MATHEMATICAL MODELS IN AIR QUALITY PROBLEMS

Jean Roux
Environmental Research and Teaching Institute, École Normale Supérieure,Paris, France.

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Contents

Summary

The problem of air quality is modeled by a reaction-advection-diffusion 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 ODE's, 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 chapter 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 industrialized 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 (VOC's) 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 starts 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 PDE representing the one change

in concentrations of chemical species:

$$\frac{\partial \mathbf{C}}{\partial t} + \mathrm{div}(\mathbf{VC}) = \mathrm{div}(\mathbf{KC}) + \mathbf{P}(\mathbf{C},t) - \mathbf{L}(\mathbf{C},t). \qquad (1)$$

Here $\mathbf{C}$ is a vector containing the concentrations of all m model chemical species depending on space and time t, $\mathbf{V}$ is three dimensional wind vector, $\mathbf{K}$ is turbulent diffusive matrix, and $\mathbf{P}$ and $\mathbf{L}$ represent production and loss terms due to chemical reactions, emissions and depositions. The wind field $\mathbf{V}$ 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 $\mathbf{P}$ and $\mathbf{L}$ is quadratically non-linear (it is by this mechanism that $\mathbf{P}$ and $\mathbf{L}$ depend on, for a specific concentration chemical species c, the concentrations of other constituents). Without the chemical mechanism the m equations of the PDE system (1) are uncoupled.

In methods of solution often used in air pollution modeling, the PDE system (1) with its boundary conditions is first discretized in space on a three-dimensional Eulerian grid. On the discretized space grid the system of ODE's 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 ODE's 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 ODE's system together which the large number of cells in 3D, ODE integrators based on standard numerical routines are not feasible in a 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 method for solving ODE's: the Euler methods. Due to the production-loss form of the ODE's 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 write 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 present 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, furthermore 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 ODE's 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:

$$\begin{aligned} &NO_2 + h\nu \xrightarrow{k_1} NO + O\left(^{3P}\right) \\ &O\left(^{3P}\right) + O_2 \xrightarrow{k_2} O_3 \\ &NO + O_3 \xrightarrow{k_3} O_2 + NO_2 \end{aligned} \qquad (2)$$

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 that 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 hydroperoxyl 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)) 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). We note by [x] the concentration of the chemical species x. Let $c_1 = [O(^{3P})]$, $c_2 = [NO]$, $c_3 = [NO_2]$, $c_4 = [O_3]$, then (2) can be written as:

$$\begin{aligned} \dot{c}_1 &= k_1 c_3 - k_2 c_1 \\ \dot{c}_2 &= k_1 c_3 - k_3 c_2 c_4 \\ \dot{c}_3 &= k_3 c_2 c_4 - k_1 c_3 \\ \dot{c}_4 &= k_2 c_1 - k_3 c_2 c_4 \end{aligned} \qquad (3)$$

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:

$$\begin{cases} \dfrac{\partial a}{\partial t} + \dfrac{\partial (au)}{\partial x} = 0 & \forall (x,t) \in \mathbb{R} \times [0,T] \\ a(x,0) = a_0(x) & \forall x \in \mathbb{R} \end{cases} \qquad (4)$$

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

Since (4) 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 (4): 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 (4) becomes

$$\frac{\partial a}{\partial t} + u\frac{\partial a}{\partial x} = 0 \qquad \forall (x,t) \in \mathbb{R} \times [0,T] \tag{5}$$

The exact solution of (5) becomes

$$a(x,t) = a_0(x - ut) \tag{6}$$

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.

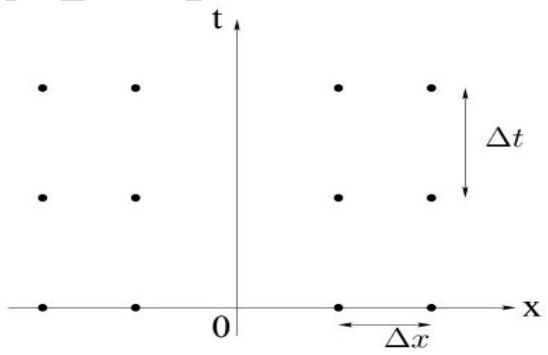

Figure 1. Discrete network of the points $(j\Delta x, n\Delta t)$ ($j \in \mathcal{Z}$ and $n \in \mathcal{N}$) for finite difference approximation.

3.1.2. Simple Finite Difference Schemes

For the advection equation (5) when $u \geq 0$, perhaps the most simple scheme is the left one-sided scheme (see Figure 2):

$$a_i^{n+1} = a_i^n - u\frac{\Delta t}{\Delta x}\left(a_i^n - a_{i-1}^n\right). \tag{7}$$

This particular form of the method in Eq. (7) is called explicit, since the advance in time is done directly without any matrix inversion.

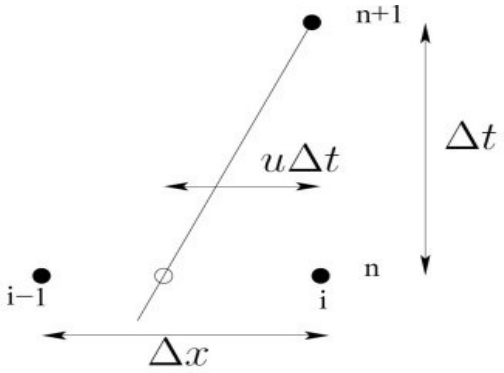

Figure 2. Left one-sided scheme.

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 (7) the CFL condition is

$$0 \le u\frac{\Delta t}{\Delta x} \le 1. \tag{8}$$

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 $u \le 0$, is the right one-sided method

$$a_i^{n+1} = a_i^n - u\frac{\Delta t}{\Delta x}\left(a_{i+1}^n - a_i^n\right) \tag{9}$$

We refer to (7) with $u > 0$ as upwind scheme and to (9) 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 (4). 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 (4) (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 Section 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 (4).

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Biographical Sketch

Jean Roux ,after completing his PhD, Jean Roux was a Research-Engineer at the Direction of "Études et Recherches" at Électricité de France (EdF). For a number of years, he has worked in many fields of applied mathematics (dynamical problems, inverse problems, etc.), as well as teaching at various institutions (École Nationale des Ponts et Chaussées, University Paris XIII and at some Écoles d'Été etc.) in numerical analysis and mathematics. In the last years of his career at EdF he focused on pollution problems (working on reduction and lumping technics in chemistry) together with the Institut Pierre-Simon Laplace du Centre National de la Recherche Scientifique (CNRS). Specifically he has collaborated with Robert Vautard's team at the « Laboratoire de Météorologie Dynamique » (LMD). After leaving EdF, he has worked on the CHIMERE software, in LMD at École Normale Supérieure of Paris (ENS), bringing his experience in numerical analysis. By doing this, he has experienced different aspects of modeling the air quality problem. Presently he is working at "Environmental Research and Teaching Institute" at ENS. His principal subject of interest is the averaging of Time Periodic Systems (essentially without small parameter) with the perspective to apply these methods to Partial Differential Equations.