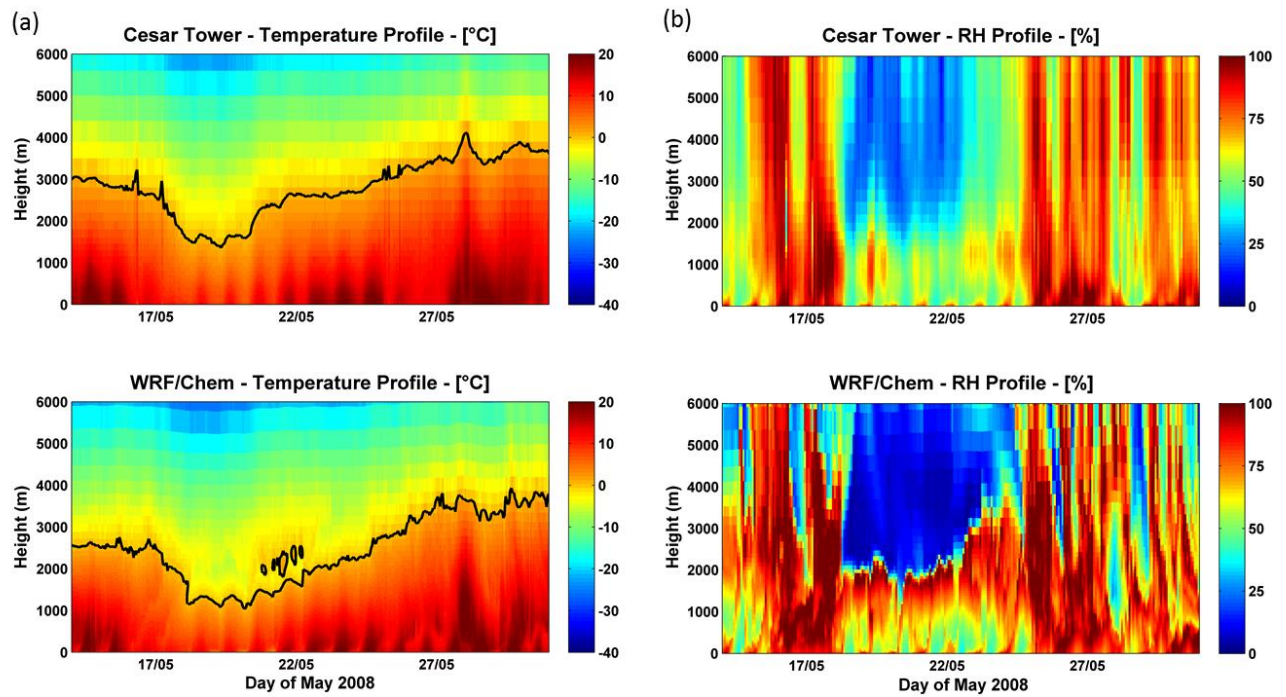
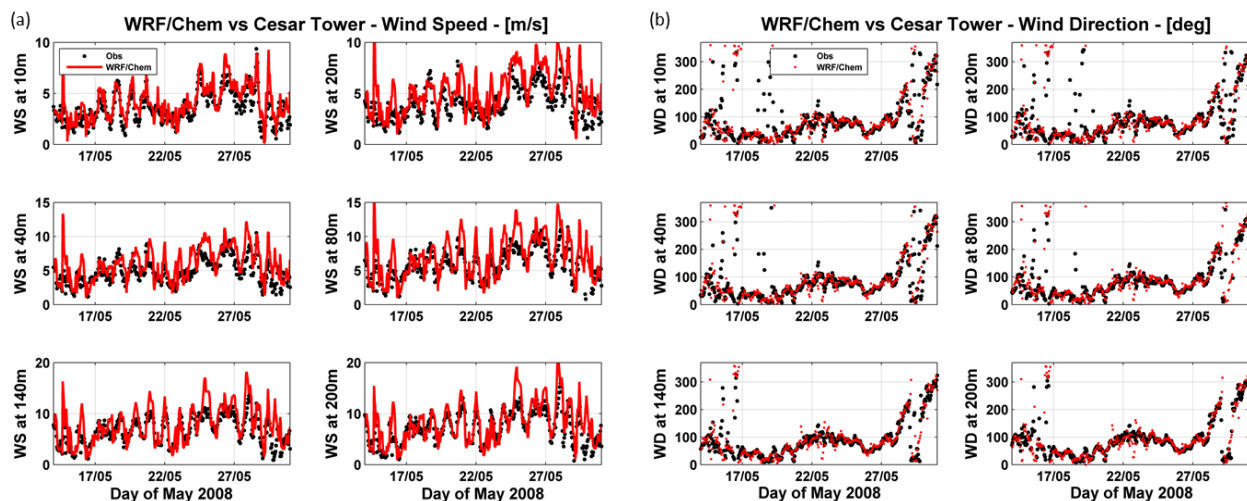


Figure 2. Observed and simulated time series of vertical profile of the temperature (a) and relative humidity (b), observed at Cesar observatory. The black line on the temperature profile represents the 0°C isotherm.

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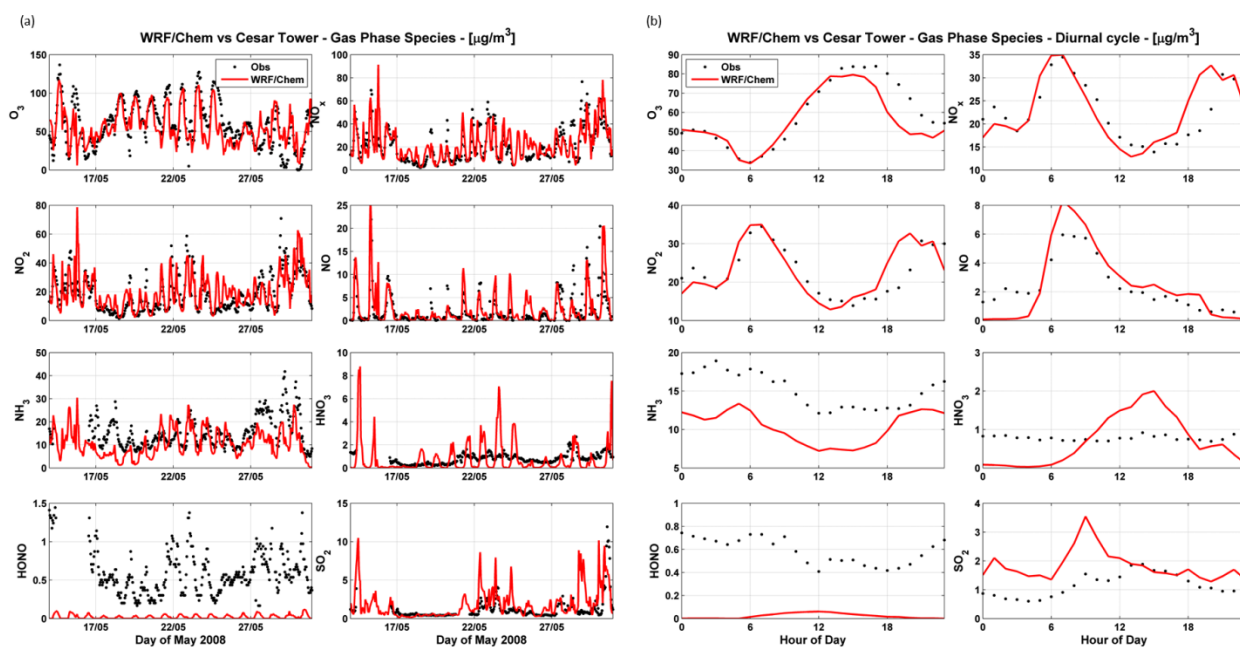


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3 Figure 3. Observed (black lines) at Cesar Tower and simulated (red lines) time series of wind speed  
 4 (a) and wind direction (b) at different height.

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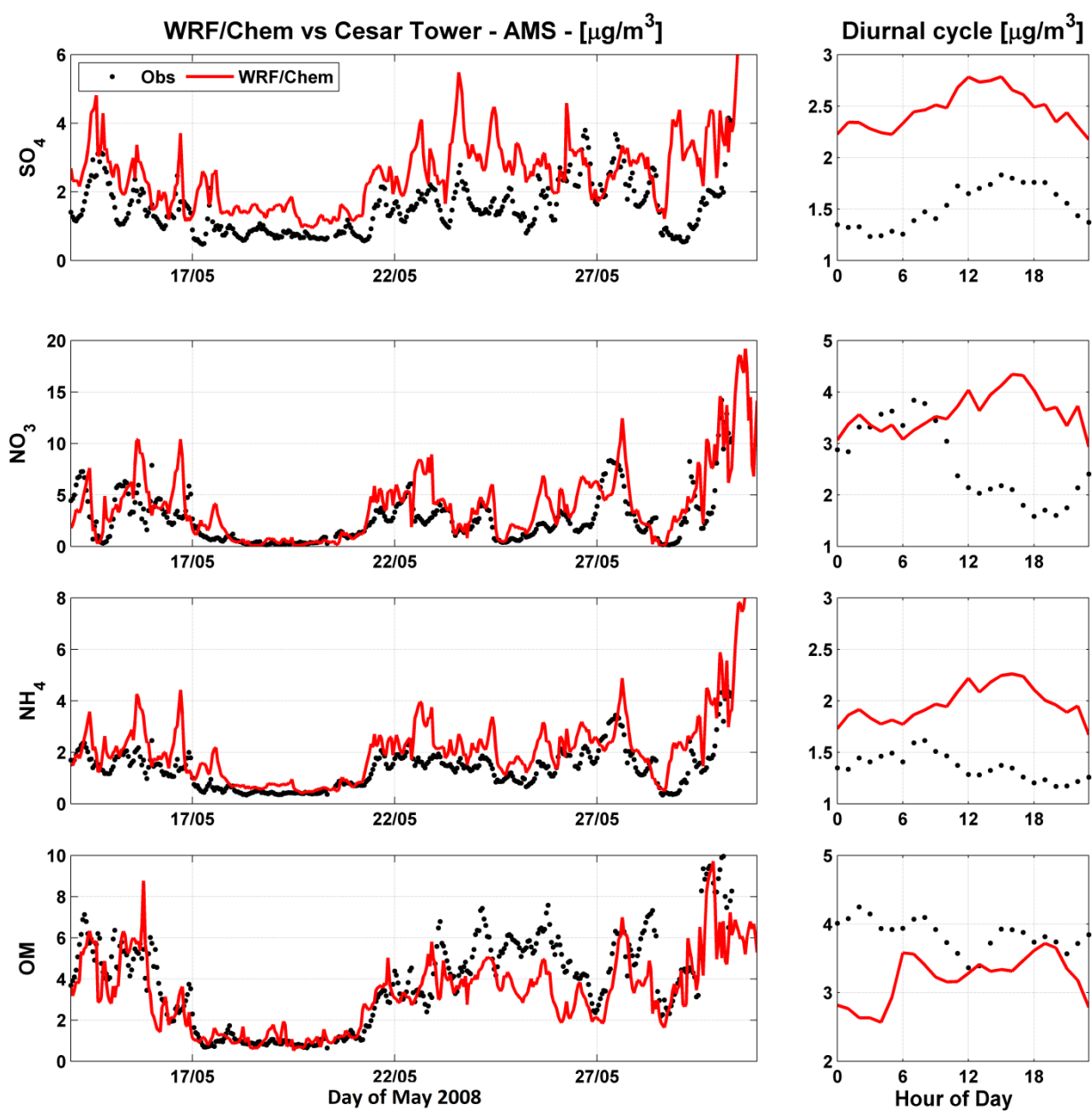
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3 Figure 4. Observed and simulated time series of gas-phase species (a) and their average diurnal  
 4 cycle (b), at Cabauw Zijdeweg EMEP station (NL0011R).

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3 Figure 5. As Figure 4, but for aerosol mass speciation at Cesar Observatory observed at 60m height.

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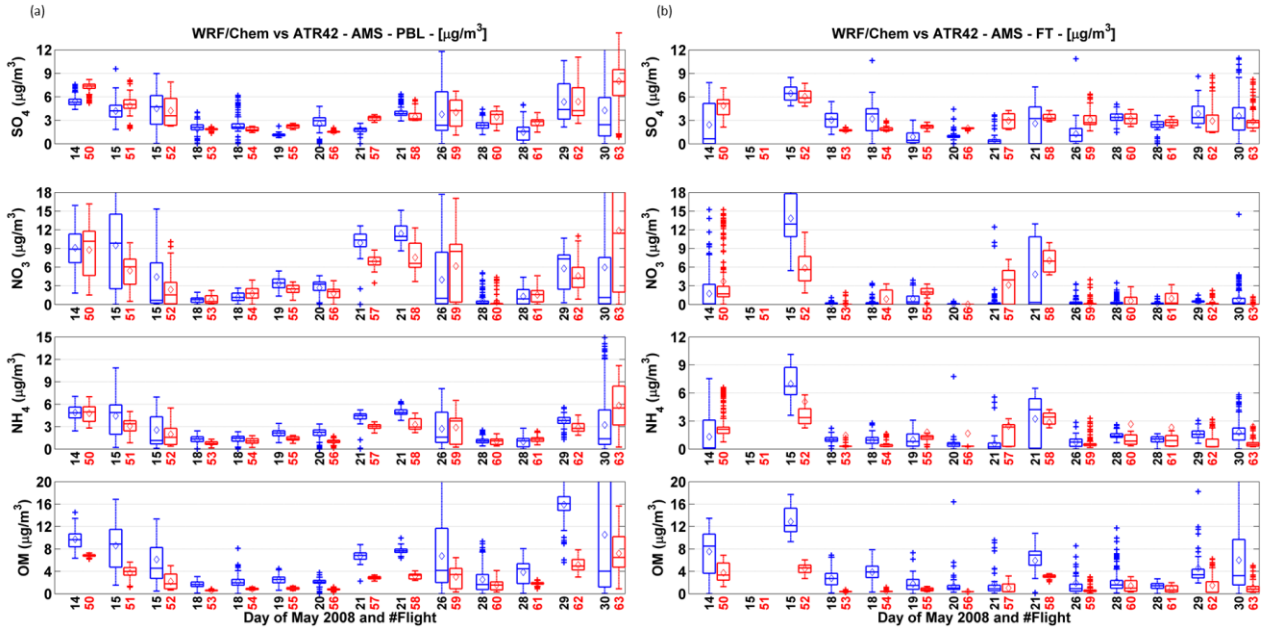
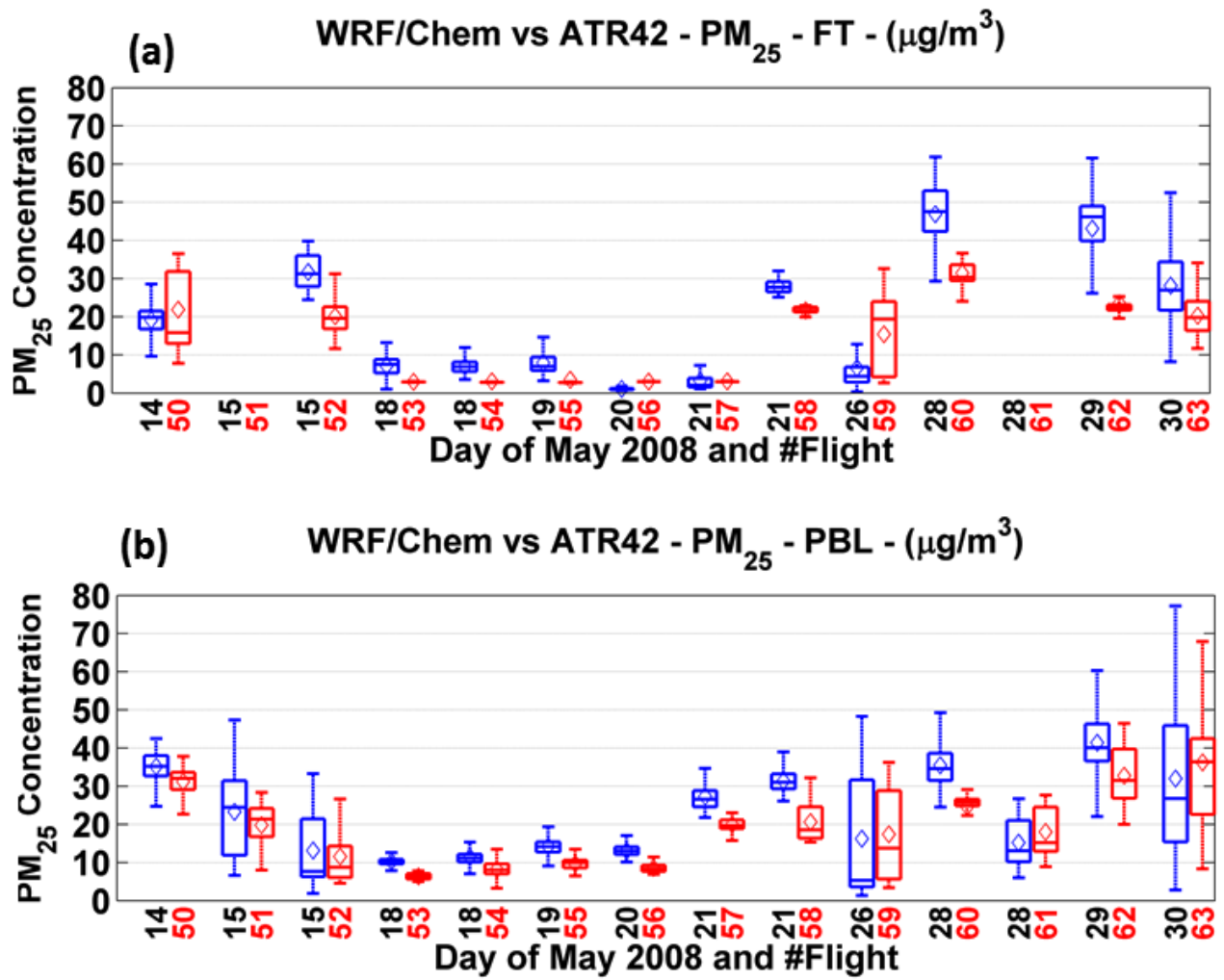


Figure 6. Box plot of  $\text{SO}_4$ ,  $\text{NO}_3$ ,  $\text{NH}_4$ , and OM mass concentrations measured by AMS aboard the ATR-42 (blue) and simulated by WRF/Chem (red) within boundary layer (panel a) and free troposphere (panel b). The x-axis reports the day of May 2008 (black) and the number of the research flight (red). The whisker plots denote median, 25th and 75th percentiles,  $1.5 \times$  (inter-quartile range), and outliers. The squares represent the mean values.

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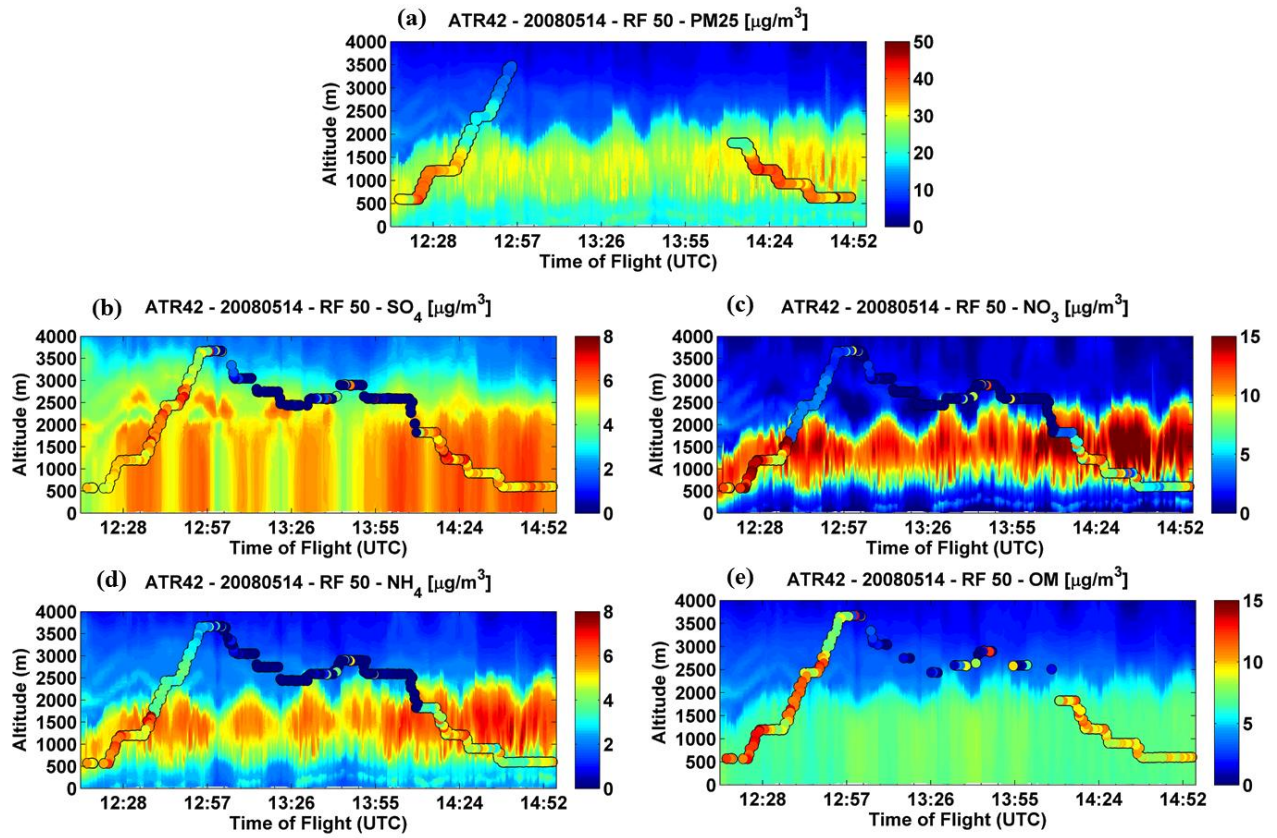


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3 Figure 7. Same as Figure 6 but for observed and simulated PM<sub>2.5</sub> mass concentrations. The blue  
 4 colour represents the observations will the model is displayed in red colour.

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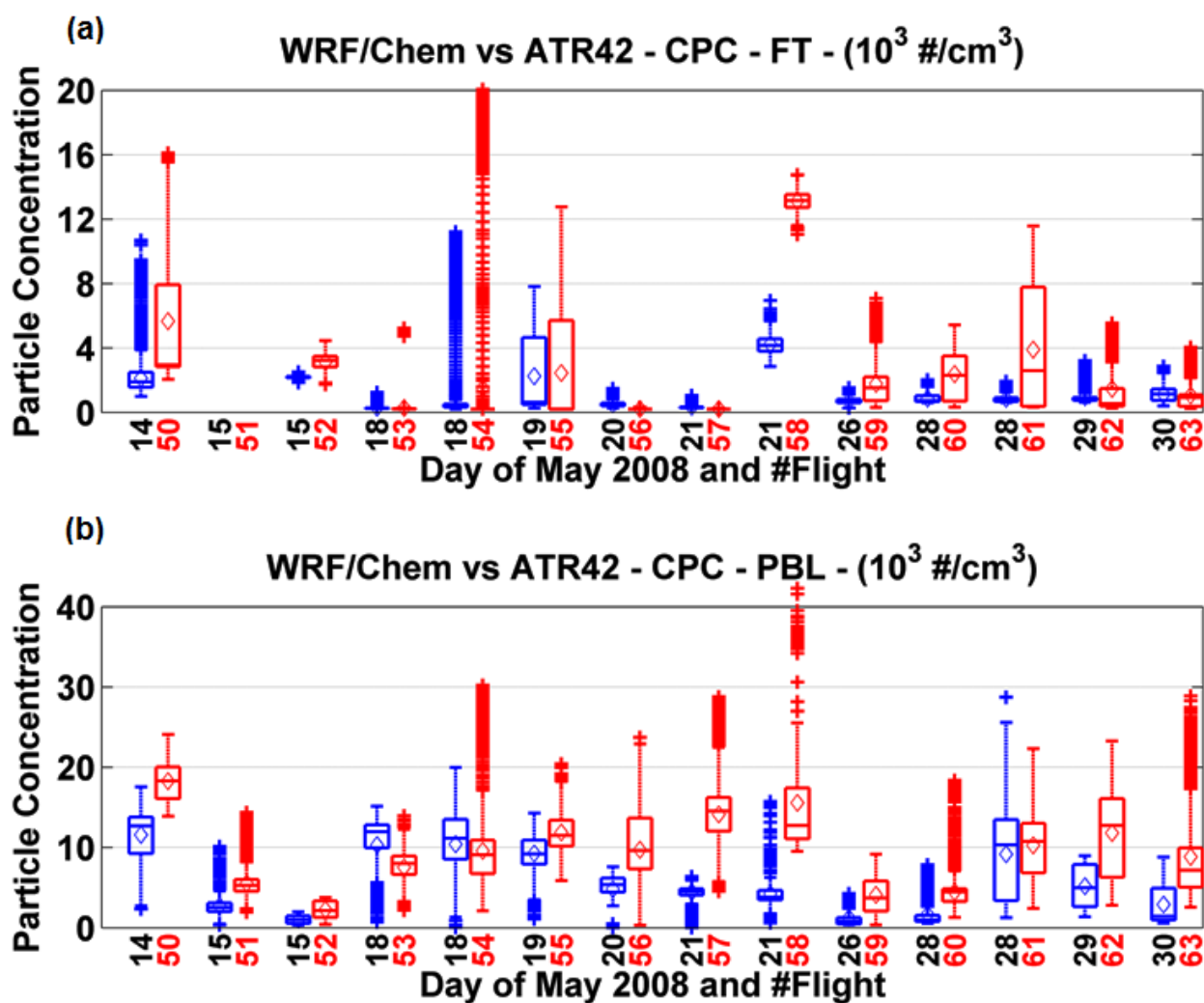
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3 Figure 8. Vertical profiles (shadow) along the flight track of 14 May (RF50) of modelled PM<sub>2.5</sub> (a),  
 4 SO<sub>4</sub> (b), NO<sub>3</sub> (c), NH<sub>4</sub> (d), and OM (e). The circles are the measurements collected aboard the  
 5 ATR42.

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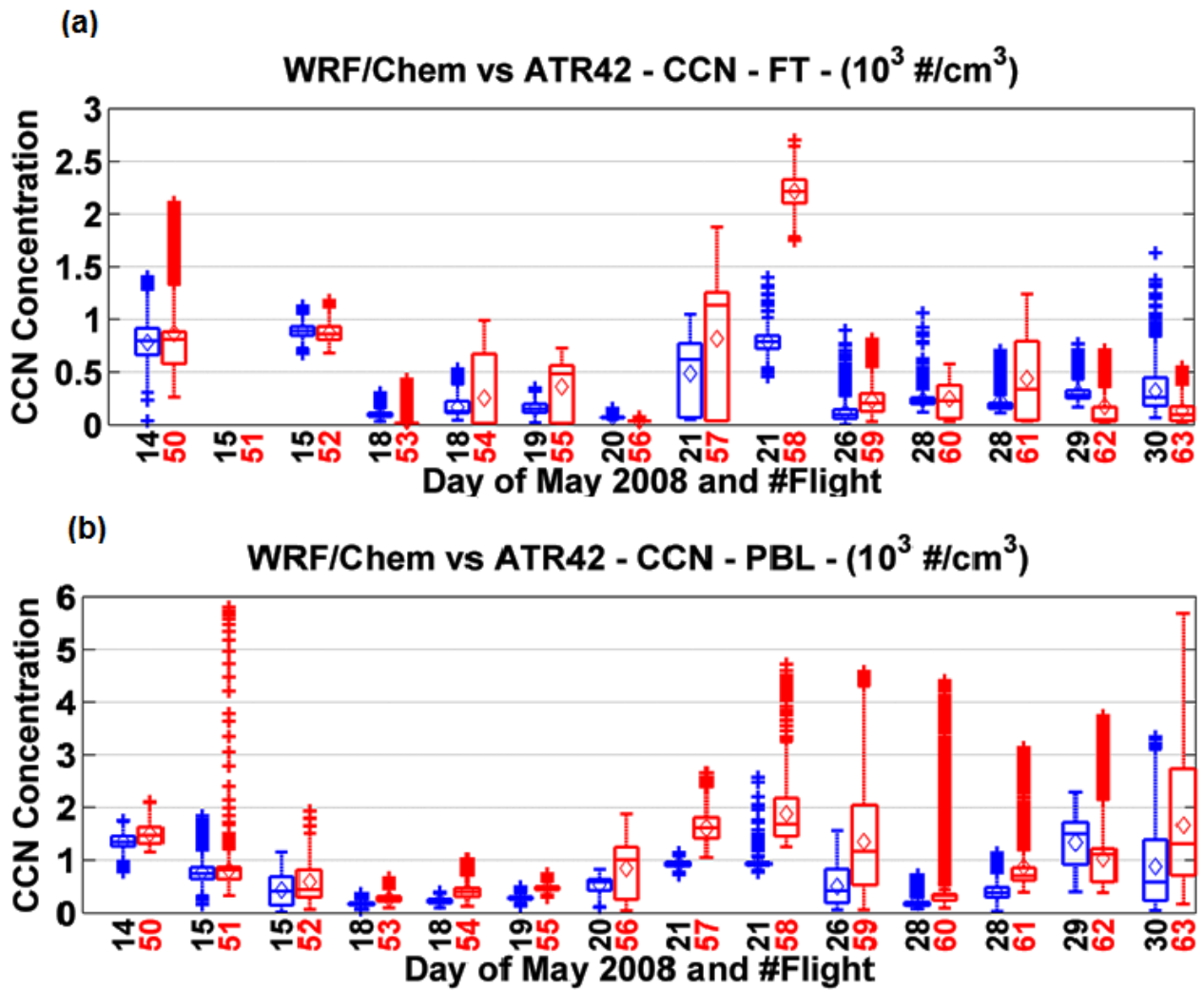
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4 Figure 9. Same as Figure 6 but for observed and simulated condensation nuclei (CN)  
 5 concentrations. The blue colour represents the observations while the model is displayed in red  
 6 colour.

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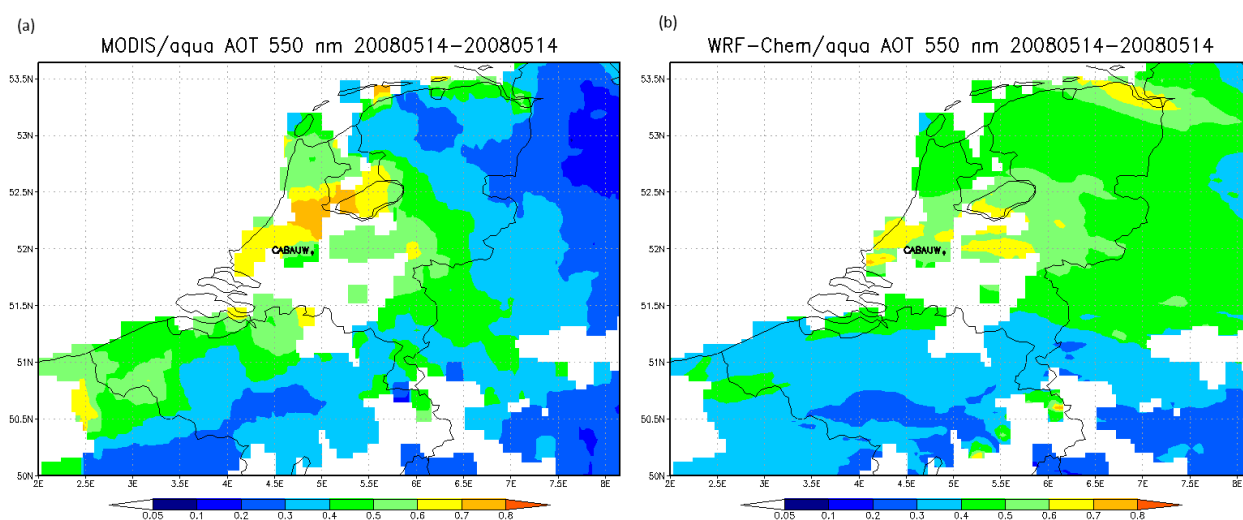
3 Figure 10. Same as Figure 6 but for observed and simulated cloud condensation nuclei (CCN)

4 concentrations at 0.2% of supersaturation. The blue colour represents the observations, the model is

5 displayed in red color.

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Figure 11. Aerosol optical thickness at 500 nm from MODIS-Aqua (panel a) and WRF/Chem simulations (panel b) on 14 May 2008.



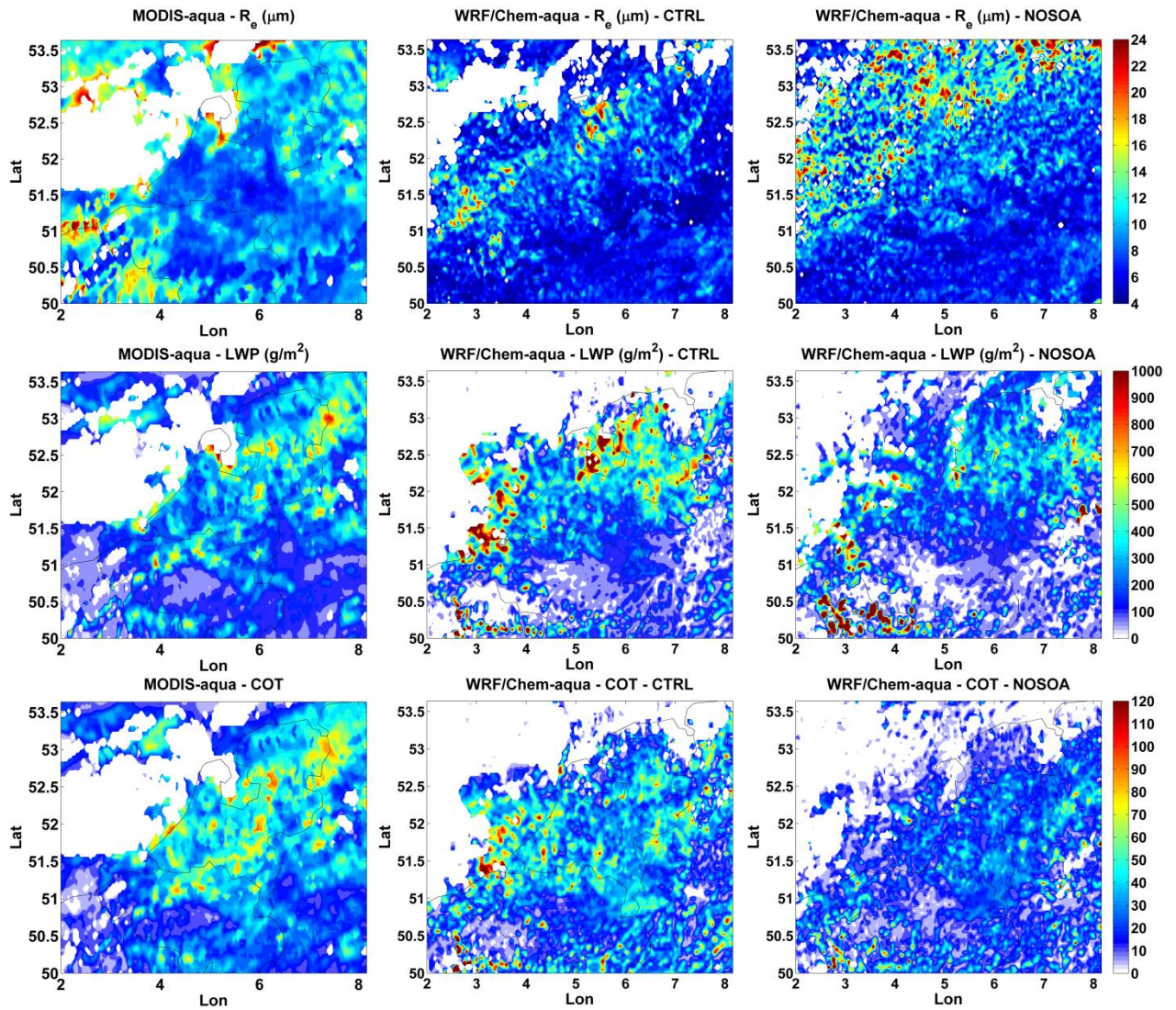
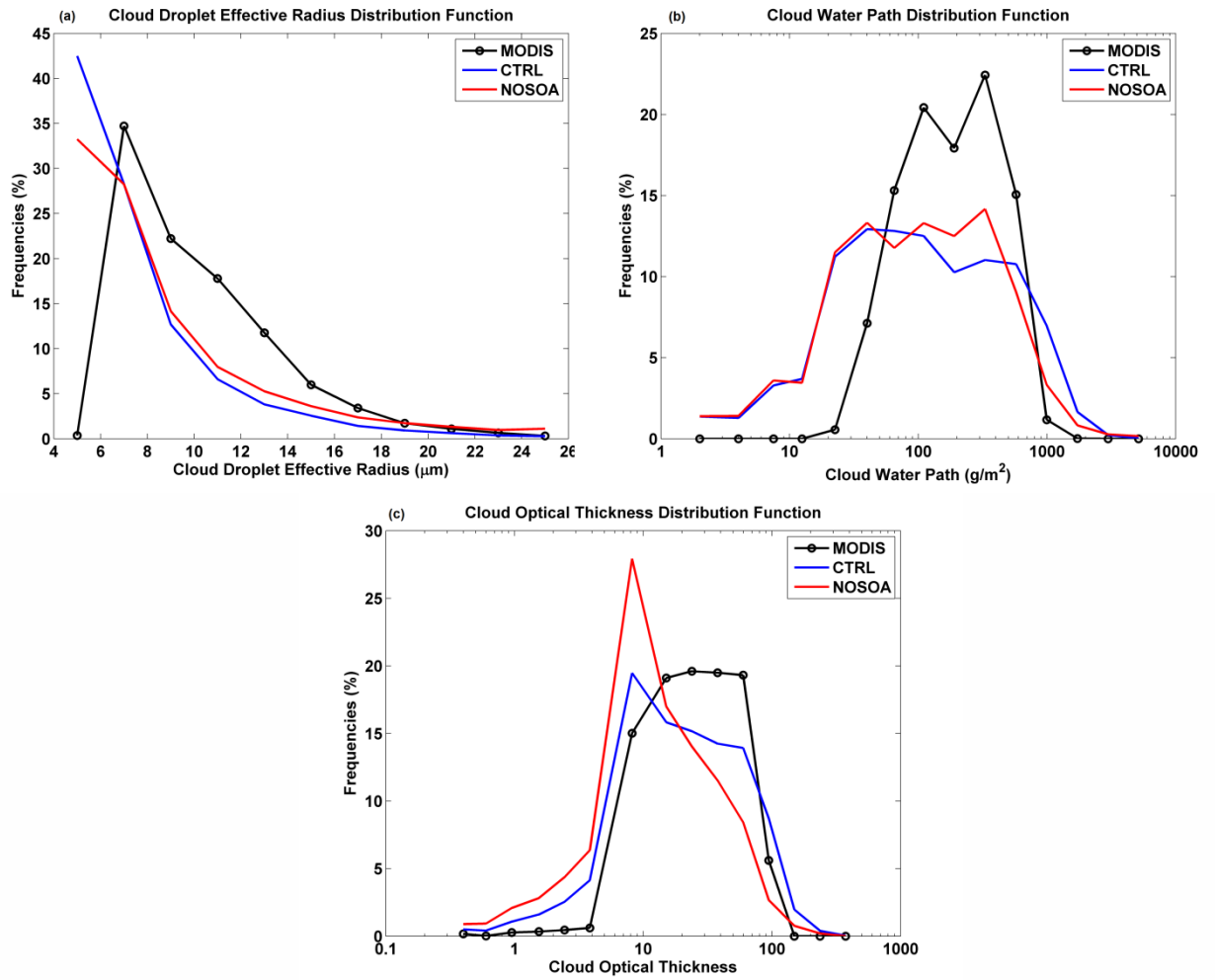


Figure 12. 17-19 May 2008 averages of droplet effective radius at cloud top (first row), liquid water path (second row), and liquid cloud optical thickness (third row), retrieved using MODIS-aqua observations (first column), predicted by model in the references run (CTRL, second columns) and sensitivity test without SOA (NOSOA, third column).



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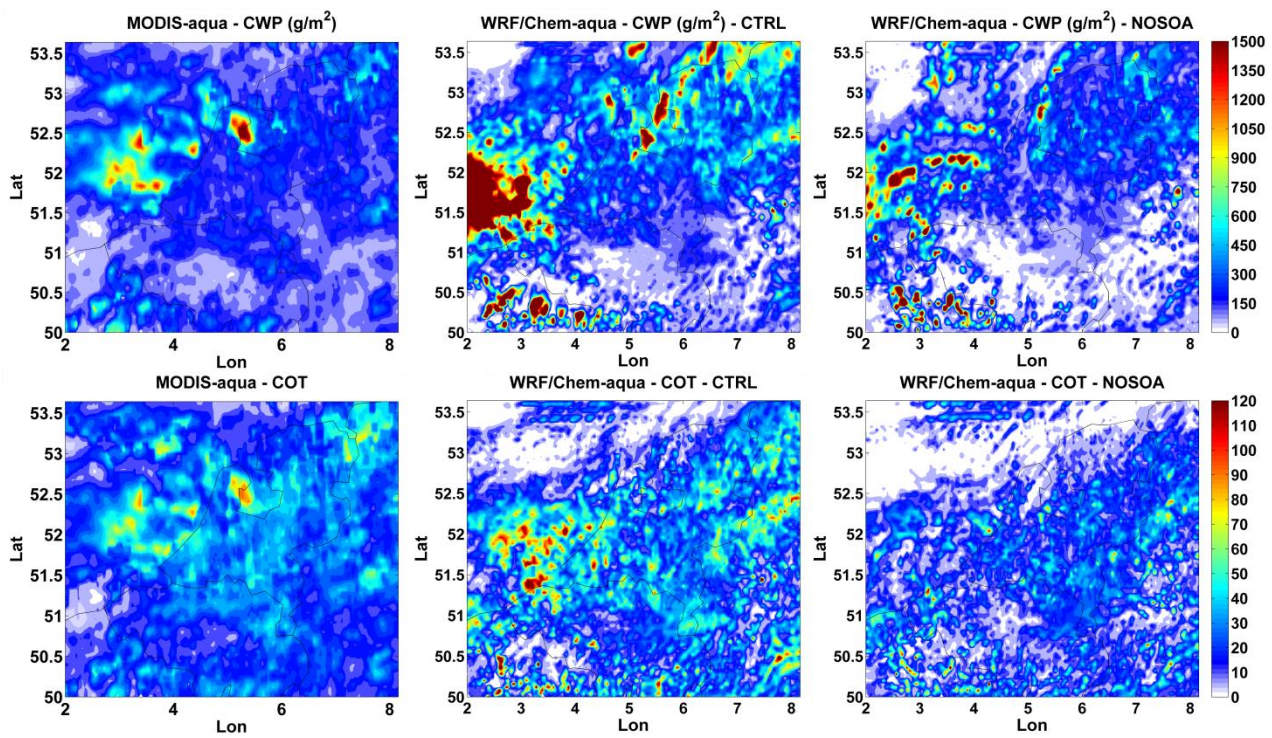


2

3 Figure 13. 17-19 May 2008 averages of observed and simulated distribution function of droplet  
4 effective radius at cloud top (a), liquid water path (b) and liquid cloud optical thickness (c). The  
5 black line represents the observations retrieved by MODIS, blue and red colours correspond to  
6 model predictions from the reference run (CTRL) and sensitivity test without SOA (NOSOA),  
7 respectively.

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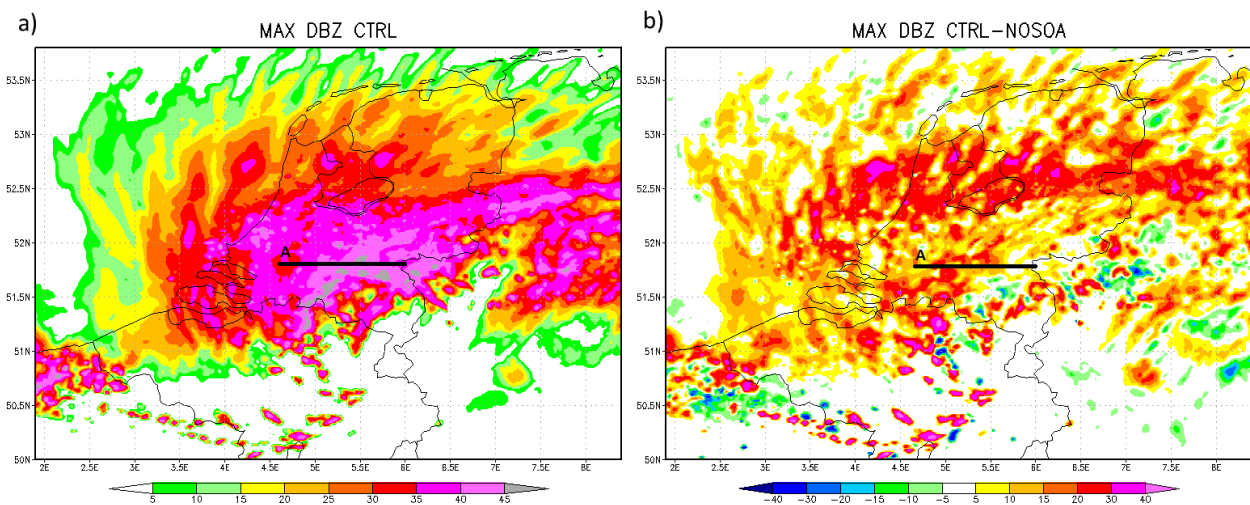
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4 Figure 14. As Figure 12, but for clouds in mixed phase.

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3 Figure 15. Maximum dBZ at 6 UTC of 17 May for CTRL run (a) and difference of maximum dBZ  
 4 between CTRL and NOSOA simulations (b). The solid black line represents the cross section A  
 5 used to plot vertical profiles reported in Figure 13.

6

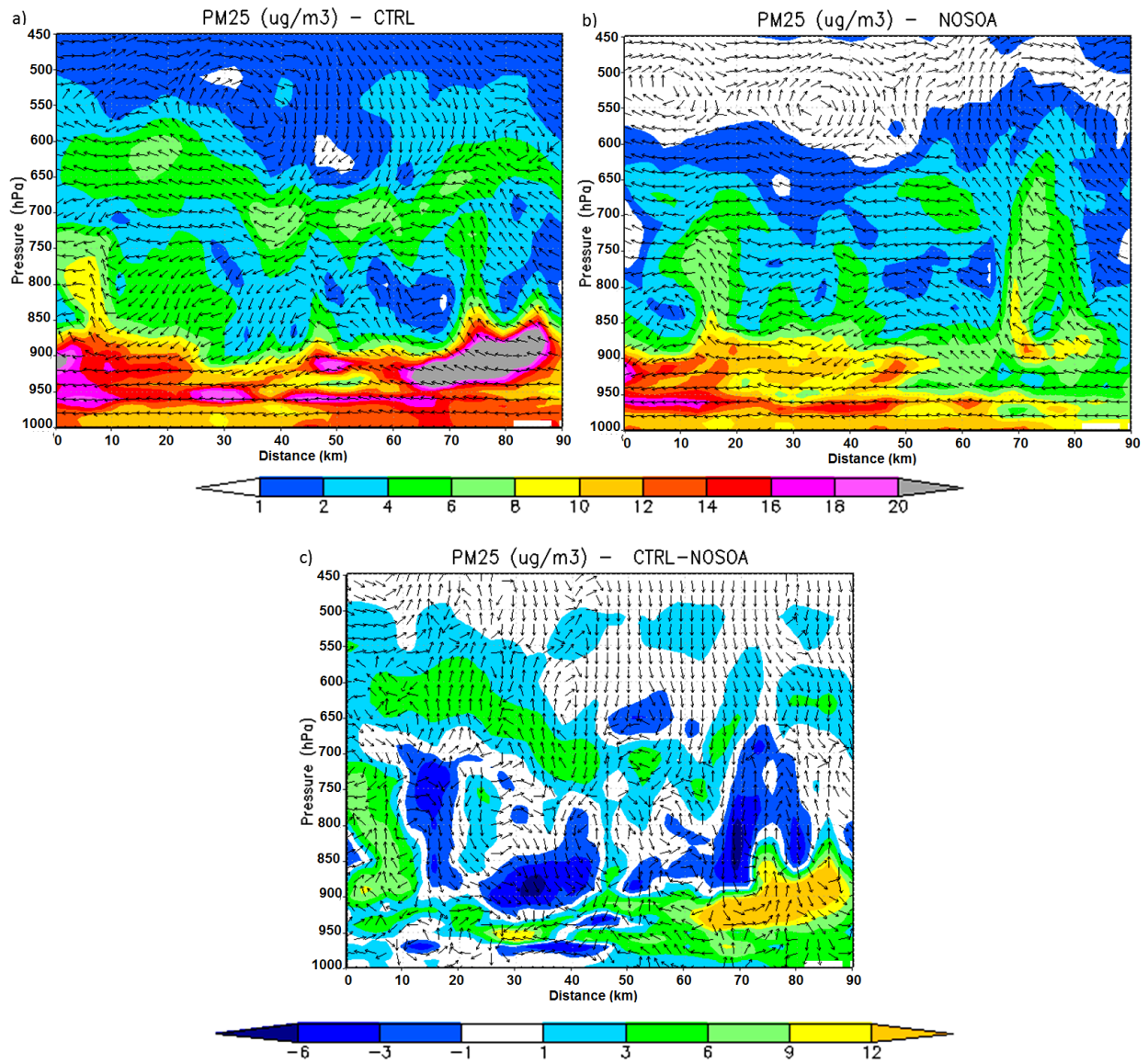
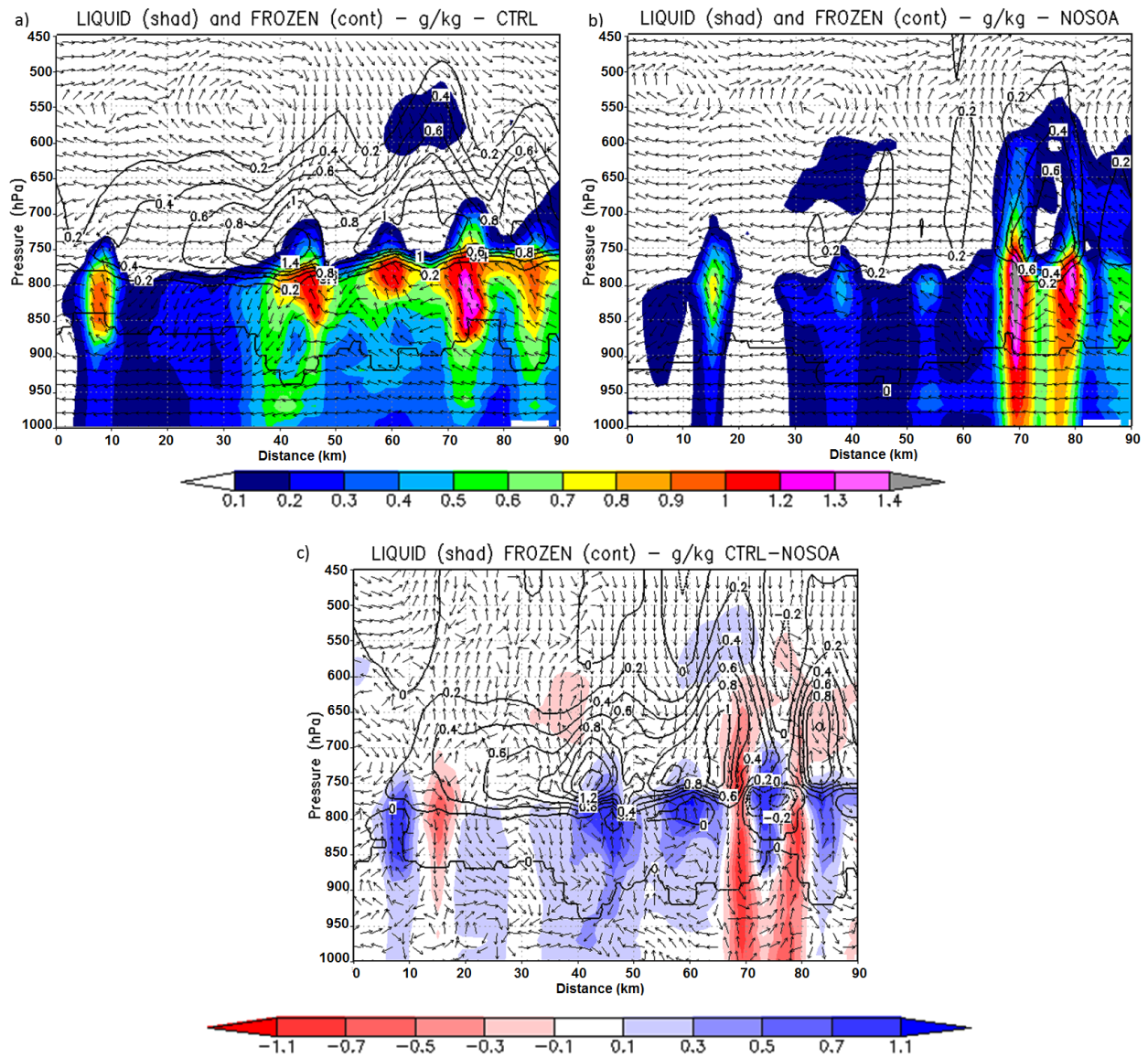


Figure 16. Vertical profile of PM2.5 mass (color) and wind (vector) for CTRL run (a), NOSOA run (b) and their differences (c). The fields are extracted along the cross section A (see Figure 12) at 6 UTC of 17 May. The x-axis reports the west-east distance in km along the cross section.



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3 Figure 17. As Figure 16, but for water (color), and frozen (black contours) hydrometeors.

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