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# Simulation of size-segregated aerosol chemical composition over northern Italy in clear sky and wind calm conditions

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## ABSTRACT

The present article compares the outputs of the 3-D regional chemistry-transport model (CTM) CHIMERE against observations of the size-resolved aerosol chemical composition over northern Italy in clear sky and wind calm conditions. Two 4-day intensive field campaigns were carried out in July 2007 and February 2008 at three sites (urban, rural and mountain backgrounds) in the framework of the AEROCLOUDS project. Predicted levels are in reasonable agreement with observations for the urban and rural sites. Bias ranges from -30%, for the rural site in winter, to + 38%, for the urban site during summer. In addition, the model is able to capture both the daily evolution of the bulk aerosol mass as well as its spatial gradients. Aerosol size distribution and chemical composition remain difficult to predict. The largest discrepancies were found for secondary organic aerosol (SOA) during summer and nitrates during the cold season. Compared with observations, modelled size distribution is shifted towards fine mode in winter, and towards coarse mode in summer. More accurate predictions can be achieved for both seasons by tuning the gas to particle absorption process. By reducing the SOA absorption rate by 25% at the urban sampling site in summer, the correlation between observed and simulated SOA size distributions increases from -0.30 to +0.70, and the bias is reduced from 200% to 0%. In winter, increasing the intra-sectional flux of particles from smaller to larger ones by a factor of 5, the Pearson correlation coefficient calculated over the nitrate size distribution goes up to +0.85, compared to +0.50 from CTRL, also resulting in a better agreement with the size distribution of PM<sub>10</sub>. As expected, the nitrate bulk mass concentration does not vary with respect to the base-case, and therefore nitrate overestimation remains present in the model. © 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

The impact of aerosols on health and climate strongly depends on their size and chemical composition. Thus, a correct characterization of their high variability over space and time is one of the main issues in atmospheric chemistry and physics studies (IPCC, 2007). Several comprehensive chemistry-transport models (CTM) on the global and regional

\* Corresponding author. Tel.: +39 3200636360. *E-mail address:* t.landi@isac.cnr.it (T.C. Landi). scale (e.g. STEM (Carmichael et al., 1991); GEOS-CHEM (Bey et al., 2001); ECHAM5-HAM (Stier et al., 2005); WRF/Chem (Grell et al., 2005); CHIMERE (Bessagnet et al., 2008); PMCAMx (Fountoukis et al., 2011)) have been developed in the last two decades. They are now generally able to reproduce annual  $PM_{2.5}$  and  $PM_{10}$  levels with an acceptable uncertainty, varying according to initialization data, boundary conditions, emissions and meteorological fields used (e.g. De Meij et al., 2006, 2009a, 2009b). Nevertheless, daily aerosol levels are generally underestimated by a factor of 2 (e.g. Stern et al., 2008). Earlier modelling studies suggested that a large part of







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this underestimation rises from (i) uncertainties in the magnitude and spatial-temporal allocation in the emission inventory of primary compounds (Mathur et al., 2008; Stern et al., 2008), and (ii) a combination of current uncertainties in emissions of secondary organic aerosols precursors and the estimation of chemical production pathways for secondary constituents (Myhre et al., 2009; Simpson et al., 2007; Stern et al., 2008: Bessagnet et al., 2010: Kim et al., 2011). Moreover, focusing on one of Europe's most polluted areas, the Po Valley in northern Italy, major experimental campaigns have been carried out over the last decade in the context of projects such as MINATROC (MINeral dust And TROpospheric Chemistry, (Hanke et al., 2003)) ADRIEX (Aerosol Direct Radiative Impact Experiment, (Myhre et al., 2009)) and QUITSAT, (Di Nicolantonio et al., 2009). Such recent, and often multidisciplinary projects have contributed to a better understanding of (i) how the gas/dust interactions affect estimates of radiative forcing by ozone and anthropogenic aerosols, (ii) aerosol direct effects, and (iii) aerosol monitoring through a synergy among satellite and ground-based observations, and chemical transport models. However, to date, few studies are available on the size distribution and chemical composition of aerosols observed in northern Italy, like those of Myhre et al. (2007) and Fountoukis et al. (2011).

For the first time to our knowledge, the present article reports a comparison between the size-segregated PM<sub>10</sub> chemical composition and CTM model results. The CHIMERE (Bessagnet et al., 2008) model was used for the experiments conducted over northern Italy (Po Valley) during two periods of four days, one in summer and one in winter, respectively. The Po Valley is a wide plane located in a semi-closed basin bordered by the Alps to the North and the Apennines to the South-east, and closed to the East by the Adriatic Sea, where pollutants emitted at ground level often remain trapped under stagnant weather conditions (Minguzzi et al., 2005). Calm wind conditions prevailing throughout the valley favour the formation and accumulation of pollutants, mainly comprising secondary particulate matter from aging processes. Species like primary particulate matter (PPM), organic material and inorganic aerosols (sulphate, nitrate and ammonium) from sources, such as industrial combustion plants, domestic heating and road traffic, are the main components of PM<sub>10</sub> in the Po Valley (Putaud et al., 2004, 2010; Finardi and Pellegrini, 2004; De Meij et al., 2007; Rodriguez et al., 2007). In spite of the application of current legislation devoted to air pollution control, particulate matter levels are expected to remain problematic at least until 2020 in northern Italy and will still be responsible for a loss of ten months of life expectancy (Amann et al., 2005). In view of this, establishing a robust and effective methodology for monitoring the spatial-temporal variability of the main aerosol components (i.e. secondary organic and inorganic aerosols, and black carbon), over the whole domain, rather than only at single sampling sites, is a crucial issue.

In Section 2, the observational data set collected during the AEROCLOUDS project (study of the direct and indirect effects of aerosol and clouds on climate) is presented. In Section 3 the CHIMERE model and its aerosol module are briefly described. In Section 4, simulations are compared with observations of the aerosol size-segregated compositions found for the two campaign periods (winter and summer), and sensitivity test results are described in an attempt to elucidate the reasons for the discrepancies against the observations. Section 5 contains the conclusions.

## 2. Observational data set

The experimental data used in the present work refer to the organic and inorganic chemical characterizations of size-segregated aerosol samples collected over northern Italy in typical summer and winter conditions. In the framework of the AEROCLOUDS project-mainly devoted to the investigation of aerosol radiative properties and their direct climatic effects (see Carbone et al., 2010), and funded by the Italian Ministry of Education, University and Research (MIUR), aerosol samples were collected concurrently at three sites over the Po Valley: the urban background site in Milan (MI, 45°30'N, 9°12'E, 140 m above sea level), the rural background station of San Pietro Capofiume, near Bologna (SPC, 44°39'N, 11°37' E, 11 m a.s.l.), and the mountain site of Mt. Cimone (CMN, 44°11′N, 10°42′E, 2165 m a.s.l.). Aerosols were sampled for summer (winter) during night-time, from 20 (18) to 5 (7) UTC, and during daytime from 5 (7) to 20 (18) UTC. Two 4-day field campaigns were carried out from 14 to 17 July, 2007, and from 6 to 10 February, 2008, both under prevailing stable atmospheric conditions favourable to aerosol accumulation.

Five-stage Berner impactors (LPI 80/0.05) with 50% size cut at 0.05, 0.14, 0.42, 1.2, 3.5 and 10  $\mu$ m aerodynamic diameter (d<sub>ae</sub>), were employed for aerosol sampling and aerosol samples were analysed off-line for the characterization of the main organic and inorganic components.

Table 1 reports the observed chemical classes and the associated species used for subsequent model comparisons. Water-insoluble carbonaceous matter (WINCM) is considered to be representative of primary carbonaceous matter, while water-soluble organic matter (WSOM) is associated with secondary organic aerosol (SOA). Nevertheless, the separation of WINCM and WSOM into the two classes cannot be considered a strict and universal definition. The approximation is based on the evidence that WINCM is more influenced by direct local emissions, especially freshly generated particles from combustion sources (i.e. high volume of road traffic in cities), whereas WSOM is richer in background aerosol. In fact, since atmospheric processing induces an increase in the water

#### Table 1

Matching between observed and predicted species for MI, SPC and CMN in winter and summer.

Observations (Carbone et al., 2010)	CHIMERE
WINCM (water insoluble carbonaceous matter) = EC + WIOM	BCAR + OCAR
WSOM (water soluble organic matter) SO <sub>4</sub> <sup>2</sup> NH <sub>4</sub> <sup>4</sup> NO <sub>3</sub> <sup>-</sup> Seasalt	$\label{eq:AnA1D} \begin{array}{l} AnA1D + AnBmP + AnA0D + AnA2D; \\ AnBIP + BiA1D + BiBmP + BiA0D + BiA2D; \\ ISOPA1 + ISOPA2 \\ H_2SO_4 \\ NH_3 \\ HNO_3 \\ SALT \end{array}$
Unk	DUST + DUSTout + PPM

solubility of organic aerosol corresponding to secondary particle formation, WSOM may be considered a good proxy of SOA (Decesari et al., 2001).

Inorganic ions were determined by ion chromatography, and the "sea-salt" concentration included all the ions of marine origin, considering the mass ratio with Na<sup>+</sup> in standard seawater. Unaccounted (unk) was calculated as the difference between the weighed mass and the sum of concentrations of the analysed chemical compounds, which do not include insoluble and soluble crustal components. All samples were fielded blank corrected. Concentration values below the limit of detection (LOD) were represented as zero. The LODs were calculated as field blank averages, plus twice the standard deviation. Further details on the sampling set up and analytical methods adopted in the AEROCLOUDS experiments are reported in Carbone et al. (2010).

## 3. Model description

CHIMERE is a 3-dimensional chemical transport model (CTM) that simulates gas-phase chemistry, aerosol formation, transport and deposition on the European and urban scales, as reported in Bessagnet et al. (2004, 2008). In the present application, version 2008c of the model is run in nested configuration, with a coarse domain covering western Europe at 50 km horizontal resolution, and one nested domain covering northern Italy, with a 10 km grid size resolution. The vertical grid contains 8 layers from the surface up to 500 hPa, and the layer top altitude in meters of each is approximately 15, 50, 100, 250, 500, 1000, 2300 and 5000, respectively.

The CHIMERE model is driven by the meteorological model MM5 for dynamical parameters (wind, temperature, humidity, pressure, etc.), which is run at a horizontal resolution of 36 km over the coarse domain, and 12 km over the nested one (centred over the Po Valley), both with 29 vertical levels from surface to 10 hPa. The MRF scheme for boundary layer physics (Hong and Pan, 1996) was chosen. Global meteorological forcing is taken from six-hourly NCEP analyses in combination with the grid nudging option (FDDA). Over the coarse domain, anthropogenic emission data are taken from the EMEP database (Verstreng, 2003; http://www.ceip.at/), while over the nested one they are taken from a higher resolution inventory (5 km) developed by the Italian National Focal Point on Atmospheric Emissions (Deserti et al., 2008). Biogenic emissions are calculated with the MEGAN algorithm (Guenther et al., 2006), and dust emissions from local erosion are simulated according to Vautard et al. (2005). Sea salt emissions are those calculated by Monahan (1986), while gas and aerosol boundary conditions for the larger domain are given by 5-year climatology (2001-2005) of the global model LMDzT-INCA. For aerosol boundary conditions, only elemental and organic carbon, desert dust and sulphate are taken into account.

The particle size distribution ranges from 0.04 µm to 10 µm and is distributed into 8 log-spaced bins. As illustrated in Table 1, WINCM is associated to primary carbonaceous species, represented in CHIMERE as organic material (OCAR) and black carbon (BCAR). WSOM is associated with SOA (ISOPA1, ISOPA2, AnAOD, AnA1D, AnA2D, AnBmP, AnBIP, and BiAOD, BiA1D, BiA2D, BiBmP), produced by the oxidation of anthropogenic (benzene, toluene and other mono-substituted aromatics, xylene, tri-methyl-benzene and other poly-substituted aromatics, higher alkanes) and biogenic pollutants (isoprene,  $\alpha$ -pinene, sabinene,  $\beta$ -pinene,  $\delta^3$ -carene, limonene, ocimene, myrcene). In CHIMERE's aerosol module, SOA formation is represented according to a simplified approach described by Pun et al. (2006). The formation of the secondary organic fraction is represented according to the oxidation of semivolatile and volatile products that can be absorbed into aerosols. following the gas/particle equilibrium partitioning theory. In particular, the thermodynamic equilibrium of the inorganic mixture (i.e. sulphate, nitrate, and ammonium) is computed using the ISORROPIA model (Nenes et al., 1998) and the time rate of the processes of coagulation and condensation are dynamically calculated, based on the difference between actual and equilibrium Gibbs free energies (see CHIMERE user guide for full details). The model dynamically computes the gas/ particle conversion in time steps of about 5 min, adopting the approach described in Bowman et al. (1997). The absorption or desorption flux of each species is computed using formula (1):

$$J_i = \frac{1}{\tau_i} \left( G_i - G_i^{eq} \right) \tag{1}$$

where  $J_i$  [µg m<sup>-3</sup> s<sup>-1</sup>] is the absorption or desorption flux of species *i*,  $\tau_i$  [s] is a characteristic time of the mass transfer, which depends on particle size and the chemical properties of species *i*,  $G_i$  is the bulk gas-phase concentration of species *i*, and  $G_i^{eq}$  is the gas-phase concentration of species *i* at thermodynamic equilibrium (i.e., at the particle surface). The equilibrium gas-phase concentrations of the particle chemical composition, temperature and, for hydrophilic species, relative humidity, as described by Pun et al. (2006). A more detailed description of the SOA scheme deployed in CHIMERE is reported in Bessagnet et al. (2008).

In the coarse fraction, the unspeciated (unk) mass may be considered as mainly comprising insoluble crustal components, and has been associated to the sum of re-suspended local dust (DUST), dust from long-range transport (DUSTout), and primary insoluble inorganic particles (PPM) predicted by CHIMERE.

A spin-up run of 10 days was made to initialize the model. CHIMERE was then run from 14 July to 17 July, 2007, and from 6 February to 10 February, 2008. The simulations were performed in 1-day time slices, continuously restarting from the concentrations of the previous run.

## 4. Results

A large range of  $PM_{10}$  concentrations (8–22 µg m<sup>-3</sup> in summer and 4–39 µg m<sup>-3</sup> in winter) is observed across the three sampling sites. The range of  $PM_{10}$  levels calculated by CHIMERE (13–28 µg m<sup>-3</sup> in summer and 8–33 µg m<sup>-3</sup> in winter) are comparable to the observed ones (see Table 2). As expected, an increasing gradient in particulate matter concentration is observed passing from the mountain to the urban site. This trend is well reproduced by the model in both seasons.

Fig. 1 shows the daily evolution of observed and calculated  $PM_{10}$  concentrations. As reported in Section 2, two  $PM_{10}$  measurements a day were performed. Along the

# Table 2

Site	SUMMER				WINTER			
	РМ <sub>10</sub> [µg m <sup>-3</sup> ]				РМ <sub>10</sub> [µg m <sup>-3</sup> ]			h
	Obs (mean; std)	Mod (mean; std)	R <sup>a</sup>	NMB <sup>D</sup>	Obs (mean; std)	Mod (mean; std)	R <sup>a</sup>	NMB⁵
MI SPC CMN	22; 7 <b>20; 5</b> 8; 5	28; 6 <b>20; 4</b> 13; 3	0.40 <b>0.80</b> 0.22	+ 38% + <b>5%</b> > 100%	<b>39; 20</b> 31; 10 4; 1	<b>33</b> ; <b>18</b> 19; 18 8; 2	<b>0.79</b> 0.25 0.13	<b>15</b> % 30% 80%

Mean, standard deviation, Pearson correlation coefficient, and normalized mean bias of both observed and model-predicted PM<sub>10</sub> concentrations for the three sampling sites in northern Italy. The bold entries point out the best agreement between observations and predictions we achieved for our experiments.

<sup>a</sup> Pearson correlation coefficient.

<sup>b</sup> Normalized mean bias, expressed as percentage.

x-axis the decimal days denote night and daytime by 0 and .5, respectively. In general, infra-day variability dominates over inter-day variability, indicating that aerosol mass is primarily driven by local atmospheric circulation, rather than larger scale atmospheric forcing. As noted by Carbone et al. (2010), both daytime and seasonal growth of the planetary boundary layer result in a dilution effect at ground level, contributing to decreased concentrations at ground level during daytime and summer time. The model qualitatively captures these features, especially in summer at the rural site (SPC) and in winter at the urban site (MI).

Table 2 reports some statistical indices (mean, standard deviation, Pearson correlation coefficient and mean normalized bias) of the observation/prediction comparison. The observations indicate that CMN is the only sampling site where aerosol levels are higher in summer than in winter. These results are in agreement with those reported by Marinoni et al. (2008), who argued that CMN is in the free troposphere in winter and, at night-time, also in summer. In fact, during the warm season, more pronounced PBL daily evolution favours the transport of pollutants from the highly urbanized Po Valley towards the top of Mt. Cimone. In addition, the frequent episodes of Saharan dust transported in summer could also explain the high aerosol levels observed at CMN in summer rather than in winter.

The best model performance is found in summer at SPC, where the measurements and predictions are highly correlated (R = 0.8) and also essentially unbiased (NMB = +5%), and in winter at MI, where the Pearson correlation coefficient is equal to 0.79, and the mean normalized bias is -15%.



**Fig. 1.** Comparison of modelled  $PM_{10}$  daily evolution-mean (red dots) and standard deviation (transparent red)-with observations (black squares) at each sampling site (urban-MI, rural-SPC, mountain-CMN), for summer (upper panel, 14–18 July 2007) and winter (lower panel, 6–9 February 2008). Labels on the x-axis denote the day of month and period of the day. (For interpretation of the references to colours in this figure legend, the reader is referred to the web version of this article.)

Furthermore, for MI, the model compares reasonably well also in summer, even if  $PM_{10}$  levels are somewhat higher than observations (MNB = + 38%). At SPC in winter the aerosol mass concentrations are underestimated by 30%. As reported by Bessagnet et al. (2005), this discrepancy is strongly related to the meteorological output, emission inventory, and spatial resolution used. With respect to the mountain site, the model greatly overestimates the particulate matter levels compared with other sampling sites. In summer the mean normalized bias is above 100%, and in winter it reaches + 80%.

Furthermore, some of the observations may not necessarily be representative of the spatial scales that a regional model like CHIMERE is able to reproduce. The spatial representativeness of the three sampling sites can be categorized according to the criteria proposed by the European Environmental Agency (Larssen et al., 1991), which consider the distance of the station from large pollution sources, such as cities, power plants and major motorways, as well as traffic volume. The temporal representativeness is limited by the cost of observations (which involve expensive and time-consuming chemical analyses), which can be made only during intensive observational campaigns. It should be noted that severe pollution episodes are generally associated with high-pressure and stagnant conditions, which are very frequent during summer in the Po Valley. In addition, since CMN is located at 2165 m a.s.l., during winter-when the maximum of the PBL in the Po Valley does not exceed 800 m-and also at night-time during the summer the collected data are representative of free troposphere conditions (Marinoni et al., 2008).

Fig. 2 compares the campaign average concentrations normalized by the maximum of observations and models. The best model performance was for the predictions of WINCM and ammonium in both seasons. Their spatial variability, as well as the maximum observed for the urban and rural sites in winter, respectively, is correctly reproduced. Moreover, nitrates are reasonably well simulated, even if the summer trend differs slightly compared to that of Berner. In contrast, the largest observations/predictions discrepancy concerns the WSOM. In fact, the model does correctly reproduce either the seasonal levels of water-soluble organic matter, the highest concentrations being predicted for summer rather than winter, or the maximum WSOM concentrations during winter at rural and urban sites. Nevertheless, during the cold season, except for WSOM and sulphate, the spatial variation of the remaining species is consistent with the observed one.

In summary, the following statements can be made:

- WINCM levels, influenced by freshly generated particles from combustion sources (i.e. road traffic and domestic heating), decrease on passing from urban to rural and, then, towards the high mountain site, in both seasons. The model well reproduces this behaviour both in terms of spatial gradient and WINCM mass concentrations predicted for the three sampling sites.
- WSOM, which may be considered a good proxy of SOA (Decesari et al., 2001), decreases from the urban to the mountain site in summer, while during winter season the maximum is observed at the rural sampling site. In



Fig. 2. Spatial-temporal variability during summer and winter of aerosol composition. Bars denote the campaign average concentrations normalized by the maximum of observations (black) and model (red). From top to bottom: WINCM, WSOM, sulphate, ammonium and nitrate. (For interpretation of the reference to colour in this figure legend, the reader is referred to the web version of this article.)

continental regions like the Po Valley, the main component of submicrometre-size particles is usually organic matter, which in urban, rural and remote areas is often dominated by SOA. Recent studies (Lewis and Stiles, 2006; Szidat et al., 2004, 2006; Gelencsér et al., 2007) have pointed out that biogenic precursors dominate regional SOA formation, even if measurements of secondary organic aerosols, performed on the regional scale, found them to be strongly coupled with traces of anthropogenic emissions (Sullivan et al., 2006; Weber et al., 2007). Thus, the anthropogenic (mostly produced in urban areas) and biogenic (mostly produced in remote areas) fractions of SOA on local and regional scales, remain poorly constrained. Because of this, there is a need for the characterization of emissions, measurements and parameterization of the evolving volatility distribution (SOA yields) upon the oxidation, and inclusion of these processes into CTM. The experiment carried out here found that CHIMERE overestimates WSOM at MI and CMN, and predicts higher concentrations at CMN than at SPC. In winter, the model greatly underestimates WSOM concentrations by a factor of 5, most probably because of a potentially important source from wood burning, which is missing in our model (Decesari et al., 2001).

- Sulphate concentrations observed at SPC are higher than those measured at MI and CMN. This is attributable to

higher emissions in the eastern sector of the Po Valley (power plants and harbours) compared to the Milan conurbation. The model reproduces the bulk mass concentrations with a small bias, but it does not capture the enhanced concentrations observed at the rural station in both seasons.

- The largest concentrations of nitrate and ammonium were observed at the rural site, possibly because of its location downwind of urban areas and major highways, and combination with enhanced agriculture-related sources of ammonium. The high nocturnal relative humidity may also contribute to enhancing ammonium nitrate formation at SPC. The model captures the higher ammonium nitrate concentrations for the rural site in winter, as well as its spatial variability.

Figs. 3 and 4 compare simulations with the average size-segregated aerosol composition observed during the two campaigns. Modelled concentrations were interpolated over the five log-spaced dimensional classes of the Berner impactor to facilitate comparison, also because by comparing the 8 dimensional classes from CHIMERE with the instrument ones, the discrepancies found are very similar. Besides, the model's underestimation of temperature, here shown in Fig. 5 for MI, is comparable to the bias reported by Bessagnet et al. (2008).



**Fig. 3.** Average size-segregated chemical composition of measured and modelled PM<sub>10</sub> during the summer campaign. Top and bottom panels show daytime and night-time values, respectively. Chemical composition from Berner (left bin) to the CHIMERE model (right bin) is compared for each of the five dimensional classes. Boxes report the observed and modelled temperature at ground level in black and red, respectively. (For interpretation of the reference to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 4. Same as Fig. 3, but for the winter campaign.

The present comparison was undertaken, in view of the fact that temperature is one of most important variables for SOA formation (Bessagnet et al., 2008).

Although the aerosol bulk mass concentrations are reasonably well reproduced by CHIMERE across the stations considered, a more careful inspection reveals significant discrepancies between observed and predicted size-distributions. Compared to observations, the peaks of modelled size distributions are shifted towards the coarse mode in summer and towards the fine and ultrafine mode in winter. During summer, the model greatly overestimates the water soluble organic particles with dry diameter larger than 1.2 µm. In winter, the largest discrepancy concerns nitrates, which fall into the first two dimensional classes (dry diameter smaller than 1.2  $\mu$ m). WSOM in summer and nitrates in winter are the strongest contributors to the differences between measured and calculated size distributions. To better investigate these discrepancies, two sensitivity tests are presented in the next section.

## 4.1. Sensitivity analysis

This section focuses on the results of two sensitivity tests on the aerosol module of CHIMERE, the first by reducing the



Fig. 5. Comparison of observed (black) and modelled (red) hourly 2-m temperature in July 2007 (left) and February 2008 (right) at MI. (For interpretation of the reference to colour in this figure legend, the reader is referred to the web version of this article.)

SOA (25\_SOA run) formation rate in summer, the second by increasing the intra-sectional flux (ISFLX run) over all the dimensional classes. Only the results of the two mentioned tests are shown here, since they were found to generate the most important modifications in the simulation of SOA and size distribution.

Figs. 6 and 7 show the comparison of the results for the control run (CTRL) compared with a simulation performed by reducing the SOA absorption flux by 25% (25\_SOA) and ISFLX runs at MI sampling site in daytime in summer and winter, respectively. In particular, the right side of the figures show a species-by-species comparison between the CTRL run and the considered experiment. In addition, the legend of each subplot reports the total mass concentration  $[\mu g/m^3]$  of observed (black) and predicted (red) species (title denotes the species' name).

It is worth noting that, in the 25\_SOA experiment, the absorption process was modified by reducing the formation rate of secondary particles yielded by pathways among semi-volatile organic compounds (SVOC). Interestingly, the 25\_SOA simulation shows lower concentrations of WSOM, with a decrease of 75% against the CTRL run, even though the formation rate decreased by 25%. The 25\_SOA run partially corrects the model's shift toward coarser particles and alleviates the model bias, indicating that details of the calculation of SOA production rates require further investigations. This new setting does not induce marked differences compared to the CTRL run for winter simulations.

Table 3 reports the comparison for the three sampling sites in summer-daytime, for both the CTRL and 25\_SOA runs with the observations of  $PM_{10}$  concentrations. In addition, the Table 3 reports the Pearson correlation and the mean normalized error calculated for WSOM size distributions and bulk mass concentration, respectively.

The results (see Fig. 6) indicate that the 25\_SOA simulations seem to be more suitable than the CTRL for representing secondary organic aerosols. Also secondary inorganic aerosols (SIA) show some variations for the 25\_SOA simulation compared to the CTRL. As stated above, in the 25\_SOA experiment, the SOA formation rate was reduced by 25%. The tuning affects the absorption process, which involves both inorganic and organic species. Indeed, both inorganic and organic species make up the aerosol substrate upon which further material is accumulated. Thus a change in the inorganic mass will indirectly influence the organic mass, and vice-versa. In the literature, it is not perfectly clear how the interaction of inorganic and organic should be treated, so this point is left open for further analysis. However, it should be noted that the effect of interaction, as simulated here, is small.

In another test, the intra-sectional fluxes were increased from smaller to larger dimensional classes (ISFLX) by multiplying by a factor of 5 the transition rate of particles throughout the size distribution. In particular, the transition rate was calculated as "gain" in each dimensional bin expressed in kg m<sup>-3</sup> s<sup>-1</sup>. As mentioned earlier, the flux was calculated dynamically as a characteristic time of adjustment



Fig. 6. Comparison between control run (CTRL—upper part of figure) and the simulation performed using a reduced rate of both anthropogenic and biogenic SOAs (25\_SOA—lower part of figure) for MI urban site, in summer daytime.



Fig. 7. Comparison between control run (CTRL–upper part) and the simulation performed using an increased factor of intra-sectional fluxes of all particles throughout the size distribution (ISFLX–lower part of figure) for the MI urban site, during winter daytime.

toward thermodynamic equilibrium, expressed in terms of the difference between the actual and the equilibrium Gibbs energy. Further details are given in the CHIMERE user guide. Fig. 7 shows the comparison of CTRL and ISFLX simulations during winter 2008 at MI.

Although the simulated size distribution for the ISFLX experiment is generally more similar to observations than the CTRL run, nitrate overestimation is still present in the model. For the ISFLX experiment, this overestimation mostly concerns the third dimensional class, rather than the first two (CTRL). The Person correlation of the nitrate size distribution for the ISFLX simulations goes up to +0.85, against +0.50 for the base case. The bulk mass concentration does not vary

### Table 3

Comparison of  $\rm PM_{10}$  levels among observations, CTRL and 25\_SOA runs for the three sampling sites during summer time. In addition, Pearson correlation ( $\rm R^a)$  computed for the size distribution of WSOM and the mean normalized bias (MNB) of its bulk mass concentration. The bold entries emphasizes the improvements achieved by tuning the SOA rate formation.

	РМ <sub>10</sub> [µg m <sup>-3</sup> ]			R <sup>a</sup> (size distribution of WSOM)		MNB (bulk mass concentration of WSOM)	
Site	Obs	CTRL	25_SOA	CTRL	25_SOA	CTRL	25_SOA
MI SPC CMN	17 15 10	26 18 12	18 15 12	$-0.30 \\ -0.20 \\ +0.10$	+ 0.70 + 0.65 + 0.90	>200% >100% 200%	0% - 50% + 5%

against the base case (OBS: 28  $\mu$  g m<sup>-3</sup>, CTRL: 28  $\mu$  g m<sup>-3</sup>, ISFLX: 27  $\mu$  g m<sup>-3</sup>).

In addition, Table 4 reports the percentage values of each aerosol compound observed and predicted both for control runs and the two experiments performed. As expected, the greater variation concerns the WSOM mass concentration, which decreases by a factor of 3, thus approaching observed levels. As mentioned above, the reduction of SOA formation yields a slight variation also in other species. On the other hand, no significant variations of percentage mass concentrations emerge from the ISFLX run, since it prevalently affects the PM<sub>10</sub> size distribution, rather than the total mass of each compound.

#### Table 4

Percentage mass concentrations of each aerosol compound from observations, the control run and two sensitivity tests-25\_SOA for summer and ISFLX for winter-for the urban (MI) sampling site. The bold entries emphasizes the improvements achieved by tuning the SOA rate formation.

MI	Summe	r	Winter	
Daytime	Obs	CTRL-25_SOA	Obs	CTRL-ISFLX
WINCM WSOM $SO_4^{2-}$ $NH_4^+$ $NO_3^-$ See selt	24% <b>14%</b> 12% 5% 6%	11%-16% <b>37%-13%</b> 16%-23% 7%-11% 7%-6% 2% 2%	23% 11% 4% 7% 20%	16%-17% 4%-3% 5%-5% 16%-15% 50%-50%
Unk	35%	20%-30%	32%	2%-2% 8%-8%

## 5. Conclusions

Observations of size-segregated aerosol speciation in two 4-day intensive field campaigns, at three sampling sites (MI-urban, SPC-rural, and CMN-mountain) in northern Italy are compared to the outputs of the 3-D regional chemistrytransport model (CTM) CHIMERE.

The model well reproduces the daily evolution of the bulk aerosol mass, as well as the spatial gradient of the main chemical components, from urban to remote sites. However, it does not reproduce the aerosol size distributions. The largest discrepancies are found for the secondary organic components during summer and for nitrate during winter. The gas/particle conversion process is one factor that strongly affects the SOA and SIA predictions, and consequently the PM<sub>10</sub> concentrations.

Sensitivity tests indicate that a better agreement with observations can be achieved by tuning the absorption processes computed in CHIMERE. In summer, the formation rate of secondary organic compounds (25\_SOA) was reduced, while in winter larger (by a factor 5) intersectional mass fluxes (ISFLX) were set.

By decreasing the SOA formation rate in summer, a reduction of WSOM concentrations by 80% against the reference (CTRL) run was observed, even though the formation rate was reduced by 25%. Decreasing the WSOM amount, the bulk aerosol mass concentration agrees with observations (OBS : 17  $\mu$  g m  $^{-3}$  , CTRL : 27  $\mu$  g m  $^{-3}$  , 25\_SOA : 18  $\mu$  g m  $^{-3}$  ). For example, at the urban sampling site, the Pearson correlation coefficient for SOA size distribution goes up to +0.70 from -0.30, since the model's large positive bias in the coarse mode disappears in the 25\_SOA run. This results in a significant reduction in the mean normalized bias (MNB) of WSOM mass concentrations, which tend to become even though zero compared with >200% for the base case. In this case, even SIA shows some variation, since the nitrate bulk mass concentration compares better than in the CTRL run. The bias associated with  $NO_3^-$  becomes + 15% against the initial + 95%.

By increasing the intra-sectional fluxes, the comparisons made for the urban site during winter show that the  $PM_{10}$  bulk mass concentration does not vary, as well as the nitrates concentration, thus  $HNO_3$  overestimation remains. Despite this discrepancy, the Pearson correlation coefficient calculated over nitrate size distribution goes up to +0.85 against +0.50 from the CTRL. It also results in a better agreement with the  $PM_{10}$  size distribution.

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### References

- Bessagnet, B., Hodzic, A., Vautard, R., Beekmann, M., Rouil, L., Rosset, R., 2004. Aerosol modelling with CHIMERE–first evaluation at continental scale. Atmos. Environ. 38, 2803–2817.
- Bessagnet, B., Hodzic, A., Blanchard, O., Lattuati, M., Le Bihan, O., Marfaing, H., Rouil, L., 2005. Origin of particulate matter pollution episodes in wintertime over the Paris Basin. Atmos. Environ. 39 (33), 6159–6174.
- Bessagnet, B., Menut, L., Curci, G., Hodzic, A., Guillaume, B., Liousse, C., Moukhtar, S., Pun, B., Seigneur, C., Schulz, M., 2008. Regional modeling of carbonaceous aerosols over Europe and focus on secondary organic aerosols. J. Atmos. Chem. 61 (3), 175–202. http://dx.doi.org/10.1007/ s10874-009-9129-2.
- Bessagnet, B., Seigneur, C., Menut, L., 2010. Impact of dry deposition of semi volatile organic compounds on secondary organic aerosols. Atmos. Environ. 344, 1781–1787.
- Bey, I., Jacob, D.J., Yantosca, R.M., Logan, J.A., Field, B.D., Fiore, A.M., Li, Q., Liu, H.Y., Mickley, L.J., Schultz, M.G., 2001. Global modeling of tropospheric chemistry with assimilated meteorology: model description and evaluation. J. Geophys. Res. 106, 23,073–23,089.
- Bowman, F.M., Odum, J.R., Seinfeld, J.H., Pandis, S.N., 1997. Mathematical model for gas-particle partitioning of secondary organic aerosols. Atmos. Environ. 31, 3921–3931.
- Carbone, C., Decesari, S., Mircea, M., Giulianelli, L., Finessi, E., Rinaldi, M., Fuzzi, S., Marinoni, A., Duchi, R., Perrino, C., Sargolini, T., Vardè, M., Sprovieri, F., Gobbi, G.P., Angelini, F., Facchini, M.C., 2010. Size-resolved aerosol chemical composition over the Italian Peninsula during typical summer and winter conditions. Atmos. Environ. 44 (39), 5269–5278.
- Carmichael, G.R., Peters, L.K., Saylo, R.D., 1991. The STEM-II regional scale acid deposition and photochemical oxidant model-I. An overview of model development and applications. Atmos. Environ. 25 (10), 2077–2090. http://dx.doi.org/10.1016/0960-1686(91)90085-L.
- De Meij, A., Krol, M., Dentener, F., Vignati, E., Cuvelier, C., Thunis, P., 2006. The sensitivity of aerosol in Europe to two different emission inventories and temporal distribution of emissions. Atmos. Chem. Phys. 6, 4287–4309.
- De Meij, A., Wagner, S., Gobron, N., Thunis, P., Cuvelier, C., Dentener, F., 2007. Model evaluation and scale issues in chemical and optical aerosol properties over the greater Milan area (Italy), for June 2001. Atmos. Res. 85, 243–267.
- De Meij, A., Thunis, P., Bessagnet, B., Cuvelier, C., 2009a. The sensitivity of the CHIMERE model to emissions reduction scenarios on air quality in Northern Italy. Atmos. Environ. 43, 1897–1907.
- De Meij, A., Gzella, A., Cuvelier, C., Thunis, P., Bessagnet, B., Vinuesa, J.F., Menut, L., Kelder, H.M., 2009b. The impact of MM5 and WRF meteorology over complex terrain on CHIMERE model calculations. Atmos. Chem. Phys. 9, 6611–6632.
- Decesari, S., et al., 2001. Chemical features and seasonal trend of water soluble organic compounds in the Po valley fine aerosol. Atmos. Environ. 35, 3691–3699.
- Deserti, M., et al., 2008. Rapporto tecnico sulla applicazione di modellistica al Bacino Padano Adriatico. Agenzia per la Protezione dell'Ambiente e per i servizi Tecnici (APAT) e Centro Tematico Nazionale-Atmosfera Clima ed Emissioni in Aria (CTN-ACE) (Available at: http://www.arpa.emr.it/ dettaglio\_documento.asp?id=1533&idlivello=64).
- Di Nicolantonio, W., Cacciari, A., Tomasi, C., 2009. Particulate matter at surface: Northern Italy monitoring based on satellite remote sensing, meteorological fields, and in-situ samplings. IEEE J. Sel. Top. Appl. Earth Obs. Remote Sens. 2 (4) (December).
- Finardi, S., Pellegrini, U., 2004. Systematic analysis of meteorological conditions causing severe urban air pollution episodes in the central Po Valley. 9th International Conference on Harmonisation Within Atmospheric Dispersion Modelling for Regulatory Purposes. Forschungszentrum Karlsruhe, Garmisch-Partenkirchen, Germany, pp. 250–254.
- Fountoukis, C., et al., 2011. Evaluation of a three-dimensional chemical transport model (PMCAMx) in the European domain during the EUCAARI May 2008 campaign. Atmos. Chem. Phys. 11, 10331–10347. http://dx.doi.org/10.5194/acp-11-10331-2011.
- Gelencsér, András, et al., 2007. Source apportionment of PM2. 5 organic aerosol over Europe: primary/secondary, natural/anthropogenic, and fossil/biogenic origin. J. Geophys. Res. 112 (D23), D23S04.
- Grell, G.A., et al., 2005. Fully coupled "online" chemistry within the WRF model. Atmos. Environ. 39, 6957–6975. http://dx.doi.org/10.1016/j.atmosenv. 2005.04.027.
- Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P.I., Geron, C., 2006. Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). Atmos. Chem. Phys. 6, 3181–3210.
- Hanke, M., Umann, B., Uecker, J., Arnold, F., Bunz, H., 2003. Atmospheric measurements of gas-phase HNO3 and SO2 using chemical ionization mass spectrometry during the MINATROC field campaign 2000 on

Amann, M., Bertok, I., Cabala, R., Gyarfas, F., Heyes, C., Klimont, Z., Schopp, W., Wagner, F., 2005. A further emission control scenario for the Clean Air for Europe (CAFE) Program, IIASA. CAFE Scenario Analysis Report no. 7.

Monte Cimone. Atmos. Chem. Phys. 3, 417–436. http://dx.doi.org/10. 5194/acp-3-417-2003.

- Hong, S.-Y., Pan, H.L., 1996. Non-local boundary layer vertical diffusion in a medium-range forecast model. Mon. Weather Rev. 124, 2322–2339.
- IPCC (Ed.), 2007. Climate change: The Scientific Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change (http://www.ipcc.ch/).
- Kim, Y., Sartelet, K., Seigneur, C., 2011. Formation of secondary aerosols over Europe: comparison of two gas-phase chemical mechanisms. Atmos. Chem. Phys. 11 (2), 583–598.
- Larssen, S., Sluyter, R., Helmis, C., 1991. Criteria for EUROAIRNET, the EEA air quality monitoring and information network. http://reports.eea.eu.int. TEC12/en.
- Lewis, Charles W., Stiles, David C., 2006. Radiocarbon content of PM2.5 ambient aerosol in Tampa, FL. Aerosol Sci. Technol. 40 (3), 189–196.
- Marinoni, A., Cristofanelli, P., Calzolari, F., Roccato, F., Bonafè, U., Bonasoni, P., 2008. Continuous measurements of aerosol physical parameters at the Mt. Cimone GAW station (2165 m asl, Italy). Sci. Total Environ 391 (2), 241–251.
- Mathur, R., Yu, S., Kang, D., Schere, K.L., 2008. Assessment of the wintertime performance of developmental particulate matter forecast with the Eta-Community Multiscale Air Quality modeling system. J. Geophys. Res. 113, D02303. http://dx.doi.org/10.1029/2007JD008580.
- Minguzzi, E., Bedogni, M., Carnevale, C., Pirovano, G., 2005. Sensitivity of CTM simulations to meteorological inputs. Int. J. Environ. Pollut. 24 (1/2/3/4).
- Monahan, E.C., 1986. The ocean as a source of atmospheric particles. The Role of Air-Sea Exchange in Geochemical Cycling. Kluwer Academic Publishers, Dordrecht, Holland, pp. 129–163.
- Myhre, G., et al., 2009. Modelling of chemical and physical aerosol properties during the ADRIEX aerosol campaign. Q. J. R. Meteorol. Soc. 135, 53–66.
- Nenes, A., Pilinis, C., Pandis, S., 1998. ISORROPIA: a new thermodynamic model for inorganic multicomponent atmospheric aerosols. Aquat. Geochem. 4, 123-152.
- Pun, B.K., Seigneur, C., Lohman, K., 2006. Modeling secondary organic aerosol formation via multiphase partitioning with molecular data. Environ. Sci. Technol. 40, 4722–4731.
- Putaud, J.P., Raes, F., van Dingenen, R., Brüggemann, E., Facchini, M.C., Decesari, S., Fuzzi, S., Gehrig, R., Hüglin, C., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N., Müller, K., Querol, X., Rodriguez, S., Schneider, J., Spindler, G., ten Brink, H., Torsenth, K., Wiedensohler, A., 2004. A European aerosol phenomenology-2: chemical characteristics of partic-

ulate matter at kerbside, urban, rural and background sites in Europe. Atmos. Environ. 38, 2579–2595.

- Putaud, J.P., van Dingenen, R., Alastuey, A., Bauer, H., Birmili, W., Cyrys, J., Flentje, H., Fuzzi, S., Gehrig, R., Hansson, H., Harrison, R., Herrmann, H., Hitzenberger, R., Hüglin, C., Jones, A., Kasper-Giebl, A., Kiss, G., Kousa, A., Kuhlbusch, T., Löschau, G., Maenhaut, W., Molnar, A., Moreno, T., Pekkanen, J., Perrino, C., Pitz, M., Puxbaum, H., Querol, X., Rodriguez, S., Salma, I., Schwarz, J., Smolik, J., Schneider, J., Spindler, G., ten Brink, H., Tursic, J., Viana, M., Wiedensohler, A., Raes, F., 2010. A European aerosol phenomenology e 3: physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside sites across Europe. Atmos. Environ. 44, 1308–1320. http://dx.doi.org/10.1016/j.atmosenv. 2009.12.011.
- Rodriguez, S., et al., 2007. A study on the relationship between mass concentrations, chemistry and number size distribution of urban fine aerosols in Milan, Barcelona and London. Atmos. Chem. Phys. 7, 2217–2232.
- Simpson, D., Yttri, K.E., Klimont, Z., Kupiainen, K., Caseiro, A., Gelencser, A., Pio, C., Puxbaum, H., Legrand, M., 2007. Modeling carbonaceous aerosol over Europe: analysis of the CARBOSOL and EMEP EC/OC campaigns. J. Geophys. Res. 112. http://dx.doi.org/10.1029/2006JD008158.
- Stern, et al., 2008. A model inter-comparison study focusing on episodes with elevated PM<sub>10</sub> concentrations. Atmos. Environ. 42, 4567–4588.
- Stier, P., et al., 2005. The aerosol–climate model ECHAM5-HAM. Atmos. Chem. Phys. 5, 1125–1156.
- Sullivan, A.P., et al., 2006. Airborne measurements of carbonaceous aerosol soluble in water over northeastern United States: method development and an investigation into water-soluble organic carbon sources. J. Geophys. Res. 111 (D23), D23S46.
- Szidat, Soenke, et al., 2004. Radiocarbon <sup>14</sup>C-deduced biogenic and anthropogenic contributions to organic carbon (OC) of urban aerosols from Zürich, Switzerland. Atmos. Environ. 38 (24), 4035–4044.
- Szidat, Sönke, et al., 2006. Contributions of fossil fuel, biomass-burning, and biogenic emissions to carbonaceous aerosols in Zurich as traced by <sup>14</sup>C. J. Geophys. Res. 111 (D7), D07206.
- Vautard, R., Bessagnet, B., Chin, M., Menut, L., 2005. On the contribution of natural aeolian sources to particulate matter concentrations in Europe: testing hypotheses with a modelling approach. Atmos. Environ. 39 (18), 3291–3303.
- Weber, Rodney J., et al., 2007. A study of secondary organic aerosol formation in the anthropogenic-influenced southeastern United States. J. Geophys. Res. 112 (D13), D13302.