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# Regional atmospheric composition modeling with CHIMERE

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## Abstract

Tropospheric trace gas and aerosol pollutants have adverse effects on health, environment and climate. In order to quantify and mitigate such effects, a wide range of processes leading to the formation and transport of pollutants must be considered, under-

- stood and represented in numerical models. Regional scale pollution episodes result from the combination of several factors: high emissions (from anthropogenic or natural sources), stagnant meteorological conditions, velocity and efficiency of the chemistry and the deposition. All these processes are highly variable in time and space, and their relative importance to the pollutants budgets can be quantified within a chemistry-
- <sup>10</sup> transport models (CTM). The offline CTM CHIMERE model uses meteorological model fields and emissions fluxes and calculates deterministically their behavior in the troposphere. The calculated three-dimensional fields of chemical concentrations can be compared to measurements to analyze past periods or used to make air quality forecasts and CHIMERE has enabled a fine understanding of pollutants transport during
- <sup>15</sup> numerous measurements campaigns. It is a part of the PREVAIR french national forecast platform, delivering pollutant concentrations up to three days in advance. The model also allows scenario studies and long term simulations for pollution trends. The modelling of photochemical air pollution has reached a good level of maturity, and the latest projects involving CHIMERE now aim at increasing our understanding of pollution
- impact on health at the urban scale or at the other end of the spectrum for long term air quality and climate change interlinkage studies, quantifying the emissions and transport of pollen, but also, at a larger scale, analyzing the transport of pollutants plumes emitted by volcanic eruptions and forest fires.

## 1 Introduction

<sup>25</sup> The rapid growth of urban areas and increased industrialization have created the need for air quality assessment and motivated the first regional-scale studies on





anthropogenic pollution in the early 1990s (Fenger, 2009, among others). The first systematic measurements have been implemented by the air quality agencies in the source regions, which often coincided with the most densely populated areas. One of the first targeted pollutants was the sulfur dioxide due to its effects on acid rain and

- <sup>5</sup> forest ecosystems. As a result of imposed emission reductions in the industrial activity sector, concentrations of sulfur dioxid were greatly reduced in the 1990s. The focus was then shifted to other gaseous pollutants such as ozone and nitrogen oxides that were shown to have adverse health effects on populations. More recently, particles have become a priority. In parallel, and although it has always existed, research on biogenic pollution has long been more modest in contrast to anthropogenic sources. Having no
- <sup>10</sup> pollution has long been more modest in contrast to anthropogenic sources. Having no possible action on biogenic pollutants, the research community, has perceived these sources, perhaps inaccurately, as less intense or less important to study.

Even if air pollution was viewed as a "local" and mostly "urban" problem, it has been shown that ozone and its precursors may be transported on long distances. There-

- fore, to study local pollution and represent effects of anthropogenic and biogenic emissions, chemistry and transport on the local pollution budget, models need to integrate processes over large spatial scales. While early models were based on statistical assumptions and could not account for sporadic changes in the atmospheric forcing, the past two decades have seen the development of deterministic and Eulerian models.
- Some of these models are very complex and dedicated to field or idealized studies of a few days, over specific regions. Others are dedicated to long-range transport only. In addition, some models allow fast simulations and are thus suitable for daily forecast calculations.

The CHIMERE model has been in development for more than fifteen years and is intended to be a modular framework available for the community use. It includes the necessary state-of-the-art parametrizations for simulating reasonable pollutant concentrations, but remains also computationally efficient for forecast applications. CHIMERE is also frequently used for local field experiment analysis studies, or for long-range transport and trends quantification studies over continental scales. Designed for both





the research community and operational agencies, the CHIMERE model needs to be computationally stable and provide robust results. It means that the model needs to be able to estimate pollution peaks at the right time and the right place, but also to be able to diagnose low pollution conditions and avoid false alerts. As a research tool, the

<sup>5</sup> model needs to be modular enough to allow adding new processes or testing specific physico-chemical interactions. In the present paper we describe the parameterizations included in the CHIMERE model, and the results of recent studies.

An overview of the CHIMERE model structure is given in Sect. 2. The domains definition and the boundary conditions are described in Sect. 3. The meteorological forcings

- and their preprocessing are described in Sect. 4 and the implementation of transport and mixing is described in Sect. 5. The emissions taken into account in the model (anthropogenic, biogenic, mineral dust, fires and the local resuspension of particulate matter) are described in Sect. 6. The chemical schemes preparation, the gaseous and aerosol chemistries are described in Sect. 7. The dry and wet deposition processes
- are described in Sect. 8 and the cloud impacts in Sect. 9. The CHIMERE model results evaluations are described in Sect. 10, the hybridation between model and observations (for sensitivity, inverse modeling and data assimilation) in Sect. 11. The experimental and operational forecasts operated with CHIMERE are described in Sect. 12. Finally, a summary and new research directions are presented in Sect. 13.

#### 20 2 CHIMERE model overview

### 2.1 Main characteristics

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CHIMERE is an Eulerian off-line chemistry-transport model (CTM). External forcings are needed to run a simulation: meteorological fields, primary pollutant emissions, chemical boundary conditions. Using these input data, CHIMERE calculates and provides the atmospheric concentrations of tens of gas-phase and aerosol species over

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local to continental domains (from 1 km to 1 degree resolution) at an hourly time step.

The key processes affecting the chemical concentrations are represented in CHIMERE: emissions, transport (advection and mixing), chemistry and deposition, as presented in Fig. 1. Note that forcings have to be known on the same grid and time step than the CTM simulation. In this sense, CHIMERE is not only a chemical model but a suite of numerous pre-processing programs able to prepare simulations. The model is now used for pollution event analysis, scenarios, operationnal forecast and more recently for impact studies of pollution over health (Valari and Menut, 2010) and vegetation (Anav et al., 2011).

The first model version (1997) was a box model covering the Paris area including only gas-phase chemistry (Honoré and Vautard, 2000; Menut et al., 2000a; Vautard et al., 2001). In 1998, the model is implemented for its first forecast version (Pollux) during the ESQUIF experiment (Menut et al., 2000b) still over the Paris area (Vautard et al., 2000). In the same time, the adjoint model is developed to estimate the sensitivity of concentrations to all parameters (Menut et al., 2000a). In 2001, the geographical domain is extended over Europe with a cartesian mesh (Schmidt et al., 2001) and the new experimental forecast platform (PIONEER) is set up in 2003, the experimental

- new experimental forecast platform (PIONEER) is set up. In 2003, the experimental forecast became operational with the PREVAIR system operated at INERIS (Honoré et al., 2008; Rouïl et al., 2009). The aerosol module is implemented in 2004 (Bessagnet et al., 2004) with further improvements concerning the dust natural emissions and
- resuspension over Europe (Vautard et al., 2005; Hodzic et al., 2006a; Bessagnet et al., 2008) and evaluated against long-term and field measurements (Hodzic et al., 2005, 2006b). The development of the mineral dust version started in 2005 (Menut et al., 2005b). Chemistry was not included in that version and a new horizontal domain had been designed to cover the whole northen Atlantic and Europe, including the Saharan
- desert and downwind regions. In 2006, an important step is achieved with the development of the parallel version of the model an its first implementation on a massively parallel computer (the ECMWF computer in the framework of the FP6/GEMS project).

The CHIMERE model is now considered as a state-of-the-art model. It has been involved in numerous intercomparison studies mainly focusing on ozone and  $\text{PM}_{10}$ 





from the urban scale (Vautard et al., 2007; Van Loon et al., 2007; Schaap et al., 2007) to continental scale (Solazzo et al., 2012b; Zyryanov et al., 2012). Moreover, the model has been mainly applied over Europe, but also more recently over Africa and North Atlantic for dust simulations, over Central America during the MILAGRO project to study organic aerosols (Hodzic et al., 2009, 2010a,b) and over the US within the AQMEII project.

Finally, the development of CHIMERE follows three main rules. First, concentrations of main pollutants are calculated with the best possible accuracy using well evaluated and state-of-the-art parameterizations. Second, a modular framework is maintained to allow updates to the code by developers but also all interested users. Third, The code is kept computationally efficient to allow long-term simulations, climatological studies and operational forecast. One goal of this paper is to finely described all the numerical and scientific choices and to explain the main reasons of these choices. In addition, ongoing and planned developments and application studies are presented.

#### 15 2.2 The CHIMERE software

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In order to have the most simple as possible code distribution, CHIMERE is under a GPL licence. The source code and the associated documentation is available on a web site www.Imd.polytechnique.fr/chimere. The documentation is both technic and scientific. It includes a chapter dedicated to the set-up of a test case simulation that allows new users to easily carry out a CHIMERE simulation: model configuration and data (meteorology and emissions) files are provided to simulate the 2003 heat wave in western Europe.

CHIMERE is a National Tool of the French "Institut des Sciences de l'Univers", meaning that support has to be provided to the model's users. Two mailing lists exist for this <sup>25</sup> support: chimere@Imd.polytechnique.fr to send questions to the model developers and chimere-users@Imd.polytechnique.fr to initiate discussions, exchange programs or data between users. In addition, two-days training courses are organised twice a year. Each training course is completely free of charge for participants and offers





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For graphical postprocessing, simple interfaces are available using either the GMT 5 or the GrADS 6 free software. Also an additional graphical user interface (GUI) software CHIMPLOT is provided. It allows making various 1-D or 2-D plots (e.g. longitude-latitude or time-altitude maps, vertical slices, time series, vertical profiles  $\dots$ ). One can also overlay multiple fields (e.g. O<sub>3</sub> concentrations, wind vectors, and

each one being processed by a worker process. Each worker performs the model integration in its geographical sub-domain as well as boundary condition exhanges with its neighbours. The master process performs initializations and file input/output. To configure the parallel sub-domains, the user has to specify two parameters in the model 20 parameter file: the number of sub-domains for the zonal and meridional directions. The

total number of CPU used is therefore the product of these two numbers, plus one CPU

- (recommended) and LAM/MPI, but should work, with minor changes in the scripts, with MPICH or other MPI compatible parallel environments. The model parallelism results 15 from Cartesian division of the main geographical domain into several sub-domains,
- ory scheme, and an MPI message passing library. It has been tested with Open MPI
- Makefiles for the libraries already installed. The model computation time for one AMDx64 node of 16 CPUs is 1 h 30 min for 10 1 month of simulation for the Paris area, at 15 km resolution, the domain size being 45 × 48 × 8 with a time step of 360 s on average. CHIMERE uses the distributed mem-
- The code is completely written in Fortran90, and running scripts are written in shell (using gnu-awk for input datafiles processing). Software required is a Fortran 95 compiler (g95 and gfortran are both free and efficient, but Makefiles with ifort compiler 5 options are also provided). The required libraries are NetCDF (either 3.6.x or 4.x.x), MPI (see below), and GRIB API (associated to the use of the ECMWF meteorological datasets). The model includes tools that can help the user to configure the model's

a complete training to be able to install the code, launch a simulation and change sur-

face emissions or other parameters in the code.

for the master process.

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pressure contours) and perform simple operations such as calculating daily maxima, daily means, vertical or horizontal averaging or integrations.

# 2.3 The CHIMERE code organization

After the pre-processing step where forcings are prepared, the CHIMERE model is
splitted into two main parts: an initialization phase and the model integration phase (Fig. 2). The *initialization phase* is dedicated to the reading of all input parameters as well as the preparation of the initial meteorological and chemical field. The *model integration* phase is splitted into three stages: (i) A *hourly time-step* that corresponds to the provision of forcings, i.e. meteorological fields, emission fluxes and chemical boundary conditions. (ii) A *user's defined coarse time step "nphour"*, corresponding to the time interpolation of "physical" parameters, such as wind, temperature, reactions rates etc. In parallel, to optimize the time simulation and prevent issues associated to the violation of the CFL criteria, a "physical" time step is dynamically estimated in the meteorological pre-processor taking into account horizontal and vertical winds and deep convective updraft. During the run, if the user time step is too low, the model

- time integration is increased to reach the recommended value. If the user's defined time-step is lower that the recommended one, the user's choice is applied (even if this is not the optimal choice) but can be changed to the recommended one. (iii) A *user's defined "fine" time step "ichemstep"*: this corresponds to the integration of the chemical
- <sup>20</sup> mechanism, including concentration's increments due to all processes. This is achieved by the two-step scheme. Due to the stiffness of the chemical system to solve, this time step must be at least 30 s (or less if possible). In practice, for large domains, such as the Western Europe, a "very quick formulation", with a 10-min physical step, no sub-chemical steps, i.e. all processes are stepped to 10 min, is realistic. It is possible
- to select one or two Gauss-Seidel iterations, but the use of two iterations is strongly recommended even if it increases by two the computer time.

The numerical integration of all processes follows a production-loss budget approach as presented in Fig. 4. This means that all production and loss terms, for each chemical





species are calculated simultaneously to avoid error propagation generally created with operator-splitting techniques (the concentration evolution being dependent on the several terms order, McRae et al., 1982). Further advantages of the scheme are (1) its stability even for quite long time steps due to the implicitness of the formulation and (2) the simplicity of the code which facilitates the development of secondary models (adjoint, tangent linear).

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The numerical method used to estimate the temporal solution of the stiff system of partial differential equations is adapted from the second-order TWOSTEP algorithm originally proposed by Verwer (1994) for gas phase chemistry only. It is based on the application of a Gauss-Seidel iteration scheme to the 2-step implicit backward differentiation (BDF2) formula:

$$c^{n+1} = \frac{4}{3}c^n - \frac{1}{3}c^{n-1} + \frac{2}{3}\Delta t R(c^{n+1})$$
(1)

with  $c^n$  being the vector of chemical concentrations at time  $t_n$ ,  $\Delta t$  the time step leading from time  $t_n$  to  $t_{n+1}$  and  $R(c) = \dot{c} = P(c) - L(c)c$  the temporal evolution of the concentrations due to chemical production and emissions (*P*) and chemical loss and deposition (*L*). Note that *L* is a diagonal matrix here. After rearranging and introducing the production and loss terms this equation reads

$$\boldsymbol{c}^{n+1} = \left(I + \frac{2}{3}\Delta t L(\boldsymbol{c}^{n+1})\right)^{-1} \times \left(\frac{4}{3}\boldsymbol{c}^n - \frac{1}{3}\boldsymbol{c}^{n-1} + \frac{2}{3}\Delta t P(\boldsymbol{c}^{n+1})\right)$$
(2)

The implicit nonlinear system obtained can be solved pertinently with a Gauss-Seidel <sup>20</sup> method (Verwer, 1994).

In CHIMERE the production and loss terms *P* and *L* in Eq. (2) are replaced by the modified terms  $\tilde{P} = P + P_h + P_v$  and  $\tilde{L} = L + L_h + L_v$ , respectively.  $P_h$  and  $P_v$  denote the temporal evolution of the concentrations due to horizontal (only advection) and vertical (advection and diffusion) inflow into a given grid box,  $L_h$  and  $L_v$  gives the temporal evolution due to the respective outflow divided by the concentration itself.





## 3 Domains and boundary conditions

## 3.1 Domains geometry

Model domains are entirely defined by their grid cell centres description. The user has a complete control of the horizontal model grid by writing a simple longitude/latitude

ASCII file, in decimal degrees. The input meteorological fields are automatically interpolated on the CHIMERE grid. Each pair of coordinates stands for a grid cell centre, described (from the top to the bottom of the file) from West to East then from South to North.

In the definition of a new CHIMERE domain, the user must check carefully whether
 the domain is quasi-rectangular. Most projections work, including a regular grid in geographic coordinates (longitude-latitude), provided the resolution is not too coarse (more than ≈ 2 degrees). The model grid can be any quasi-rectangular grid with a slowly varying spatial step. It is assumed, in particular for the Parabolic Piecewise Method for transport, that the grid size is constant in each direction locally (over 5 consecutive cells), with the sizes equal to those of the locally central cell. The sphericity effects,

although taken into account, are therefore linearized.

The model uses any number of vertical layers described in hybrid sigma-p coordinates. The pressure in hPa at the top of each layer k is given by the following formula:

<sup>20</sup>  $P_k = a_k 10^5 + b_k P_{surf}$ 

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where  $P_{surf}$  is the surface pressure and the coefficients  $a_k$  and  $b_k$  must be given. These hybrid coefficients  $a_k$  and  $b_k$  are provided by the user in an input file. The vertical grid can be defined automatically given the pressure at the top of the model and sigma at the top of the surface layer. If not otherwise specified by the user, the resolution varies upward in a geometric progression.



(3)



## 3.2 Landuse types

Land use types, or categories, are needed by CHIMERE to calculate a number of processes, such as deposition, biogenic emissions, or surface layer momentum and heat transfer. Land use files need to be constructed only once per model domain. There are currently 9 land use categories in CHIMERE. Those categories are calculated from available global land use databases, which can contain different number of classes. The source code version comes with land use data and interfaces for two databases: the Global Land Cover Facility (GLCF) and the GlobCover Land Cover (LC).

GLCF is a 1 km × 1 km resolution database from the University of Maryland, following the methodology of Hansen and Reed (2000). This global land cover classification is based on the imagery from the AVHRR satellites analyzed to distinguish 14 land cover classes. The GlobCover LC is a global land cover map at 10 arc second (300 m) resolution (Bicheron et al., 2011). It contains 22 global land cover classes defined within the UN Land Cover Classification System (LCCS). GlobCover database is based on

 the ENVISAT satellite mission's MERIS sensor (Medium Resolution Image Spectrometer) Level 1B data acquired in Full Resolution (FR) mode with a spatial resolution of 300 m. GlobCover LC was derived from an automatic and regionally-tuned classification of a time series of MERIS FR composites covering the period December 2004– June 2006. The global land cover NetCDF files are provided along with the CHIMERE distribution.

The nine CHIMERE land use types are described in Table 1. The correspondance table between the database landuse types and the CHIMERE landuse types is provided with the model. The user can choose either GLCF or GlobCover by simply selecting a flag; a dedicated sequence of scripts and programs prepares the landuse file in the

CHIMERE format. An additional class "inland water" has been added to the classifications in both land cover databases to distinguish between the sea water and fresh water. This was needed to avoid model emissions of the sea salt over the fresh water surfaces. The separation was done using a land-sea mask. So instead of the original 14





GLCF and 22 GlobCover classes, CHIMERE land use pre-processor employs 15 and 23 classes for GLCF and GlobCover, respectively. An example of CHIMERE regridded landuse is displayed in Fig. 5.

## 3.3 Boundary and initial conditions

- As a limited area model, CHIMERE requires chemical initial and boundary conditions. The boundary conditions are three-dimensional fields covering the whole simulation. These fields provide the concentrations of chemical species (gaseous and particulate) at the lateral and upper layers of the CHIMERE simulation domain. Some CTMs use tabulated vertical profiles derived from observational climatologies. Considering that
- observation-based boundary conditions are too restrictive in terms of available species, as well as time and space coverage, CHIMERE get its boundary conditions from global CTMs. The sensitivity study (Szopa et al., 2009) illustrates the importance of using a domain that is large enough to minimize boundary effects and allow for recirculations within the CHIMERE domain.
- <sup>15</sup> To ensure the best possible simulation quality, a common practice is to use the nesting option of CHIMERE, with a coarse domain to provide the most consistent boundary conditions for the smaller nested domains. An example of such a configuration is displayed in Fig. 6 for a specific study in the Paris area with the horizontal resolution dx = 5 km. The local simulation is nested into a larger domain with dx = 15 km, which itself is nested into a domain with dx = 45 km. Only the largest domain makes use of external boundary conditions (Fig. 6).

Szopa et al. (2009) also investigated the sensitivity of the model to the temporal increment of the boundary conditions. They found that using a time-variable large scale forcing improves the variability at the boundary of the domain compared to the monthly

<sup>25</sup> average, but the magnitude of the sensitivity decreases towards the centre of the domain. Schere et al. (2012) confirmed this finding during the AQMEII intercomparison exercise. Colette et al. (2011) argued that the selection of the large scale model had a larger impact than its temporal resolution.





Depending on the research projects that have been conducted in the past, preprocessing tools have been implemented to build boundary conditions from a variety of global models. The most widely employed is LMDz-INCA (Folberth et al., 2006), for which a climatology (average monthly fields) is available on the CHIMERE website. Alternatively, the MOZART model was also used, for instance for the GEMS

- (Hollingsworth et al., 2008), MACC II, and AQMEII (Rao et al., 2011) projects, and an interface with OsloCTM2 (Sovde et al., 2008) was also developed for the CityZen project. For the specific case of mineral dust, the GOCART (Ginoux et al., 2001) monthly average fields are also available. The current version of the model includes in its namelist
- a series of flags in order to define which model is to be used for the following three groups of species: gases, dust aerosols, and non-dust aerosols. For each of them either climatological or time-varying fields can be used. A suite of pre-processing tools is made available in order to facilitate the implementation of new forcing datasets in the appropriate format.
- The initial conditions is a three-dimensional field corresponding to the starting date of the simulation. The same global model fields used for boundary conditions can be used to initiate the simulation. If there are no global model fields available, it is also possible to start a simulation with zero concentrations for all species. In this case, the spin-up time of the simulation has to be adjusted to the domain size: from a few days for a local domain to one month for a continental domain (to take into account the
- long-range transport and possible recirculations).

# 4 Meteorology

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CHIMERE is an off-line chemistry-transport model driven by meteorological fields, e.g. from a weather forecast model, such as WRF or MM5. CHIMERE contains a meteorological pre-processor that prepares standard meteorological variables to be read by the model core.





The input meteorological data are processed in two stages, as presented in Fig. 7. This choice constitutes a strength of the CHIMERE model: the user can use CHIMERE providing only very basic meteorological variables: wind speed, temperature, humidity and pressure. In this case, a complete suite of diagnostic tools for all other mandatory

- variables (turbulent fluctuations and fluxes) may be used. On the other hand, if the meteorological model provides all the necessary meteorological variables, the meteorological interface only interpolates data on the CHIMERE grid, with an hourly time step. The diagnostic interface may also be used even if turbulent parameters are provided with the meteo model. The user can decide to bypass turbulent parameterizations of
   the input meteorological model and make use of the CHIMERE diagnostics in order to
- increase the consistency of the forcing fields accross a range of input models.

The meteorological interface first transforms original variables from any input spatial grid and temporal frequency onto standard variables given on the CHIMERE horizontal grid as hourly values. The operations performed include: horizontal and temporal

interpolation, wind vector rotation, temporal deaccumulation of precipitations, transformation from perturbation and mean values to full values, etc. The vertical interpolation is performed at a later stage, since a higher vertical resolution might be required for the turbulence and fluxes diagnostics. In the current CHIMERE version, meteorological interfaces are provided for ECMWF (ERA-INTERIM, IFS), WRF (Skamarock et al., 2007) and MM5 models.

If all required fields are not provided, the pre-processor diagnostic model is used. It takes meteorological variables and transforms them into variables necessary for the CHIMERE core. These parameters are (i) the radiation attenuation, (ii) the boundary layer height, (iii) the friction velocity  $u_*$ , the aerodynamical resistance  $r_a$ , the sensible heat flux  $Q_0$ , the Monin–Obukhov length L and the convective velocity  $w_*$ .

For the photochemistry, the cloud liquid water content is necessary to estimate the radiative attenuation. If rain water or ice are available, they are added to the cloud water for the attenuation effects. Note that for gaseous species (such as HNO<sub>3</sub>) and aerosols





calculations, additional parameters related to convective and large-scale precipitation are required for the scavenging.

Finally, and since most large-scale weather models do not include any "urban parameterization", the possibility of correcting the wind speed in the surface layer (due
to increased roughness) in urban areas is offered. This will automatically be balanced by a vertical wind component calculated in the mass balance (see vertical transport below). This correction has however no effect at continental scale where the fraction of urban areas in the model grid cells are limited (see Fig. 5 for example, where the Paris city, a urban site, is not a "dominant" landuse for the corresponding cell). This urban parameterization has however a strong impact on urban versions of the model, mostly for primary pollutants.

## 4.1 Diagnostic of turbulent parameters

If the boundary layer height and some energy fluxes are not directly available in the meteorological model, they can be diagnosed in CHIMERE. The following variables are computed: the friction velocity  $u_*$ , the surface sensible heat flux  $Q_0$ , the vertical convective velocity  $w_*$ , the boundary layer height  $\overline{h}$ , the Monin–Obukhov length L and the vertical diffusivity profile  $K_z$ .

The friction velocity  $u_*$  is used for the deposition and calculation of diffusivities. It is a particularly sensitive parameter for ozone in Summer through the calculation of aerodynamic resistance  $r_a$ . Friction velocity is thus sensitive to the land use type, which is critical to deposition. In large scale meteorological models, roughness lengths are often too coarse for the implementation of high-resolution deposition. Therefore an update of  $u_*$  is proposed following the Louis et al. (1982) formulation which is particularly robust. We recommend to use this alternative formulation, no matter whether  $u_*$  is available in the input fields, in order to have a deposition that is consistent with the high-resolution land use.

$$u_* = \sqrt{C_{\rm DN}^2 \cdot F_{\rm m} \cdot |U|^2}$$



(4)

with  $F_{\rm m}$  is the Louis et al. (1982) stability function and  $C_{\rm DN}$  the neutral drag coefficient as:

$$C_{\rm DN} = \frac{k}{\ln\left(\frac{z+z_{\rm 0m}}{z_{\rm 0m}}\right)}$$

 $F_{\rm m} =$ 

with k = 0.41 the Karman constant, *z* the altitude where the wind speed |U| is known <sup>5</sup> and  $z_{0m}$ , the momentum roughness length. The momentum stability function  $F_m$  is estimated depending on the bulk Richardson number value.

- Under *stable cases* (if  $Ri_b < 0$ ):

$$F_{\rm m} = 1 - \frac{2 \cdot b \cdot Ri_{\rm b}}{1 + 3 \cdot b \cdot c \cdot C_{\rm DN}^2 \cdot \sqrt{\frac{Z + Z_{\rm 0m}}{Z_{\rm 0m}}} \sqrt{|Ri_{\rm b}|}}$$

- Under *unstable cases* (if  $Ri_b > 0$ ):

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$$\frac{1}{1 + \frac{2 \cdot b \cdot Ri_{b}}{\sqrt{1 + d \cdot Ri_{b}}}}$$

with the constant b = c = d = 5. Under neutral case, i.e.  $Ri_b = 0$ ,  $F_m = 1$ . The bulk Richardson number is estimated as:

$$Ri_{\rm b}(z) = \frac{gz}{\overline{\theta_{\rm v}(z)}} \frac{\Delta \overline{\theta_{\rm v}}}{\Delta |U|^2}$$
(8)

with  $g = 9.81 \text{ m}^2 \text{ s}^{-2}$  the gravitational acceleration,  $\Delta \overline{\theta_v} = \overline{\theta_v}(z) - \overline{\theta_v}(z_0)$ ,  $\Delta |U| = |U|(z)$ . Heat fluxes are used to compute  $w_*$  and therefore mixing, and the height of the boundary layer. In fact only the virtual heat flux is required, which can be recomputed

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from an empirical formula (Priestley, 1949) using temperatures in the first model layers. This formula is not very accurate. It is strongly advised to use heat fluxes from the meteorological model if available. If the surface sensible heat flux  $Q_0$  is provided by the meteorological model, it is directly used for the computation of the convective velocity  $W_*$ :

$$W_* = \left(\frac{gQ_0\overline{h}}{\rho c_p\overline{\theta_v}}\right)^{1/3}$$

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where  $Q_0$  is the surface sensible heat flux,  $\overline{h}$  the convective boundary layer height,  $c_p$  the specific heat of air at constant pressure,  $\overline{\theta_v}$  the mean virtual potential temperature representative of the surface layer.

The Monin–Obukhov length is estimated as:

 $L = \frac{-\overline{\theta_{\rm v}}u_*^3}{kgQ_0}$ 

The boundary layer height  $(\overline{h})$  is derived from different formulation depending on the atmospheric static stability. When stable, i.e. when L > 0,  $\overline{h}$  is estimated as the altitude when the Richardson number reaches a critical number here chosen as  $Ri_c = 0.5$ , following Troen and Mahrt (1986).

In unstable situations (i.e. convective),  $\overline{h}$  is estimated using a convectively-based boundary layer height calculation. This is based on a simplified and diagnostic version of the approach of Cheinet and Teixeira (2003) which consists in the resolution of the (dry) thermal plume equation with diffusion. The in-plume vertical velocity and buoyancy equations are solved and the boundary layer top is taken as the height where calculated vertical velocity vanishes. Thermals are initiated with a non-zero vertical velocity and potential temperature departure, depending on the turbulence similarity parameters in the surface layer.

(9)

(10)



Once the depth of the boundary layer is computed, vertical turbulent mixing takes can be applied following the *K*-diffusion framework following the parameterization of Troen and Mahrt (1986), without counter-gradient term. In each model column, diffusivity  $K_z$  (m<sup>2</sup>s<sup>-1</sup>) is calculated as:

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$$K_z = k w_s \frac{z}{h} \left( 1 - \frac{z}{h} \right)^2$$

where  $w_s$  is a vertical scale given by similar formulas:

- In the stable case (when the surface sensible heat flux is negative):

$$w_{\rm s} = \frac{u_*}{(1+4.7z/L)}$$

- In the unstable case:

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$$W_{\rm s} = (u_{*}^3 + 2.8eW_{*}^3)^{1/3}$$

where  $e = \max(0.1, z/h)$ . A minimal K(z) is assumed, with a value of  $0.01 \text{ m}^2 \text{ s}^{-1}$  in the dry boundary layer and of  $1 \text{ m}^2 \text{ s}^{-1}$  in the cloudy boundary layer. K(z) is capped to a maximal value of  $K_z = 500 \text{ m}^2 \text{ s}^{-1}$  to avoid unrealistic mixing. Above the boundary layer, a fixed value of  $K_z = 0.1 \text{ m}^2 \text{ s}^{-1}$  is prescribed. As for many CTMs considered as numerically diffusive, horizontal turbulent fluxes are not considered.

## 4.2 Diagnostic of deep convection fluxes

The deep convection scheme describes the effects of subgrid scale clouds on tropospheric convection, following Tiedtke (1989). The hourly fluxes of entrainment and detrainement in the updrafts and the downdrafts are estimated during the meteorological diagnostic stage.



(11)

(12)

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Deep convection occurs when cumulus or cumulo-nimbus clouds (referred to as convective clouds) are present. These clouds are formed when air masses are unstable, when warm air is at the surface or cold air is transported in upper layers (cold front). High vertical wind speed are observed leading to large cloud structures along the ver-

tical direction. On the other hand, when clouds are only due to mechanical forcings (mountains, warm fronts), they are referred to as stratiform clouds and generally exhibit low vertical velocity.

Air masses shall be quickly mixed in the troposphere when convective unstabilities occur under a cloud. To describe this phenomenon, mixing schemes generally consider a cloud (and the whole column including this cloud) and its environment. In the main part of deep convection parameterizations, the hypothesis of a small cloud surface compared to the total studied surface is used.

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Under the cloud, updrafts and downdrafts are observed. The updraft originates from air masses lighter than their environment when downdrafts represent the downfall of colder air (often with rain). In the updraft and the downdraft, air may be exchanged between the cloud and its environment. Entrainment refers to the air that flows from the environment into the cloud, detrainment refers to the air that flows from the cloud towards the environment. In order to ensure mass conservation, a compensatory subsidence is observed in the environment.

<sup>20</sup> In CHIMERE, the Tiedtke scheme (Tiedtke, 1989) is implemented. The main goal of this scheme is to estimate a convection mass flux:

$$M(z) = \rho(z)(a_{\rm up}\overline{w_{\rm up}(z)} + a_{\rm dw}\overline{w_{\rm dw}(z)}) = -\rho(z)a_{\rm env}\overline{w_{\rm env}(z)}$$
(14)

with  $\overline{w_{up}(z)} > 0$ ,  $\overline{w_{dw}(z)} < 0$  and  $\overline{w_{env}(z)} < 0$  the vertical wind speed in the updrafts, downdrafts and environment, respectively. The vertical gradient of this mass flux is:

$$_{25} \quad \frac{\partial M(z)}{\partial z}(z) = E(z) - D(z) \tag{15}$$



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with E(z) > 0 et D(z) > 0, the entrainment and detrainment fluxes (kgm<sup>-2</sup>s<sup>-1</sup>). This equation works both for updrafts and downdrafts, with, for example for the updraft:

$$E(z) = E_{up}(z) + E_{dw}(z)$$
  

$$D(z) = D_{up}(z) + D_{dw}(z)$$
(16)

An example of these four fluxes is displayed in Fig. 8. In order to use this convection scheme, new calculations were added in the meteorological pre-processor, providing an estimate of the vertical wind speed (independently of the input from the meteorological model). In the CHIMERE model itself, these fluxes are used to estimate mass fluxes for the poollutant species as follows:

$$\frac{\partial M_{up}(z)c_{up}(z)}{\partial z} = E_{up}(z)c_{env} - D_{up}(z)c_{up}$$

$$\frac{\partial M_{dw}(z)c_{dw}(z)}{\partial z} = E_{dw}(z)c_{env} - D_{dw}(z)c_{dw}$$
(17)
(18)

with the concentrations  $c_{up}$ ,  $c_{dw}$  and  $c_{env}$  in the updraft, downdraft and environment, respectively. The calculation is done from surface to the top of the domain in order to ensure mass conservation.

### 5 Transport and mixing

For a given chemical species with concentration c, the following conservation equation is solved numerically in the CHIMERE CTM, where  $\rho$  is the air density:

<sup>20</sup>  $\partial_t(C\rho) + \partial_i \mathbf{F}^i = 0$ 

with **F** indicating a mass flux :

 $\mathbf{F} = \rho c \mathbf{v}$ 

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(19)

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As CHIMERE is designed for structured grids where the grid cells are nearly parallelepipedic, this equation can be discretized and solved separately for each of the three orthogonal directions: zonal, meridional and vertical. This strategy is known as *operator splitting*. Even though the use of operator splitting may generate some numerical problems, this technique is very widely used in weather modelling and chemistry-transport modelling, both because it is more computationnally efficient and also sometimes more stable and accurate than a bi- or tri-dimensional approach, particularly when it is applied to high-order models (Byun et al., 1999). Therefore, the tendancy  $c_t$  in the concentration *c* is equal to  $c_t^{(1)} + c_t^{(2)} + c_t^{(3)}$ , where  $c_t^{(i)}$  is the time derivative of concentration due to transport in the *i*th direction. When it is also assumed that the time variations of  $\rho$  are much slower than the time variations of c ( $|\rho c_t| \ll |c \rho_t|$ , which is implicitly assumed in CHIMERE since air density is updated at each coarse time step while concentrations are updated at each fine time step), we have:

$$\rho c_t^{(i)} = -\partial_i \mathbf{F}^i \tag{21}$$

After time and space discretization, if we note  $\delta^{(i)}c$  the variation of c due to transport in direction *i*, the discretized transport equations are the following:

$$\delta^{(i)}c = -\left(\frac{F_{n+\frac{1}{2}}^{i}(t) - F_{n-\frac{1}{2}}^{i}(t)}{\Delta x}\right)\Delta t$$
(22)

The concentration increments are calculated successively for each direction from the initial concentration field (parallel strategy). This equation secures mass conservation because the inward and outward fluxes cancel out in each direction. The time integration is of order 1. The key issue in solving this equation is the estimation of the fluxes at the cell interfaces ( $F_{n\pm\frac{1}{2}}^{i}(t)$ ). The way these fluxes are defined determines the characteristics of the transport scheme (scheme type, scheme order, diffusivity, numerical stability etc.).





In chemistry-transport models, various types of numerical schemes have been tested and are proposed to users to solve the advection equations. These numerical schemes range from simple order-1 numerical schemes such as the classical upwind method to higher-order methods such as the Piecewise-parabolic method (Colella and Woodward, 1984) proposed in CHIMERE and CMAQ, the Yamartino-Blackman cubic scheme, proposed in CMAQ (Byun et al., 1999), or the Walcek scheme in BRAMS (Freitas et al., 2011).

# 5.1 Horizontal transport

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In the horizontal directions, it is assumed that the grid cell length does not vary substantially from one grid cell to its neighbours. As in the CHIMERE model, species concentrations and meteorological variables are represented on the same grid, the wind speed at the interfaces in the direction orthogonal to the interface is interpolated linearly from the wind speeds at the centers of the two gridcells separated by the interface. The wind speed at the interface will be noted  $u_{n\pm\frac{1}{2}}(t)$ , and is assumed constant during

each coarse time step. We will drop in the following the superscript *i* to indicate the direction. The definition of the wind speed at the cell interface is independant of the scheme used, so that the definition of the fluxes at the interfaces only depends on the evaluation of the concentration at the interface.

Three schemes for horizontal transport of chemical concentrations in the model are now available in the model.

# 5.1.1 Upwind scheme

In the upwind scheme (Courant et al., 1952), the fluxes at the cell interfaces are defined by the following equations according to the sign of the wind speed at the cell interface:

$$\begin{split} F_{n\pm\frac{1}{2}}(t) &= c_n \rho_n u_{n+\frac{1}{2}}(t) \quad \text{if } u_{n+\frac{1}{2}}(t) > 0 \\ &= c_{n+1} \rho_n u_{n+\frac{1}{2}}(t) \quad \text{if } u_{n+\frac{1}{2}}(t) < 0 \end{split}$$



(23)

The assumption made in this scheme is that the tracer concentration is constant in each grid cell, and that the flux at the interface is determined by the direction of the mass flux at the cell interface, which imposes the tracer concentration at the cell interface.

#### 5 5.1.2 Van Leer scheme

The Van Leer scheme used in CHIMERE is commonly called Van Leer I because it is the first one described in the seminal paper of Van Leer (1979). This scheme is of order 2 in space, it assumes that the concentration inside a grid cell is described by a linear slope between the two cell interfaces:

10  $C_n(x) = C_n + (x - x_n)\Delta_n$ 

where the slope  $\Delta_n$  is determined according to the following cases. If  $c_{n-1} \le c_n \le c_{n+1}$ or  $c_{n-1} \ge c_n \ge c_{n+1}$  then

$$\Delta_{n} = \operatorname{sign}\left(c_{n+1} - c_{n-1}\right) \times \min\left(\frac{c_{n+1} - c_{n-1}}{2\Delta x}, \frac{c_{n+1} - c_{n}}{\Delta x}, \frac{c_{n} - c_{n-1}}{\Delta x}\right)$$
(25)

where, in this case,  $\Delta_n$  is the smallest slope that can be estimated between cell *n* and <sup>15</sup> its closest neighbours.

Otherwise,  $c_n$  is an extremum of concentration and the concentration within cell *n* is assumed constant ( $\Delta_n = 0$ ) which ensures that the scheme is monotonic.

This scheme, which is recognized in meteorology for its good numerical accuracy and smaller diffusion than the first-order upwind scheme, is also slightly more time-<sup>20</sup> consuming than the first-order upwind scheme. In meteorology, it can be considered as a good compromise solution between numerical accuracy and computational efficiency for long-range transport (Hourdin and Armengaud, 1999).



(24)



## 5.1.3 The Parabolic Piecewise Method scheme

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Another scheme that is proposed in CHIMERE for horizontal transport is the Parabolic Piecewise Method (PPM) scheme, with slope-limiting and monotonicity-preserving conditions, such as presented in Colella and Woodward (1984). As for the upwind and the Van Leer schemes, this schemes is applied separately to the two horizontal dimensions, which formally limits the model order to second-order accuracy in solving the two-dimensional transport problem because the second-order cross derivatives (the terms as  $\partial c/\partial x \partial y$ ) are not taken into account. However, since this scheme is symmetric, it can be considered that the errors due the neglection of cross-derivatives approximately compensate (Ullrich et al., 2010), so that for practical cases this scheme is still less diffusive than the Van Leer scheme (see, e.g. Vuolo et al., 2009b).

### 5.1.4 Comparison between the three available transport schemes

Vuolo et al. (2009b) have performed a comparison between the three horizontal transport schemes presented above in the context of an event of long-range transport of saharian dust over Europe. They found that the choice of one or another of these transport schemes has a strong impact on modelled dust concentrations. As can be expected

- from the well-known numerical behaviour of these schemes, simulated peak values of the dust plume are reduced by 32 % (upwind) or 17 % (Van Leer) compared to the less diffusive PPM scheme, while the plume area, defined as the surface around the peak
- where dust concentration exceeds 40 % of the peak value, is increased by 48 % (upwind) or 25 % (Van Leer) compared to the PPM scheme. Horizontal transport schemes also have an indirect impact on vertical transport and diffusion, the most diffusive horizontal schemes tending to increase dust transport towards the lowest layers, increasing there domain-averaged surface concentrations and decreasing domain-averaged con-
- <sup>25</sup> centrations in and above the boundary layer. The authors conclude that the modelling uncertainty due to the choice of one or another numerical transport scheme is among







the limiting factors for the use of dust-transport models for operational air-quality monitoring over Europe.

# 5.2 Vertical transport

# 5.2.1 Explicit vertical transport

In the vertical direction, unless otherwise specified by the user the thickness of the layers increases quasi-exponentially with altitude in order to provide a better vertical resolution in the lower model levels. The value of the thickness ratio between two neighbouring layers is typically close to 1.5. Therefore the hypothesis of constant length for the grid cells cannot be made for vertical transport in CHIMERE, and other numerical schemes have to be used.

First, vertical mass fluxes are calculated to secure zero flux divergence at each grid cell. The vertical mass flux at the lower boundary of the lowest layer is zero, and the vertical mass flux at the top of each grid cell is computed successively, from the lowest layer to the highest.

- <sup>15</sup> Once these mass fluxes are known, the vertical transport scheme can be applied. As the number of vertical layers in CHIMERE is much lower than the horizontal size of the domain (typically 8–15 vertical layers), while horizontal domains have typically at least 40 × 40 grid cells, it is not clear whether using high-order transport schemes relying on the concentration values of several neighbouring cells is useful for vertical transport.
- Therefore, historically, only the classical upwind scheme was used for vertical transport in CHIMERE, with the same formulation as presented above for horizontal transport. However, more recent applications concern long-range transport of species having long lifetimes (e.g. mineral dust, volcanic ashes, particulate matter from forest fires) which also can occur above the boundary layer. Therefore, it seems important to reduce
- <sup>25</sup> numerical diffusion also in the vertical direction. This is particularly important to reduce numerical diffusion reduces the ability of the model to adequately represent dense plumes that are located in thin vertical layers such as mineral dust or volcanic ashes.



Therefore, a current development in CHIMERE is to include the Van Leer I transport scheme, which is less diffusive than the upwind scheme, in a version adapted to grid cells with nonuniform thickness. This scheme has been tested with encouraging results in terms of preserving sharp concentration gradients and higher peak values than the upwind scheme during long-range transport and shall therefore be proposed to the community in the next distributed version of CHIMERE.

## 5.2.2 Turbulent mixing

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At each interface between layers k and k + 1, an equivalent turbulent vertical velocity  $w_k$  is calculated:

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$$W_k = \frac{K_z}{\frac{1}{2}(h_k + h_{k+1})}$$

This enables to diagnose the net incoming flux at the upper interface of cell k as:

$$F_{i} = \frac{W_{k}\left(c_{k+1}\frac{\rho_{k}}{\rho_{k+1}} - c_{k}\right)}{h_{k}}$$

where  $c_k$  is the concentration at the *k*th layer,  $\rho_k$  the air density,  $h_k$  the thickness of the *k* layer.

The profiles of  $K_z$  and  $w_k$  are computed in the meteorogical diagnostic code at each coarse time step, while the flux for each species depending on its concentration is computed at each fine time step (see Sect. 4.1).

### 6 Emissions

Emissions of pollutants have different origins and include a number of different gaseous and aerosol species, chemically inert or not. The sources can be located at the surface



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(traffic, biogenic) or along vertical profiles (industrial emissions, biomass burning). These emissions are splitted in several families, representing their origin:

- The anthropogenic emissions: represent the whole human activities. They may be very localized and emissions inventories are often dedicated to specific simulation domain. Often operated for studies in the Paris area, CHIMERE uses in this case the AIRPARIF air quality network inventory (Valari and Menut, 2008, 2010). For European studies, the EMEP inventory is usually used (Menut et al., 2012), but the TNO inventory has also been used (Timmermans et al., 2009). In studies over North America it has also used the US EPA inventory (Solazzo et al., 2012b). Finally, the EDGAR global emissions inventory was recently added in CHIMERE and comparisons with EMEP over Europe are in the course.
- The biogenic emissions represent activities linked to the vegetation. These emissions are calculated using the global MEGAN model (Guenther et al., 2006).
- The mineral dust emissions represent the other part of "natural" emissions, but in this case for non-reactive particle and mainly generated by the surface layer dynamics (Menut et al., 2009a). They are specific of several regions (Western Africa, Sahel and Saudi Arabia) but are described globally. Some other sources exist in Europe but are not yet implemented and this specific physics is an ongoing project in CHIMERE. This is the case of the resuspension, actually parameterized following the Loosmore and Cederwall (2004) scheme.
- The fire emissions are more sporadic and require numerous and very differet data: satellite to estimate the burned area each day, a vegetation model to estimate the emitted amount for each chemical species (gas and particles). These emissions are also a specific project in development in CHIMERE.





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# 6.1 Anthropogenic emissions

The anthropogenic emissions are the key point in pollution management, since they are the only reducible sources. Contrarily to the dust and biogenic emissions (only dependent on the surface types and the meteorology), the anthropogenic emissions have

to be prepared in a bottom-up way, using a number of input data and information to build up an inventory of fluxes of chemical species. These various input informations are generally given for a reduced number of classes of chemical species and often provided under an activity sectors classification (e.g. following the SNAP nomenclature), as masses per surfaces for various domains and resolutions and as totals over a period
 of one year.

As input to CHIMERE and for a realistic simulation, these emissions have to be provided every hour, for the specific species of the chemical mechanism used and projected over the gridded domain, regardless of the original data projection. From the raw data to the data required for a specific simulation, a sequence of preprocessing actions is necessary, including a temporal disaggregation, the application of VOC, NOx and PM shares and the final species lumping into model species. A standard procedure is proposed but preprocessing actions can be bypassed by directly providing hourly anthropogenic emissions. For the standard procedure, it is proposed to prepare these data following two distinct stages:

- Step 1: Create a yearly total gridded database per activity sector adapted to the horizontal simulation grid. This enables then to create monthly masses of emitted model species, already projected on the horizontal simulation grid, by application of seasonal factors (provided only for Europe). This step is performed only once each time a new domain is used. The complete suite of programs is provided to the user only for the EMEP format, but can be adapted to other formats.
  - Step 2: Disaggregate the monthly emissions into hourly emissions by applying daily and weekly factors, and then produce hourly emission time series for each species adapted to the specific simulation period (real days) and the model





vertical grid. This step is performed for each simulation. The complete suite performing this second step is provided to the user and does not need to be modified.

Instead of going through Step 1, the user can also provide monthly anthropogenic emissions files (except soil NO) built by other means. This leads to 12× nspec files for a typical year, nspec being the number of emitted species and one file per month (or two files per month if a distinction is done between surface and point sources). For example, these nspec species are listed in the Table 2 for the MELCHIOR chemical mechanism implemented by default in CHIMERE.

Depending on the spatial domain, CHIMERE has been used with several anthropogenic emissions datasets. The largest number of studies was over the western Europe and two datasets were used: (i) the EMEP database (Vestreng, 2003) and, more recently, the TNO database during the GEMS and MACC projects. In both cases, the data were provided over specific domains grids, needing a spatial interpolation for the target modelled domains. This is performed using an intermediate fine grid with a 1 km

- <sup>15</sup> resolution (GLCF dataset, Hansen and Reed, 2000). Soil types being described on the fine grid allows for a better apportionment of the emissions according to urban, rural, forest, crops and maritime areas. This pre-processing is provided with the model distribution to all users. The data being delivered as tons per year, a sensitivity study was done in Menut et al. (2012) to quantify the improvement of more realistic hourly profile:
- it was shown that each European country has particular traffic emissions time profiles and the use of an unique and averaged profile over large domain impacts the modelled concentrations. By default, CHIMERE is proposed with the SNAP diurnal profiles following Vestreng et al. (2009) as a first guess.

More recently, continental scale modelling was done over the United States and the <sup>25</sup> model used USEPA inventory to model air quality during the AQMEII project (Rao et al., 2011; Schere et al., 2012; Solazzo et al., 2012b). Several other applications were also performed over Mexico City in the framework of the MILAGRO project (Hodzic et al., 2009).





At a finer scale, CHIMERE is used with more specific anthropogenic emissions inventories. This is the case of all studies done over the Paris area, using the Airparif air quality network data (from Menut et al., 2000a to Valari et al., 2011). A sensitivity study was presented in Valari and Menut (2008) showing the impact of the emissions horizontal resolution on the modelled concentrations: the effect of spatially "averaged" areas may lead to large changes in the emissions fluxes and therefore concentrations: due to nonlinearity in chemical regimes, the modelled concentrations are not varying

linearly with the NO<sub>x</sub> and VOCs emissions fluxes changes. As one of the strongest "air pollution" hotspot in Europe, the model is also used to simulate the Po Valley pollution with a specific inventory as described in de Meij et al. (2009), among others.

Whatever the database and its resolution, the species  $NO_x$  and NMVOCs have to be distributed into the chemical mechanism species. Annual emissions of  $NO_x$  are first speciated as 8% of  $NO_2$  and 92% of NO following GENEMIS recommendations (Friedrich, 2000). The GENEMIS NMVOC speciation is used for the same districts and for 6 types of emission activity sectors: traffic, solvents, industry (except solvents),

- and for 6 types of emission activity sectors: traffic, solvents, industry (except solvents), energy extraction/production, residential (except solvents) and agriculture. For each activity, a speciation is obtained over 32 NMVOC NAPAP classes (Middleton et al., 1990). Once the disagregation step is performed, an aggregation step for the lumping of NMVOCs into model species is achieved following Middleton et al. (1990).
- For the anthropogenic emissions of primary particles,  $H_2SO_4$ , PPM, BaP, BbF, BkF, OCAR, BCAR are splitted over three modes: XXX\_fin for  $\phi < 2.5 \,\mu$ m; XXX\_coa for  $2.5 < \phi < 10 \,\mu$ m and XXX\_big for  $\phi > 10 \,\mu$ m. PPM\_fin refers to PM<sub>2.5</sub>, PPM\_coa to PM<sub>10</sub>-PM<sub>2.5</sub>. H<sub>2</sub>SO<sub>4</sub>, BaP, BbF, BkF, OCAR, BCAR are assumed to be in the fine mode. In rural areas, NO emissions from ammonium used in fertilizer application, followed by
- <sup>25</sup> microbiological processes may be significant. Since these emissions strongly depend on temperature, they are processed in the model as "biogenic" emissions and often called in this manual "biogenic NO emissions". CHIMERE uses an European inventory of soil NO emissions from Stohl et al. (1996). This inventory estimates the soil emissions to be during the summer months at the order of about 20 % of the emissions from





combustion on a European average but with large differences between the countries. In the model, these NO emissions are only considered during the months of May to August.

# 6.2 Biogenic emissions

<sup>5</sup> Emissions of six Chimere species: isoprene,  $\alpha$ -pinene,  $\beta$ -pinene, limonene, ocimene, and NO, are calculated using the MEGAN model data and parameterizations. The MEGAN model (Guenther et al., 2006, v. 2.04) exploits most recent measurements in a gridded and canopy scale approach, more appropriate for use in CTMs since it estimates the effective burden of gases that mix and react in the boundary layer. Estimates of biogenic VOCs from vegetation and NO emissions are calculated as:

 $ER_i = EF_i \times \gamma_i(T, PPFD, LAI) \times \rho_i$ 

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where ER<sub>*i*</sub> ( $\mu$ gm<sup>-2</sup>h<sup>-1</sup>) is the emission rate of species *i*, EF<sub>*i*</sub> ( $\mu$ gm<sup>-2</sup>h<sup>-1</sup>) is an emission factor at canopy standard conditions,  $\gamma_i$  (unitless) is an emission activity factor that accounts for deviations from canopy standard conditions, and  $\rho_i$  is a factor that accounts for production/loss within canopy.

As a first step, canopy standard conditions are set to: air temperature (T) of 303 K, photosynthetic photon flux density (PPFD) of 1500  $\mu$ molm<sup>-2</sup>s<sup>-1</sup> at the top of the canopy, leaf area index (LAI) of 5 m<sup>2</sup>m<sup>-2</sup> and a canopy with 80 % mature, 10 % growing and 10 % old foliage.

<sup>20</sup> The MEGAN model parameterizes the bulk effect of changing environmental conditions using three time-dependent input variables specified at top of the canopy: temperature (*T*), radiation (PPFD), and foliage density (LAI). The production/loss term within canopy is assumed to be unity ( $\rho = 1$ ). The equation can then be expanded as:

 $\mathsf{ER}_i = \mathsf{EF}_i \times \gamma_{T,i} \times \gamma_{\mathsf{PPFD}} \times \gamma_{\mathsf{LAI}}$ 

<sup>25</sup> The MEGAN model provides input EF and LAI data over a global grid, hereafter projected on the CHIMERE model grid. The current available choice for EF's is restricted



(28)

(29)



to following species: isoprene,  $\alpha$ -pinene,  $\beta$ -pinene, myrcene, sabinene, limonene,  $\delta^3$ carene, ocimene, and nitrogen oxide. NO biogenic emissions include contribution from both forest and agricultural (fertilizers) soils. EF's are static and refer to years 2000– 2001. They are obtained summing up over several plant functional types (e.g. broadleaf

- and needle trees, shrubs, etc.). LAI database is given as a monthly mean product derived from MODIS observations, referred to base year 2000. Hourly emissions are calculated using 2-m temperature and short-wave radiation from a meteorological model output. Terpene and humulene emissions are not calculated in this model version and are set to zero.
- For European studies with CHIMERE, a comparison of the simulated formaldehyde column was presented in Curci et al. (2010). Formaldehyde concentrations variability is primarily driven by the oxidation of biogenic isoprene over Europe. By comparison to satellite based observations (Aura/OMI), it was showed that MEGAN isoprene emissions might be 40 % and 20 % too high over the Balkans and Southern Germany, respectively, and 20 % too low over Iberian Peninsula, Greece and Italy (Curci et al., 15)
- respectively, and 20% too low over Iberian Peninsula, Greece and Italy (Curci et al., 2010).

Sea salt emissions processed as biogenic emissions in CHIMERE because they depend on meteorology. They are calculated by Monahan (1986):

$$\frac{dF}{dr} = 1.373U_{10}^{3.41}r^{-3}(1+0.057r^{1.05})10^{1.19e^{-B^2}}$$
(30)  
$$B = \frac{0.38 - \log(r)}{0.65}$$
(31)

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*F* is the flux of sea salt particle number expressed in particles  $m^{-2} s^{-1} \mu m^{-1}$ , *r* the particle radius in  $\mu m$  and  $U_{10}$  is the wind speed at 10 m in m s<sup>-1</sup>.

# 6.3 Dust emissions

<sup>25</sup> The goal of the mineral dust modeling is twofold: improve our understanding on this physical problem (emissions, transported thin layers) and, after long-range transport,





estimate the relative part of mineral dust in the total budget of aerosols near the surface (and thus accounted for air quality in Europe, for example).

The analysis and forecast of mineral dust was primarily done in a parallel version of CHIMERE called CHIMERE-dust. The developments of the dust emissions and trans-

port are still ongoing but the development of CHIMERE-dust was frozen in 2010 and 5 all dust calculations are now integrated in the current CHIMERE model, ensuring more homogeneous developments.

The dust emission fluxes are calculated using the parameterization of Marticorena and Bergametti (1995) for saltation and the dust production model (DPM) proposed

- by Alfaro and Gomes (2001) for sandblasting. In order to have a better accuracy and 10 a lower computational cost, the DPM is optimized as presented in Menut et al. (2005b). Before calculating the fluxes, the estimation of the threshold friction velocity is required and is estimated following the Shao and Lu (2000) scheme. A complete description of the dust calculation is presented in Menut et al. (2007).
- For long-range transport simulations, the modelled domain is very large and must 15 include at the same time Africa (for emissions) and Europe (for the long-range transport and deposition). This leads to a coarse horizontal resolution of  $1^{\circ} \times 1^{\circ}$  in many studies. In order to take into account the subgrid scale variability of observed winds, the dust emissions are thus estimated using a Weibull distribution for the wind speed, following
- Cakmur et al. (2004) and Pryor et al. (2005). 20

An extension of the African dust emission scheme was done in Europe to model a huge dust event in Ukraine (Bessagnet et al., 2008). This shows this is possible to calculate local European erosion and retrieve an extreme event of particles, observed in the northern-western Europe (Netherlands, Belgium).

In Menut (2008), the impact of the meteorological forcing (NCEP or ECMWF) on the 25 dust emissions fluxes was quantified. In Vuolo et al. (2009a), the model results were compared to CALIOP lidar data and the vertical diffusion was guantified. In Menut et al. (2009a), an intensive observation period of the AMMA program was modelled in forecast mode to study the variability of the preditability of modelled surface dust





concentrations. It was shown that the sum of all model uncertainties (emissions, transport, deposition) and of the spread of the forecasted meteorology induces a variability in surface concentrations still higher than the required precision for European air quality forecast. A sensitivity study was presented in Menut et al. (2009b) and it was shown that a vary email area in the Scheren depart (around the position of the former French

<sup>5</sup> that a very small area in the Saharan desert (around the position of the former French nuclear tests site during the 60's) may explain the sporadic (but low) radionuclides concentrations measured sometimes in the South of France.

## 6.4 Fire emissions

Fires are now recognized to be a major source of emissions of aerosols and trace
gases. Depending on the area studied, the species of interest and the time period analyzed, it may be necessary to account for this additional contribution in the model simulations. Several studies have used CHIMERE to evaluate the impact of large fire events on air quality at regional scale, for example Hodzic et al. (2007) for fires in Portugal in 2003 or Konovalov et al. (2011) for fires in Russia in 2010. A new emission preprocessor is currently being developed in order to allow the evaluation of emissions either from pre-existing emission inventories (e.g. van der Werf et al., 2010; Wiedinmyer et al., 2011), or from the fire location points and estimated area burned directly. The latter allows the construction of an emission inventory for the CHIMERE grid and time-period chosen by the user. It is adaptable to near-real time observations for forecasting

This inventory is based on the general formulation of Seiler and Crutzen (1980). For each model species *i*, the emission associated to a specific fire  $E_i$  (kg species) is estimated by multiplying the area burned in the corresponding vegetation type  $A_{veg}$  (m<sup>2</sup>) by the fuel load FL<sub>veg</sub> (kg dry matter (DM) m<sup>-2</sup>) and the specific emission factor





 $EF_{i,veg}$  (g(kgDM)<sup>-1</sup>), as summarized in Eq. (32):

 $E_{i} = \sum_{v=1}^{\text{nveg}} \left( A_{\text{veg}} F L_{\text{veg}} E F_{i,\text{veg}} \right)$ 

The emissions are then binned into the specified model grid. The temporal and horizontal resolutions of the fire emissions depend on the resolution of the different pa-

rameters. The area burned parameter is estimated from the global observations of fire activity and areas burned at a daily and 1 km resolution from the MODIS instrument (Giglio et al., 2010), coupled to the SEVIRI/METEOSAT observations Roberts and Wooster (2008) for the regions covered (Europe and Africa) to allow the evaluation of a diurnal cycle. An example is presented in Fig. 11 for 8 May 2012. Depending
 on the fire location, a specific vegetation burned is attributed using the USGS landuse database (at 1 km resolution) and the corresponding fuel load (or carbon content) is evaluated from simulations by the ORCHIDEE vegetation and carbon cycle model

(Krinner et al., 2005).

Finally, the emissions are converted from carbon (or DM, considering that it is 45% carbon as in van der Werf et al., 2010) to each species using emission factors from the Akagi et al. (2011) review. Any species may be included in the inventory provided that emission factors are available. For a full description of each step of the calculation, the reader is referred to Turquety (2012).

In addition to the amount of trace gases and aerosols, the injection altitude is a critical parameter. Indeed, fires can release enough energy to trigger or reinforce convection (Freitas et al., 2007; Rio et al., 2010). These events will be accounted for by using a parameterization of pyroconvection – still being implemented – to evaluate emission profiles based on the fire intensity and the meteorological conditions (e.g. WRF simulations used for the CHIMERE simulations). A database including all CHIMERE

<sup>25</sup> species will be made available to users via the ECCAD portal (ECCAD, 2006–2012) and the near-real time evaluation of the emissions is under experiment at LMD (COSY,



(32)


governed by:  $F = Pf(w)u_{*}^{1.43}$ 

2013). Updates on the availability of the fire emissions module will be available from the CHIMERE web page.

### 6.5 Particles local erosion and resuspension

- The dust emissions are mostly modelled over Africa. Over Europe the local contribution is rarely taken into account, even if the relative part may be non negligible as shown by Colette et al. (2008) (by comparisons between lidar data, surface air quality measurements in the Paris area). This was only shown by deriving a specific source over Ukraine to test the capability of CHIMERE to model dust emissions during a specific event (Bessagnet et al., 2008). In addition, saltation is not the only natural aerosol upward entrainment process. Resuspension of freshly deposited small particles lying at the surface by turbulent wind is a distinct process, their extraction resulting from the imbalance between adhesive and lifting forces. Such particles can originate from the atmosphere or the biosphere, and are particularly easy to extract shortly after deposition (Loosmore and Cederwall, 2004).
- In CHIMERE, for the sake of simplicity, we assume that this biogenic aerosol com-15 ponent is of primary origin. In order to represent these processes, we use a bulk formulation based on the simple resuspension rate empirical formula of Loosmore and Cederwall (2004), which was shown to provide a very good fit to the available resuspension measurement data. The particles are first deposited then resuspended. In
- reality, deposition and resuspension are simultaneous, and the available dust concen-20 tration on the ground is governed by resuspension, washout by runoff and absorption by soil water, production by deposition and other biological or mechanical processes. The detail of all these processes is essentially unknown, and we assume here that the available concentration of dust does only depend on the wetness of the surface, as 25
  - fully described in Vautard et al. (2005). In this empirical view, the resuspension flux is (33)

where f(w) is a function of the soil water content, P is a constant tuned in order to approximately close the PM<sub>10</sub> mass and the  $u_*$  dependency follows the Loosmore and Cederwall (2004) formulation. In the absence of any information, the reentrained PM<sub>10</sub> particle mass is supposed to be distributed in a standard atmospheric size distribution:  $_{5}$  2/3 of the mass as PM<sub>2.5</sub> and 1/3 as coarse PM<sub>1</sub>-PM<sub>2.5</sub>. Within PM<sub>2.5</sub>, particles are

# distributed as for the anthropogenic emissions.

## 7 Chemistry

# 7.1 Chemical preprocessor

CHIMERE offers the option to include different gas phase and aerosol chemical mechanisms. The originality in CHIMERE is that these chemical mechanisms are written in 10 a "human readable" format, and, thus, do not need to be compiled. The user can easily change some reactions or add new ones. When the model is launched, the availability of chemistry input files corresponding to the specific simulation is checked. If the data already exist, the run continues. If not, a pre-processor script will create the data directory. The strength of this approach is that the user may easily create very particular 15 chemical schemes. All chemical parts being independent, the user may choose to have gas chemistry or not, aerosols chemistry or not (and the number of bins), sea salt, dust, secondary organic aerosols persistent organic pollutants, tracers or not. At the end of all these choices, one single file is created. To add or change chemical reactions is also simple: an ascii file has to be edited and manually changed. The nomenclature 20 was defined to be easily understandable and the user can build chemistry sensitivity studies by changing reactions rates, photorates etc. The list of active species may

also be changed and the pre-processor recognizes the sum operator to define families: one user defined species is the sum of numerous model species, for example:  $NO_x = NO + NO_2$  and  $NO_x$  is directly an output species in the simulation output file.





# 7.2 Gas phase chemistry

By default, two gas phase and one aerosol scheme are provided. The gas phase mechanisms are MELCHIOR1 (the complete mechanism) and MELCHIOR2 (a reduced version, useful for forecast). The complete chamical mechanism used by CHIMERE is <sup>5</sup> built using a suit of scripts and programs called chemprep.

The original, complete scheme (Lattuati, 1997), hereafter called MELCHIOR1, describes more than 300 reactions of 80 gaseous species. The hydrocarbon degradation is fairly similar to the EMEP gas phase mechanism (Simpson, 1992). Adaptations are made in particular for low  $NO_x$  conditions and  $NO_x$ -nitrate chemistry. All rate constants are updated according to Atkinson et al. (1997) and De Moore et al. (1994). Heterogeneous formation of HONO from deposition of  $NO_2$  on wet surfaces is considered, using the formulation of Aumont et al. (2003). For other heterogeneous reactions, see also Sect. 7.3.3.

Inorganic chemistry (42 reactions) is treated in a classical way, similarly to the original EMEP mechanism, and including the chemistry of SO<sub>2</sub>, NO<sub>x</sub> species, HONO<sub>x</sub>, CO, O<sub>3</sub>, HO<sub>x</sub> radicals etc. Organic chemistry is based on the simplified degradation of 8 hydrocarbons and two alcohols. These compounds represent either individual species, generally for the smallest molecules of a class (methane, ethane, ethene, isoprene and methanol), or families of compounds (*n*-butane for alkanes, propene for alkenes, o-xylene for aromatics, *α*-pinene for terpenes and ethanol for alcohols). These VOCs undergo oxidation reactions with OH, NO<sub>3</sub>, and ozone (the latter being for the unsaturated compounds) leading to the formation of peroxy (RO<sub>2</sub>) radicals. All major reaction pathways of the 25 RO<sub>2</sub> radicals (including those formed by the oxidation of carbonyl compounds or nitrates, see below) are represented in the mechanism (Fig. 12):

- Reactions with NO leading to the formation of carbonyl compounds (including, when significant, the fragmentation pathway)
  - For some RO<sub>2</sub> + NO reactions, a second pathway yielding nitrates is taken into account





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- RO<sub>2</sub> reactions with NO<sub>3</sub>, important during night time, and resulting in the same COV species than the RO<sub>2</sub> + NO reaction
- $\mathrm{RO}_2$  reactions with  $\mathrm{NO}_2$  resulting in the formation of peroxynitrates (including PAN)
- Reaction with HO<sub>2</sub> yielding hydroperoxides. Individual hydroperoxides (15) are taken into account. Their oxidation with OH or by photolysis is treated and yields the carbonyls that would have been resulted from the RO<sub>2</sub> + NO reaction.
  - Recombination reactions of RO<sub>2</sub> radicals. A full treatment would require the treatment of  $1/2(N^2 + N)$  reactions (i.e. 325 for N = 25) and would be too time consuming. This mechanism is simplified by taking into account only the RO<sub>2</sub> reaction with itself, with the most abundant (CH<sub>3</sub>O<sub>2</sub>) and the most reactive (CH<sub>3</sub>COO<sub>2</sub>)RO<sub>2</sub> species. Both the radical terminating and non-terminating recombination pathways are included (101 reactions).

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- Secondary VOC species formed from these reactions are carbonyl compounds (9),
  hydroperoxydes (15), nitrates (9) and peroxynitrates (4). As the primary VOCs, they can undergo reactions with OH, NO<sub>3</sub> and O<sub>3</sub> in addition to photolysis (only for oxidized VOCs). A 0-D study conducted by Dufour et al. (2009) under low and high NO<sub>x</sub> conditions allowed the comparison of formaldehyde yields from 10 organic compounds, simulated by MELCHIOR1 and three reference mechanisms (Master Chemical Mechanism from Saunders et al. (2003), the SAPRC99 scheme developed by Carter (2000) and the fully explicit self-generated chemical scheme SGMM of Aumont et al. (2005)). The results show that MELCHIOR simulated yields agree within 20% with the reference mechanisms, this fair agreement going up to 5% in high NO<sub>x</sub> conditions for C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, CH<sub>3</sub>CHO, *n*-C<sub>4</sub>H<sub>10</sub> and CH<sub>3</sub>OH oxidation.
- <sup>25</sup> In order to reduce the computing time a reduced mechanism with a bit more than 40 species and about 120 reactions is derived from MELCHIOR1 (Derognat et al., 2003). This scheme (MELCHIOR2) is intended for use under polluted conditions. In particular,

the concept of "chemical operators" (Carter, 1990) has been introduced. In a general way, in this concept,  $RO_2$  radicals are treated as virtual species independently of their organic rest R. VOC degradation results in secondary compounds as if the corresponding  $RO_2$  radical reacted with NO. In our scheme, some individual  $RO_2$  radicals are surflicitly token into account (CLL Q. CLL CO(Q.)). C. LL (QLL)Q.

<sup>5</sup> are explicitly taken into account (CH<sub>3</sub>O<sub>2</sub>, CH<sub>3</sub>CO(O<sub>2</sub>), C<sub>5</sub>H<sub>8</sub>(OH)O<sub>2</sub>). As a further reduction step, minor reaction pathways under polluted conditions are neglected. Under polluted and moderately conditions (NO<sub>x</sub> > 100 ppt), differences between the reduced and the complete mechanism are below 5 % for ozone, below 10 % for NO<sub>x</sub> and HO<sub>x</sub>, and below 20 % for OH. These differences are acceptable, in view of often much larger differences with respect to observations.

Photolysis rates are calculated under clear sky conditions as a function of height using the TUV model (Madronich et al., 1998). Then clouds are taken into account in a highly parameterized fashion, where clear sky photolysis rates are multiplied throughout model columns by an attenuation coefficient *A* depending on the total Cloud Optical

<sup>15</sup> Depth COD. Three options for the calculation of COD are available in CHIMERE, thus allowing to fit several meteorological forcings. A future version of CHIMERE will include an on-line version of TUV to take into account hourly variations of aerosols concentrations and their impact of photolysis rates.

A comparison of MECHIOR2 and SAPRC07 (Carter, 2010) for the production of sec ondary organic gaseous species within CHIMERE was recently conducted by Siour et al. (2012) for Europe over a whole summer season in year 2005, with a resolution of 0.16°. For this purpose, SAPRC07 was implemented in CHIMERE, together with a new aggregation table for anthropogenic emitted species and a specific preprocessing of boundary conditions in order to fit the SAPRC lumped species. Also, an up-to-date
 photolysis rate table, using recent data from Sander et al. (2006) and IUPAC (2006, http://www.iupac.org/) was provided for both schemes using the most recent version of the TUV model. The results for ozone show quite comparable correlation coefficients, RMSE and bias (see Table 3) with a slight tendency for SAPRC07 to reduce the averaged overestimation of ozone, compared with a set of 1300 Air Base measurement





stations. A longitudinal cut in a city plume also showed that the two mechanisms produce similar quantities of  $HO_x$  radicals (albeit somewhat lower with SAPRC due to reduced ozone production), the main difference being the speciation of organic nitrogen (approximately 25% of oxidized NOx species in both schemes), which is more in

favor of PAN species when using MELCHIOR2 while SAPRC produces a larger amount of organic nitrates RNO<sub>3</sub> (10% against 5% with MELCHIOR2). This may impact the geographical extent of ozone production. The possibility to select either SAPRC07 or MELCHIOR will be given in the next version of CHIMERE.

In order to reduce the computing time a reduced mechanism with less than species and about 120 reactions is derived from MELCHIOR (Derognat et al., 2003), following the concept of "chemical operators" (Carter, 1990). This reduced mechanism is called MELCHIOR2.

Photolysis rates are calculated under clear sky conditions as a function of height using the TUV model (Madronich et al., 1998). Then clouds are taken into account in a highly parameterized fashion. A future version of CHIMERE will include an on-line version of TUV to take into account hourly variations of aerosols concentrations and their impact of photolysis rates.

# 7.3 Aerosol module

## 7.3.1 Aerosols size distribution

<sup>20</sup> CHIMERE contains a sectional aerosol module which accounts for primary particle material, nitrate, sulfate, ammonium, biogenic secondary organic aerosol (SOA), an-thropogenic SOA and water, as listed in the Table 4 (Bessagnet et al., 2010).

Sulfate is formed by SO<sub>2</sub> oxidation through both gaseous and aqueous phase pathways. Nitric acid is produced in the gas phase by NO<sub>x</sub> oxidation.  $N_2O_5$  is converted into

nitric acid via heterogeneous pathways by oxidation on aqueous aerosols. Ammonia is a primary emitted base converted in the aerosol phase by neutralization of nitric and sulfuric acids. Ammonia, nitrate and sulfate exist in aqueous, gaseous and particulate





phases in the model. As an example, in the particulate phase the model species  $pNH_3$  represents an equivalent ammonium as the sum of  $NH_4^+$  ion,  $NH_3$  liquid,  $NH_4NO_3$  solid, etc.

Atmospheric aerosols are represented by their size distributions and chemical compositions (Bessagnet et al., 2005). The sectional representation described by Gelbard and Seinfeld (1980) has been used for the density distribution function. The sectional approach is quite useful to solve the governing equation for multicomponent aerosols. It discretizes the density distribution function in a finite number of size sections (Warren, 1986) so that all particles in section / have the same composition and are characterized by their mass-median diameter  $D_n$ .

The discretization of the density distribution function q for a given aerosol component, follows Eq. (34)

$$q(x) = \frac{\mathrm{d}Q}{\mathrm{d}x} \tag{34}$$

where x is the logarithm of the mass m of the particle ( $x = \ln(m)$ ) and Q is the mass concentration function.

If  $Q_l^k$  (µg m<sup>-3</sup>) is the mass concentration of the *k*th aerosol component within the size section *l*, then the total mass concentration in the size section *l* is given by Eq. (35)

$$Q_{i} = \int_{x_{i-1}}^{x_{i}} q(x) dx = \sum_{k} Q_{i}^{k}$$
(35)

The range of the discretized size distribution and the number of size sections  $(n_b)$  are both user defined. The default range of the distribution is set to  $40 \text{ nm}-10 \mu\text{m}$ . A good compromise between numerical accuracy and computational time is  $n_b = 8$ , as used in the PREVAIR system (Rouïl et al., 2009) with the following mass-median diameter intervals:  $D_p = 0.039, 0.078, 0.156, 0.312, 0.625, 1.25, 2.5, 5, 10 \mu\text{m}$ .





### 7.3.2 Aerosols dynamics

### Coagulation

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Coagulation is modeled following the classical theory described in Gelbard and Seinfeld (1980). Considering that  $Q_l^k$  is the mass concentration of component k in size section l, the mass balance equation for coagulation follows Eq. (36):

$$\left[\frac{\mathrm{d}Q_{l}^{k}}{\mathrm{d}t}\right]_{\mathrm{coag}} = \frac{1}{2} \sum_{i=1}^{l-1} \sum_{j=1}^{l-1} \left[ {}^{1a}\beta_{i,j,l}Q_{j}^{k}Q_{j} + {}^{1b}\beta_{i,j,l}Q_{i}^{k}Q_{j} \right] - \sum_{i=1}^{l-1} \left[ {}^{2a}\beta_{i,l}Q_{i}Q_{l}^{k} - {}^{2b}\beta_{i,l}Q_{l}Q_{i}^{k} \right] - \frac{1}{2} {}^{3}\beta_{l,l}Q_{l}Q_{l}^{k} - Q_{l}^{k} \sum_{i=l+1}^{m} {}^{4}\beta_{i,l}Q_{i}$$
(36)

The sectional coagulation coefficients  ${}^{1a}\beta$ ,  ${}^{1b}\beta$ ,  ${}^{2a}\beta$ ,  ${}^{2b}\beta$ ,  ${}^{3}\beta$  and  ${}^{4}\beta$  depend on particle characteristics and meteorological data such as temperature, pressure and turbulence parameters (Fuchs, 1964). For submicronic particles, coagulation is essentially driven by Brownian motions.

### **Gas-particle conversion**

The implementation of the absorption process in CHIMERE is based on Bowman et al. (1997). The absorption flux J ( $\mu$ gm<sup>-3</sup>s<sup>-1</sup>) of species onto a monodisperse aerosol is:

 $J = \frac{1}{\tau} (G - G_{eq}) \tag{37}$ 

with *G* and  $G_{eq}$  (µgm<sup>-3</sup>) the gas phase and equilibrium concentrations respectively. The characteristic time  $\tau$  is:

$$\tau = \frac{1 + \frac{8\lambda}{\alpha D_{\rm p}}}{2\pi\lambda c D_{\rm p} N}$$



CC ①

(38)

with  $\lambda$  (m) the mean free path of air molecules,  $D_p$  (m) the diameter of the particles, N (particles m<sup>-3</sup>) the number concentration,  $\alpha$  the accommodation coefficient of the transferred species and c (ms<sup>-1</sup>) the mean molecular velocity. For a semi-volatile species k, a mean absorption coefficient  $H_l^k$  (s<sup>-1</sup>) is defined at section l as:

$$= \left[\frac{\mathrm{d}Q_{j}^{k}}{\mathrm{d}}\right]_{\mathrm{abso}} = H_{j}^{k}Q_{j} \tag{39}$$

$$H_{l}^{k} = \frac{12\lambda c_{k}}{\rho_{p}D_{p}^{2}(1 + (8\lambda/\alpha_{k}D_{p}))}(G^{k} - G_{l,eq}^{k})$$

where  $\rho_{\rm p}$  is the particle density (fixed at 1500 kg m<sup>-3</sup> here).

Different absorption modules are implemented in CHIMERE for the inorganic and organic aerosols.

For *inorganic species* (sulfate, nitrate, ammonium), the equilibrium concentration  $G_{eq}$  is calculated using the thermodynamic module ISORROPIA (Nenes et al., 1998). This model also determines the water content of particles. Chloride and sodium can be optionally included with a significant increase in computational time. The model calculates the thermodynamical equilibrium of the sulfate/nitrate/ammonium/sodium/chloride/water system at a given temperature and relative humidity. The possible species for each phase are the following:

– Gas phase:  $NH_3$ ,  $HNO_3$ , HCI,  $H_2O$ .

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- Liquid phase:  $NH_4^+$ ,  $Na^+$ ,  $H^+$ ,  $CI^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $HSO_4^-$ ,  $OH^-$ ,  $H_2O$ ,  $HNO_{3(aq)}$ ,  $HCI_{(aq)}$ ,  $NH_{3(aq)}$ ,  $H_2SO_{4(aq)}$ .
- Solid phase:  $(NH_4)_2SO_4$ ,  $NH_4HSO_4$ ,  $(NH_4)_3H(SO_4)_2$ ,  $NH_4NO_3$ ,  $NH_4CI$ , NaCI,  $NaNO_3$ ,  $NaHSO_4$ ,  $Na_2SO_4$ .

Due to their low vapor pressure, sulfuric acid and sodium are both assumed to reside completely in the condensed phase. The solid/liquid phase transition is solved with



(40)



ISORROPIA by computing the deliquescence relative humidities (relative humidity at the transition point between the two phases).

Two ways are possible:

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- Reading a look-up table already prepared using ISORROPIA (and provided with the model input data files);
- Using the implemented on-line coupling of ISORROPIA in CHIMERE.

In the case of using the look-up table, the calculation can be done by interpolating a precalculated look-up table (Table 5). The partitioning coefficient for nitrates, ammonium and the aerosol water content has been calculated for a range of temperatures from 260 to 312 K, relative humidities from 0.3 to 0.99 and concentration ranges from  $10^{-2}$ to 65 µg m<sup>-3</sup>. Because of numerical limitations, Sodium and Chloride are not accounted for in this table. In case of the active "sea salt" version, the model automatically switch to the on-line coupling.

The use of the look-up table allows to run the model faster, some errors can occur <sup>15</sup> around each deliquescent point. Comparisons with on-line coupling was done and presented in Hodzic (2005). The use of an on-line coupling leads to a weak decrease of the mean concentrations (13% for the nitrates, and no more than 2% for the sulfates). Ammonium concentrations are slightly increased (1 to 5%). In absolute values, the differences never exceed 0.5  $\mu$ gm<sup>-3</sup> in average for the nitrates and 0.1  $\mu$ gm<sup>-3</sup> for the sulfates and ammonium. The aerosol water content is slightly decreased (3 to 13%, 0.1 to 2.8  $\mu$ gm<sup>-3</sup>).

For *semi-volatile organic species*, the equilibrium concentration of the aerosol component *k* at the size section *l* ( $G_{l,eq}^{k}$ ) is related to the particle concentration  $Q_{l}^{k}$  through a temperature dependent partition coefficient  $K^{p}$  (in m<sup>3</sup>µg<sup>-1</sup>) (Pankow, 1994):



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with OM ( $\mu$ gm<sup>-3</sup>) the concentration of the absorptive organic material. Considering the thermodynamic equilibrium between the gas and particulate phases, this coefficient is given by

$$\kappa_k^p = \frac{10^{-6}RT}{\mathsf{MW}_{\mathsf{om}}\zeta_k p_k^0}$$

- <sup>5</sup> with *R* the ideal gas constant (8.206 × 10<sup>-5</sup> m<sup>3</sup> atmmol<sup>-1</sup> K<sup>-1</sup>), *T* the temperature (K), MW<sub>om</sub> the mean molecular weight (gmol<sup>-1</sup>),  $p_i^0$  the vapor pressure of product *i* as a pure liquid (atm) and  $\zeta$  the activity coefficient of species in the bulk aerosol phase. The coefficient  $\zeta$  is difficult to calculate and is assumed constant and equal to one.
- For the *nucleation* process of sulfuric acid, the parameterization of Kulmala and Pirjola (1998) is used. This process, favoured by cold humid atmospheric conditions, affects the number of ultrafine particles. The nucleated flux is added to the smallest bin in the sectional distribution. Nucleation of condensable organic species has been clearly identified in many experimental studies (Kavouras et al., 1998), there is no available parameterization. Since, the sulfuric acid nucleation process competes with absorption processes, it is expected to occur in low particle polluted conditions.

# 7.3.3 Aerosols chemistry

# **Multiphase chemistry**

Sulfate production in the aqueous-phase occurs from the following reactions (Berge, 1993; Hoffman and Calvert, 1985; Lee and Schwartz, 1983):

$$- \operatorname{SO}_2^{\operatorname{aq}} + \operatorname{O}_3^{\operatorname{aq}} \to \operatorname{SO}_4^{2-}$$

 $- \operatorname{HSO}_{3}^{-} + \operatorname{O}_{3}^{\operatorname{aq}} \to \operatorname{SO}_{4}^{2-}$  $- \operatorname{SO}_{3}^{2-} + \operatorname{O}_{3}^{\operatorname{aq}} \to \operatorname{SO}_{4}^{2-}$ 

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(42)



- $SO_2^{aq} + H_2O_2^{aq} \rightarrow SO_4^{2-}$ -  $SO_2^{aq} + NO_2^{aq} \rightarrow SO_4^{2-}$ -  $SO_3^{2-}(Fe^{3+}) \rightarrow SO_4^{2-}$ -  $HSO_3^{-}(Mn^{2+}) \rightarrow SO_4^{2-}$
- SO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> in the aqueous phase are in equilibrium with the concentrations in the gas phase. Moreover, aqueous SO<sub>2</sub> is dissociated into HSO<sub>3</sub><sup>-</sup> and SO<sub>3</sub><sup>2-</sup>. Catalyzed oxidation reactions of sulfur dioxide in aqueous droplets with iron and manganese are considered, following Hoffman and Calvert (1985) among others. Henry's law coefficient and other aqueous equilibrium constants are used (Seinfeld and Pandis, 1997).
   Sulfur chemistry is very pH sensitive and to avoid large but uncontroled variations, the pH may vary only between 4.5 and 6.0 to be realistic.

A few heterogeneous reactions are also considered. Nitric acid is produced onto existing particles and fog droplets. Although aerosol particles and cloud droplets represent a small fraction of the atmosphere, it is well established that reactions involving

- gas species onto their surfaces may significantly contribute to atmospheric chemistry cycles. For ozone modeling, Jacob (2000) recommends to include a minimal set of reactions:
  - HO<sub>2</sub>  $\rightarrow$  0.5H<sub>2</sub>O<sub>2</sub>  $\gamma$  = 0.2
  - $\text{NO}_3 \rightarrow \text{HNO}_3 \qquad \gamma = 0.001$

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- $NO_2 \rightarrow 0.5HNO_3 + 0.5HONO$   $\gamma = 0.0001$ 
  - N<sub>2</sub>O<sub>5</sub>  $\rightarrow$  2HNO<sub>3</sub>  $\gamma = 0.01-1$

with  $\gamma$  the associated uptake coefficients are provided in Harrison and Kito (1990), and other references in Jacob (2000).





The first-order rate constant k for heterogeneous loss go gases onto particles is given by:

$$k = \sum_{l} \left( \frac{D_{\rm p}(l)}{2D_{\rm g}} + \frac{4}{v\gamma} \right)^{-1} A_{l}$$

with  $D_p$ , the particle diameter (m),  $D_g$ , the reacting gas molecular diffusivity (m<sup>2</sup> s<sup>-1</sup>),  $\nu$ , the mean molecular velocity (m s<sup>-1</sup>),  $A_I$ , the total surface area in the particle bin

/ and  $\gamma$  the uptake coefficient of reactive species. The uptake coefficient for N<sub>2</sub>O<sub>5</sub> is assumed to be temperature-dependent in the range 0.01–1 (De Moore et al., 1994) with increasing values for decreasing temperatures. A recent study (Aumont et al., 2003) suggests that NO<sub>2</sub> reactions on wet surfaces could be an important source for HONO production during wintertime smog episodes, so, a new reaction is added (also present in the gas-phase mechanism, see above).

### Secondary organic aerosol chemistry

The complete chemical scheme implemented in CHIMERE includes biogenic and anthropogenic precursors (Table 6) as described in Bessagnet et al. (2009). Biogenic precursors include API ( $\alpha$ -pinene and sabinene), BPI ( $\beta$ -pinene and  $\delta^3$ -carene), LIM (limonene), OCI (myrcene and ocimene) and ISO (isoprene). Anthropogenic precursors include TOL (benzene, toluene and other mono-substituted aromatics), TMB (Trimethylbenzene and other poly-substituted aromatics), and NC4H10 (higher alkanes). SOA formation is represented according to a single-step oxidation of the relevant precursors and gas-particle partitioning of the condensable oxidation products.

vant precursors and gas-particle partitioning of the condensable oxidation products. The gas-particle partitioning formulation has been described in detail by Pun et al. (2006). The overall approach consists in differentiating between hydrophilic SOA that are most likely to dissolve into aqueous inorganic particles and hydrophobic SOA that are most likely to absorb into organic particles. The dissolution of hydrophilic SOA is governed by Henry's law whereas the absorption of hydrophobic particles is governed



(43)



by Raoult's law. The large number of condensable organic compounds is represented by a set of surrogate compounds that cover the range of physico-chemical properties relevant for aerosol formation, i.e. water solubility and acid dissociation for hydrophilic compounds and saturation vapor pressure for hydrophobic compounds. These surrogate compounds were selected by grouping identified particulate-phase molecular products with similar properties. The molecular weight of each surrogate compound

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is determined based on its structure and functional groups. The Henry's law constant or the saturation vapor pressure of the surrogate species is derived from the average properties of the group. Other properties are estimated using the structure of each surrogate compound. Enthalpy of vaporization are given in brackets (kJ mol<sup>-1</sup>) for each SOA coumpounds: AnA0D (88), AnA1D(88), AnA2D(88), BiA0D(88), BiA1D(88), BiA2D(109), AnBmP(88), AnBIP(88), BiBmP(175). The full name of compounds are

explicited in Table 6 caption.
 The base SOA module was tested against the smog chamber data of Odum et al.
 (1997) for anthropogenic compounds and those of Griffin et al. (1999) for biogenic compounds and was shown to satisfactorily reproduce SOA formation for those compounds (Pun et al., 2006). Higher alkanes and isoprene were added to the original chemical mechanism of Pun et al. (2006). The formation of SOA from higher alkanes follows the formulation of Zhang et al. (2007) for the stoichiometric SOA yield and it is assumed

<sup>20</sup> that the SOA species can be represented by a hydrophobic surrogate compound with a moderate saturation vapor pressure. The formation of SOA from the oxidation of isoprene by hydroxyl radicals is represented with two surrogate products and follows the formulation of Kroll et al. (2006) and (Zhang et al., 2007).

The base SOA module described here was compared with the Aerosol Mass Spec-<sup>25</sup> trometer measurements in Mexico City during the MILAGRO-2006 field project (Hodzic et al., 2009), and the results have shown that the current parameterization tends to severely underpredict, i.e. by 2–8 times the observed levels of SOA in the city as well as at the regional scale downwind of the city. The model has been updated to include the SOA formation from primary organic vapors that has been proposed as an additional





and important source of SOA (Robinson et al., 2007), and that has allowed to significantly improve the comparison with measurement in Mexico City (Hodzic et al., 2010a). Additional constraints from measurements have been included through the calculation of the oxygen to carbon ratios, or the modern carbon amounts (Hodzic et al., 2010b). The code is available upon request

5 The code is available upon request.

## 8 Dry deposition

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The dry deposition process is, as commonly, described through a resistance analogy (Wesely, 1989). These resistances are not expressed in the same way, considering gas or particles as displayed in Fig. 13.

The deposition process is a sink and only acts on a concentration *c* along the vertical, as:

$$\Delta c = \frac{\partial}{\partial z} (V_{\rm d} \cdot c) \tag{44}$$

with  $V_d$  the dry deposition velocity. For each gaseous species or particles, the deposition is due to three different processes. First, the turbulent diffusivity is needed to estimate the aerodynamical resistance,  $r_a$ . Second the diffusivity near the ground, in the "laminar" layer, is needed to estimate the surface resistance  $r_b$ . Third, and for gaseous species only, the species solubility is needed to estimate the canopy resistance  $r_c$ . For particles, there is no solubility, the particle only reaches the ground but this is done under an additional force called the settling velocity,  $v_s$ .

The dry deposition velocity (in  $cm s^{-1}$ ) is expressed for gaseous species as:

$$v_{\rm d} = \frac{1}{r_{\rm a} + r_{\rm b} + r_{\rm c}}$$

and for particles as:

$$v_{\rm d} = v_{\rm s} + \frac{1}{r_{\rm a} + r_{\rm b} + r_{\rm a}r_{\rm b}v_{\rm s}}$$

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### 8.1 Settling velocity v<sub>s</sub>

The settling velocity represents the effect of gravity on particles. This velocity is expressed as:

$$v_{\rm s} = \frac{1}{18} \frac{D_{\rm p}^2 \rho_{\rm p} g C_{\rm c}}{\mu}$$
(47)

<sup>5</sup> with  $\rho_p$ , the particle density (chosen as  $\rho_p = 2.65 \text{ g cm}^{-3}$  for mineral dust),  $D_p$  the mean mass median diameter of particles,  $C_c$  a "slip correction factor". *g* is the gravitational acceleration with  $g = 9.81 \text{ ms}^{-2}$ ,  $\mu$  the dynamic viscosity (here the air dynamic viscosity is used as  $\mu_{air} = 1.8 \times 10^{-5} \text{ kgm}^{-1} \text{ s}^{-1}$ ).

The slip correction factor has to be estimated as:

<sup>10</sup> 
$$C_{\rm c} = 1 + \frac{2\lambda}{D_{\rm p}} \left[ 1.257 + 0.4 \exp\left(-\frac{1.1D_{\rm p}}{2\lambda}\right) \right]$$

with  $\lambda$  the mean free path of air, estimated as:

$$\lambda = \frac{2\mu_{\text{air}}}{\rho\sqrt{\frac{8M_{\text{air}}}{\pi RT}}}$$
(49)

with  $M_{air}$  the molecular mass of dry air (here 28.8 gmol<sup>-1</sup>), T the temperature (K), p the pressure (Pa),  $\mu$  the air dynamic viscosity.

#### 15 8.2 The resistances

The aerodynamical resistance  $r_a$  depends on several turbulent parameters such as L the Monin–Obukhov length, the friction velocity  $u_*$ , the dynamical roughness length



(48)



Z<sub>0m</sub>.

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$$r_{\rm a} = \frac{1}{ku_*} \left[ \ln \left( \frac{z}{z_0} \right) - \Psi_{\rm M} \left( \frac{z}{L} \right) \right]$$

where  $\Psi_{\text{M}}$  is the stability function, defined and calculated during the meteorological diagnostic before a CHIMERE simulation.

The quasi-laminary boundary layer resistance  $r_{\rm b}$  factor is estimated as:

$$r_{\rm b} = \frac{2v}{k \times D {\rm H}_2 {\rm O}_{\rm w} {\rm Pr}} D {\rm H}_2 {\rm O}_{\rm g}^{2/3}$$
(51)

with *k* the Karman number (here k = 0.41),  $DH_2O_w$  and  $DH_2O_g$  the molecular diffusivity of water and gaseous species, respectively, and Pr the Prandl number. For gaseous species, the molecular diffusivity is expressed as:

$$_{0} DH_{2}O_{g} = \sqrt{\frac{dMx}{18}}$$
(52)

The main land/seasonal parameters follow seasonal variations of resistances. Most land parameters are taken from Wesely (1989), but LAI are drawn from the NASA/EOSDIS Oak Ridge National Laboratory using average LAI field measurements for Summer. The molar masses used in CHIMERE are displayed in Table 7.

<sup>15</sup> The formulation of the surface resistance  $r_c$  follows Erisman et al. (1994). It uses a number of different other resistances accounting mainly for stomatal and surface processes which are again dependent on the land use type and season. Necessary chemical parameters for the calculation of  $r_c$  are also taken from Erisman et al. (1994) except for carbonyls (Sander et al., 1999; Baer and Nester, 1992) and peroxide species (Hall et al., 1999). As presented in Table 7, dHx and df0 are used for the mesophyllic resistance value as described in Seinfeld and Pandis (1997). The mesophyllic resistance



(50)



 $r_{\rm m}$  is calculated for each deposited species as:

$$r_{\rm m} = \frac{1}{\rm dHx \times 3.310^{-4} + \rm df0 \times 10^2}$$

Over vegetal canopies, corrections have been implemented according to Zhang et al. (2001); Giorgi (1986) and Peters and Eiden (1992).

#### 5 9 Impact of clouds

The clouds may impact the photolysis, the chemistry via dissolution of gases in precipitating drops and wet scavenging.

#### 9.1 Impact of clouds on photolysis

In this model version and only for the photolysis attenuation, clouds are assumed to <sup>10</sup> lie above the model top, so that there is no cloud albedo effect within the model domain depth. For all photolysed species, clear sky photolysis rates  $J_c(z)$  are multiplied throughout model columns by an attenuation coefficient A(d) depending on the total cloud optical depth (COD) *d*. Using the TUV model, and a large set of CODs for clouds at various altitudes, the attenuation relative to the clear-sky case has been fitted as <sup>15</sup> a function of COD with the formula:

$$A(d) = e^{-0.11d^{2/3}}$$

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Several options are offered in order to calculate the COD. Total COD, d, is the sum of partial CODs from 3 cloud layers, low clouds  $d_1$ , medium clouds  $d_m$  and high clouds  $d_h$ . The limits between these clouds is user-chosen, but depend on the meteorological model. For WRF or MM5, limits of 2000 m and 6000 m are proposed. For each cloud layer, three options are possible for the calculation of the partial cloud optical depth:

(53)

(54)



- Calculation as a function of liquid/ice water content in the column; using an assumption of sphericity and equivalent droplet size of 6 microns, an assumption of hexagonal shape for ice particles, the formula for cloud optical depth is  $180 \cdot C_w + 67 \cdot C_i$ , where  $C_w$  and  $C_i$  are respectively the liquid water column (in kgm<sup>-2</sup>) and ice column for this cloud layer.
- Liquid/Ice water are generally unverified and unstable parameters in atmospheric models. Basing a cloud parameterization on such parameters can be risky. A more robust parameterization consists in using relative humidity only. The proposed parameterization consists in parameterizing the COD as a function of the integral *R*, over the cloud depth, of the relative humidity above 75%. It is assumed that small cloud formation (in particular cumulus clouds) starts at 75% relative humidity. Normalization of *R* leads to the formulation (for instance for low clouds):  $d_1 = aR/dz$ , where a = 0.02 is chosen such that a 1000 m-thick layer has an optical cloud depth of 20.
- An even simpler parameterization can be achieved by making the COD simply proportional to the cloud fraction (if available) for each cloud layer. Coefficient tuning led to proportionality coefficients of: 50 for low-clouds, 10 for medium clouds and 2 for high clouds. This means, for instance, that a sky covered with 100% of high clouds has an optical depth of 2. Tuning was performed with ECMWF cloud fraction data and should change with the meteorological model.

### 9.2 Wet scavenging

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Scavenging for gas/aerosols in clouds or rain droplets is taken into account as follows:

- For gases in clouds: Nitric acid, ammonia in the gas phase are scavenged by cloud droplets and this process is assumed to be revertible. During cloud dissipation, and for a non precipitating cloud, dissolved gases may reappear in the gas
- phase (Bessagnet et al., 2004). For a gas denoted A, the processes between the





two phases, gas and aqueous, the two following simultaneous reactions may be written:

$$A^{g} \xrightarrow{k^{+}} A^{aq}; A^{g} \xleftarrow{k^{-}} A^{aq}$$

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The constants  $k^{-}$  and  $k^{+}$  (s<sup>-1</sup>) are estimated following the relations:

$$k^{-} = \frac{6w_{\rm l}\rho_{\rm a}}{\rho_{\rm e}D} \left(\frac{D}{2D_{\rm A}^{\rm g}} + \frac{4}{c_{\rm A}\alpha_{\rm A}}\right)^{-1}$$
(56)  
$$k^{+} = \frac{600}{RH_{\rm A}T} \left(\frac{D}{2D_{\rm A}^{\rm g}} + \frac{4}{c_{\rm A}\alpha_{\rm A}}\right)^{-1}$$
(57)

with  $\rho_e$  and  $\rho_a$  the water and air densities, respectively, in kgm<sup>-3</sup>,  $w_l$  the liquid water content (kgkg<sup>-1</sup>), *D* the droplet mean diameter (*m*),  $c_A$  the mean molecular velocity of the gas *A* (ms<sup>-1</sup>),  $D_A^g$  the molecular diffusion of the gas *A* in air (in m<sup>2</sup>s<sup>-1</sup>) and  $\alpha_A$  the gas *A* accomodation coefficient. *H* is the Henry's constant (Matm<sup>-1</sup>), *T* the air temperature (*K*) and *R* the molar gas constant.

 For gases in rain droplets below the clouds: Dissolution of gases in precipitating drops is assumed to be irrevertible, both for HNO<sub>3</sub> and NH<sub>3</sub>. The scavenging coefficient is expressed as:

$$\Gamma = \frac{\rho D_{\rm g}}{6.10^5 u_{\rm g} D^2} (2 + 0.6 R e^{1/2} {\rm Sc}^{1/3})$$
(58)

*p* being the precipitation rate (mmh<sup>-1</sup>),  $D_g$  the molecular diffusion coefficient (m<sup>2</sup>s<sup>-1</sup>),  $u_g$  the raindrop velocity (ms<sup>-1</sup>), *Re* and Sc respectively the Reynolds and Schmidt numbers of drops. Mircea and Stefan (1998) and references therein

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(55)



give relationships between  $u_g$  and hydrometeor diameter for various types of precipitation. In the model, sulfur dioxide and hydrogen peroxide are also scavenged by precipitation.

 For particles in clouds: particles can be scavenged either by coagulation with cloud droplets or by precipitating drops. Particles also act as cloud condensation nuclei to form new droplets. This latter process of nucleation is the most efficient one in clouds. According to Tsyro (2002) and Guelle et al. (1998), the deposition flux is written as:

$$\left[\frac{\mathrm{d}Q_{l}^{k}}{\mathrm{d}t}\right] = -\frac{\varepsilon_{l}P_{\mathrm{r}}}{w_{\mathrm{l}}h}Q_{l}^{k}$$

- where  $P_r$  is the precipitation rate released in the grid cell (gcm<sup>-2</sup>s<sup>-1</sup>),  $w_l$  the liquid water content (gcm<sup>-3</sup>), h the cell thickness (cm) and  $\epsilon$  an empirical uptake coefficient (in the range 0–1) depending on particle composition. *I* and *k* are respectively the bin and composition subscripts.
  - For *particles* in *rain droplets below the clouds*: particles are scavenged by raining drops, the deposition flux of particles being:

$$\left[\frac{\mathrm{d}Q_{I}^{k}}{\mathrm{d}t}\right] = -\frac{\alpha p E_{I}}{u_{g}} Q_{I}^{k} \tag{60}$$

with  $\alpha$  is an empirical coefficient, p the precipitation rate in the grid cell (gcm<sup>-2</sup>s<sup>-1</sup>), E a collision efficiency coefficient between particles and raining drops (Slinn, 1983) and  $u_g$  the falling drop velocity (cms<sup>-1</sup>). Assuming a constant drop diameter (2 mm), this parameterization is an approximation of equations described in Seinfeld and Pandis (1997) and Jung et al. (2002). In the next developments, this equation will be improved.



(59)

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# 10 Model results evaluation

CHIMERE integrates a large set of complex processes and delivers chemical concentrations. These chemical concentrations fields have to be compared to available measurements in order to: (i) understand complex and non-linear processes and investigate geophysical hypotheses; (ii) validate the model for specific chemical species

vestigate geophysical hypotheses; (ii) validate the model for specific chemical species and location against measurements and therefore estimate the realism of the parameterizations in the model; (iii) make sensitivity and scenario studies in order to quantify changes in emissions or meteorology under climate change etc.

For all these reasons, the comparisons between modeled concentrations and mea-<sup>10</sup> surements were always carefully performed during the various stages of the model developments. These comparisons were carried out with three different options:

- Improve the processes:

The comparisons to field campaings measurements allow an assessment of the model ability to reproduce specific air quality episodes using a wide range of available measurements;

- Dynamic evaluation:

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Long-term simulations can be used to evaluate the sensitivity of the model to changing situations (monthly variability, seasonal cycles, long term trends in emissions,  $\dots$ );

20 – Compare to other numerical tools:

Model inter-comparison exercices allow comparing the performances of the model with respect to other state of the art models and developping ensemble approaches.

### 10.1 International projects

<sup>25</sup> The Table 8 summarizes some of the international projects where CHIMERE was involved. Some of them include large-scale field campaigns, with data measurements





during Intensive Observations Periods that were used to understand pollution events, for the model development and its validation. Many other national projects (french, spanish, italian etc.) were conducted during the last years and are not listed here.

Some of these projects include field campaigns which constitute an opportunity to use a wide range of measurements during selected pollution events. The measurements are limited in space (a region) and time (several days) but they include a larger set of physical and chemical parameters than basic monitoring networks.

The first field campaign using CHIMERE was ESQUIF during the summers 1998 and 1999. In this first version, the model was a box model: five boxes with a central one representing the Paris city and only two vertical levels (the surface and the bound-

ary layer) (Menut et al., 2000a). Even if that model version was very simple, the model was used in forecast mode and was of great help to choose the best periods to launch the intensive observation periods (IOPs), more particularly for airborne measurements (Menut et al., 2000b; Vautard et al., 2003). During ESQUIF, the relative part of local

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- <sup>15</sup> ozone production and long-range transport was quantified and it was shown that Paris pollution episodes can not be above the legal limits with local production only. For the first time, the predicted aerosol chemical and optical properties were evaluated against chemically specified aerosol data and lidar measurements (Hodzic et al., 2006b). In 2001, CHIMERE was also used for forecast and analysis during the ESCOMPTE cam-
- <sup>20</sup> paing that was also devoted to photo-oxidant pollution (ozone) but in the Marseille area, in southern France (Menut et al., 2005a). Between ESQUIF and ESCOMPTE, the horizontal grid became cartesian (Schmidt et al., 2001) and covered the lower troposphere with 8 levels.

For the GEMS project, the model was spatially extended to the whole Western Europe, switching the anthropogenic source to the EMEP emissions. These emissions have been changed for the MACC project and the TNO inventory was implemented (Zyryanov et al., 2012).

In 2006, mineral dust emissions and transport were added in the model and used during the AMMA campaing. The model ran in forecast mode and the previsibility of





mineral dust emissions was thus quantified (Menut et al., 2009a). During the same period, aerosols were implemented in the model. The model version with gaseous and aerosols species was used during several projects such as MILAGRO, over the Mexico area (Hodzic et al., 2009, 2010a,b; Hodzic and Jimenez, 2011); MEGAPOLI over

- the Paris area (Royer et al., 2011), EC4MACS for the climate and air pollution miti-5 gation strategies in Europe, AQMEII for model inter-comparisons between the United States and Europe (Pirovano et al., 2012). More recently, two European projects have been the opportunity of new developments: the CIRCE project where the first on-line coupling between chemistry and vegetation was done between CHIMERE and OR-CHIDEE, and ATOPICA for the development of a new module for the pollen modelling.
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#### 10.2 Evaluation in extreme events

Air quality simulations are particularly relevant during extreme events in order to anticipate potentially detrimental situations. CHIMERE was used to simulate air quality in several such events. It was shown to faithfully reproduce observed ozone concentrations during the 2003 European heat wave (Vautard et al., 2005) and transport of

- 15 aerosol smoke plumes (Hodzic et al., 2007) across Europe during the 2003 heat wave. The extreme particulate matter episode that took place in Germany earlier in 2003 was also simulated but with less success by CHIMERE as well as other models (Stern et al., 2008).
- In 2008, an unexpected event of high particulate matter concentrations at the surface 20 was observed in Belgium and Netherlands. First thought to be long-range transport of mineral dust from Africa, these huge concentrations were finally identified as coming from Ukraine. This assessment was achieved by including a new dust mineral source representing the erodible Chernozemic soil. The validation was done with surface (Air-Base) and space-borne lidar (Caliop) measurements (Bessagnet et al., 2008). 25

CHIMERE was used to simulate the transport of the plume of the extreme fire incident that occurred in the Buncefield oil depot in late 2005 (Vautard et al., 2007). It was shown in particular that the lack of major air quality degradation was due to the





dispersion and transport of the enormous plume of particulate matter above the boundary layer.

More recently, the dispersion of the Eyjafjallajökull in April 2010 was modelled by adding a volcanic source in Iceland. This source was roughly estimated to deliver <sup>5</sup> a near real-time assessment of the ash plume dispersion which was validated against monitoring stations and lidar remote sensing (Colette et al., 2011a). The main challenge for atmospheric volcanic emission is the knowledge of the total mass emitted as well as the granulometry and the injection height. As a first estimate, volcanic tracers are considered to be chemically inert.

#### 10 10.3 Long term evaluation

The long term evaluation of a model is certainly the oldest way to estimate its accuracy during pollution events: not only should the model be able to simulate specific and huge pollution events, it also has to calculate accurately low concentrations in absence of pollution.

- <sup>15</sup> For a CTM, the air quality networks are able to continuously deliver hourly concentrations of O<sub>3</sub>, NO<sub>2</sub> and particulate matter over the past decades. Depending on the model domain and resolution, CHIMERE results have always been compared to surface data: the changes during the last ten years were the duration of these comparisons which is directly related to the computational capabilities. The first comparisons were done for
- <sup>20</sup> a few days and over a limited region, the Paris area (Menut et al., 2000b) to a full year (Hodzic et al., 2004, 2005), then a few month and over largest domains: for example, Spain in Vivanco et al. (2009) and the western Europe in Colette et al. (2011b) and Wilson et al. (2012). In Europe, the AirBase network is used in a lot of studies to compare CHIMERE results to surface observations of O<sub>3</sub>, NO<sub>2</sub>, SO<sub>2</sub>, PM<sub>10</sub>, PM<sub>2.5</sub>. To extend
- the comparison to vertical profiles, several data types were used: for ozone, vertical profiles of sondes and ozone analyser aboard commercial aircraft (MOZAIC/IAGOS) were compared to model outputs (Coman et al., 2012; Zyryanov et al., 2012).





Satellite data have also been used for long-term evaluation studies as listed in Table 9. CHIMERE has been confronted to  $NO_2$  satellite observations (tropospheric columns) from SCIAMACHY (Blond et al., 2007), OMI (Huijnen et al., 2010) and GOME (Konovalov et al., 2005). CHIMERE has been evaluated against AOD measurements from MODIS and POLDER satellites (Hodzic et al., 2006c, 2007).

Satellite ozone observations from satellite and AQ models can now be used synergistically either to evaluate models, to interpret satellite observations or to constrain models through assimilation. In this way, Konovalov et al. (2006) used SCIAMACHY  $NO_2$  columns to optimize  $NO_x$  surface emissions. Zyryanov et al. (2012) have evaluated

<sup>10</sup> CHIMERE and MACC AQ models against IASI 0–6 km ozone columns over one summer. Coman et al. (2012) have recently shown the possibility to use IASI observations to correct CHIMERE model using an assimilation approach. Dufour et al. (2009) and Curci et al. (2010) applied inverse modeling of fomaldehyde columns (SCIAMACHY and OMI, respectively) to estimate and validate biogenic VOC emissions at the European scale.

### 10.4 Models inter-comparisons and ensembles

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CHIMERE has been involved and tested in a number of inter-comparison studies with other air pollution models. In order to evaluate the sensitivity of air quality to emission control scenarios and its uncertainty, several models were evaluated over a reference year and then used with emission scenarios. This work was conducted in the framework of the Clean Air For Europe program (Cuvelier et al., 2007; Thunis et al., 2007), over four European cities. The evaluation part of the project (Vautard et al., 2007) showed the large spread of model simulations for ozone close to the sources due to combined effects of titration and poor representation of lower-layer mixing in stable boundary layers. This spread gave rise to a spread of response to emission control scenarios (Thunis et al., 2007). At continental scale, this spread was less marked (Van Loon et al., 2007). In this inter-comparison over Europe, CHIMERE was found to have among the best skills for ozone daily maxima but an overestimation of nighttime





ozone concentration, leading to a general positive bias, not generally shared by other models. This bias is thought to be due in large parts to overestimation of mixing in stable conditions. For particulate matter, CHIMERE was shown to exhibit a negative bias, shared by other models, at least over several high wintertime episodes in Germany

- Stern et al., 2008). Such biases were also found in a more recent and extensive intercomparison over two continents and a full evaluation year (Rao et al., 2011; Solazzo et al., 2012b,a). In this unprecedented exercise, models used in Europe and in North America were considered. CHIMERE also participated to the first multi-model decadal air quality assessment in the CityZen project (Colette et al., 2011b) and proved to be in-
- <sup>10</sup> line with other state-of-the-art tools. The same biases as previously reported (positive for mean ozone and negative for particulate matter) where obtained by the majority of the models. As far as CHIMERE was concerned, the usual strenght in capturing ozone variability through a good temporal correlation was found.

In these inter-comparison studies, the potential to use these ensemble of models to (i) improve the simulation of air pollutant concentrations by a proper averaging of results and (ii) to estimate the uncertainty in the simulations was evaluated (Solazzo et al., 2012b). It was shown in particular that the average of model results outperformed each individual model results (Van Loon et al., 2007), and that for most pollutants the spread of models was representative of their uncertainty and skill (Vautard et al., 2009).

### 20 11 Hybridation between model and observations

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The direct chemistry-transport model uses meteorology and emissions as forcings to calculate pollutants concentrations fields. The hybridation consists in assimilating observations during a simulation in order to: (i) optimize one of the forcing parameter (inverse modelling), (ii) build more realistic concentrations fields (data assimilation analysis).





### 11.1 Sensitivity studies

For several of these applications, the adjoint model is a powerful tool and may be used for sensitivity studies and inverse modelling. The first adjoint of CHIMERE was developed in 1998 and used to optimize the boundary conditions of the box-model version

<sup>5</sup> (Vautard et al., 2000; Menut et al., 2000a). An updated version was developed when CHIMERE was modified to use a cartesian mesh (Menut, 2003). CHIMERE being updated every year, the adjoint model should follow the same evolution: unfortunately, the last adjoint version was the one developed for the gaseous species. When the aerosols were added (Bessagnet et al., 2004), the adjoint part was not upgraded. Currently, a new branch of the model ajoint is under development to have a parallel version to apply to regional CO<sub>2</sub> fluxes inversion over western Europe (Broquet et al., 2011).

The adjoint model was used to quantify to which input parameter the modelled concentrations are sensitive (Menut, 2003). The studies done with CHIMERE were for the Paris area pollution: the calculations were performed to calculate the sensitivity of

- $_{15}$  O<sub>3</sub>, O<sub>x</sub> and NO<sub>x</sub> to various meteorological parameters and surface emissions fluxes (per activity sectors). An example of synthesized results is presented in Fig. 14. The sensitivity is estimated for a specific concentration (here NO<sub>x</sub> at 09:00 UTC and O<sub>3</sub> at 15:00 UTC in the Paris center grid cell) to the whole domain emissions of traffic and solvents. This shows that NO<sub>x</sub> are more sensitive to emissions than O<sub>3</sub>, quantifying the direct effect of modelling primary and secondary species. The sensitivity may be
- positive (a direct addition of  $NO_x$  by traffic emissions will increase instantaneously NO concentrations) or negative (O<sub>3</sub> titration by NO<sub>2</sub>). This kind of study allowed us to classify the most important parameters in a chemistry-transport model, depending on the modelled pollutants, the location and the time.
- <sup>25</sup> Another way to make sensitivity studies is the Monte Carlo modelling. The same pollution events were studied over the Paris area and results have allowed us to quantify the variability of pollutants and thus to refine the uncertainty of the modelled







concentrations as a function of the uncertainties of the input parameters (Deguillaume et al., 2008).

### 11.2 Inverse modelling

Over the Paris area, the inversion of anthropogenic emissions was done for specific
pollution events and seasonal simulations. These studies were an opportunity to develop a new approach. The surface measurements used are less numerous than the grid points to invert: this weak-constrained problem is often circumvented at the global scale by inverting the emissions of the same specie than the measured one and considering large areas and long timescale. For regional studies and photo-oxidant pollution,
the time and spatial variability is large and a methodology of dynamical areas was developed and applied (Pison et al., 2006, 2007). For the Paris area, the results enabled us to optimize the diurnal profiles of the emissions and show that the city center emissions were over-estimated in emissions inventories whereas the suburb emissions

were often underestimated. An example of optimized coefficients is displayed in Fig. 15 for NO emissions at 05:00 UTC, when the traffic becomes important.

### 11.3 Data assimilation

Following the approach developed in meteorology and oceanography, data assimilation has been applied to air quality since the beginning of this century. In the case of ozone, ground based observations from air quality networks have been used to correct regional CTMs (Hanea et al., 2004; Wu et al., 2008). In the case of the CHIMERE model, Blond et al. (2003) and Blond and Vautard (2004) have developed an optimal interpolation method where they used an anisotropic statistical interpolation approach to determine a climatological background covariance matrix (Blond et al., 2003). This matrix allows them to give weights to innovations (differences between model and observations) and to propagate this information where no observations are directly avail-



able. Over a European domain they improve RMSE by about 30%. As already stated

by Elbern and Schmidt (2001), forecast using these analyses as initial conditions were only slightly improved in few particular cases. The work of Blond and Vautard (2004) has been implemented in the PREVAIR platform that produces operationally ozone analysis (Honoré et al., 2008). Such analyses are also produced in the framework of the FP7/MACC-II project as well as  $PM_{10}$  analysis derived from a similar approach

(http://www.gmes-atmosphere.eu/services/raq/).

5

Since 2006, an ensemble Kalman filter (EnKF; Evensen, 1994) has been coupled to the CHIMERE model. It is also a sequential assimilation method but it allows calculating a time-evolutive background covariance matrix that takes into account the variability

- of model errors with time and space. It is based on a Monte Carlo approach using an ensemble of direct simulation to calculate the background covariance matrix. To do so, we have followed the precursor work of Hanea et al. (2004) that coupled an EnKF to the LOTOS-EUROS model. One of our goals was to assimilate satellite data that would complement surface observations. Indeed, since 2006, the IASI instrument on
- <sup>15</sup> board the METOP platform (Clerbaux et al., 2009) allows us to observe ozone concentrations in the lower atmosphere (0–6 km partial columns) with a good accuracy (Eremenko et al., 2008; Dufour et al., 2012). Coman et al. (2012) have shown that assimilating IASI 0–6 km columns in the CHIMERE model allows correcting significantly tropospheric ozone fields, Fig. 16. Corrections were higher at about 3–4 km height
- where the instrument and retrieval method exhibit maximum sensitivity. In spite of a reduced sensitivity of the instrument in the planetary boundary layer, Coman et al. (2012) also showed that surface ozone fields were systematically improved.

In the near future, it is planned to produce analyses by assimilating simultaneously surface ozone and satellite ozone. Such a product could be of great interest to study

tropospheric ozone variability and trends especially in region were in situ observations are scarce such as the Mediterranean basin. This CHIMERE-EnKF software will be tested operationally during the FP7/MACC-II project. Moreover, assimilation of other species such as NO<sub>2</sub> and CO (from satellite) is planned in the framework of the same MACC-II project.





### 12 Forecast

Air quality forecast is one main goal of chemistry-transport modeling, but it is also a specific way to improve and to validate models (Menut and Bessagnet, 2010). Indeed, forecast makes it possible to quantify day by day the model accuracy and to measure its sensitivity to the various parameters and parameterizations, by studying its predictability.

### 12.1 Experimental forecast

Since its early developments, CHIMERE has been used both for analysis and forecast. For the release of every new model version, the developments priorities were driven by
 the results of test case analyses and daily experimental forecasts. A recent example of this is the COSY project which aims at producing systematic comparisons between observations and a set of CHIMERE forecasts and making them available on a web site (www.lmd.polytechnique.fr/cosy/). This project has provided sensitivity analyses of modelled concentrations fields when using the different land surface schemes of the WRF meteorological driver (Khvorostyanov et al., 2010): this leads to a better understanding of the impact of LSM on modelled surface concentrations and thus quantify the concentrations biases only due to meteorological surface fluxes. Another example

comes from dust modeling. Figure 17 presents modelled dust surface concentrations over Rome, Italy, for several leads of the same period (Menut et al., 2009a). The variability of the meteorological forecast impacts directly the emissions and, finally, the remote surface concentrations: the daily forecasted maxima may show differences up to a factor of 2. Unfortunately, this variability is of the same order of magnitude as the background particle concentrations often recorded in Europe: this clearly shows that the forecast of mineral dust transport over Europe remains a challenging scientific problem.





## 12.2 Operational forecast

CHIMERE is implemented in several air quality platforms which provide daily forecasts up to 3 days ahead for a set of regulatory pollutants ( $O_3$ ,  $NO_2$ ,  $PM_{10}$ ,  $PM_{2.5}$ ...). Firstly developed as experimental platforms, such tools (www.prevair.org; Rouïl et al., 2009;

- <sup>5</sup> Menut and Bessagnet, 2010) became operational in France after the 2003 summer heat wave (Vautard et al., 2005) and are foreseen to be operational in Europe at the end of the FP7 project MACCII in 2014. Forecasts are used to inform people about air quality regarding pollutant threshold values, to anticipate pollution events and to make recommendations for the protection of sensitive people. Moreover, air quality models
- <sup>10</sup> offer two essential functionalities. They can help the identification of the reasons why pollutant concentrations increase (giving for instance PM speciation), and the results of operational runs conducted with emission control scenarios allow selecting the most efficient measures to set-up. As a consequence, these modelling tools provide support to national authorities to communicate on air quality management, and they assist the
- 15 selection of regulatory measures that may be efficient to limit the intensity of pollution episodes. In this context, CHIMERE is now involved in the prototype toolbox dedicated to air quality episode management in the MACC-II project.

Another contribution of such platforms to air quality issues is the provision of daily assessments of the model ability to predict pollutant concentrations. Daily scores are

- indeed an important parameter, which gives insights into the research efforts that need to be made to improve the model behaviour. Current (research) works are thus focusing on the implementation of dynamical input data such as biomass burning emissions (Kaiser et al., 2012) or emissions from agricultural activities (Hamaoui-Laguel et al., 2012). In both cases, the starting date of emissions is crucial for forecasting their im-
- pacts in time, place and magnitude on pollutant concentrations. The modulation, with climatic contitions (temperature), of wood burning emissions from residential heating is also strongly improving the forecasts of wintertime PM episodes. Finally, in the MACC-II project, it was shown that imports of pollutants due to cross-Atlantic ozone plumes





or African dust plumes could have significant contributions to the European pollutant levels computed with CHIMERE (Menut et al., 2009b), and that the implementation in CHIMERE of near real time boundary conditions delivered by global models provided reliable pollutant background concentrations to the European regional domains. Cur-

5 rently, CHIMERE forecasts are used by more than 50 local agencies in Europe, either to refine the PREV'AIR forecasts using their own modelling platform or to produce a local air quality index value (such as the CITEAIR index, http://www.airqualitynow.eu).

### 13 Conclusions

CHIMERE was initially developed for regional and short-term (a few days) pollution
 episodes. During the last years, new projects and demand gave rise to several needs for model developments, leading to changes in (i) the spatial domains resolution and size, (ii) the simulations duration and (iii) the processes and parameters covered. Spatially, the model domains were extended to near semi-hemispheric scales for mineral dust, forest fires and volcanic plumes. At the same time, urban versions were devel oped to better understand and quantify the impact of air pollution on health. Pollen emissions and transport is also under development, to complete our knowledge of air quality evolution. The time scales were also extended since CHIMERE is now used for long-term simulations, trend analysis and future projections.

#### 13.1 Chemistry in fire plumes

Quantifying the impact of fires on air quality requires not only accurate emissions but also a realistic representation of the chemical processes occuring inside the plumes. The main specificity of fire plumes (besides their high spatial variability) is that they consist of large amounts of trace gases (including the main ozone precursors) and aerosols. The corresponding emissions are included in the emission inventory. But these dense plumes will induce a significant modification of the UV light reaching the





surface, and thereby the photolysis rates for photochemical reactions. For example, Alvarado and Prinn (2009) estimate that, if this effect is accounted for, the ozone levels in plumes from savanna fires in South Africa decrease by 10-20%, and Hodzic et al. (2007) estimate a 10-30% decrease for Portuguese forest fires.

- <sup>5</sup> CHIMERE currently uses tabulated photolysis rates precalculated using the Troposphere Ultraviolet and Visible (TUV) model (Madronich et al., 1998) for different cloud cover situations. In order to account for the impact of dense plumes (critical for fires but also dust and anthropogenic sources), the photolysis rates need to be reevaluated depending on the evolution of the aerosol optical depth (AOD) at different vertical
- <sup>10</sup> levels and locations. Several approaches have been used for CHIMERE. A simplified parameterization based on satellite observations of the AOD has been used by Hodzic et al. (2007), and Konovalov et al. (2011) have refined this approach by recalculating the photolysis rates online with the TUV model using the observed AOD as constrain. More recently, an online calculation of the aerosol properties has been implemented
- and coupled to the TUV model (Péré et al., 2011). It is currently being integrated in the default version of CHIMERE, with a numerical optimization of the calculation of aerosol optical properties to maintain computational efficiency. Large variations in ozone production are also observed depending on PAN formation, heterogeneous chemistry or oxygenated volatile organic compounds amounts for different fire situations (Jaffe and
- <sup>20</sup> Wigder, 2012; Konovalov et al., 2012), that are still not well represented by CTMs. Once the effect of aerosols on radiation is included, further analysis will be undertaken on the chemical evolution in fire plumes simulated by CHIMERE.

#### 13.2 Heavy metals

Metals are considered as important pollutants that can be responsible for a range of hu-<sup>25</sup> man health effects. Diseases such as cancer, neurotoxicity, immunotoxicity, cardiotoxicity, reproductive toxicity, teratogenesis and genotoxicity can be related with the presence of metal particles in the air (HEI, 1998; EPA, 1999). Organisms could assimilate the particles via inhalation (because particles settle into bronchial regions of the lungs)





or ingestion (because the particles are deposited and accumulated on soils or water, and this accumulation produces an increase of the risk of future exposure through food). In Europe, Directive 2008/50/CE sets an annual limit value of  $500 \text{ ngm}^{-3}$  for Pb. Annual target levels for As, Cd and Ni are regulated by Directive 2004/107/CE (6 ngm^{-3})

<sup>5</sup> for As, 5 ngm<sup>-3</sup> for Cd, 20 ngm<sup>-3</sup> for Ni). For other metals (with the exception of mercury), no normative is available.

In the atmosphere, metals are attached to particles, especially those in the fine fraction (Milford and Davidson, 1985; Allen et al., 2001; Molnar et al., 1995; Kuloglu and Tuncel, 2005). A preliminary description of heavy metals (Pb, Cd, As, Ni, Cu, Zn, Cr and Se) air concentration has been implemented in a dedicated version of

- In Zr, Cr and Se) air concentration has been implemented in a dedicated version of the CHIMERE model. At this stage, these metals are treated as inert fine particles. According to Finlayson-Pitts and Pitts (2000), the aerodynamic mass median diameters for Pb, Cd, As, Ni, Cu, Zn, Cr and Se are 0.55, 0.84, 1.11, 0.98, 1.29,1.13, 1.11 and 4.39 µm, respectively. As in this approach all the metals are considered as fine
- <sup>15</sup> particles, more refinement could be necessary for Se. Physical processes such as anthropogenic emissions, transport, mixing and deposition are considered. For some of these metals, such as Pb and Cd, the inert status consideration is generally adopted. They are believed to be transported in the atmosphere with no change in their chemical and aggregate state (Ryaboshapko et al., 1999). For other metals this approach must
- <sup>20</sup> be reconsidered and reactions in the aqueous phase could be required. In the case of Cr, Seigneur and Constantinou (1995) have highlighted the importance of the reactions converting Cr(III) to Cr(VI) and vice-versa associated to particle and droplet chemistry. For Ni, aqueous phase chemistry could also be important. Regarding arsenic, airborne particulate matter has been shown to contain both inorganic and organic arsenic com-
- <sup>25</sup> pounds (Johnson and Braman, 1975; Attrep and Anirudhan, 1977). Unfortunately, there are few studies on the chemistry of these pollutants in the atmosphere.

A preliminary study applying this heavy metal CHIMERE version has been presented in Vivanco et al. (2011), where the model performance was evaluated for Spain. Figure 18 presents the mean annual concentrations of lead for 2009. This preliminary





version has also recently been applied for a European domain at a horizontal resolution of 0.2° for 2008 (González et al., 2012). Important limitations were associated to metal emissions. Only anthropogenic sources have been considered, although some metals can be released into the environment by both natural sources and human activities.

- <sup>5</sup> Moreover, only Cd and Pb emissions are available in the EMEP expert database for 2008 (Vestreng et al., 2009); for the other metals, emissions were taken from TNO totals estimated for 2000 (Van der Gon et al., 2005), except in the Spanish part of the domain, where emissions were provided by the Spanish Ministry of Environment and Rural and Marine Affairs for 2006. Original emissions were spatially and temporally disag-
- <sup>10</sup> gregated and adapted to the simulated domain by taking into account the land use information of GLCF (Global Land Cover Facility, http://change.gsfc.nasa.gov/create.html). In the case of TNO emissions, only the total amount for each EMEP grid-cell was available. The temporal disaggregation of these totals is normally performed in the CHIMERE emission processor considering the SNAP activity. As we did not have this
- information for the metals coming from TNO database, we used a SNAP disaggregation similar to PM<sub>2.5</sub> particles for those species. We also used a temporal profile similar to PM fine particles. A better knowledge of the temporal behavior of metal emissions for each SNAP activity would reduce the input errors. Other aspects, such as boundary contours should also be considered in order to improve model results. At this stage, no boundary conditions were applied, as no information on many of these metals is
- available from global models.

### 13.3 Pollens

A new research direction involving CHIMERE is modeling the dispersion of pollen grains in the atmosphere. The prevalence of pollen allergy in European countries is estimated between 12 and more than 35% (Burney et al., 1996). The quantity of some highly allergenic pollens, such as ragweed, is increasing and seems to correlate with allergic diseases (Rybnicek and Jäger, 2001). Conclusions from a number of European and international climate research projects suggest that future climate change and


variability may strongly affect pollen emission and dispersal in Europe (Christensen and et al., 2007), thereby influencing the prevalence of atopic diseases.

The European (FP7) project Atopica aims to evaluate, using numerical modeling, statistical data analysis, and laboratory experiments, the influence of changes in cli-<sup>5</sup> mate, air quality, land use, and the subsequent distribution of invasive allergenic plant species and allergic pollen distribution on human health. Modelling of ragweed and birch pollen emission and dispersion in the atmosphere using CHIMERE plays a key role in this project.

Pollen grains are about 5–50 times larger in size than conventional atmospheric aerosols. The scale analysis (Sofiev et al., 2006) shows that the assumption of pollen grains being transported together with air masses following the airflow, including small turbulent eddies, still applies. Pollens are implemented in CHIMERE as a special aerosol type having a single size distribution bin of 20–22 µm depending on the pollen type. The density is prescribed for a particular pollen species and varies between 800 and 1050 kgm<sup>-3</sup>, which yields the sedimentation velocity of 1.2–1.3 cms<sup>-1</sup>. Gravitational settling is the main deposition process for pollens and the only one considered in the model. The simulated pollen grains are transported by the atmospheric circulation and turbulent mixing, settled under the gravity, and washed out by rains and clouds, following the parameterizations already implemented for other CHIMERE aerosols.

<sup>20</sup> The main challenge for the state-of-the art pollen dispersion modeling is accurate description of pollen emissions. This requires a fair knowledge of plant distribution, phenology, and adequate assumptions regarding the sensitivity to meteorological factors, such as humidity, temperature, wind and turbulence. Unlike industrial pollutants or mineral aerosols, pollen emissions depend not only on the instantaneous meteo-

<sup>25</sup> rological conditions but also on the conditions during the pollen maturation within the plants before the pollination starts. Additional factors such as the  $CO_2$  and  $O_3$  concentrations can influence pollen production and emissions (Rogers et al., 2006; Darbah et al., 2008).





Pollen episodes have been simulated with CHIMERE for ragweed (Chaxel et al., 2012) and for birch, the latter using the emission methodology developed by Sofiev et al. (2012). Figure 19 shows daily mean birch pollen concentration simulated with CHIMERE for 12 April 2007, during the seasonal concentration maximum in Paris. CHIMERE was forced by the WRF model in the forecast mode without nudg-5 ing at 15 km resolution for the North of France. The model concentration in Paris peaks at 390 grains m<sup>-3</sup> on 12 April, while the RNSA observations show the peak of  $965 \text{ grains m}^{-3}$  on 16 April. The model underestimation can be related to the birch distribution map used for pollen emission calculation: its French contribution is mostly based on the satellite data prone to large uncertainties (Sofiev et al., 2006).

#### Subgrid scale exposure modeling for health impact assessment 13.4

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Air guality models, by integrating different emission scenarios are valuable tools for the evaluation of alternative mitigation policies and possible adaptation strategies with respect to public health and climate change. CHIMERE model is involved in two different projects on the evaluation of the health impact of air quality under changing conditions (ACHIA and ACCEPTED). This ongoing research requires several model developments in order to account for the variability of exposure at the intra-urban scale. A subgrid scale module has been added to the classical computation of the gridaveraged pollutant concentration based on the Reynolds-average approach. Since grid

cell surfaces cover generally a few square kilometers in meso-scale models, the large heterogeneities in emissions over urban areas can not be represented, although this may result in concentrations near sources that are very different from the grid averaged levels. From a health outcome perspective, it is important to know how much local concentrations deviate from grid-averaged values due to the proximity to emission sources (e.g. near roads, in residential zones, industrial parks etc.). 25

To address the issue of subgrid-scale emission heterogeneity, an emission scheme has been developed and implemented in the CHIMERE model (Valari and Menut, 2010). Instead of adding together emissions from all sources and all activity sectors





at each model grid cell we split them into four different categories: traffic, residential, outdoor activities (entertainment) and all other sources (including point sources). Grid area fractions corresponding to each type of emission are calculated based on high resolution landuse data (CORINE land cover at 100 m resolution). Thus, instead of a single emission from each model grid cell  $\sum E_i/A$ , four different emission scenarios  $A \times E_i/A_i$  are used. At each model time-step, and for the grid cells where we are interested in applying the subgrid scale calculation, instead of the single "grid-averaged" scenario, concentrations are calculated following all four subgrid scale scenarios. At the end of the time-step, weighted averages of the four estimates for all model species are propagated to the next time-step.

In Fig. 20, modeled NO<sub>2</sub> concentrations are compared to surface measurements of the IIe-de-France air-quality network AIRPARIF. Model resolution is  $3 \text{ km} \times 3 \text{ km}$  and results are shown for a model grid cell with in which lay two AIRPARIF sites: a traffic monitor (red circles) and a background monitor (blue crosses). The black line correspondence to the standard model grid averaged concentrations whereas calered lines

- responds to the standard model grid-averaged concentrations whereas colored lines stand for the results of the subgrid scale scheme (red for the traffic sector and blue for the residential sector). The added value of the subgrid implementation is that instead of a single grid-averaged concentration we now have two additional estimates for what pollutant levels are near a road or inside a residential block inside the grid area. This
- <sup>20</sup> information is especially useful when we are interested to use air-quality model outputs to estimate population exposure levels. Subgrid model concentrations weighted with activity data on the time people spend at home, at the office or in transit, give an estimate of personal exposure. This method has been applied to the Paris area in Valari et al. (2011).

### 25 13.5 Towards regional on-line modeling

Historically, and for computational reasons, many CTMs such as CHIMERE have been essentially used offline, i.e. they are forced with precalculated meteorological fields and surface state. In order to consider the numerous feedbacks between atmospheric,





radiative and chemical processes, the development of platforms coupling online meteorology, chemistry and vegetation has been identified as a priority for both research and forecast applications. One next big step in CHIMERE development will be to build an online-coupled platform putting together a meteorological model (WRF), a groundvegetation-hydrology model (ORCHIDEE) and a CTM (CHIMERE). This coupling will be done through the OASIS coupler, which will offer greater flexibility and computational advantages compared to a direct hard-coded implementation of a supermodel that includes all these three models. The resulting modelling platform will be used for fundamental research purposes, for assessing the importance of the retroactions between meteorology, vegetation and chemistry, and it will be available for research and forecast applications.

To quantify the potential benefit of such on-line coupling, some preliminary studies were conducted with CHIMERE. A lot of interactions are identified and will be studied, as described in the general Fig. 21. With CHIMERE, the first study of this kind has <sup>15</sup> explored the impact of the radiation attenuation due to aerosols on the ozone photolysis during the 2003 heat wave (Péré et al., 2011). The second one was dedicated to the retroactions between surface ozone concentrations and vegetation through dry deposition (Anav et al., 2011).

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30 (http://www.msceast.org).







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Table 1. Landuse categories used in CHIMERE.

#	Description	#	Description
1	Agricultural land/crops	6	Shrubs
2	Grassland	7	Needleaf forest
3	Barren land/bare ground	8	Broadleaf forest
4	Inland Water	9	Ocean
5	Urban		





**Table 2.** List of MELCHIOR anthropogenic emitted species.

Model species	Name
NO	Nitrogen monoxide
NO <sub>2</sub>	Nitrogen dioxide
HONO	Nitrous acid
SO <sub>2</sub>	Sulphur dioxide
NH <sub>3</sub>	Ammoniac
CO	Carbon monoxide
CH <sub>4</sub>	Methane
C <sub>2</sub> H <sub>6</sub>	Ethane
$NC_4H_{10}$	<i>n</i> -Butane
$C_2H_4$	Ethene
C <sub>2</sub> H <sub>6</sub>	Ethane
C <sub>3</sub> H <sub>6</sub>	Propene
C <sub>5</sub> H <sub>8</sub>	Isoprene
OXYL	<i>o</i> -Xylene
HCHO	Formaldehyde
CH₃CHO	Acetaldehyde
CH₃COE	Methyl ethyl Ketone
APINEN	$\alpha$ -pinene
PPM_fin	Primary particulate matter
PPM₋coa	Primary particulate matter
PPM₋big	Primary particulate matter
H₂SO₄₋fin	Primary sulfuric acid
BaP₋fin	Benzo(a)pyrene
BbF_fin	Benzo(b)fluoranthene
BkF₋fin	Benzo(k)fluoranthene
OCAR_fin	Primary organic carbon
BCAR_fin	Primary black carbon





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**Table 3.** Averaged values, with their standard deviation, of the correlation coefficient, the root mean square error and the bias, calculated for the comparison of simulated ozone with Air Base data over Europe for summer 2005, using MELCHIOR2 (left) and SAPRC07 (right).

	MELCHIOR2	SAPRC07
R	$0.71 \pm 0.08$	$0.71 \pm 0.08$
RMSE (ppbv)	$13.69 \pm 2.14$	$13.18 \pm 2.03$
Bias (ppbv)	$9.29 \pm 2.65$	$8.19 \pm 2.65$

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**Table 4.** List of aerosol species. (\*): ions, molecules, crystals. (P) and (S) stand for "primary" and "secondary", respectively. Note that pNH3 may be both primary (emitted) and secondary (transferred) aerosol.

Model species	Type and Species	
pPPM	(P) Anthropogenic primary species EC, OC, and other industrial dusts	
pSOA	(S) Anthropogenic and Biogenic secondary organic aerosol (ASOA + BSOA)	!
pH <sub>2</sub> SO <sub>4</sub>	(S) Equivalent Sulfate(*)	
pHNO <sub>3</sub>	(S) Equivalent Nitrate(*)	(
pNH <sub>3</sub>	(P,S) Equivalent Ammonium(*)	(
pWATER	Water	

**Table 5.** Look-up table used for the calculation of the thermodynamic equilibrium with ISOR-ROPIA. The minimum and maximum values represent the range of the values calculated. Their values are defined to cover a large range of possible meteorological situations. In case of temperature, relative humidity or concentrations less than the minimum or up to the maximum, the thermodynamic equilibrium is chosen as the value corresponding to the last defined value (minimum or maximum). The increment is defined to ensure a realistic linearity between two consecutive values and for the interpolation.

Variable	Value		Increment
	Min.	Max.	
Temperature (K)	260	312	2.5
Relative Humidity	0.3	0.99	0.05
$H_2SO_4$ , $HNO_3$ , $NH_3$ (µg m <sup>-3</sup> )	10 <sup>-2</sup>	65	×1.5





**Table 6.** Gas phase chemical scheme for SOA formation in CHIMERE. The surrogate SOA compounds consist of six hydrophilic species that include an anthropogenic nondissociative species (AnA0D), an anthropogenic once-dissociative species (AnA1D), an anthropogenic twice-dissociative species (AnA2D), a biogenic non dissociative species (BiA0D), a biogenic once-dissociative species (BiA1D) and a biogenic twice-dissociative species (BiA2D), three hydrophobic species that include an anthropogenic species with moderate saturation vapor pressure (AnBmP), an anthropogenic species with low saturation vapor pressure (AnBIP) and a biogenic species with moderate saturation vapor pressure (AnBmP), an anthropogenic species with low saturation vapor pressure compounds for the isoprene oxidation products.

Reactions	kinetic rates (molec $cm^{-3}s^{-1}$ )
TOL + OH $\rightarrow$ 0.004 × AnA0D + 0.001 × AnA1D + 0.084 × AnBmP + 0.013 × AnBIP	1.81 × 10 <sup>-12</sup> exp(355/T)
$TMB + OH \rightarrow 0.002 \times AnA0D + 0.002 \times AnA1D + 0.001 \times AnA2D + 0.088 \times AnBmP + 0.006 \times AnBIP$	$9.80 \times 10^{-9}/T$
NC4H10 + OH $\rightarrow$ 0.07 × AnBmP	$1.36 \times 10^{-12} \exp(190/T)^{-2}$
API + OH $\rightarrow$ 0.30 × BiA0D + 0.17 × BiA1D + 0.10 × BiA2D	1.21 ×10 <sup>-11</sup> exp(444/ <i>T</i> )
$API + O_3 \rightarrow 0.18 \times BiA0D + 0.16 \times BiA1D + 0.05 \times BiA2D$	1.01 ×10 <sup>-15</sup> exp(-732/T)
$API + NO_3 \rightarrow 0.80 \times BiBmP$	1.19×10 <sup>-12</sup> exp(490/T)
$BPI + OH \rightarrow 0.07 \times BiA0D + 0.08 \times BiA1D + 0.06 \times BiA2D$	$2.38 \times 10^{-11} \exp(357/T)$
$BPI + O_3 \rightarrow 0.09 \times BiA0D + 0.13 \times BiA1D + 0.04 \times BiA2D$	$1.50 \times 10^{-17}$
$BPI + NO_3 \rightarrow 0.80 \times BiBmP$	2.51 × 10 <sup>-12</sup>
$LIM + OH \rightarrow 0.20 \times BiA0D + 0.25 \times BiA1D + 0.005 \times BiA2D$	1.71 ×10 <sup>-10</sup>
$LIM + O_3 \rightarrow 0.09 \times BiA0D + 0.10 \times BiA1D$	2×10 <sup>-16</sup>
$OCI + OH \rightarrow 0.70 \times BiA0D + 0.075 \times BiA1D$	$5.10 \times 10^{-8}/T$
$OCI + O_3 \rightarrow 0.50 \times BiA0D + 0.055 \times BiA1D$	$7.50 \times 10^{-14}/T$
$OCI + NO_3 \rightarrow 0.70 \times BiA0D + 0.075 \times BiA1D$	$4.30 \times 10^{-9}/T$
ISO + OH $\rightarrow$ 0.232 × ISOPA1 + 0.0288 × ISOPA2	$2.55 \times 10^{-11} \exp(410/T)$

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**Table 7.** The main characteristics of the dry deposited species with their names, dMx the molar mass of the model species, dHx the effective Henry's law constant (Matm<sup>-1</sup>) for the gas, df0 the normalized (0 to 1) reactivity factor for the dissolved gas.

Species	dMx	dHx	df0
0 <sub>3</sub>	48	0.01	1
SO <sub>2</sub>	64	1e+5	0
$NO_2$	46	0.01	0.1
NO	30	2e-3	0
$NH_3$	17	1e+5	0



Climate change and impact research: The Mediterranean Environ-Feedbacks between ozone and ment - Curci et al. (2009); Anav et al. (2011) vegetation. Implementation of MEGAN. Global Earth Observation and Monitoring Pollution trends over Europe

> Fast chemistry and aerosols over the Paris area

Model improvement

gaseous pollutants only

Mineral dust addition

properties

Regional modeling of aerosol and

Regional cartesian mesh model, for

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Secondary Organic Aerosols

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Emissions reduction scenarios

AQMEII Models intercomparisons over Europe and United-States - Pirovano US domain et al. (2012); Solazzo et al. (2012b)

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Atopic diseases in changing climate, land use and air quality

Pollens addition in the model





Table 8. International projects involving CHIMERE (in chronological order). Names with a \* also

correspond to field campaigns for which data were used.

Vautard et al. (2003); Hodzic et al. (2006c)

Mineral dust (western Africa) - Menut et al. (2009a)

Regional pollution (Paris area) - Rover et al. (2011)

Regional photochemistry (Paris area, France) - Menut et al. (2000b):

Regional photochemistry (Marseille area, France) - Menut et al.

Monitoring Atmospheric composition and climate - Hollingsworth

Regional pollution (Mexico City) - Hodzic et al. (2010a): Hodzic and

Main goals (+ references)

(2005a)

et al. (2008)

Jimenez (2011)

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Project

ESQUIF\*

**FSCOMPTF**\*

GEMS, MACC

AMMA<sup>\*</sup>

CIRCE

GEOMON

MEGAPOLI\*

FC4MACS

MILAGRO\*



## Table 9. Satellite data used for model/data comparisons and analysis.

Satellite	Parameter	Goal
SCIAMACHY, OMI, GOME	$NO_2$ , HCHO	Improve total column and biogenic emissions
MODIS, POLDER	Surface properties	Fires emissions calculation. Improve aerosol emissions and transport
IASI	$O_3$ , CO	Improve the tropospheric columns and vertical distribution
CALIOP	Dust, aerosols	Improve the vertical transport





**Fig. 1.** General principle of a chemistry-transport model such as CHIMERE. In the box "Meteorology",  $u_*$  stabds for the friction velocity,  $Q_0$  the surface sensible heat flux, L the Monin–Obukhov lenght and BLH the boundary layer height.  $c_{\rm mod}$  and  $c_{\rm obs}$  are for the chemical concentrations fields for the model and the observations, respectively.







Fig. 2. General CHIMERE structure for time integration of all processes.






**Fig. 3.** Calculation of the number of integration steps per hour to respect the CFL over a complete 120 h simulation.







Fig. 4. Principle of "operator-splitting" versus Chimere integration.















**Fig. 6.** Example of simulation domains for CHIMERE, and corresponding surface ozone concentrations maps. The largest domain (dx = 45 km) use a global model climatology for boundary conditions, and forces itself the medium domain, dx = 15 km over the North of France, itself forcing the small domain, dx = 5 km, over the Paris area.





Fig. 7. Treatment of meteorological fields: two options are available (i) using a meteorological dataset restricted to the mean parameters (u, v, T, q, P, precipitation) and (ii) using a complete meteorological dataset that includes turbulent parameters.



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Fig. 8. Entrainment and detrainment fluxes in the updrafts and downdrafts.







Fig. 9. General principle of the CHIMERE anthropogenic emissions procedure.







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Fig. 11. Example of area burned  $(km^2)$  calculated using the fire emissions preprocessor and for 8 May 2012 over western Europe.







Fig. 12. Reaction pathways of the RO<sub>2</sub> radical in MELCHIOR 1.

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Fig. 13. Main principle of dry deposition for gas and particles.





Fig. 14. Time series of the sensitivity of pollutants (NO<sub>x</sub> and O<sub>3</sub>) to anthropogenic surface emissions (from "traffic" and "solvents" activity sectors).



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**Fig. 15.** Optimized coefficients for the NO emissions in the Paris area for 7 August 1998 (ES-QUIF campaign).







Fig. 16. Assimilation with CHIMERE of ozone profiles recorded by the IASI instrument and comparisons of the obtained gain with MOZAIC data (data courtesy of A. Coman).



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**Fig. 17.** Time series of dust forecast for the period of 17 to 23 March 2006. The results are for dust surface concentations in Rome, Italy.







Fig. 18. Mean annual concentrations of lead for 2009 over Spain and Portugal.







Fig. 19. Birch pollen distribution simulated with CHIMERE for 12 April 2007.







**Fig. 20.** Surface concentrations of NO<sub>2</sub> time series, using the subgrid scale variability module. The symbols represent AIRPARIF measurements of two stations, one background and one traffic, located in the same CHIMERE cell in Paris, with a horizontal resolution of  $3 \text{ km} \times 3 \text{ km}$ . The plain lines represent the corresponding modelled surface concentrations and show the subgrid scheme is able to reproduce the large variability of NO<sub>2</sub> depending on the sources in an urban environment. After Valari and Menut (2010).







**Fig. 21.** Interactions between meteorology, soil-vegetation and air-quality in the future modelling platform using CHIMERE.



