Cerea

Centre d'Enseignement
et de Recherche
en Environnement
Atmosphérique

RAPPORT 2006-29

Simulation of aerosols and related species over Europe with the Polyphemus system.
Part I: model-to-data comparison for 2001

K.N. Sartelet, E. Debry, K. Fahey, Y. Roustan.
M. Tombette, B. Sportisse[1]

Submitted to Atmospheric Environment

---

[1]

Centre d'Enseignement et de Recherche sur l'Environnement Atmosphérique
Laboratoire Commun ENPC/EDF R&D
Ecole Nationale des Ponts et Chaussées
6-8 Avenue Blaise Pascal, Cité Descartes, 77455 Champs sur Marne
EDF R&D, 6 Quai Watier, 78401 Chatou
Tel : (33) 01 64 15 21 57
Fax : (33) 01 64 15 21 70

Simulation of aerosols and related species over Europe with the POLYPHEMUS system. Part I: model-to-data comparison for 2001

K.N. Sartelet [a,*] E. Debry [a] K. Fahey [a] Y. Roustan [a]
M. Tombette [a] B. Sportisse [a]

[a] *CEREA, 6-8 avenue Blaise Pascal, Cité Descartes Champs-sur-Marne 77455
Marne la Vallée Cedex 2*

Abstract

Aerosol modeling is a challenging task due to the complexity of multiphase processes and the related uncertainties. Chemistry-Transport models are now used for forecast and emission reduction studies for atmospheric aerosols. In order to have confidence in these models, comprehensive model-to-data comparisons are required. We present in this paper a preliminary validation study of the POLYPHEMUS system applied to annual aerosol modeling over Europe for 2001. The aerosol model is the SIze REsolved Aerosol Model (SIREAM). It is a sectional model that describes the temporal evolution of the size/composition distribution of atmospheric particles containing a mix of black carbon, mineral dust, inorganic species, and primary and secondary organics. In addition to a brief model description, we present an overview of the model validation. A comprehensive set of model-to-data statistics is computed with observational data extracted from three European databases (the EMEP, AirBase and BDQA databases). Model performance criteria are verified for ozone and Particulate Matter (PM) and its inorganic components. Comparisons of correlations and root mean square errors with those generated by other models run over Europe for 2001 indicate an acceptable performance of the POLYPHEMUS system. Modifications of the system configuration and parameterizations may have a significant impact on error statistics, which may question the robustness of such models. Because large differences exist between databases, the robustness of model-to-data error statistics is also questioned.

Key words: aerosol, monitoring network, chemistry transport model, model performance criteria

---

[*] Corresponding author.
Email address: `sartelet@cerea.enpc.fr` (K.N. Sartelet).

Preprint submitted to Elsevier Science *6 September 2006*

Introduction

Aerosol modeling is a field of growing interest for many reasons. Particles, especially fine particles, have been implicated in adverse effects on human health. Atmospheric particles also affect the manner in which radiation passes through the atmosphere and represent an uncertain component of the atmospheric response to the increasing emissions of greenhouse gases. The first motivation for better understanding the behavior of atmospheric aerosol is then related to air quality, while the second is related to climate change.

Many regulations for air quality now focus on Particulate Matter (PM) mass. This is the case with the EPA standards in the United States and also the case in Europe with Clean Air For Europe (CAFE). Models are powerful tools to assess the effects of proposed emission reductions on particulate concentrations. In order to have confidence in these models, however, it is necessary to validate them with observational data. Several models are now available in Europe and have been validated and compared for gaseous species and sometimes aerosols. Among many others, one can cite EMEP (Simpson et al. (2003)), LOTOS-EUROS (Schaap et al. (2005)), EURAD (Ackermann et al. (1995)), DREAM (Brandt (1998)), and CHIMERE (Schmidt et al. (2001)). A specific exercise (the EURODELTA program) has also been carried out in order to analyze the responses of different models to emission changes.

One complication is that observational data for PM are rarely very detailed and generally do not offer a precise description of the aerosol size aand composition distribution, with exception of data taken during intensive field campaigns. In this respect, once validated, models may provide rich supplemental information compared to that offered by routine monitoring networks.

Polyphemus is a modeling system that has been developed for forecasts and assessment of emission reduction strategies over Europe. Its novelty is that it is not an “all-in-one” model: it has been designed as a modular system able to host different model configurations and is thus well-suited for ensemble modeling. It is the basis of the future forecast system of the French Institute for Nuclear Safety (Quelo et al. (2006); Isnard et al. (2005)) and has been involved in operational testing for photochemistry forecasts (Mallet and Sportisse (2006a)) on the French Prév'air platform since July 2006 (`www.prevair.org`). A key focus of Polyphemus is devoted to the model sensitivity with respect to emissions (Mallet and Sportisse (2005)). Many topics related to uncertainties have already been investigated with Polyphemus (Mallet and Sportisse (2006b)). Polyphemus has already been applied to aerosol modeling, through its Chemistry-Transport Model (Polair3D), in the MICS (Model Intercomparison Study, Phase II) Asia exercise (Sartelet et al. (2006)). Previous European studies with Polyphemus have focused on gas-phase chemistry, and this paper is the logical extension to aerosol modeling. The focus of this paper is a preliminary validation with a model-to-data comparison for the year 2001 over Europe.

This paper is structured as follows. A brief description of the Polyphemus system and of the aerosol model SIREAM (SIze REsolved Aerosol Model) are given in the first section. The model validation exercise is presented in Section 2. The Polyphemus system is used for simulating aerosol over Europe for the year 2001. Error statistics for model-to-data comparisons are computed on the basis of observational data given by three different databases (EMEP, AirBase and BDQA). The focus is on inorganic species and PM10 due both to model uncertainties and the lack of measured data for Secondary Organic Aerosol. The results are discussed in the third section. The paper ends with a conclusion and the presentation of future work. A companion paper (Part II) is devoted to a sensitivity analysis.

1 Model description

1.1 The POLYPHEMUS *system*

Polyphemus and its Chemistry-Transport Model Polair3D (Boutahar et al. (2004)) have already been used for many applications: sensitivity analysis of ozone with respect to emissions (Mallet and Sportisse (2005)), evaluation of uncertainties (Mallet and Sportisse (2006b)), inverse modeling of NOx emissions at regional scale (Quelo et al. (2005)), ensemble forecast for ozone (Mallet and Sportisse (2006a)), modeling of mercury and heavy metals at continental scale (Roustan and Bocquet (2006b,a)), dispersion of radionuclides at continental scales (Bocquet (2005); Quelo et al. (2006)), etc. The Polyphemus platform is made of four distinct components:

- Physical parameterizations and preprocessing of input fields (meteorological fields, boundary conditions and emissions) are performed within the AtmoData library. One purpose of the AtmoData library is to perform the preprocessing of input fields, especially of meteorological fields (from Numerical Weather Forecasts or from mesoscale models). It does not depend on the numerical model. The outputs are typically gridded data necessary to model dispersion (for instance: wind field, vertical diffusion, air density and parameterizations for scavenging processes). These fields are given for a specific model grid (here, the Chemistry-Transport Model Polair3D).

  AtmoData also includes all the relevant parameterizations to be used by the numerical models (see below for the aerosol processes).
- Drivers have been defined in order to handle high-level use of the models,

which can be viewed as black boxes. This includes a driver for Monte Carlo simulations, a driver for ensemble forecast, a driver for sequential data assimilation and a driver for variational data assimilation. These drivers do not depend on the chosen model.

- Models (for instance the Chemistry-Transport Model POLAIR3D) constitute the third level of the system. Other models can be plugged into the system. This is already the case for Gaussian-like (plume and puff) models used for risk modeling and for the Chemistry-Transport Model CASTOR based on CHIMERE (Schmidt et al. (2001)).
- the last level is composed of postprocessing tools, especially the Python module ATMOPY. This library (which does not depend on the previous components) performs model-to-data comparisons (on the basis of the indicators recommended by the US EPA for model validation) and ensemble computations when required (the combination of different model outputs on the basis of appropriate algorithms).

POLYPHEMUS is developed with a GNU/GPL licence and the source code is downloadable from the web site `http://www.enpc.fr/cerea/polyphemus`.

1.2 The SIze REsolved Aerosol Model (SIREAM)

Two aerosol models are hosted by POLYPHEMUS: MAM (a Modal Aerosol Model, Sartelet et al. (2005)) and SIREAM (a SIze REsolved Aerosol Model, Debry et al. (2006)). Both models rely on the same parameterizations hosted by the ATMODATA library (Sportisse et al. (2006)). SIREAM is used for this study.

1.2.1 Composition

The aerosol mixture is assumed to be *internally mixed*: for a given size section, there is a unique, uniform chemical composition.

The following components are taken into account : liquid water, inert species (mineral dust, elemental carbon and, in some applications, heavy trace metals such as lead or cadmium), inorganic species (Na^+, SO_4^{2-}, NH_4^+, NO_3^- and Cl^-), Primary Organic Aerosol (POA) and 8 species representing Secondary Organic Aerosol (see below).

1.2.2 Parameterizations used for GDE

The time and size evolution of distribution functions is given by the General Dynamic Equation for aerosol (GDE). The processes that are taken into account are nucleation, coagulation and condensation/evaporation.

1.2.2.1 Nucleation

The nucleation process corresponds to the formation of the smallest particles through the stable aggregation of gaseous molecules into clusters. Two parameterizations are available: Vehkamaki et al. (2002) for the binary mixture H_2O-H_2SO_4 and Napari et al. (2002) for the ternary mixture H_2O-H_2SO_4-NH_3.

1.2.2.2 Coagulation

We only take into account Brownian coagulation of aerosols, parameterized by classical coagulation kernels (Seinfeld and Pandis (1998)).

1.2.2.3 Condensation/evaporation

The condensation/evaporation mass transfer is governed by the gradient between the gas-phase concentration and the concentration at the aerosol surface. The surface concentration is supposed to be at equilibrium with the aerosol mixture ("local" equilibrium). The mass flux for condensation/evaporation is given by:

$$I_i = 2\pi D_i^g d_p f_{FS}(K_{n_i}, \alpha_i)\bigg(c_i^g - c_i^s(d_p, t)\bigg) \tag{1}$$

D_i^g and c_i^g are the diffusion coefficient in the air and the gas-phase concentration of species $\mathrm{X_i}$, respectively. The concentration c_i^s at the aerosol surface is supposed to be at *local* thermodynamic equilibrium with the aerosol composition: $c_i^s(d_p, t) = \eta(d_p)\ c_i^{eq}(q_1, \ldots, q_{n_e}, RH, T)$. $\eta(d_p)$ is a correction factor for the Kelvin effect. RH is the relative humidity and T is the temperature. The function f_{FS}, the Fuchs-Sutugin function, describes the non-continuous effects (Dahneke (1983)). It depends on the Knudsen number of species $\mathrm{X_i}$, K_{n_i}, and on the accommodation coefficient α_i with a default value of 0.5.

The current model version does not describe the mixed thermodynamics between inorganics and organics. In practice, two independent equilibria are assumed. This assumption is a limitation of the current model because some organic species may exhibit hydrophilic behavior (Griffin et al. (2002b,a); Pun et al. (2002)). The local equilibrium is computed with the model ISORROPIA (Nenes et al. (1998), version v1.7) for inorganics, with an absorption law for organics (Schell (2000); Schell et al. (2001)).

Moreover, some specific corrections may be applied in the case of liquid aerosol (limitation of the H^+ flux). In the case of solid aerosol, a specific computation describing the interactions between the gas phase and the solid surface is also performed (Pilinis et al. (2000)).

In the model version that is used as a reference for this study, chloride and sodium are not considered when computing the local equilibrium for inorganics. In other words, the condensation/evaporation of chloride and sodium is ignored, and their concentrations do not influence the condensation/evaporation of other inorganic species. As such, one can consider that a kind of external mixing hypothesis is used for sea-salt aerosol.

1.2.3 Other processes related to aerosols

1.2.3.1 Aqueous-phase chemistry The description of aqueous-phase chemistry is a key point, especially for sulfate production. The model is based on the chemical mechanism of the VSRM developed at Carnegie Mellon University (Fahey and Pandis (2003); Strader et al. (1998)). It contains 18 gas-phase species and 28 aqueous-phase species. Aqueous-phase chemistry is modeled by a chemical mechanism of 99 chemical reactions and 17 equilibria (for ionic dissociation). Radical chemistry is not included.

The microphysical processes that govern the evolution of cloud droplets are parameterized and not described explicitly. If the liquid water content (LWC) is above a threshold (of magnitude $0.05\,\mathrm{g.m^{-3}}$), the grid cell is assumed to contain a cloud or fog and the fraction of the aerosol distribution above $d_{activ} = 0.7\,\mu\mathrm{m}$ is activated. A cloud droplet is formed on the activated aerosols and disappears instantaneously (after one numerical time step). The objective is to take into account the impact of aqueous-phase chemistry for the activated part of the aerosol distribution.

In order to lower the computational burden, the activated distribution is a monomodal distribution of median diameter $0.4\,\mu\mathrm{m}$ and of variance $1.8\,\mu\mathrm{m}$. The tests in Fahey (2003) illustrate the low impact of the choice made for this distribution. The chemical composition of the cloud droplet is then based on that of the activated aerosols.

Aqueous-phase chemistry and mass transfer between the gaseous phase and the cloud droplet are then solved with the DVODE solver (Brown et al. (1989)). At the end of the time step, the cloud droplet distribution is then mapped to the initial aerosol distribution.

1.2.3.2 Heterogeneous chemistry Heterogeneous reactions at the surface of aerosols and cloud droplets may have a significant impact on ozone and tropospheric chemistry. Following Jacob (2000), these processes are usually parameterized as first-order reactions for the following reactions: $HO_2 \rightarrow 0.5\ H_2O_2$, $NO_2 \rightarrow 0.5\ HONO + 0.5\ HNO_3$, $NO_3 \rightarrow HNO_3$ and $N_2O_5 \rightarrow 2\ HNO_3$.

For cloud droplets, the reactions for HO_2, NO_2 and NO_3 are already described by the diphasic model and are considered separately.

The kinetic rate is computed with $k_i = \left(\frac{a}{D_i^g} + \frac{4}{\bar{c}_i^g \gamma}\right)^{-1} S_a$ with a the particle radius and $\bar{c}_i^g$ the gas-phase thermal velocity in the air. S_a is the available surface of condensed matter per air volume. γ strongly depends on the chemical and size distribution of particles and are highly uncertain. In the simulations presented in this paper, the uptake coefficients are fixed at the smallest values: $\gamma_{HO_2} = 0.1$, $\gamma_{NO_2} = 10^{-6}$, $\gamma_{NO_3} = 2.10^{-4}$ and $\gamma_{N_2O_5} = 0.01$.

1.2.3.3 SOA The oxidation of VOCs leads to Semi Volatile Organic Compounds (SVOC) that have increasingly complicated chemical functions, high polarizations and lower saturation vapor pressure. The current version of SIREAM use a “two-product” formulation. The gas-phase chemical mechanism RACM (Stockwell et al. (1997) has been extended by adding SVOCs as products in some oxidation reactions by OH, O_3, and NO_3. The basis is the SORGAM model (Schell et al. (2001); Schell (2000)). Eight SOA classes are taken into account (4 anthropogenic and 4 biogenic). Anthropogenic species include two from aromatic precursors, one from higher alkanes and one from higher alkenes. The biogenic species represent two classes from α-pinene and two from limonene degradation. An updated version of yields and thermochemical data has been developed. However, the focus of this preliminary validation is not SOA and we do not present the module in detail.

1.2.4 Solving the GDE

Several numerical algorithms have been implemented (Debry (2004)). The numerical strategy is based on methods that ensure stability with a low computational burden: a splitting approach for coagulation and condensation/evaporation, a sectional method based on partitioning coefficients for coagulation (Fernandez-Diaz et al. (2000); Debry and Sportisse (2005b)) and a Lagrangian treatment for condensation/evaporation in order to avoid numerical diffusion with Eulerian schemes due to the low number of discretization points in 3D models.

The time integration of the coagulation model is performed with a second-order explicit scheme (Debry and Sportisse (2005b)). Simulating the condensation/evaporation process leads to the largest computational burden. The resulting system of Ordinary Differential Equations is stiff due to the wide range of timescales and an implicit method, the second-order Rosenbrock method (Verwer et al. (1999); Djouad et al. (2002)), is used. Apart from kinetic mass transfer for condensation/evaporation, SIREAM offers two other options based on equilibrium between the gaseous phase and aerosols: a bulk approach or a hybrid approach (Capaldo et al. (2000); Debry and Sportisse (2005a)). The method consists of assuming that the fine fraction (below a cut-off diameter, of default value 1.25 or 2.5 μm) rapidly reaches equilibrium while the coarse fraction obeys a law of kinetic mass transfer. In practice, we use either a hybrid approach or a bulk approach in the case for long-term simulations, as for this article.

Using a Lagrangian approach for condensation/evaporation implies the redistribution of number and mass concentrations onto the fixed size grid of 3D models. Two algorithms that ensure mass conservation during the redistribution can be used (Sportisse et al. (2006)).

For this study, the aerosol size distribution is separated into 5 sections. The dry diameters are log-distributed between 0.01 μm and 10 μm.

1.2.5 Parameterization of the wet diameters for 3D processes

The wet diameter is a key input for many parameterizations used for three-dimensional processes (such as deposition and scavenging). The wet diameter can be computed on the basis of the chemical composition and the thermodynamic conditions with ISORROPIA (for the inorganic part). In order to lower the computational burden, we use a parameterization based on Gerber's formula (Gerber (1985)). The parameters used in this formula have been tuned on the basis of ISORROPIA (with a comprehensive learning data basis of 10^6 runs describing most situations, Sportisse et al. (2006)).

2 Simulation of year 2001 over Europe

2.1 Model simulation characteristics

2.1.1 Domain

Simulations are performed over Europe. The coordinates of the southwestern-most point are (10.75°W, 34.75°N) in longitude/latitude. The domain of simulation covers an area of 33.5° x 23° with a step of 0.5° along both longitude and latitude. Five vertical levels are considered from the ground to 3000m. The heights of the cell interfaces are 0m, 50m, 600m, 1200m, 2000m and 3000m.

2.1.2 Meteorological data

Meteorological data are provided by ECMWF (31 vertical levels with a horizontal resolution of 0.36° x 0.36° every three hours). Vertical diffusion is computed using the Troen and Mahrt parameterization (Troen and Mahrt (1986)) within the boundary layer, and using the Louis parameterization (Louis (1979)) above it. For land use coverage the USGS (United States Geological Survey) land cover map (24 categories) is used.

2.1.3 Gas-phase chemistry

The chemical mechanism chosen for the simulation is RACM (Stockwell et al. (1997)). Photolysis rates are computed off-line, as done in the photolysis rate preprocessor JPROC of CMAQ (Roselle et al. (1999)).

2.1.4 Boundary conditions

For boundary conditions, daily means are extracted from outputs of the global Chemistry-Transport Model Mozart 2 run over a typical year for gas, and from outputs of the Goddard Chemistry Aerosol Radiation and Transport (GOCART Chin et al. (2000)) model for the year 2001 for sulfate, dust, black carbon, and organic carbon.

40% of organic carbon is assumed to be primary aerosol. The remaining 60% is equally distributed amongst the eight organic species of POLYPHEMUS on a molar basis. Boundary conditions for sea salt are also provided by GOCART, but they are not used because local emissions of sea salt are taken into account in the system.

As recommended in Vautard et al. (2005), boundary conditions of dust are drastically lowered (here divided by 4), because high dust events are very sporadic and the use of mean values may lead to overestimation of dust concentrations.

Boundary conditions for ammonium are deduced from the sulfate boundary conditions by assuming electro-neutrality of sulfate and ammonium. GOCART provides only total concentrations of sulfate and carbon. Therefore they need to be redistributed amongst the 5 sections of the aerosol module. The GOCART concentrations are assumed to follow a trimodal lognormal distribution of parameters ($N_1 = 8128 \times 10^6$ m^3, $d_1 = 0.014\mu$m, $\sigma_1 = 1.92$) for the first mode, ($N_2 = 4633 \times 10^6$ m^3, $d_2 = 0.045\mu$m, $\sigma_2 = 1.87$) for the second mode and ($N_3 = 1235 \times 10^6$ m^3, $d_3 = 0.162\mu$m, $\sigma_3 = 1.71$) for the third mode. N_i is the number of particles in the mode, d_i the geometric mean diameter and σ_i the geometric standard deviation (Putaud et al. (2003)). Integrating this lognormal distribution over each section gives the percentage of the mass to be allocated to each section. For dust concentrations, GOCART provides concentrations for 5 bins ranging between 0.1 μm and 10 μm. For each GOCART bin, the percentage of the mass to be allocated to each section is computed similarly to sulfate and carbon. The trimodal lognormal distribution is integrated over each section.

2.1.5 Deposition and wet scavenging

2.1.5.1 Gases The dry deposition velocities are preprocessed by using the parameterization of Zhang et al. (2003). As in Simpson et al. (2003), the surface resistance is modeled following Wesely (1989) for sub-zero temperatures, and the surface resistance of HNO_3 is assumed to be zero for positive temperatures. Below-cloud scavenging (washout) is parameterized following Sportisse and Dubois (2002). During below-cloud scavenging, equilibrium concentrations of soluble gaseous species can be significantly affected by the ion dissociation during dissolution in water. To take this ionization process into account, effective Henry coefficients are computed given the raindrop pH for the following species: SO_2, NH_3, HNO_3, HNO_2 and HCl.

2.1.5.2 Aerosols Dry deposition is parameterized with a resistance approach, following Zhang et al. (2001). Below-cloud scavenging is parameterized with the washout coefficient $\Lambda(d_p) = \frac{3}{2} \frac{E(D_r, d_p)\, p_0}{D_r}$, with p_0 the rain intensity in ISU (m/s), d_p the particle diameter, D_r the raindrop diameter and E the collision efficiency. The representative diameter for the rain is given as a function of p_0 following Loosmore and Cederwall (2004). The raindrop velocity is computed as a function of the raindrop diameter following Loosmore and Cederwall (2004).

In-cloud scavenging (rainout) is parameterized following Roselle and Binkowski (1999).

In the case of a fog, diagnosed as a cloud whose first level is at ground, the fog settling velocity is parameterized following Pandis et al. (1990).

2.1.6 Emission

2.1.6.1 Gases Anthropogenic emissions are generated with the EMEP expert inventory for 2001. A typical time distribution of emissions, given for each month, day and hour (GENEMIS (1994)) is applied to each emission sector or SNAP category. For the SNAP 10 (agriculture), monthly emission and hourly emission factors are applied following Schaap (2003) (page 4-64). The inventory species are disaggregated into real species using speciation coefficients (Passant (2002)). NOx emissions are split into 90% of NO (in mass), 9.2% of NO_2 and 0.8% of HONO. SOx emissions are split into 95% of SO_2 and 5% of H_2SO_4 (in molar concentrations) following Simpson et al. (2003). The aggregation into model species (for RACM) is done following Middleton et al. (1990). Because of the coarse discretization used in the modelling, 25% of NH3 emissions are deposited locally (Tsyro (2001), Loubet et al. (2003)). Biogenic emissions are computed as in Simpson et al. (1999). Two third of terpene emissions are allocated to apinene and one third to limonene (Johnson et al. (2006)).

2.1.6.2 Aerosols Primary particle emissions are usually given in total mass. For example, the EMEP European emission inventory provides yearly quantities for PM2.5 and PM10 (particles with diameters less than 2.5 μm and 10 μm respectively) or PM coarse (particles with diameters between 2.5 and 10 μm). These brute data have to be temporally, chemically, and granulometrically speciated. We follow the recommendations of Simpson et al. (2003). The PM coarse fraction is attributed to mineral dust. The PM2.5 fraction is first chemically speciated into three species (mineral dust, MD, primary organics aerosols, POA, and black carbon, BC) by source sector or SNAP code and the resulting species are then distributed into two modes (the Aitken and the accumulation modes). The redistribution of the quantities in the model bins is based on the assumption that each bin belongs to one mode. The emissions of a mode are then equally partitioned amongst the bins that are included in this mode. Sensitivity tests (not reported here) show that the distribution of emissions does not have a great influence compared to other sources of uncertainties.

Sea-salt emissions are parameterized following (Monahan et al. (1986)), which models the generation of sea-salt by the evaporation of sea spray produced by bursting bubbles during whitecap formations due to surface wind. This parameterization is valid at 80% relative humidity. To generalize it, it is expressed in terms of dry radius, which is assumed to be approximatively half the radius at 80% humidity (Gerber (1985)). The emitted mass of sea-salt is assumed to be made of 55.14% of chloride, 30.61% of sodium and 7.68% of sulfate (Seinfeld and Pandis (1998)).

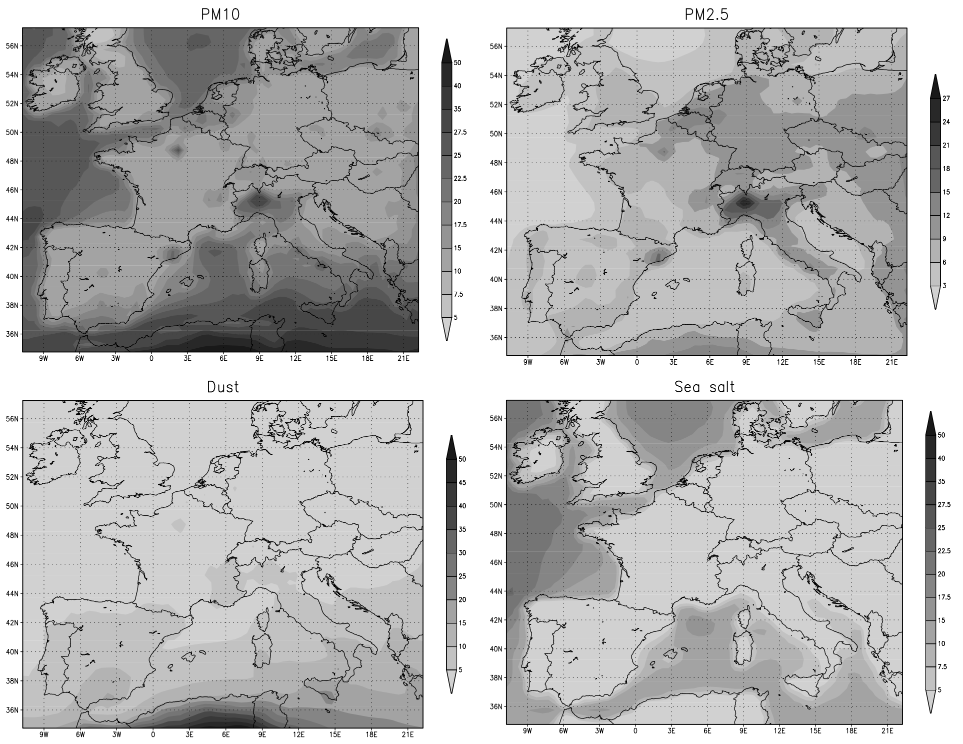

Fig. 1. Yearly mean concentrations (in μg m^{-3}) of PM components in 2001.

2.2 Error statistics

2.2.1 Simulated fields

The simulation is run over the year 2001, and the evaluation is made for both gases and aerosols. Hourly, daily, and peak statistics are computed for O_3. Daily statistics are computed for NO_2, SO_2, NH_3, HNO_3 and particulate matter (PM_{10}, sulfate, nitrate, ammonium, sodium and chloride).

The spatial distribution of pollutants over Europe is shown on Figure 1 for PM_{10}, $PM_{2.5}$, dust, sea salt, nitrate and ammonium. The spatial distribution of $PM_{2.5}$ shows similar patterns to the distribution computed by Bessagnet et al. (2004) for the year 1999, with high concentrations over northern Italy, the north east of Spain, The Netherlands, Germany and eastern European countries. The spatial distribution of PM_{10} differs from that of Bessagnet et al. (2004), which did not include sea salt and dust. As shown in Figure 1, the high PM_{10} concentrations observed in the south part of Europe are made mostly of Saharan dust, while the high concentrations in the west part of the domain are mostly due to sea salt.

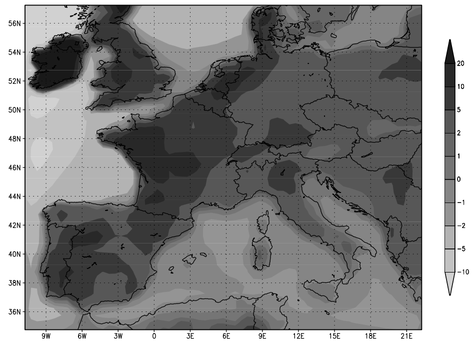

Fig. 2. Mean simulated gas ratio in 2001.

Figure 2 shows the simulated gas ratio GR (Park et al. (2004))

$$GR = \frac{\left[NH_3^T\right] - 2\left[SO_4^{2-}\right]}{\left[HNO_3^T\right]}. \tag{2}$$

where concentrations are in molar units, $\left[NH_3^T\right]$ is the sum of ammonium and ammonia, $\left[HNO_3^T\right]$ is the sum of aerosol nitrate and nitric acid and $\left[SO_4^{2-}\right]$ is the sulfate concentration. As shown by Park et al. (2004) over the United States, negative GR values, which indicate an acidic sulfate aerosol, are limited to the the oceans. Although in Park et al. (2004) over the United States, the supply of ammonia limits the formation of ammonium nitrate (GR ¡ 1), in Europe and especially in western Europe, the ammonium nitrate formation is limited by the formation of nitric acid (GR ¿ 1).

2.2.2 Measured data

The model results are compared to observational data provided by three databases:

- the EMEP database, available on the EMEP Chemical Co-ordinating Centre (EMEP/CCC) web site at `http://www.emep.int`;
- the AirBase database, available on the European Environment Agency (EEA) web site at `http://air-climate.eionet.europa.eu/databases/airbase`;
- The BDQA database (“Base de Données Qualité de l’Air”: the French Data Basis for Air Quality that covers France).

The location of the stations is given in Figure 3 for each of the three databases.

The measurement sites of the EMEP network are assumed to be representative of the regional background concentrations (Torseth and Hov (2003)). The AirBase database contains observational data from the European Air Quality monitoring network (EuroAirnet). For our comparisons only the stations labeled as “background” representative have been used. However it should

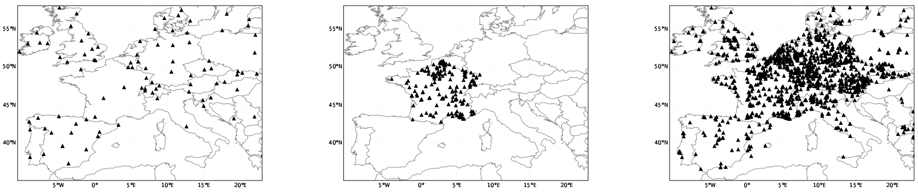

Fig. 3. Locations of the stations for the EMEP (left panel), the BDQA (middle panel) and the AirBase (right panel) databases.

be kept in mind that "background" does not have exactly the same meaning between AirBase and EMEP. For instance traffic and industrial stations have been excluded but stations representative of urban or suburban background have been kept. The same kind of filter has been applied to data from the BDQA, "rural" and "suburban" stations have been retained.

Measurement data used in this paper are given on a daily average basis except for ozone, for which hourly averages are available. Since AirBase contains observational data from several European networks, some time series measurements may be provided by both AirBase and BDQA or EMEP databases.

There are many uncertainties in the observational data. First, some sites may be not representative of background values (not far enough from important emissions). Second, some sites may be strongly impacted by local conditions (for instance orography). Third, the observational error may be large due to artifacts in the measurement methods (we refer for instance to Schaap et al. (2004) for a deeper understanding; a key process is evaporation of the samples, for example).

The aerosol water content is not taken into account in the model-to-data comparisons. Moreover, although the aerodynamic diameter is used for PM_{10} and $PM_{2.5}$ in measurements, the Stokes diameter is used in the modeling and for the comparison to measurements. The discrepancy in the results is not significant as compared to other uncertainties.

2.2.3 Statistical indicators

The key statistical indicators are the correlation coefficient (%) and the root mean square error RMSE (μg m^{-3}) (given in Appendix). The smaller the RMSE and the larger the correlation, the better the model fits the observations. The US EPA (EPA (1991), Russell and Dennis (2000)) recommends using the mean normalized bias error (MNBE) and the mean normalized gross error (MNGE) with an observation-based minimum threshold of 40 to 60 ppb (about 80 to 120 μg m^{-3}) to evaluate hourly ozone. The suggested performance criteria are MNBE $\leq \pm 15\%$ and MNGE $\leq 30\%$. When computing statistics for ozone in this paper, a threshold of 80μg m^{-3} is chosen. Bias indicates

	Obs. mean	Mod. mean	RMSE	correlation
O_3	56.0 - 57.1	57.6 - 65.2	23.1 - 28.1	54 - 69
O_3 peak	79.6 - 79.9	68.6 - 84.6	18.1 - 22.1	73 - 83
NO_2	14.8 - 15.7	7.0 - 16.0	11.7 - 13.9	30 - 46
SO_2	3.2 - 3.7	2.7 - 11.0	3.2 - 10.1	39 - 49
PM_{10}	20.0 - 20.5	9.4 - 13.8	12.4 - 15.2	38 - 55
Sulfate	2.3 - 2.8	2.0 - 3.2	1.8 - 2.9	50 - 62
Ammonium	1.1 - 1.9	0.8 - 2.4	0.8 - 2.1	44 - 56
Nitrate	1.7 - 2.9	1.5 - 2.9	1.6 - 2.7	17 - 46

Table 1
Range of values obtained for observed and modeled means, RMSE and correlation over Europe in 2001 according to van Loon et al. (2004)

whether the model tends to under or overpredict the observations, and error and RMSE indicates how large the deviation is. According to Boylan and A.G. (2006), the MNBE and MNGE may not be appropriate to evaluate particulate matter. They suggested using instead the mean fractional bias MFB (%) and the mean fractional error MFE (%). They propose that a model performance goal is met when both the MFE and the MBE are less than or equal to +50% and ±30% respectively, and a model performance criteria is met when both MFE $\leq +$ 75% and MFB $\leq \pm$60%.

An inter-comparison of seven models over Europe for 2001 is presented in van Loon et al. (2004), hereafter referred to as TNO-04. The data used in the report differ from one model to another, e.g. for meteorological data, boundary conditions, emissions... However, it provides a good basis for evaluating the reliability of the results obtained with Polyphemus over Europe for the year 2001. Table 1 shows the range of error statistics (correlation and RMSE) that were presented in this report. Measurements from both the EMEP and the AirBase database were used to compute the statistics.

2.2.4 Results

Statistics obtained with Polyphemus over Europe in 2001 are shown for the three monitoring networks in Tables 2 and 3.

	Database	Stations	Obs. mean	Mod. mean	RMSE	corr	MFB	MFE	MNBE	MNGE
O_3	EMEP	96	63.2	57.0	24.3	63.9	40	-10	-18	22
	AirBase	1017	49.8	52.9	25.9	67.8	12	56	-16	20
	BDQA	135	53.1	55.5	25.2	69.1	12	50	-16	20
O_3 peak	EMEP	96	80.2	73.5	21.4	72.1	24	-7	-14	18
	AirBase	1022	73.6	72.4	23.5	76.6	5	31	-14	18
	BDQA	139	77.4	73.7	23.2	77.4	1	27	-15	18
NO_2	EMEP	35	7.5	9.0	5.7	50.0	22	59		
	AirBase	1049	23.9	15.3	14.2	57.2	-37	62		
	BDQA	75	22.1	13.4	14.6	55.9	-47	70		
NH_3	EMEP	3	7.4	6.3	5.5	28.8	12	52		
	AirBase	7	12.7	6.6	13.7	27.3	-23	101		
HNO_3	EMEP	7	0.7	1.3	1.4	26.2	40	89		
SO_2	EMEP	43	2.0	5.3	4.9	46.7	97	106		
	AirBase	992	6.5	7.3	6.6	44.2	25	70		
	BDQA	10	7.8	6.8	6.5	35.7	-13	59		

Table 2

Statistics obtained with POLYPHEMUS over Europe in 2001 for gaseous species: number of stations used to compute the statistics, observed mean (μg m^{-3}), modeled mean (μg m^{-3}), RMSE (μg m^{-3}), correlation (%), MFB (%), MFE (%), MNBE (%) and MNGE (%)

	Database	Stations	Obs. mean	Mod. mean	RMSE	corr	MFB	MFE	MNBE	MNGE
PM_{10}	EMEP	26	16.9	15.4	12.5	55.1	-9	50		
	AirBase	537	25.4	15.2	17.0	44.9	-45	59		
	BDQA	23	19.8	15.5	9.6	57.7	-27	41		
$PM_{2.5}$	EMEP	17	12.6	8.3	8.6	54.4	-40	61		
Sulfate	EMEP	57	2.5	2.0	1.7	55.6	-6	50		
	AirBase	11	1.9	2.3	1.7	49.4	39	65		
Nitrate	EMEP	14	2.6	4.0	3.1	41.3	30	75		
	AirBase	8	3.5	4.3	2.7	71.7	6	54		
Ammonium	EMEP	9	1.8	2.0	1.3	51.9	19	49		
	AirBase	8	1.8	2.0	0.9	74.4	14	36		
Sodium	EMEP	3	1.3	2.4	2.2	62.8	47	68		
Chloride	AirBase	7	0.9	3.1	3.5	69.8	83	102		

Table 3

Statistics obtained with POLYPHEMUS over Europe in 2001 for aerosols: number of stations used to compute the statistics, observed mean (μg m^{-3}), modeled mean (μg m^{-3}), RMSE (μg m^{-3}), correlation (%), MFB (%), MFE (%), MNBE (%) and MNGE (%)

The EPA criteria for ozone and ozone peaks have been met. Although MNBE goes to values as high as the criteria of ±15%, the MNGE is always largely under the criteria of 30%. For PM_{10}, the model performance criteria are met for the three networks. Furthermore, the results obtained for EMEP and BDQA are very well under the model performance goal. Although the criteria were designed for PM_{10} and $PM_{2.5}$, the model performance criteria are met for all aerosol species except chloride.

Statistics vary strongly depending on the observational data network used. For example, NO_2 and SO_2 observed values are 3 times higher with AirBase or BDQA stations than with EMEP stations. These differences stress the importance of the filtering of the stations used for the comparisons. Although urban stations are filtered out of all data bases, stations that are not truly background stations, such as suburban stations, may not be filtered out in some databases.

For ozone, compared to TNO-04, the observed values reported in Table 2 covers a large range. Values as low as 50 for AirBase and as high as 63 for EMEP are reported. However, the statistics (RMSE and correlation) obtained with POLYPHEMUS are within the range of those of TNO-04, with RMSE in its low range and correlation in its high range, suggesting that the results obtained with POLYPHEMUS are comparatively good for hourly ozone. However for ozone peaks, although the results are acceptable, RMSE obtained with POLYPHEMUS are in the high range and correlation in the low range.

For NO_2, good results are observed for the EMEP data base with RMSE as low as 5.7. However, POLYPHEMUS has difficulties representing the high concentrations observed with AirBase or BDQA. These high concentrations may be explained by suburban stations that have not been filtered out. Note that these high concentrations are much higher than the observed mean of TNO-04. However, the RMSE associated with these observations are similar to the highest RMSE of TNO-04 (14.6 against 13.9), and better correlations are obtained with POLYPHEMUS (46% for the highest of TNO-04 against 50% for the lowest of POLYPHEMUS).

For SO_2, as for NO_2, observed values differ by a factor 3 or 4 depending on the network. The low SO_2 concentrations observed with the EMEP network are largely overestimated by POLYPHEMUS (2.0 against 5.3). However, the higher concentrations observed with AirBase and BDQA are well represented. If the high concentrations in AirBase and bdqa are explained by suburban stations that are not filtered out, POLYPHEMUS has a tendency to over-estimate SO_2 concentrations. The RMSE are in the range of those of TNO-04, which spans from 3.2 to value as high as 10.1. Although very high correlations are obtained for NO_2, the correlations for SO_2 are similar to those of TNO-04. However, the lowest correlation obtained with POLYPHEMUS is slightly lower than the lowest correlation of TNO-04 (36% against 39%).

For PM_{10}, the concentrations observed at EMEP stations are lower than those observed at AirBase stations (16.9 against 25.4), although Polyphemus does not reproduce these high concentrations. In TNO-04, because all models underestimate the PM_{10} concentrations, carbonaceous primary emissions are suspected to be severely underestimated. As the range of observed values is large and the observed values of TNO-04 are in the middle of this range, the range of RMSE predicted by Polyphemus is also large (9.6 to 17.0 against 12.4 to 15.2). However, the correlations obtained with Polyphemus are in the high range of the TNO-04 correlations, with the highest value slightly higher than the highest of TNO-04 (62 against 55).

For sulfate, the concentrations observed with AirBase are slightly lower than the minimum concentrations of TNO-04 (1.9 against 2.3). The RMSE obtained with Polyphemus are slightly lower, while correlations are in the range of TNO-04.

For ammonium, the observed values as well as the modelled mean and the RMSE are in the range of TNO-04. The correlations obtained with Polyphemus with AirBase are much higher however (74 against a maximum of 56 in TNO-04).

For nitrate, the modelled concentrations are higher than those of TNO-04. The RMSE tends to be slightly higher with Polyphemus (3.1 against a maximum of 2.7 in TNO-04). Correlations are however much better with Polyphemus (72 against a maximum of 46 in TNO-04). The concentrations of nitrate are strongly influenced by those of sulfate, ammonium, NH_3 and HNO_3. Although good comparisons of NH_3 concentrations are obtained with the EMEP network, the high NH_3 concentrations observed with AirBase are not reproduced with Polyphemus. HNO_3 concentrations are largely overestimated compared to the EMEP network.

Polyphemus overpredicts sodium and chloride, especially chloride, even though good correlations with measurements are obtained (63% and 70%). This seems to indicate that the intensity of sea-salt emissions is too strong. However, the results are very localized: the 3 stations for sodium are in Denmark and the 7 stations for chloride in the Netherlands.

2.3 Discussion

The results obtained with Polyphemus for a 1-year simulation over Europe are acceptable. Model performance criteria are met for ozone and particulate species like PM_{10}, sulfate, nitrate, and ammonium. Comparisons of correlations and RMSE with those of other models run over Europe for 2001 point out the strengths and limitations of POLYPHEMUS.

Good results are obtained with POLYPHEMUS for hourly ozone, sulfate and ammonium. Correlations tend to be in the high range for different pollutants such as NO_2, PM_{10}, sulfate, ammonium, nitrate and even chloride and sodium. However, SO_2 and nitrate concentrations tend to be overestimated.

The robustness of the results obtained with POLYPHEMUS may be questioned. The system is likely sensitive to different parameterizations, inputs, and numerics.

Concerning parameterizations, taking into account sodium and chloride in ISORROPIA is likely to influence the concentrations of nitrate. For example, nitrate may condense to form sodium-nitrate or it may evaporate and chloride may condense depending on the ambient conditions. Nitrate concentrations may also be influenced by computing local equilibrium dynamically rather than assuming thermodynamic equilibrium as done here, and by heterogeneous reactions. They may enhance the formation of HNO_3, which in turn may condense onto aerosols. Aqueous chemistry may also greatly influence aerosol concentrations. The influence of the aqueous module may be less important if the threshold for the liquid water content is modified (the aqueous module is called for a liquid water content greater than 0.05 g m^{-3}). Different parameterizations for wet deposition are available for use, with large differences in the representative diameter for the rain as well as the raindrop velocity (Sportisse (2006)). What would be the influence of such parameterizations on the PM_{10} concentrations? Parameterizations of sea-salt emissions would also modify PM_{10} concentrations. In the parameterization used in this paper, only the indirect mechanism is taken into account (bubbles bursting). However, the direct mechanism (spume) may influence large aerosols.

Concerning inputs, we may wonder what is the impact of allocating 5% of SOx emissions to H_2SO_4, or to consider the time variations of NH_3. What is the impact of boundary conditions on particulate matter concentrations? This could be checked by using other boundary conditions than those offered by Gocart, and by changing the redistribution of Gocart's boundary conditions into the 5 POLYPHEMUS' sections (by changing the parameters of the trimodal lognormal distribution).

Concerning numerics and discretization, the results may be strongly sensitive to the choice of the number of sections or to the vertical layer structure. The integration of condensation/evaporation is an issue with the assumption of thermodynamic equilibrium.

As shown in Tables 4 and 5, the results vary strongly with the season. In general, results tend to be better in summer than in winter. For ozone, although the RMSE is higher in summer, lower MFB, MFE and higher correlation are observed between April and August. NH_3 tends to be underestimated in summer and overestimated in winter. For SO_2, best results are obtained between May and August, when SO_2 is not as strongly overestimated as the rest of the year. PM_{10} is underestimated in the summer and overestimated in winter. For sulfate, results tend to be best between June and August. Although SO_2 is strongly overestimated throughout the year, sulfate is underestimated between December and March. For ammonium, the seasonality is not as clear as for other pollutants. It has a slight tendency to be less overpredicted in the summer. Nitrate is slightly underestimated between May and August, but strongly overestimated during the rest of the year. Results tend to be best in terms of RMSE and MBF during the summer.

Each parameterization or input is likely to influence the pollutants differently in winter and summer. For example, parameterizations related to the aqueous module are more likely to impact aerosol concentrations in winter. On top of differences in ambient conditions, the sensitivity study proposed above may allow us to understand which processes cause pollutants to be overestimated or underestimated, which, as shown above, often depends on the season.

On top of questioning the robustness of the modeling system, one may question the robustness of model-to-data error statistics. Large differences exist between the EMEP and the AirBase measurements, although both databases cover Europe (Figure 3). For example, the observed mean for O_3 and NO_2 are 63.2μg m^{-3} and 7.5μg m^{-3} respectively with EMEP and 49.8μg m^{-3} and 23.9μg m^{-3} respectively with AirBase. The observed mean for PM_{10} is 16.9μg m^{-3} with EMEP and 25.4μg m^{-3} with Airbase. These differences may not only be caused by the observational error due to artifacts in measurement methods but also by the way the stations are filtered in the database. For example, some sites may not be truly representative of background values, and some sites may be strongly impacted by local conditions, such as orography. This difficulty in comparing different database measurements is reflected in the error statistics, which differ depending on the database used. For PM_{10}, the RMSE is only 12.5μg m^{-3} for EMEP, but becomes as high as 17μg m^{-3} for AirBase.

		Jan.	Feb.	March	April	May	June	July	August	Sept.	Oct.	Nov.	Dec.
O_3	RMSE	21.3	22.4	25.7	23.7	25.9	25.4	25.7	27.3	23.3	22.4	20.2	21.9
	Correlation	43	48	46.1	51	48	58	58	56	45	44	50	47
	MFB	-23	-19	-26	-9	-3	-12	-4	3	7	7	-17	-24
	MFE	54	44	43	30	30	29	31	34	38	43	50	56
NH_3	RMSE	9.3	2.4	4.6	1.4	7.0	4.6	4.3	5.8	0.9	0.9	1.1	5.5
	Correlation	-15	25	43	23	47	31	43	33	22	25	12	25
	MFB	19	20	49	61	-49	-13	-7	6	30	12	35	42
	MFE	61	51	56	69	52	48	32	37	43	46	58	74
SO_2	RMSE	7.5	5.8	5.6	4.3	2.7	2.2	2.2	2.5	3.4	4.4	5.0	7.0
	Correlation	40	42	39	39	38	37	40	28	33	34	38	41
	MFB	110	103	105	103	77	79	77	76	101	101	108	103
	MFE	119	109	111	109	88	92	88	92	113	108	115	110

Table 4
Statistics obtained with POLYPHEMUS over Europe in 2001 for the EMEP network for gaseous species: monthly variations (from January to December) of the statistics RMSE (μg m^{-3}), correlation (%), MFB (%), MFE (%) for different pollutants.

		Jan.	Feb.	March	April	May	June	July	August	Sept.	Oct.	Nov.	Dec.
PM_{10}	RMSE	16.5	11.8	11.0	6.7	8.6	8.8	9.6	11.8	8.9	21.3	10.2	9.4
	Correlation	60	54.4	63	59	45	66	76	64	60	67	51	41
	MFB	7	-3	-3	6	-15	-12	-40	-28	-22	3	18	15
	MFE	60	46	52	45	40	42	51	49	56	57	53	53
Sulfate	RMSE	1.8	1.3	1.4	1.3	1.7	1.5	1.5	1.8	1.5	1.7	1.2	1.7
	Correlation	58	50	58	50	52	62	64	59	61	57	47	48
	MFB	-22	-17	-21	5	12	-2	-2	-4	5	-4	-2	-22
	MFE	59	51	50	46	46	43	43	46	51	50	57	59
Ammonium	RMSE	1.5	1.4	1.2	1.3	1.1	0.8	0.9	1.1	1.0	1.8	1.2	1.1
	Correlation	51	48	60	53	35	55	45	48	59	52	59	60
	MFB	13	29	38	43	15	12	3	10	31	10	26	4
	MFE	53	55	53	55	48	45	41	45	52	47	53	48
Nitrate	RMSE	3.5	3.5	3.4	3.6	2.1	1.7	1.7	2.2	2.4	3.7	3.1	2.9
	Correlation	47	46	46	42	19	29	22	32	42	41	48	45
	MFB	62	50	76	70	-18	6	-28	0	37	29	39	50
	MFE	82	81	86	81	74	66	77	74	71	68	72	71

Table 5
Statistics obtained with POLYPHEMUS over Europe in 2001 for the EMEP network for aerosols: monthly variations (from January to December) of the statistics RMSE (μg m^{-3}), correlation (%), MFB (%), MFE (%) for different pollutants.

Conclusion and future work

The POLYPHEMUS system has been extended to aerosol modeling by hosting the SIREAM model. The simulation of 2001 over Europe has been studied through an extensive model-to-data comparison for 3 observational networks (EMEP, AirBase and BDQA). The results, while variable between the chemical species, are acceptable given the results of other such models. The limitations of the model have been pointed out. Some processes have a strong impact on error statistics.

Apart from the conclusions related to the performance of the modeling system, one may question the robustness of such models. A comprehensive sensitivity analysis is required and is the subject of a companion paper that investigates the sensitivity of model results with respect to many modeling inputs (physical parameterizations, numerics). Moreover, the error statistics may differ significantly from one network to another, which underlines the difficulty of having fair and robust model-to-data error statistics.

Acknowledgements

Part of this project has been funded by the French Research Program, Primequal-Predit, in the framework of the PAM Project (Multiphase Air Pollution). Some of the authors (K.Fahey, K.Sartelet and M.Tombette) have been partially funded by the Region Ile de France.

We thank Spyros Pandis (Carnegie Mellon University and the University of Patras) for his help in aerosol modeling. We also thank our colleague Hadjira Houdhil for her help in the development of POLAIR3D. We thank our colleagues Vivien Mallet and Denis Quélo for having helped to adapt the POLYPHEMUS system for

References

Ackermann, I., Hass, H., M., M., Ziegenbein, C., Ebel, A., 1995. The parameterization of the sulfate-nitrate-ammonia aerosol system in EURAD. Meteorol.Atmos.Phys. 57, 101:114.

Bessagnet, B., Hodzic, A., Vautard, R., Beekmann, M., Cheinet, S., Honore, C., Liousse, C., Rouil, L., 2004. Aerosol modeling with chimere – preliminary evaluation at the continental scale. Atmos. Env. 38, 2803–2817.

Bocquet, M., 2005. Reconstruction of an atmospheric tracer source using the principle of maximum entropy II : Applications. Quart. J. Roy. Meteor. Soc. 131 (Part B(610)).

Boutahar, J., Lacour, S., Mallet, V., Qulo, D., Roustan, Y., Sportisse, B., 2004. Development and validation of a fully modular platform for numerical modelling of air pollution: Polair3D. Int. J. Env. and Pollution 22 (1-2).

Boylan, J., A.G., R., 2006. PM and light extinction model performance metrics, goals, and criteria for three-dimensional air quality models. Atmos. Env. in press.

Brandt, J., 1998. Modelling transport, dispersion and deposition of passive tracers from accidental releases. Ph.D. thesis, NERI, Denmark.

Brown, P., Byrne, G., Hindmarsh, A., 1989. VODE: A Variable Coefficient ODE Solver. SIAM J. on Sci. and Stat. Comp. 10, 1038–1051.

Capaldo, K., Pilinis, C., Pandis, S., 2000. A computationally efficient hybrid approach for dynamic gas/aerosol transfer in air quality models. Atmos. Env. 34, 3617–3627.

Chin, M., Rood, R., Lin, S.-J., Muller, J., Thomspon, A., 2000. Atmospheric sulfur cycle in the global model GOCART: Model description and global properties. J. Geophys. Res. 105, 24671–24687, 10.1029/2000JD900384.

Dahneke, B., 1983. Theory of Dispersed Multiphase Flow. Academic press, New York.

Debry, E., 2004. Modelling and simulation of an atmospheric aerosol distribution. Ph.D. thesis, ENPC, CEREA.

Debry, E., Fahey, K., Sartelet, K., Sportisse, B., Tombette, M., 2006. Technical note: A new SIze REsolved Aerosol Model: SIREAM. Atmos. Chem. Phys. Discuss.Submitted.

Debry, E., Sportisse, B., 2005a. Reduction of the condensation/evaporation dynamics for atmospheric aerosols: theoretical and numerical investigation of hybrid methods. J. Aerosol Sci.Accepted for publication.

Debry, E., Sportisse, B., 2005b. Solving aerosol coagulation with size-binning methods. Appl. Numer. Math.In revision.

Djouad, R., Sportisse, B., Audiffren, N., 2002. Numerical simulation of aqueous-phase atmospheric models : use of a non-autonomous Rosenbrock method. Atmos. Env. 36, 873–879.

EPA, 1991. Guideline for regulatory application of the urban airshed model. Tech. rep., EPA, technical report.

Fahey, K., 2003. Cloud and fog processing of aerosols: modeling the evolution of atmospheric species in the aqueous phase. Ph.D. thesis, Carnegie Mellon University.

Fahey, K., Pandis, S., 2003. Size-resolved aqueous-phase chemistry in a three-dimensional chemical transport model. J. Geophys. Res. 108, 4690, doi:10.1029/2003JD003564.

Fernandez-Diaz, J., Gonzalez-Pola Muniz, C., Rodriguez Brana, M., Arganza Garcia, B., Garcia Nieto, P., March 2000. A modified semi-implicit method to obtain the evolution of an aerosol by coagulation. Atmos. Env.

34, 4301–4314.

GENEMIS, 1994. GENEMIS (generation and evaluation of emission data. Tech. rep., EUROTRAC, annual report 1993.

Gerber, H., 1985. Relative-humidity parameterization of the navy aerosol model (NAM). Tech. Rep. 8956, National Research Laboratory, Washington, D.C.

Griffin, R., Dabdub, D., Kleeman, M., Fraser, M., Cass, G., Seinfeld, J., 2002a. Secondary organic aerosol 3. Urban/regional scale model of size- and composition-resolved aerosols. J. Geophys. Res. 107 (D17), 4334, doi:10.1029/2001JD000544.

Griffin, R., Dabdub, D., Seinfeld, J., 2002b. Secondary organic aerosol 1. Atmospheric chemical mechanism for production of molecular constituents. J. Geophys. Res. 107 (D17), 4332, doi:10.1029/2001JD000541.

Isnard, O., Krysta, M., Bocquet, M., Dubiau, P., Sportisse, B., December 2005. Data assimilation of radionuclides atmospheric dispersion at small scale: a tool to assess the consequences of radiological emergencies. In: Proceedings of the IAEA Conference. Rio Conference.

Jacob, D., 2000. Heterogeneous chemistry and tropospheric ozone. Atmos. Env. 34, 2131–2159.

Johnson, D., Utembe, S., Jenkin, M., Derwent, R., Hayman, G., Alfarra, M., Coe, H., McFiggans, G., 2006. Simulating regional scale secondary organic aerosol formation during the TORCH 2003 campaign in the southern UK. Atmos. Chem. Phys. 6, 403–418.

Loosmore, G., Cederwall, R., 2004. Precipitation scavenging of atmospheric aerosols for emergency response applications: testing an updated model with new real-time data. Atmos. Env. 38, 993:1003.

Loubet, B., Cellier, P., Genermont, S., Laville, P., Flura, D., 2003. Measurement of short-range dispersion and deposition of ammonia over a maize canopy. Agric. For. Meteor. 114, 175–196.

Louis, J., 1979. A parametric model of vertical eddy fluxes in the atmosphere. Boundary-Layer Meteor. 17, 197:202.

Mallet, V., Sportisse, B., 2005. A comprehensive study of ozone sensitivity with respect to emissions over Europe with a chemistry-transport model. J. Geophys. Res. 110 (D22).

Mallet, V., Sportisse, B., 2006a. Toward ensemble-based air-quality forecasts. J. Geophys. Res.Accepted for publication.

Mallet, V., Sportisse, B., 2006b. Uncertainty in a chemistry-transport model due to physical parameterizations and numerical approximations: an ensemble approach applied to ozone modeling. J. Geophys. Res. 111, D01302, doi:10.1029/2005JD006149.

Middleton, P., Stockwell, W., Carter, W., 1990. Aggregation and analysis of voc emissions for regional modelling. Atmos. Env. 24, 1107–1133.

Monahan, E., Spiel, D., Davidson, K., 1986. A model of marine aerosol generation via whitecaps and wave disruption. In: Oceanic whitecaps. D. Reidel, pp. 167–174.

Napari, I., Noppel, M., Vehkamki, H., Kulmala, M., 2002. Parametrization of ternary nucleation rates for H2SO4-NH3-H2O vapors. J. Geophys. Res. 107 (D19), 4381, doi:10.1029/2002JD002132.

Nenes, A., Pandis, S., Pilinis, C., 1998. ISORROPIA : A new thermodynamic equilibrium model for multicomponent inorganic aerosols. Aquatic geochemistry 4, 123–152.

Pandis, S., Seinfeld, J., Pilinis, C., 1990. The smog-fog-smog cycle and acid deposition. J. Geophys. Res. 95, 18489–18500.

Park, R., Jacob, D., Field, B., Yantosca, R., 2004. Natural and transboundary pollution influences on sulfate-nitrate-ammonium aerosols in the united states: Implications for policy. J. Geophys. Res. 109, D15204, doi:10.1029/2003JD004473.

Passant, N., 2002. Speciation of UK emissions of NMVOC. Tech. rep., AEA Technology, tech. Rep. AEAT/ENV/0545.

Pilinis, C., Capaldo, K., Nenes, A., Pandis, S., 2000. MADM - a new Multicomponent Aerosol Dynamic Model. Aerosol Sc. and Tech. 32, 482–502.

Pun, B., Griffin, R., Seigneur, C., Seinfeld, J., 2002. Secondary organic aerosol 2. Thermodynamic model for gas/particle partitioning of molecular constituents. J. Geophys. Res. 107 (D17), 4333, doi:10.1029/2001JD000542.

Putaud, J., Dingenen, R., Baltensperger, U., Brggemann, E., Charron, A., Facchini, M., Decesari, S., Fuzzi, S., Gehrig, R., Hansson, H., Harrison, R., Jones, A., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N., Mller, K., Palmgren, F., Querol, X., Rodriguez, S., Schneider, J., Spindler, G., Brink, H., Tunved, P., Torseth, K., Weingartner, E., Wiedensohler, A., Wahlin, P., Raes, F., 2003. A european aerosol phenomenology. Tech. rep., Joint Research Centre, Institute for Environment and Sustainability.

Quelo, D., Krysta, M., Bocquet, M., Isnard, O., Minier, Y., Sportisse, B., 2006. Validation of the POLYPHEMUS system: the ETEX, Chernobyl and Algeciras cases. Atmos. Env.Submitted.

Quelo, D., Mallet, V., Sportisse, B., 2005. Inverse modeling of NO_x emissions at regional scale over Northern France. Preliminary investigation of the second-order sensitivity. J. Geophys. Res. 110, D24310, doi:10.1029/2005JD006151.

Roselle, S., Binkowski, F., 1999. Cloud dynamics and chemistry. Tech. rep., U.S. Environmental Protection Agency, EPA/600/R-99/030 chapter 11.

Roselle, S., Schere, K., Pleim, J., 1999. Photolysis rates for CMAQ. Tech. rep., U.S. Environmental Protection Agency, EPA/600/R-99/030 chapter 14.

Roustan, Y., Bocquet, M., 2006a. Inverse modeling for mercury over Europe. Atmos. Chem. Phys. Discuss., 795–838SRef-ID: 1680-7375/acpd/2006-6-795.

Roustan, Y., Bocquet, M., 2006b. Sensitivity analysis for mercury over Europe. J. Geophys. Res. 111, D14304, doi:10.1029/2005JD006616.

Russell, A., Dennis, R., 2000. NARSTO critical review of photochemical models and modeling. Atmos. Env. 34, 2,283–2,234.

Sartelet, K., Hayami, H., Sportisse, B., 2006. MICS-Asia Phase II: sensitivity to the aerosol module. Atmos. Env.Submitted.

Sartelet, K. N., Hayami, H., Albriet, B., Sportisse, B., 2005. Development and preliminary validation of a modal aerosol model for tropospheric chemistry: MAM. Aerosol Sc. and Tech. 40 (2), 118–127.

Schaap, M., 2003. On the importance of aerosol nitrate over europe. data analysis and modelling. Ph.D. thesis, University of Utrecht, The Netherlands.

Schaap, M., Timmermans, M., Sauter, F., Roemer, M., Velders, G., Boersen, G., Beck, J., Builtjes, P., 2005. The LOTOS-EUROS model: description, validation and latest development. Int. J. Env. and Pollution.

Schaap, M., Van Der Gon, H., Dentener, F., Visschedijk, A., Van Loon, M., ten Brink, H., Putaud, J.-P., Guillaume, B., Liousse, C., Builtjes, P., 2004. Anthropogenic black carbon and fine aerosol distribution over europe. J. Geophys. Res. 109, D18207, doi:10.1029/2003JD004330.

Schell, B., 2000. Die behandlung sekundrer organischer aerosole in einem komplexen chemie-transport-modell. Ph.D. thesis, Univ. Kln.

Schell, B., Ackermann, I., Hass, H., Binkowski, F., Ebel, A., 2001. Modeling the formation of secondary organic aerosol within a comprehensive air quality model system. J. Geophys. Res. 106, 28275–28294.

Schmidt, H., Derognat, C., Vautard, R., Beekmann, M., 2001. A comparison of simulated and observed ozone mixing ratios for the summer of 1998 in Western Europe. Atmos. Env. 35, 6277:6297.

Seinfeld, J., Pandis, S., 1998. Atmospheric Chemistry and Physics. Wiley-interscience.

Simpson, D., Fagerli, H., Jonson, J. E., Tsyro, S., Wind, P., Tuovinen, J.-P., 2003. Transboundary acidification, euthrophication and ground level ozone in Europe. Part I: Unified EMEP model description. Tech. rep., EMEP.

Simpson, D., Winiwarter, W., Brjesson, G., Cinderby, S., Ferreiro, A., Guenther, A., Hewitt, C., Janson, R., Khalil, M., Owen, S., Pierce, T., Puxbaum, H., Shearer, M., Skiba, U., Steinbrecher, R., Tarrason, L., Oquist, M., 1999. Inventorying emissions from nature in Europe. J. Geophys. Res. 104 (D7), 8113–8152.

Sportisse, B., 2006. A review of parameterizations for modeling dry deposition and scavenging of radionuclides. Atmos. Env.Submitted.

Sportisse, B., Dubois, L., 2002. Numerical and theoretical investigation of a simplified model for the parameterization of below-cloud scavenging by falling raindrops. Atmos. Env. 36, 5719–5727.

Sportisse, B., Sartelet, K., Debry, E., Fahey, K., Roustan, Y., Tombette, M., 2006. PAM project (multiphase air pollution): description of the aerosol models SIREAM and MAM. Tech. Rep. 2006-08, CEREA, available at http://www.enpc.fr/cerea/polyphemus.

Stockwell, W., Kirchner, F., Kuhn, M., Seefeld, S., 1997. A new mechanism for regional atmospheric chemistry modeling. J. Geophys. Res. 95 (D10), 16343:16367.

Strader, R., Gurciullo, C., Pandis, S., Kumar, N., Lurmann, F., 1998. Development of gas-phase chemistry, secondary organic aerosol and aqueous-phase chemistry modules for PM modeling. Tech. rep., STI.

Torseth, K., Hov, O., 2003. The EMEP monitoring strategy 2004-2009. Tech. rep., EMEP/CCC, eMEP/CCC report - 9/2003.

Troen, I. B., Mahrt, L., 1986. A simple model of the atmospheric boundary layer; sensitivity to surface evaporation. Boundary-Layer Meteor. 37, 129–148.

Tsyro, S., 2001. Description of the Lagrangian Acid Deposition Model. Tech. rep., EMEP, technical report.

van Loon, M., Roemer, M., Builtjes, P., 2004. Model inter-comparison in the framework of the review of the unified EMEP model. Tech. rep., TNO Environment Energy and Process Innovation, TNO report - R2004/282.

Vautard, R., Bessagnet, B., Chin, M., Menu, L., 2005. On the contribution of natural Aeolian sources to particulate matter concentrations in Europe: Testing hypotheses with a modelling approach. Atmos. Env. 39, 3291–3303.

Vehkamaki, H., Kulmala, M., Napari, I., Lehtinen, K., Timmreck, C., Noppel, M., Laaksonen, A., 2002. An improved parameterization for sulfuric acid-water nucleation rates for tropospheric and stratospheric conditions. J. Geophys. Res. 107 (D22), 4622, doi:10.1029/2002JD002184.

Verwer, J., Spee, E., Blom, J., Hundsdorfer, W., 1999. A second order Rosenbrock method applied to photochemical dispersion problem. SIAM J. Sci. Comp. 20 (4), 1456–1480.

Wesely, M., 1989. Parameterization of surface resistance to gaseous-dry deposition in regional scale numerical models. Atmos. Env. 23, 1293:1304.

Zhang, L., Brook, J., Vet, R., 2003. A revised parameterization for gaseous dry deposition in air-quality models. Atmos. Chem. Phys. 3, 2067–2082.

Zhang, L., Gong, S., Padro, J., Barrie, L., 2001. A size-segregated particle dry deposition scheme for an atmospheric aerosol module. Atmos. Env., 549–560.

Appendix: statistical indicators

The following indicators are computed by the AtmoPy module in order to evaluate error statistics for model-to-data comparisons. Let $(o_i)_i$ and $(c_i)_i$ be the observed and the modeled concentrations at time and location i, respectively. Let n be the number of data.

We define the following indicators:

- Root mean square error (RMSE)

$$\sqrt{\frac{1}{n}\sum_{i=1}^{n}(c_i - o_i)^2}$$

- Correlation

$$\frac{\sum_{i=1}^{n}\left(c_i-\bar{c}\right)\left(o_i-\bar{o}\right)}{\sqrt{\sum_{i=1}^{n}\left(c_i-\bar{c}\right)^2}\sqrt{\sum_{i=1}^{n}\left(o_i-\bar{o}\right)^2}}$$

$$\text{with: } \bar{o}=\frac{1}{n}\sum_{i=1}^{n}o_i \text{ and } \bar{c}=\frac{1}{n}\sum_{i=1}^{n}c_i$$

- Mean normalized bias error (MNBE)

$$\frac{1}{n}\sum_{i=1}^{n}\frac{c_i-o_i}{o_i}$$

- Mean normalized gross error (MNGE)

$$\frac{1}{n}\sum_{i=1}^{n}\frac{\left|c_i-o_i\right|}{o_i}$$

- Mean fractional bias (MFB)

$$\frac{1}{n}\sum_{i=1}^{n}\frac{c_i-o_i}{\left(c_i+o_i\right)/2}$$

- Mean fractional error (MFE)

$$\frac{1}{n}\sum_{i=1}^{n}\frac{\left|c_i-o_i\right|}{\left(c_i+o_i\right)/2}$$