

MATHEMATICAL MODELS IN AIR QUALITY PROBLEMS

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Contents

1	Introduction	3
2	A Fundamental Chemical Kinetics System	5
3	Modeling of Linear Advection	6
3.1	Modeling in 1D	6
3.1.1	Generalities and Finite Difference Methods	6
3.1.2	Simple Finite Difference Schemes	7
3.2	Finite Volume Method in 1D	8
3.2.1	Formulation of the Finite Volume Method	8
3.2.2	Godunov Type Methods: General Principle and Formulation	9
3.2.3	Examination of usual Godunov Methods	11
3.3	Modeling of the Advection Problem in 3D	13
4	Modeling of Chemical Ordinary Differential Equations	14
4.1	Formulation of the Problem and Classical Methods	14
4.2	Special Methods for Chemistry Modeling	15
4.2.1	The QSSA Method	15
4.2.2	The Two-step Method	16
5	One Example of the Modeling of the Air Pollution Problem: the CHIMERE software	17
5.1	Chemical Mechanism	17
5.2	Emissions	18
5.3	Depositions	19
5.4	Advection, diffusion and boundary layer modeling	19
5.5	The Model in 3D	21
5.6	An Illustrative Example	21

Glossary Ozone: The main greenhouse gas for our air quality problem.
Cells: Partition of the simulation domain.

Finite Volume Method: Method which calculates the average of the solution in each cell.

CFL condition: Courant-Friedrichs-Lewy condition. It is a necessary condition for the stability of any explicit numerical method for solving linear advection.

TVD (Total Variation Diminishing): Property at least necessary for proving the convergence of the numerical solution towards the solution of the conservative equation.

Slope Limiter: Condition that insures, for any scheme, the TVD property.

Conservative Scheme: Property of a scheme which preserves against the convergence of the method towards a non-solution of the advection problem put in conservative form.

Flux Function: The cell averages of the solution are evaluated by differences of the flux functions on the boundaries of the cells.

Godunov Methods: Framework and algorithm in finite volume method, which calculates the approximate fluxes of the field.

MUSCL: One of the Godunov schemes.

PPM: Piecewise Parabolic Method- another Godunov scheme.

Euler Method for ODEs: The simplest scheme to solve a system of ODEs.

Stiff Problems: ODEs systems whose solutions are characterized by very different time scales.

QSSA: Method used essentially for solving systems of ODEs arising from chemical kinetics.

Two-step method: Appropriate method to solve the stiff chemical ODEs.

Summary The problem of air quality is modeled by a reaction-advection-diffusion partial differential equation(PDE), where the unknown is the vector of the concentrations of model chemical components depending on space and time. Generally the flow fields are pre-processed by meteorological computations or parameterizations. The coupling of all chemical components is given by the chemical mechanism considered. Essentially this mechanism appears in the right member of the previous equation. The first question to solve is to introduce the fundamental chemical kinetic system producing ozone (the main pollutant and greenhouse gas). Subsequently, one needs to choose a solution method for the PDE. The finite volume method is the right framework for that, and we present it in the context of Godunov schemes (Van Leer, PPM). For didactic reasons we consider the 1D case (in space) then the 3D case. After using the finite volume method, we obtain a large system of stiff ordinary differential equations (taking into account, furthermore, depositions and emissions). Due to the stiffness and the size of the system of ODEs, a method especially dedicated to this system has been developed (two-step). Space editorial constraints do not allow for a comprehensive description and comparison of the models used in the field of air pollution problems. Rather we concentrate in a last section on one model with an illustrative example: the simulation of the episode of unusually persistent high ozone concentrations in western European countries during August 2003.

1 Introduction

In this article on air pollution modeling we emphasize mainly models on air quality forecasting. This is a challenging scientific problem, which has recently received considerable attention in many industrialised countries due to the increasing awareness of the effects, on health and environment, of the emissions into the urban atmospheres of pollutants, especially volatile organic compounds (VOCs) and nitrogen oxides (NO_x). The environmental benefits of reliable air quality forecasts are obvious : populations can be more efficiently protected by means of information on hazardous conditions or real-time emission abatement strategies. The scientific aspects of air-quality forecasting are of major scientific interest, since prediction lies at the end of the understanding process. In this presentation we focus on models based on the physical equations (often called “deterministic models”) driving the chemistry and the transport of pollutants. Deterministic models require input of numerous data (e.g. emissions, meteorology, input cover), which are difficult to collect in real time. Problems with data may eventually become less and less significant with time, due to increase in computer capabilities and to improvements in the data bases required for the deterministic approach of forecasting. Obviously the methods presented here are generic and valid for any problem related to air quality modeling.

Air pollution modeling always start with atmospheric chemical kinetics systems. These describe chemical reactions between trace gases, such as ozone, nitrogen oxides, methane, hydrocarbons, etc. One often studies ozone in the lower atmosphere, as ozone is dangerous for humans and animals during short term smog episodes and can damage crops when levels are too high over longer seasonal periods. Ozone is also a greenhouse gas, similar to methane, carbon dioxide and other species. Air pollution models are therefore also used in connection with climate studies. Ozone itself is not emitted but formed in very many different reactions. In Section 2 we give the fundamental chemical mechanism accountable for ozone production. A nice introduction to the field of atmospheric chemistry can be found in Graedel and Crutzen [14].

Air pollution modeling is based on the assumption of no feedbacks between chemical species and flow fields (wind velocity, turbulent diffusivity, temperature). After having pre-processed the flow fields by meteorological computations or parameterizations, ones solves thereafter a reaction-advection-diffusion partial differential equation (PDE), representing the one change in concentrations of chemical species :

$$\frac{\partial \vec{C}}{\partial t} + \text{div}(\vec{V}\vec{C}) = \text{div}(\mathbf{K}\vec{C}) + P(\vec{C}, t) - L(\vec{C}, t). \quad (1.1)$$

Here \vec{C} is a vector containing the concentrations of all m model chemical species depending on space and time t , \vec{V} is three dimensional wind vector, \mathbf{K} is turbulent diffusive matrix, and P and L represent production and loss terms due to chemical reactions, emissions and depositions. The wind field \vec{V} and the diffusion coefficient matrix \mathbf{K} are given, so that the problem is linear with respect to the transport part. The chemical reactions between these components are of first or second order, so that the contribution of the chemical mechanisms in terms P and L is quadratically non-linear (it is by this mechanism that P and L depend on, for a specific concentration chemical species c , the

concentrations of other constituents). Without the chemical mechanism the m equations (1.1) are uncoupled.

In methods of solution often used in air pollution modeling, the PDE system (1.1) with its boundary conditions are first discretized in space on a three-dimensional Eulerian grid. On the discretized space grid the system of ODEs is then solved in time.

The major transport mechanism in air pollution models is advection by the wind field: hence the quality of the advection computation is crucial. The finite volume method is an appropriate one for the advection calculation. In Section 3 we examine the scalar advection problem in one space dimension. We start by considering a finite difference method (the upwind method) by contrast to a finite volume method. Next we consider several finite volume methods in the Godunov framework, as pioneered by Godunov, van Leer and others (see for instance [21]). The modeling of the 3D advection problem is presented in Section 3.3.

The wide range of chemical timescales (10^{-9} s for excited oxygen radical O^{1D} to be compared with several months for methane) induces the well-known stiffness of the resulting equations, as seen in Section 2. The time integration of such ODEs has then to be carefully designed in order to avoid excessively high computational cost. Implicit numerical schemes are highly recommended even if they are however associated with CPU costs which can remain large (due to inversions of matrices whose dimension is large : currently the number m of species is about one hundred). In view of the dimension and stiffness of the ODEs system together with the large number of cells in 3D, ODE integrators based on standard numerical routines are not feasible in an operational way. This has led to the use of time integration methods especially dedicated to the chemical models.

In Section 4 we start by reviewing classical and very simple methods for solving ODEs: the Euler methods. Due to the production-loss form of the ODEs descended from the chemical mechanism, specific methods of solutions have been designed. A traditional tool for modeling the chemistry is the well-known QSSA method, advocated long ago by Hessvedt and co-workers [18]. The scheme must be heavily tuned by “lumping” in order to be efficient. An alternative is to use a Backward Differentiation Formula (BDF method, see [4] chapter 7 for instance, for a nice presentation of these methods) (implicit by construction and well-suited for stiff problems) and adapt it to the special form of the chemistry modeling. By that, for instance the BDF2 method (number 2 is linked with the order of this method) can be written in a particular form; the resulting implicit scheme can be solved by a Gauss-Seidel process. This algorithm (BDF2 applied to production-loss form, with resolution of the implicit scheme by Gauss-Seidel), is proposed by Verwer [38] like the two-step method. This two-step method is more or less comparable to the QSSA method. The two-step and QSSA methods are presented in the Section 4.2.

Space constraints do not allow for a comprehensive description and comparison of the models used in the field of air pollution problem. Rather, we concentrate in the last section on the CHIMERE-continental software, a European scale Eulerian chemistry transport model recently developed at *Laboratoire de Météorologie Dynamique, Ecole Polytechnique, Palaiseau, France*. The description provided by a chemistry-transport model can be more detailed than that from a survey only. We precise one possible chemical mechanism, together with the emissions and dry depositions modeling. The modeling of advection, diffusion mechanisms and boundary layer (where essentially the pollution exits, further-

more it is the domain of interest for health and environment) processes are also described with any details. Taking into account the advection and diffusion operators together with the chemical mechanisms (included emissions and deposition), the resulting ODEs system is solved by a two-step procedure.

Obviously a good approach is searching for efficient numerical solvers that provide a reasonable compromise between accuracy and CPU requirements. We intend this presentation to give information on these aspects of the problem.

2 A Fundamental Chemical Kinetics System

The following are basic reactions in any tropospheric air pollution model:



In this system $O(^3P)$ is the oxygen atom in its fundamental state. The first equation is the principal source for $O(^3P)$ by photolysis of nitrogen dioxide (NO_2) in the troposphere. The second equation describes the formation of ozone (O_3). The third equation describes ozone destruction by reaction with nitrogen monoxide (NO) and formation of NO_2 . Normally, NO , NO_2 and $O(^3P)$ are in equilibrium and the ozone concentration is moderated. The formation of high ozone concentrations requires a mechanism quickly consumes NO and regenerates NO_2 . In a polluted environment, this is realized by coupling the NO/NO_2 cycle with weathering hydrocarbons (HC). The HC attacked by a hydroxyl radical (OH) becomes an alkyl radical (R) which, by a sequence of quick reactions with air-oxygen, produces peroxy and hydroperoxy radicals ((RO_2) and (HO_2) respectively) which, in turn, quickly oxidize NO to NO_2 with regeneration of the OH radical. These oxidation reactions from NO to NO_2 short-circuit that for NO by O_3 (see (2.1)) and the latter can accumulate.

The engine behind this complex chemistry is, therefore, the photolysis of participating chemical components (O_3 , NO_2 , etc.). In this way high levels of ozone can be produced during episodes of intensive solar irradiation. This condition is not sufficient, however. The precursors sources must be sufficiently important, especially in HC , and dynamical processes must favor the accumulation of precursors and products with weak dispersion and dilution. A good reference for the chemistry of the troposphere can be found in Seinfeld and Pandis [27].

For illustration, we show the ODE system associated with (2.1). Let $c_1 = [O(^3P)]$, $c_2 = [NO]$, $c_3 = [NO_2]$, $c_4 = [O_3]$, then (2.1) can be written as:

$$\begin{aligned}
 \dot{c}_1 &= k_1 c_3 - k_2 c_1 \\
 \dot{c}_2 &= k_1 c_3 - k_3 c_2 c_4 \\
 \dot{c}_3 &= k_3 c_2 c_4 - k_1 c_3 \\
 \dot{c}_4 &= k_2 c_1 - k_3 c_2 c_4
 \end{aligned}
 \tag{2.2}$$

Note that oxygen in these equations is taken as constant, which is a reasonable assumption. Typically, the first reaction is photochemical and represents rapid changes in concentrations values at sunset and sunrise.

3 Modeling of Linear Advection

We start with the one-dimensional scalar advection problem in one space dimension and discuss separately selected finite difference and finite volume methods of solution. Next, we tackle the 3D problem. For a more detailed presentation of the methods referenced in this section, the reader is referred to:

(<http://gershwin.ens.fr/houches2002/Cours/Roux/leshouches.pdf>).

3.1 Modeling in 1D

Let us consider the transport of a single pollutant (i.e. ozone). In view of the law of conservation of mass, the one-dimensional advection of this pollutant is given by:

$$\begin{aligned} \frac{\partial a}{\partial t} + \frac{\partial(au)}{\partial x} &= 0 & \forall (x, t) \in \mathbb{R} \times [0, T[\\ a(x, 0) &= a_0(x) & \forall x \in \mathbb{R} \end{aligned} \tag{3.1}$$

where a is concentration, u is wind velocity, x is distance, and t is time.

Since (3.1) is linear in space, then the transport process does not introduce more irregularities than those in the initial condition. Two numerical methods are using to solve (3.1): the finite difference method and the finite volume method.

3.1.1 Generalities and Finite Difference Methods

We next outline basics concepts of the finite difference method. For simplicity of presentation we consider in this Section 3.1 that u is constant and known. Then (3.1) becomes

$$\frac{\partial a}{\partial t} + u \frac{\partial a}{\partial x} = 0 \quad \forall (x, t) \in \mathbb{R} \times [0, T[\tag{3.2}$$

The exact solution (3.2) becomes

$$a(x, t) = a_0(x - ut) \tag{3.3}$$

Definition of a regular mesh We define a regular mesh in the (x, t) domain by the grid points $x_j = j\Delta x$, $t^n = n\Delta t$, where j and n are integers, $\Delta x = \frac{L}{M}$, $\Delta t = \frac{T}{N}$, and M and N are the number of nodes in the x and t directions, respectively (see Figure 1). We call a_i^n to an approximation of the true solution $a(x_i, t^n)$ at point x_i and at time t^n .

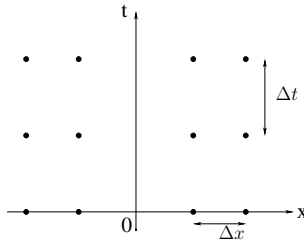


Figure 1: Discrete network of the points $(j\Delta x, n\Delta t)$ ($j \in \mathcal{Z}$ and $n \in \mathcal{N}$) for finite difference approximation.

3.1.2 Simple Finite Difference Schemes

For the advection equation (3.2) and in the case $u \geq 0$, perhaps the most simple scheme is the left one-sided scheme (see Figure 2):

$$a_i^{n+1} = a_i^n - u \frac{\Delta t}{\Delta x} (a_i^n - a_{i-1}^n) . \quad (3.4)$$

This particular form of the method in equation (3.4) is called explicit, since the advance in time is done directly without any matrix inversion.

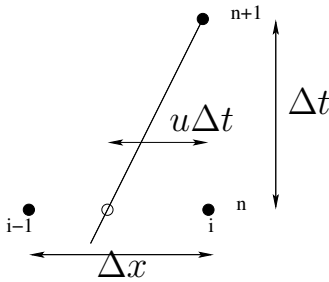


Figure 2: Left one-sided scheme.

The CFL condition Courant, Friedrichs and Lewy recognized, in 1928, a necessary stability condition for any explicit numerical method. This is known as the CFL condition.

For the left one-sided scheme(3.4) the CFL condition is

$$0 \leq u \frac{\Delta t}{\Delta x} \leq 1. \quad (3.5)$$

In general, meeting the CFL condition is not sufficient for stability. For the left one-sided scheme, however, the CFL condition is both necessary and sufficient for stability.

A similarly simple scheme for $u \leq 0$, is the right one-sided method

$$a_i^{n+1} = a_i^n - u \frac{\Delta t}{\Delta x} (a_{i+1}^n - a_i^n) . \quad (3.6)$$

We refer to (3.4) with $u > 0$ as upwind scheme and to (3.6) with $u < 0$.

The reader is referred to E. Godlewski and P. A. Raviart [12] for a discussion on the merits and demerits of these simple schemes (and other schemes).

3.2 Finite Volume Method in 1D

In finite difference methods the number of grid points tends to be very large as the resolution required to resolve relevant processes needs to be high. The location of grid points does not generally coincide with that in which we have data. In addition, the data are available as surface and/or volume averages. It is appropriate, at least for this reason, to use finite volume methods. Also, the wind speed u is not constant and we ought to consider now the conservative formulation (3.1). The aim is to generalize the upwind scheme and others schemes by application of the Godunov method, which is the right way to proceed. Indeed we know that the use of conservative numerical methods preserve us against the convergence of the method towards a non-solution of (3.1) (in the nonlinear case). The finite volume method is a particular case in the family of the conservative methods. Naturally in this family we can define methods with different orders of accuracy in space. First-order methods have the drawback of being diffusive. The use of higher order methods results in less diffusive schemes but produces eventually spurious oscillations in the vicinity of pollution propagation front: these methods are dispersive. Fortunately these oscillations can be controlled by the use of **slopes limiters**.

The first-order finite volume method is the original Godunov scheme; by extension, this scheme is the framework of many others schemes such as MUSCL or PPM (Piecewise Parabolic Method) (see the subsection 3.2.3), referred to as Godunov-type. MUSCL and PPM have an order greater than one, for which the slope limiter technique, running with any improvements in their employment, guarantees control of spurious oscillations making the scheme **TVD** (Total Variation Diminishing) (see LeVeque [21] p. 165, for definition). This important property is at least necessary for proof the convergence (by the Lax-Wendroff theorem, see for instance [21] p.130) of the numerical solution to the solution of the conservative equation (3.1).

3.2.1 Formulation of the Finite Volume Method

The first step consists of dividing the spatial domain in *cells* called *finite or controls volumes*: this division corresponds to a partition of the integration domain in segments. Next, we build discrete equations for the *integral form* of the equation.

Let $[x_{i-\frac{1}{2}}, x_{i+\frac{1}{2}}[$ $_{i \in \mathbb{Z}}$ be a partition of $[0, L]$, and $([t^n, t^{n+1}[$ $_{n \in \mathbb{N}}$ a regular partition of \mathbb{R}^+ . We define $\Delta t = t^{n+1} - t^n$ and $\Delta x_i = x_{i+\frac{1}{2}} - x_{i-\frac{1}{2}}$ steps of time and space respectively, the middle points $x_i = \frac{1}{2}(x_{i-\frac{1}{2}} + x_{i+\frac{1}{2}})$ and the control volume $\Omega_i = [x_{i-\frac{1}{2}}, x_{i+\frac{1}{2}}[$.

Integration of (3.1) on $\Omega_i \times]t^n, t^{n+1}[$ produces the **integral form of the conservation law**:

$$\bar{a}_i^{n+1} = \bar{a}_i^n - \frac{\Delta t}{\Delta x_i} (F_{i+\frac{1}{2}}^n - F_{i-\frac{1}{2}}^n) \quad , \quad (3.7)$$

where we define the **exact flux** by:

$$F_{i+\frac{1}{2}}^n = \frac{1}{\Delta t} \int_{t^n}^{t^{n+1}} (a u)(x_{i+\frac{1}{2}}, t) dt, \quad (3.8)$$

and the average values of the exact solution at the time t^n by:

$$\bar{a}_i^n = \frac{1}{\Delta x} \int_{x_{i-\frac{1}{2}}}^{x_{i+\frac{1}{2}}} a(x, t^n) dx. \quad (3.9)$$

The finite volume method consists in calculating approximations a_i^n of the \bar{a}_i^n for any time t^n and any control interval Ω_i . Fluxes F are practically unknown and we ought necessarily to make an approximation such as (3.10). We define by $A^n = (a_i^n)_{i \in \mathcal{Z}}$ the set of the discrete and approximate average values of the solution calculated at time t^n . The approximated fluxes depend only on the approximate solution A^n . Thus we should define the **numerical flux functions** \tilde{F} such that:

$$\tilde{F}_{i+\frac{1}{2}}(A^n) \approx F_{i+\frac{1}{2}}^n. \quad (3.10)$$

Finally to calculate the discrete average values (on each cell at time t^{n+1}) we write

$$a_i^{n+1} = a_i^n - \frac{\Delta t}{\Delta x_i} \tilde{F}_{i+\frac{1}{2}}(A^n) - \tilde{F}_{i-\frac{1}{2}}(A^n) . \quad (3.11)$$

This equation is the **finite volume formulation** of the problem and belongs to the general framework of **conservative schemes**. In fact the conservative property means that the mass of species A (with concentration a) is preserved (when time t move from t^n to t^{n+1}) only according to the boundaries conditions.

Remark 1. *It is necessary to keep in mind that a_i^n are now **box average** approximations of the field $a(\cdot, t)$ and not point values of this field. It is coherent with the fact that the initial condition is only given in average form by measurements in the physical ground. •*

In order to prove the convergence of this class of methods, it is necessary to introduce some new concepts: principally the conservative and consistency notions for a finite volume scheme (see [12] for a comprehensive lecture of all these notions, [13] and for the aficionados [10] (convergence theorems)).

The simplest case is when $\tilde{F}_{i+\frac{1}{2}} = F(a_i^n, a_{i+1}^n)$ is a function of only two variables. Then $\tilde{F}_{i+\frac{1}{2}} = F(a_i^n, a_{i+1}^n)$ is the numerical flux between the Ω_i and Ω_{i+1} cells, and it is an approximation of the exact flux (3.8). We have a three points explicit finite volume scheme, and (3.11) becomes

$$a_i^{n+1} = a_i^n - \frac{\Delta t}{\Delta x_i} F(a_i^n, a_{i+1}^n) - F(a_{i-1}^n, a_i^n) . \quad (3.12)$$

The use of conservative and consistent schemes prevents the convergence of the numerical solution towards a “bad” solution of the problem (for instance towards a solution with shock moving with a “bad” speed). The Godunov schemes discussed next are (happily) conservative and consistent.

3.2.2 Godunov Type Methods: General Principle and Formulation

The principal aim is to calculate numerical flux functions $\tilde{F}_{i+\frac{1}{2}} = F(a_i^n, a_{i+1}^n)$ which appear in (3.12). In 1959, Godunov proposed a way to calculate these numerical fluxes. Furthermore the Godunov method is the right procedure for the formal generalization of the upwind method.

General principle of the Godunov method Let us recall first that Godunov-type schemes for scalar conservation laws can be depicted (Harten [15], LeVeque [21] p.138) as a sequence of **three steps**:

Step 1. Reconstruction: To construct a function $\tilde{a}^n(x)$ which preserves these cell-averages:

$$\forall i \in \mathbb{Z}, \quad \frac{1}{\Delta x_i} \int_{x_{i-\frac{1}{2}}}^{x_{i+\frac{1}{2}}} \tilde{a}^n(x) dx = a_i^n. \quad (3.13)$$

Step 2. Solution: To solve **exactly** the conservation law on $[t^n, t^{n+1}]$ with $\tilde{a}^n(x)$ as the initial data, thus obtain a solution $\tilde{a}(x, t^{n+1})$ at time t^{n+1} . For the transport equation, this step consists of solving the following Cauchy problem:

$$\begin{aligned} \begin{cases} \frac{\partial \tilde{a}}{\partial t} + \frac{\partial}{\partial x} (\tilde{a} u) & = 0 \\ \tilde{a}(\cdot, t^n) & = \tilde{a}^n \end{cases} \end{aligned} \quad (3.14)$$

Step 3. Cell averaging: To define $(a_i^{n+1})_{i \in \mathbb{Z}}$ as the cell averages of the function $\tilde{a}(\cdot, t^{n+1})$:

$$a_i^{n+1} = \frac{1}{\Delta x_i} \int_{x_{i-\frac{1}{2}}}^{x_{i+\frac{1}{2}}} \tilde{a}(x, t^{n+1}) dx. \quad (3.15)$$

In all steps of the sequence we impose furthermore a **stepsize restriction** (the CFL condition):

$$\forall i, \quad -\Delta x_{i+1} \leq u_{i+\frac{1}{2}}^n \Delta t \leq \Delta x_i, \quad (3.16)$$

where we put for the wind:

$$u_{i+\frac{1}{2}}^n = u(x_{i+\frac{1}{2}}, t^n). \quad (3.17)$$

This condition is a standard one for an **explicit** scheme associates to an evolution equation where exists always a stability condition.

In other words from the numerical values of the solution at time t^n we built a function \tilde{a}^n which preserves the cell averages (in the original Godunov's method this function \tilde{a}^n is a piecewise constant function with $\tilde{a}^n(x) = a_i^n$) that we actualize during a timestep on $[t^n, t^{n+1}]$ in solving exactly the problem (3.14), then we project the function obtained at time t^{n+1} on the space of constant function by cells.

In applying this algorithm we can solve exactly the problem (3.14). First if the wind u is constant (i.e. uniform and permanent) we find

$$\tilde{F}_{i+\frac{1}{2}}(A^n) = \frac{1}{\Delta t} \int_{x_{i+\frac{1}{2}} - u \Delta t}^{x_{i+\frac{1}{2}}} \tilde{a}^n(x) dx. \quad (3.18)$$

For a speed wind u not constant we are unable to solve (3.14) numerically with exactitude (theoretically it is possible with a some assumptions on u). Here we suppose only u sufficiently regular to do the approximation:

$$\forall x \in \mathcal{V}(x_{i+\frac{1}{2}}), \forall t \in [t^n, t^{n+1}], \quad u(x, t) \approx u(x_{i+\frac{1}{2}}, t^n), \quad (3.19)$$

where $\mathcal{V}(x_{i+\frac{1}{2}})$ is a neighbourhood of $x_{i+\frac{1}{2}}$. Then we put, thanks to (3.18):

$$\tilde{F}_{i+\frac{1}{2}}(A^n) = \frac{1}{\Delta t} \int_{x_{i+\frac{1}{2}} - u_{i+\frac{1}{2}}^n \Delta t}^{x_{i+\frac{1}{2}}} \tilde{a}^n(x) dx. \quad (3.20)$$

$\tilde{F}_{i+\frac{1}{2}}(A^n)$ is a function of A^n , because function \tilde{a}^n is also define from A^n .

Remark 2. *A synthetic formulation is the following. In defining Φ_u by:*

$$\Phi_u : A^n \longmapsto -\frac{\Delta t}{\Delta x_i} \tilde{F}_{i+\frac{1}{2}}(A^n) - \tilde{F}_{i-\frac{1}{2}}(A^n) \quad , \quad i \in \mathbb{Z}, \quad (3.21)$$

the Godunov type scheme can be written :

$$A^{n+1} = (Id + \Phi_u)(A^n), \quad (3.22)$$

*which generalizes (3.12) (remember that $A^n = (a_i^n)_{i \in \mathbb{Z}}$). For our transport problem the application Φ_u is **linear** with respect to A^n . •*

3.2.3 Examination of usual Godunov Methods

We present in this context a few examples of Godunov schemes:

- the Godunov scheme, the oldest and also the simplest;
- the minmod scheme, which is an extension of the previous method; this method is a particular case of MUSCL schemes introduced by Van Leer;
- the PPM method, extension still more elaborated.

That is really not a complete review of the Godunov type methods, for instance ENO (*Essentially Non-Oscillatory*) schemes have been introduced in this context by Harten [16], Harten et al. [15], Shu and al. [28].

All the following methods differ only by the reconstruction algorithm.

The first Godunov method We build the function \tilde{a}^n by putting

$$\forall i, \forall x \in \Omega_i = [x_{i-\frac{1}{2}}, x_{i+\frac{1}{2}}[, \quad \tilde{a}^n(x) = a_i^n. \quad (3.23)$$

Remark 3. *We verify (see Figure 3) that in the original Godunov method, \tilde{a}^n is a **stair-case function**. •*

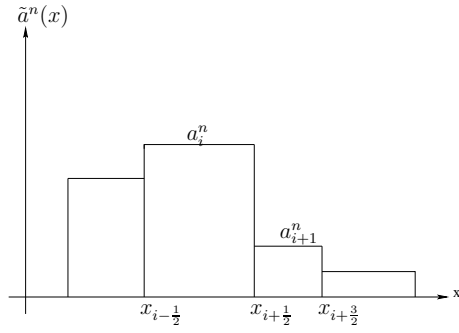


Figure 3: Field discretization at time t^n .

By direct calculation of the integral (3.20), taking into account the CFL condition (3.16), we can completely explicit the flux function for the original Godunov method with respect to the a_i^n . We have:

$$\tilde{F}_{i+\frac{1}{2}}(A^n) = F(a_i^n, a_{i+1}^n) = \begin{cases} > u_{i+\frac{1}{2}}^n a_i^n & \text{if } u_{i+\frac{1}{2}}^n \geq 0 \\ > u_{i+\frac{1}{2}}^n a_{i+1}^n & \text{if } u_{i+\frac{1}{2}}^n < 0 \end{cases} \quad (3.24)$$

N.B.: It is possible to give an explicit expression for the flux, without ambiguity, only if the CFL condition is verified. •

Suppose that the velocity wind u is constant. From (3.11), for $u_{i+\frac{1}{2}}^n = u \geq 0$ (resp. $u_{i+\frac{1}{2}}^n = u < 0$) we find again the left one-sided method (3.4) (resp. the right one-sided method (3.6)). That gives confidence in the finite volume method (perhaps less natural than finite difference method for some readers)!

The minmod scheme (MUSCL) The idea is to improve **the reconstruction phase**, by using now a function \tilde{a}^n affine by steps such that (3.13) is still true. For that we define a **slope** σ_i^n on each cell $[x_{i-\frac{1}{2}}, x_{i+\frac{1}{2}}[$, and we put:

$$\forall i, \forall x \in [x_{i-\frac{1}{2}}, x_{i+\frac{1}{2}}[, \quad \tilde{a}^n(x) = a_i^n + \sigma_i^n (x - x_i), \quad (3.25)$$

then (3.13) is obviously true by definition of x_i ($x_i = \frac{1}{2}(x_{i-\frac{1}{2}} + x_{i+\frac{1}{2}})$).

Furthermore, for convergence reasons, we should limit the slopes σ_i^n by a “slope-limiter”. A simple and convenient choice of slopes is given by *minmod* ([21], pp. 183-187)

This type of method was initially introduced by B. Van Leer (see for instance [34] and [35]) under the appellation of MUSCL (*Monotonic Upstream-centered Scheme for Conservation Laws*) scheme.

The flux function for the minmod scheme is always given by (3.20). Taking into account the CFL condition (3.16), starting from (3.25), by elementary integral calculations

we find that:

$$\tilde{F}_{i+\frac{1}{2}}(A^n) = \begin{cases} u_{i+\frac{1}{2}}^n a_i^n + \frac{1}{2}(1-\nu) u_{i+\frac{1}{2}}^n \Delta x_i \sigma_i^n & \text{if } u_{i+\frac{1}{2}}^n \geq 0 \quad \text{then} \\ u_{i+\frac{1}{2}}^n a_{i+1}^n - \frac{1}{2}(1+\nu) u_{i+\frac{1}{2}}^n \Delta x_{i+1} \sigma_{i+1}^n & \text{if } u_{i+\frac{1}{2}}^n < 0 \quad \text{then} \end{cases} \quad \text{where } \nu = \frac{u_{i+\frac{1}{2}}^n \Delta t}{\Delta x_i} \quad (3.26)$$

The PPM method Developed by Collela and Woodward [2] since 1984, the PPM (*Piecewise Parabolic Method*) method is also an extension of the original Godunov method. The reconstruction is **piecewise parabolic**: on each cell Ω_i , \tilde{a}^n is a second degree polynomial. The art of this reconstruction is the pertinent choice of the coefficients of this polynomial, essentially made by appropriate values of this polynomial at the boundary of Ω_i .

3.3 Modeling of the Advection Problem in 3D

In this section we emphasize only on the numerical modeling of the advection equation in 3D. We are concern by the advection part of (1.1), let be to solve (recall that \vec{C} is a vector containing all the unknowns concentrations of all model species, \vec{V} is the given three dimensional wind vector and \vec{C}_0 is the given vector of initial concentrations):

$$\begin{cases} \frac{\partial \vec{C}}{\partial t} + \text{div}(\vec{V}\vec{C}) = 0 & \forall (x, y, z, t) \in \mathbb{R}^3 \times [0, T[\\ \vec{C}(x, y, z, 0) = \vec{C}_0(x, y, z) & \forall (x, y, z) \in \mathbb{R}^3 \end{cases} \quad (3.27)$$

or, for a particular chemical species $a \in \vec{C}$,

$$\begin{cases} \frac{\partial a}{\partial t} + \text{div}(a\vec{V}) = 0 & \forall (x, y, z, t) \in \mathbb{R}^3 \times [0, T[\\ a(x, y, z, 0) = a_0(x, y, z) & \forall (x, y, z) \in \mathbb{R}^3 \end{cases} \quad (3.28)$$

This equation is solve with the appropriate finite volume method. We called u, v and w the components of \vec{V} : $\vec{V} = (u, v, w)^T$.

This subsection is a generalization of the Section 3.2.1. We apply in each direction the 1D calculation. Suppose a cell in 3D define like in Figure 4.

We define time and space steps respectively written by $\Delta t = t^{n+1} - t^n$, $\Delta x_i = |AB| = x_{i+\frac{1}{2}} - x_{i-\frac{1}{2}}$, $\Delta y_j = |AE| = y_{j+\frac{1}{2}} - y_{j-\frac{1}{2}}$, $\Delta z_k = |AC| = z_{k+\frac{1}{2}} - z_{k-\frac{1}{2}}$ and the cells by $\Omega_{i,j,k} = [x_{i-\frac{1}{2}}, x_{i+\frac{1}{2}}[\times [y_{j-\frac{1}{2}}, y_{j+\frac{1}{2}}[\times [z_{k-\frac{1}{2}}, z_{k+\frac{1}{2}}[$ (see Figure 4).

Then we ought define boundaries conditions: practically we impose that outside the domain the solution is given constant, we should restrict the mesh space to a bounded domain of \mathbb{R}^3 . In this way the spatial index (i, j, k) describe a finite set \mathcal{E} of \mathbb{Z}^3 , says $\mathcal{E} = \{(i, j, k) | 1 \leq i \leq p, 1 \leq j \leq q, 1 \leq k \leq r\}$.

In 3D, we repeat in each direction, the formulation of the finite volume method made in Section 3.2.1

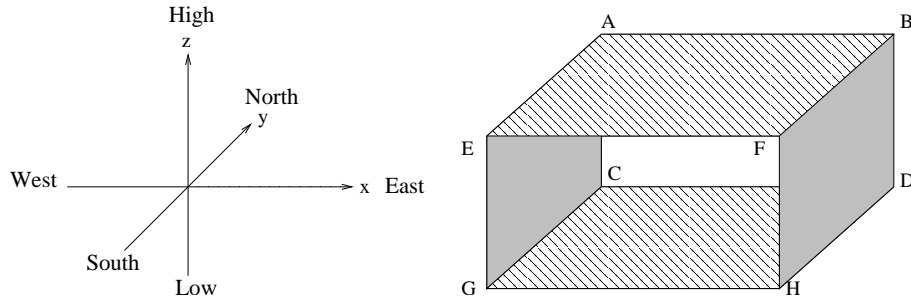


Figure 4: Cell $\Omega_{i,j,k}$ in 3D. We note, in the direction x , by F_W (resp. F_E) the flux passing through the face AEGC (resp. BFHD), in the direction y , by F_S (resp. F_N) the flux passing through the face EGHF (resp. ABDC) and finally, in the direction z , by F_L (resp. F_H) the flux passing through the face CDHG (resp. ABFE). We note by $|AB|$ the length of side AB.

Let be $A^n = a_{ijk}^n$ $(i,j,k) \in \tilde{Z}$, where a_{ijk}^n is the average value on the $\Omega_{i,j,k}$ -cell, we calculate the discrete average values (on each cell at time t^{n+1}) by the following scheme, which is an extension of (3.11), (see the legend of the Figure 4 for notations):

$$a_{ijk}^{n+1} = a_{ijk}^n - \frac{\Delta t}{\Delta x_i} (F_E(A^n) - F_W(A^n)) - \frac{\Delta t}{\Delta y_j} (F_N(A^n) - F_S(A^n)) - \dots \quad (3.29)$$

$$\dots - \frac{\Delta t}{\Delta z_k} (F_H(A^n) - F_L(A^n))$$

Now it suffices to calculate the numerical fluxes functions, in each direction and for incoming/outgoing fluxes, by one of the method given in Section 3.2.3.

If, for instance, the first component u (in direction x) of \vec{V} is positive then the face AEGC (resp. BFHD) is the incoming (resp. outgoing) face for the flux.

4 Modeling of Chemical Ordinary Differential Equations

For more information about the concepts and methods for solving ODEs, the reader can refer to [4] (in French), [11] and [17].

4.1 Formulation of the Problem and Classical Methods

The chemical system of nonlinear differential equations doesn't have generally an explicit solution. It is necessary to dispose of robust and cheap numerical methods. Furthermore the chemical system is stiff, which means that the solutions are characterized by very different scales time, and by that simple numerical method fail. The problem is the following: let be $I_0 = [t_0, t_0 + T]$, $T > 0$, a close interval of \mathbb{R} and a continuous nonlinear function f from $I_0 \times \mathbb{R}^m$ in \mathbb{R}^m , one wish to solve the following system of ordinary differential equations :

$$\begin{aligned} y'(t) &= f(t, y(t)), & t \in I_0, \\ y(t_0) &= y_0, & y_0 \text{ given in } \mathbb{R}^m \end{aligned} \quad (4.1)$$

Now let be a subdivision of the interval I_0 :

$$t_0 < t_1 < \dots < t_n < \dots < t_N = t_0 + T, \quad (4.2)$$

and we put

$$h_n = t_{n+1} - t_n \quad ; \quad h = \max_{0 \leq n \leq N-1} h_n. \quad (4.3)$$

A first natural scheme is the following

$$y_{n+1} = y_n + h_n f(t_n, y_n), \quad 0 \leq n \leq N - 1. \quad (4.4)$$

This is the **Euler-Cauchy** method or the **explicit Euler method** or the **forward Euler method**: from the initial condition y_0 we do the calculation by (4.4) of the sequence $(y_n)_{0 \leq n \leq N}$.

A second scheme is defined naturally by

$$y_{n+1} = y_n + h_n f(t_{n+1}, y_{n+1}), \quad 0 \leq n \leq N - 1. \quad (4.5)$$

At each step in the calculation of y_{n+1} one must solve sequentially an nonlinear (in general) equation in \mathbb{R}^m and by that this method is called **implicit**, y_{n+1} is not immediately given. For this reason the cost of this method can be eventually higher than those of the explicit one.

One can prove that the **explicit Euler method is inadequate** for solving stiff differential problems but that the **implicit Euler method is adequate and convenient**. This fact concerning the Euler method is representative for using implicit or explicit method to stiff problem. **The implicit methods are highly recommended for solving stiff problems.**

4.2 Special Methods for Chemistry Modeling

We present here two methods that are usually used by atmospheric chemists: 1) the method based on a **Quasi-Stationary State Approximation** called by that the **QSSA** method, and 2) the **Two-Step** method.

4.2.1 The QSSA Method

Consider for instance the following chemical system of reactions:



where the k' 's are the speed reaction constants and \mathcal{M}_1 , \mathcal{M}_2 , \mathcal{X} and \mathcal{P} are chemical species with concentrations C_1 , C_2 , C_X and C_P . The reaction speed for any reaction is

given by the elementary kinetic law, i.e. the product of the reaction constant (for this reaction) by the concentrations of chemical components consumed. If one suppose that the concentration C_X is constant, the dynamic of this system is linear and the system of ordinary differential equations is given by:

$$\begin{aligned} \circledast & < \frac{dC_1}{dt} = -(k_1 C_X)C_1 + (k_{-1} C_X)C_2 \\ \vdots & \frac{dC_2}{dt} = (k_1 C_X)C_1 - (k_{-1} C_X + k_2)C_2 \end{aligned} \tag{4.8}$$

The chemical species P is the product of a noninvertible chemical reaction and don't have an effect under the evolution of other chemical species \mathcal{X} , \mathcal{M}_1 and \mathcal{M}_2 . The first equation in (4.8) means that the chemical specie \mathcal{M}_1 is lost (produced) by the direct (inverse) way of the first chemical reaction in (4.6). It is usual to note, for a chemical species i , the production term by P_i and the loss term by L_i . For instance for the chemical species \mathcal{M}_1 we have

$$\frac{dC_1}{dt} = P_1 - L_1 C_1, \quad \text{with } P_1 = (k_{-1} C_X)C_2 \quad \text{and } L_1 = k_1 C_X. \tag{4.9}$$

Let be now the equation associated to the chemical species i

$$\frac{dC_i}{dt} = P_i - L_i C_i; \tag{4.10}$$

frequently the terms P_i and L_i depend on \vec{C} , the vector of the concentrations for all the chemical species which constitute the chemistry mechanism. It is more appropriate to write

$$\frac{dC_i}{dt} = P_i(\vec{C}) - L_i(\vec{C})C_i. \tag{4.11}$$

The entire system can be written in the nonlinear form

$$\frac{d\vec{C}(t)}{dt} = f(t, \vec{C}(t)) = P(t, \vec{C}(t)) - L(t, \vec{C}(t))\vec{C}(t), \tag{4.12}$$

where $\vec{C}(t) = (C_1(t), C_2(t), \dots, C_m(t))^T$, $P(t, \vec{C}(t))$ is a vector and $L(t, \vec{C}(t))$ is a diagonal matrix. The system (4.12) is representative of the chemistry modeling.

Now we suppose that all the concentrations are known at time t . Let a time interval be $[t, t + \Delta t]$. The basis of the QSSA method consists to suppose that during the stepsize Δt the quantities $P_i(\vec{C})$ and $L_i(\vec{C})$ are constant (it is the quasi-stationary state approximation valid for Δt sufficiently small) and equals respectively to P_i and L_i . One can find more information in E. Hesstvedt et al. [18].

4.2.2 The Two-step Method

Computational errors connected with QSSA methods are difficult to assess. So J.G. Verwer ([38] has proposed an adaptation of a standard implicit method (the Backward Differentiation Formula of order 2) to the chemical system (4.12).

If y is the vector of the unknowns concentrations of the chemical species, with variable stepsize, the scheme of the two-step method is

$$y_{i+1} = F(y_{i+1}) = (I + h_i \gamma L(t_{i+1}, y_{i+1}))^{-1} (Y_i + h_i \gamma P(t_{i+1}, y_{i+1})), \quad (4.13)$$

where index means that the unknown values of the concentrations are taken at time t_{i+1} . In this formula

$$Y_i = \sum_{j=1}^{\infty} a_{j,2}^i y_{i+1-j} = \frac{(c+1)^2 y_i - y_{i-1}}{(c^2 + 2c)}, \quad (4.14)$$

with $c = \frac{t_i - t_{i-1}}{t_{i+1} - t_i}$ and $\gamma = \frac{c+1}{c+2}$.

The relationship (4.13) is implicit in the y_{i+1} unknown. Due to this appropriate formulation it is easy, by a Gauss-Seidel iteration, to solve it. We note that this BDF formula, firstly is adapted to the typical formulation of the chemical, secondly that we calculate y_{i+1} (at time t_{i+1}) from y_i (at time t_i) and y_{i-1} (at time t_{i-1}), these are the two-step (in time). For all these reasons, in this particular situation, it is desirable to rename the BDF method of order two by two-step.

In the case of constant stepsize time we easily verify that $\gamma = \frac{2}{3}$ and $Y_i = \frac{4y_i - y_{i-1}}{3}$ because $c = 1$. Therefore we have

$$y_{i+1} = (I + h_i \frac{2}{3} L(t_{i+1}, y_{i+1}))^{-1} (\frac{4}{3} y_i - \frac{1}{3} y_{i-1} + h_i \frac{2}{3} P(t_{i+1}, y_{i+1})), \quad (4.15)$$

we find, near notations, the formula (8) in H. Schmidt et al. [26].

This scheme is very appropriate to solve stiff ordinary differential equations given by chemical models. It is stable, both in common sense and mathematical sense. This scheme is valid whatever the chemical species (slow or quick): it is not necessary to separate a priori (more or less arbitrarily) the chemical species following their characteristic reaction time.

5 One Example of the Modeling of the Air Pollution Problem: the CHIMERE software

Recall that the mass continuity equation for the concentrations of chemical species in the air pollution modeling is (1.1). In addition to the numerical resolution and meteorological input, the major steps of the modeling concerns the chemical mechanism, emissions, deposition, together with the advection, diffusion and boundary layer modeling.

5.1 Chemical Mechanism

Naturally it is desirable that a model can include different gas phase chemical mechanisms. For instance CHIMERE offers this possibility but usually use the original scheme MELCHIOR (Lattuati [20]), an updated and extended version of the EMEP mechanism

(Simpson [29]) suited to polluted as well as unpolluted environments. MELCHIOR describes more than 200 reactions of 80 gaseous chemical species. In MELCHIOR the hydrocarbon degradation is fairly similar to the EMEP gas phase mechanism and represents the major pathways of ozone build-up from industrial, traffic or biogenic (isoprene) emissions, and it has been used for many pollution studies (Simpson [29], Simpson [30]). Six hydrocarbon chemical species (ethane, butane, ethene, propene, isoprene, and *O*-xylene) represent alkane, alkene and aromatic compounds. Their oxidation by *OH*, *O*₃, yields 11 oxygenated compounds, including formaldehyde and higher aldehydes, ketones, bicarbonyls, unsaturated carbonyls and alcohols. Several adaptations have been made with respect to this mechanism, in particular for low *NO*_x conditions at nighttime for instance. All rate constants have been updated from Atkinson et al. [1] and De Moore et al. [5]. Heterogeneous reactions are not included, but the effect of the clouds on the photolysis frequency is taken into account. A list of the model species and of the complete set of chemical reactions is presented on the web site (<http://euler.polytechnique.fr/chimere>).

5.2 Emissions

The estimation of emissions is a major problem in air pollution. One ought assign emissions values to each cell at every time. This estimation of emissions (and depositions) is a physical, technical and difficult evaluation problem: a lot of data is missing together in space and in time, for each chemical specie; there are also uncertainties and it is obviously an important cause of errors in the models for pollution. A effort will be made in the future for improve these data and their use.

For example CHIMERE requires input emission data for 16 model chemical species. Annual data for anthropic emissions for the four classes *NO*_x, *SO*₂, *CO* and nonmethane volatile organic compounds (NMVOC) are taken from the EMEP data base for 1997 (see the web site <http://www.emep.int>). NMVOC emissions have been to be split into 12 classes represented within the models chemical mechanism. To this purpose they are first distributed for each country into different broad activity sectors (traffic, solvents, industrial and residential combustion, others), according to data prepared by IER (Institute for Energy Economics and Rational Use of Energy) in the framework of the EUROTRAC/GENEMIS project (GENEMIS [7]). Second, for each sector, NMVOC emissions are split into 32 classes with similar structure and reactivity, following a classification of Middleton et al. [23], and using VOC profiles again from IER. Third, VOCs from these 32 classes are aggregated into the 12 classes represented within CHIMERE, by applying mass and reactivity weighting as proposed by Middleton et al. [23]. It is clear that the uncertainty in the spatial distribution of individual VOC emissions is large, as VOC profiles are the same all over Europe, with the exception of traffic, where national differences (for example, distribution gasoline/diesel) are taken into account. Monthly, daily and hourly variations of the emissions are modeled by imposing variations available from the GENEMIS [7] data base. For biogenic emissions of isoprene and terpenes in CHIMERE we refer to Schmidt et al. [26].

5.3 Depositions

In CHIMERE, dry deposition is considered for 23 of the model chemical species. For each chemical component i considered, the dry deposition is parameterized as a downward flux $F_{d,i} = -u_{d,i}c_i$ out of the lowest model layer where c_i is the concentration of this chemical specie in this layer, and $u_{d,i}$ is the deposition velocity. This velocity is, as commonly, described through a resistance analogy (Wesley and Hicks [39]) by

$$u_{d,i} = \frac{1}{R_a + R_{b,i} + R_{c,i}}. \quad (5.1)$$

The aerodynamic $R_a = (c_D v)^{-1}$ is calculated from the drag coefficient for momentum c_D (see [39]) and the wind speed v in the lowest layer.

According to Hicks and al [8] the quasi-laminar resistance $R_{b,i}$ is calculated as

$$R_{b,i} = \frac{2}{ku_*} \frac{Sc_i}{Pr} \quad , \quad (5.2)$$

where Sc_i and Pr are respectively the Schmidt and Prandtl number, k is the von Karman's constant and the friction velocity u_* is inferred from the meteorological data by means of the Louis [22] parameterization.

Following Erisman and al. [9] the surface resistance $R_{c,i}$ can be calculated from a number of different other resistances accounting mainly for stomatal and surface processes which are again dependent on the land use type, taken from the RIVM data base ([33]). For the exact calculation of $R_{c,i}$ the reader is referred to [9]. For more information see [26].

5.4 Advection, diffusion and boundary layer modeling

We assume that the wind field is known. The ECMWF (European Centre for Medium-Range Weather Forecasts) or the MM5 ([6]) data is used for CHIMERE. Only the horizontal advection is calculated either with the upwind method or the Van Leer method or the PPM methods (see Section 3.2.3) depending on chemical species. In order to reduce computing time, PPM or Van Leer methods are used only for a reduced set of "slow" chemical species. Contrary to the horizontal wind components, vertical wind is not taken directly from the meteorological input, but calculated to enforce mass balance. This is necessary as the vertical resolution of the models for meteorology and pollution are often different (that is the case for the ECMWF (or MM5) and CHIMERE grids). Vertical mass fluxes are calculated with a first order approach (the original Godunov method).

Vertical turbulent mixing takes place in the boundary-layer only. The formulation uses K -diffusion following the parameterization of Troen and Mahrt [32], without counter-gradient term. In each model column, diffusivity $K(z)$ is calculated as:

$$K(z) = kw_s z \left(1 - \frac{z}{h}\right)^2, \quad (5.3)$$

where w_s is a vertical scale given by similarity formulae.

- In the stable case (surface sensible heat flux < 0):

$$w_s = \frac{u_*}{1 + 4.7 \frac{z}{\mathcal{L}}}, \quad (5.4)$$

- and in the unstable case:

$$w_s = (u_*^3 + 2.8\epsilon w_*^3)^{\frac{1}{3}}, \quad (5.5)$$

where $\epsilon = \max(0.1, \frac{z}{h})$, \mathcal{L} is the Obukov Length (the Obukov Length is a measure of stability of the atmosphere introduced by A.M. Obukov [25], see also R.B. Stull [31]), w_* is the convective velocity scale, u_* the friction velocity and h the boundary layer height. A minimal $K(z)$ is assumed, with a value of $0.1 \text{ m}^2/\text{s}$.

For more information about the modeling of $K(z)$, we report to Troen and Mahrt [32].

The boundary layer height h can be either directly provided by the meteorological model or recalculated by the transport model. In the latter case the boundary layer height h is considered as the maximum of the boundary layer height calculated, from the Richardson number profile, as the lowest altitude where $R_i = 0.5$, and a more convectively-based boundary layer height calculated in a similar fashion as in Cheinet [3].

The Richardson number profile is a bulk Richardson number defined as

$$R(z) = g \frac{(\theta(z) - \theta_0)(z - z_0)}{\theta(z)(\mathfrak{F}(z) + \mathfrak{F}_{\min})}, \quad (5.6)$$

where z_0 is the roughness height, $\mathfrak{F}_{\min} = 0.1 \text{ ms}^{-1}$ is a minimal wind speed in order for the Richardson number not to go to infinity, $\mathfrak{F}(z) = \frac{u^2(z) + v^2(z)}{u^2(z) + v^2(z)}$ is the horizontal wind profile in z ($u(z)$ and $v(z)$ are the horizontal components of the wind) and $\theta(z)$ denote the vertical profile of virtual potential temperature. Finally θ_0 is assumed to represent the virtual potential temperature at the base of the thermals. The modeling of this height together with the vertical eddy diffusion K is also an uncertainty problem. For more details we refer the reader to the web site (<http://euler.polytechnique.fr/chimere>).

At each interface between layers k and $k + 1$, one calculates an equivalent turbulent vertical velocity V_k , and vertical mixing is expressed in layer k by the mass flux:

$$\text{Net Flux} = \frac{V_k \left(\frac{C_{k+1} D_k}{D_{k+1}} - C_k \right)}{H_k}, \quad (5.7)$$

where C denotes concentrations, D densities and H layer thicknesses. Density ratios are applied since turbulent mixing must conserve mass in each model cell. An equivalent formula is used for the upper layer. The turbulent velocity V_k is deduced from $K(z)$ using:

$$V_k = \frac{K(z)}{\frac{1}{2}(H_k + H_{k+1})}. \quad (5.8)$$

When the top of the boundary layer is above the model top, H_{k+1} is replaced by h in the previous equation.

5.5 The Model in 3D

A chemistry-transport model calculates, given emissions, meteorological variables and lateral boundary conditions, the concentrations fields of several constituents (such as ozone). To give an idea of a spatial domain (Ile-de-France area) and resolution, we divide it into a 6×6 km cells over a domain of 150×150 km. The urban area is located around the city of Paris, in the centre, and extends with an approximate radius of 20 km. The central part covers the urban zone. We partition the central square in 5×5 cells. Depending of the versions, CHIMERE has, at least, three vertical layers above topography. Consequently we can enumerate the number of cells in thousands. For more details we refer to Vautard et al. [36].

Here we emphasize only on the link between the modeling of the advection equation and the modeling of the chemical differential equations.

In the coupling of the advection and the chemical, in (4.15), the production and loss terms P and L are replaced by the modified terms $\tilde{P} = P + P_h + P_v$ and $\tilde{L} = L + L_h + L_v$. In this way we take into account the 3D transport term $div(\vec{V}\vec{C})$ and the 3D eddy diffusion term $div(\mathbf{K}\vec{C})$. P_h and P_v denote the temporal evolution of the concentrations due to horizontal (only advection) and vertical (advection and diffusion) inflow into the concerned cell, L_h and L_v the temporal evolution due to the respective outflow, these two loss terms are divided by the concentration itself for coherence with the chemical mechanism written under the form (4.11).

The question is now: how we determine P_h and L_h ? Like we are working in 2D, for all $(i, j) \in \mathcal{E}$, k fixed, we use the following conservative scheme (see (3.29))

$$a_{i,j}^{n+1} = a_{i,j}^n - \frac{\Delta t}{\Delta x_i} (F_E(A^n) - F_W(A^n)) - \frac{\Delta t}{\Delta y_j} (F_N(A^n) - F_S(A^n)). \quad (5.9)$$

The term P_h (resp. L_h) sum the positive (resp. negative) terms (the inflow (resp. outflow) term) in $-\tilde{F}_E(A^n)$, $\tilde{F}_W(A^n)$, $-\tilde{F}_N(A^n)$ and $\tilde{F}_S(A^n)$. Finally we estimate these four terms by one (obviously the same for these four terms) of the methods seen in Section 3.2.3.

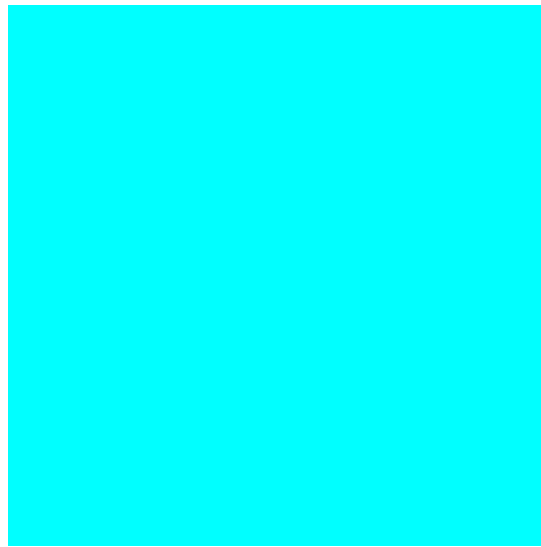
We can find a more complete description and evaluation of this model designed for seasonal simulations and real time forecasts without the use of super-computers in Schmidt & al. [26], where details about the implementation and evaluations of the modeling are given. The reader can also complete its information, and appreciated validation of the CHIMERE model, in Vautard et al. [36] for forecasts of the ozone over Paris area and in Menut et al. [24] for sensitivity studies of photochemical pollution using the adjoint of this simplified chemistry-transport model.

The web site (<http://euler.polytechnique.fr/chimere>) give more information on this model.

5.6 An Illustrative Example

During August 2003, western European countries witnessed an unprecedented 15-day long heat wave with record temperatures and unusually persistent high ozone concentrations.

The CHIMERE chemistry-transport model was used to simulate this episode (R.Vautard et al. [37]). In the presented run (Figure 5) the simulated ozone concentrations are compared to surface observations obtained from 237 monitoring stations. For this simulation, the definition of the horizontal domain is clearly given on the figure, the resolution is 0.5° . Vertical grid consists of 15 layers from the surface to 500 hPa, which is above the high boundary layers encountered during the heat wave period. Boundary conditions for a few pollutants, among which ozone and some precursors are included, are provided by monthly climatological bulletins from the second generation of the MOZART model (Horowitz et al. [19]).



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