Computational cost of the simulation of chemical reactions in a Lagrangian puff model

J. A. Souto\textsuperscript{a}, M. R. Méndez\textsuperscript{a}, J. J. Casares\textsuperscript{a} & T. Lucas\textsuperscript{b}

\textsuperscript{a}Centro de Supercomputación de Galicia, 15706 Santiago de Compostela, Spain
E-mail: jas@cesga.es
\textsuperscript{b}Central Térmica As Pontes, Endesa, Spain

Abstract

Air pollution problems, that include in their scope the solution of equations involving the chemical transformation of primary and secondary pollutants, is one of the topics that require the use of high performance computing.

The problem considered in this work implies the solution of a transport problem plus the chemical kinetic problem associated with the species transported from a single industrial source. A Lagrangian approach was used for the plume transport; so, the set of chemical equations must be solved separately to the transport subsystem. The overall problem requires the use of vector supercomputers to find good approximations in reasonable time.

Diverse chemical mechanisms involving NO\textsubscript{x}, O\textsubscript{3} and some volatile organic compounds (VOCs) have been considered in order to quantify the influence of the chemical simulation in the total CPU time. As a reference value, non-reactive simulations were performed for the same emission and meteorological conditions. The influence of the meteorological conditions (and plume mixing rate) in the computational cost of the Lagrangian transport model, is significant.

An estimation of the computational cost in the application of two different chemical mechanisms for the NO\textsubscript{x}-O\textsubscript{3} system in the Lagrangian model was obtained. For the mechanisms considered the computational effort of the chemical part is not so heavy as for the transport part, so it can be concluded that more reactions can be added to the model without a significant computational extra-cost.
1 Introduction

Air pollution models are very useful tools to study the behaviour of pollutants in the atmosphere. The pollutants concentration measurements are limited in space and time therefore, due to the different physical and chemical processes and the variability of the time scales involved, usually is more feasible to apply different numerical solutions to the physical transport problem and to the chemical processes.

For the general transport problem, two classical approaches are considered: Eulerian and Lagrangian (Seinfeld, 1986). Eulerian models apply a conservation equation, named atmospheric diffusion equation, for each pollutant as a partial differential equation in a fixed coordinate system,

$$\frac{\partial c_i}{\partial t} + \frac{\partial}{\partial x_j} u_j c_i = D_i \frac{\partial^2 c_i}{\partial x_j \partial x_j} + R_i + S_i \quad i=1,...,n \quad j=1,2,3$$

where $c_i$ is the concentration of pollutant $i$, $u_j$ is the wind component, $D_i$ is the molecular diffusivity, $R_i$ is the reaction term, $S_i$ is the source term, $x_j$ is the spatial coordinate, and $t$ is time.

The system of differential equations can be solved numerically over a discrete grid that covers all the region considered.

The chemical reaction term, $R_i$, is expressed as

$$R_i = \frac{dc_i}{dt} = \sum_{l=1}^{r} \left( k_l \cdot c_i^n c_j^m \right)$$

and represents the net production rate of pollutant $i$ due to the sum of the different reactions $l$, with $k_l$ as the kinetic coefficient and $n$, $m$ the reaction orders for the species $i$, $j$. Because of the different time scale of transport and reaction processes, these terms are usually solved separately.

Lagrangian models (Zannetti, 1990) apply a solution based in the mathematical formulation of the behaviour of representative pollutant volumes. The motion of the pollutant volumes is solved only along their trajectory, so the Lagrangian approach provides a significant saving in computational time when the pollutants are concentrated following the mean wind direction, as a single plume.

Combined simulation of plume dispersion and chemical transformation using Lagrangian models usually consider a first-order decay rate, but can not describe the relationship between different reactants and products. In a dynamic system, this relationship is defined by the same kinetic expression, $R_i$, for each pollutant $i$, as defined in [1]. When considering this expression,
Eulerian concentrations, $c_i$ and $c_j$, must be calculated to estimate the reaction rates in the chemical mechanism.

Some approximations have been considered in the past to solve non-linear chemical reactions within a Lagrangian plume model (Georgopoulos and Seinfeld, 1986; Vilà-Guerau et al., 1990). Usually, these approaches consider a steady-state plume, generated from homogeneous meteorological conditions. On the other hand, Dabdub and Seinfeld (1994) shown that the computational cost of the chemical part of an Eulerian grid model is critical to port it on a parallel machine.

In the approach followed here, two different chemical reaction mechanisms have been implemented in a non-steady Lagrangian puff model, coupled to a diagnostic wind model. As the main result, the influence of the complexity of the chemical reaction mechanism in the speed-up of this model has been determined.

2 The model

2.1 The Wind-Adaptive Puff Model system

The Wind-Adaptive Puff Model (Wind-APM) system is a combined modeling system for the simulation of plume transport from a point source. A diagnostic wind model (Ludwig et al., 1991) calculates wind, temperature and turbulence fields that are used as input data to the adaptive puff model (APM) (Ludwig et al., 1989). This system is currently applied around As Pontes Power Plant (Souto et al., 1996) for the real-time simulation of plume transport.

In the adaptive puff model, the contribution of a puff to the pollutant concentration at a point, $c_i$, is defined by a Gaussian function as,

$$c_i = \frac{Q_s}{(2\pi)^{3/2} \sigma_z^2 \sigma_z^2} \exp\left(-\frac{1}{2} \left(\frac{\nu}{\sigma_z^2}\right)^2\right) \exp\left(-\frac{Z^2(z)}{2}\right) \quad [2]$$

where $c_i$ is the pollutant concentration, $Q_s$ is the pollutant mass, $\sigma_z$ and $\sigma_x$ are the Gaussian standard desviations, $z$ is the height, $z_0$ is the height of the puff and $Z(z)$ is a vertical coordinate in $1/\sigma_z$ units, as follows,

$$Z(z) = \int^{z} \frac{dz}{\sigma_z(z)}$$

The pollutant mass, $Q_s$, represents the total pollutant mass in the puff volume; in a non-reactive puff, this mass keeps invariant along its trajectory.
2.2 The reactive & adaptive puff model (RAP)

The chemical reactions into a pollutants plume depend on the reaction rates, the primary pollutants emitted, the background pollution and the mixing rate between both of them. If these factors are favourable, the plume can either produce secondary pollutants, that increase the background pollution, or consume background pollutants.

As the pollutants emissions are known, the original adaptive puff model (APM) can calculate the pollutant mass in to each puff; after that, the puff growth along its trajectory is estimated from the meteorological conditions. In the reactive & adaptive puff model (RAP), these pollutants mix with the background air, so background pollutants flow into the plume with it. This pollutants flow, $Q_{BG}$, (figure 1) can be estimated from the plume growth along a time interval $\Delta t$ and the background pollutants concentration, $C_{BG}$,

$$Q_{BG} = C_{BG} \left( V_2 - V_1 \right) / \Delta t$$

![Diagram of puff growth](image)

Figure 1. Adaptive puff mixing with background (BG) pollution in the RAP model.

On the other hand, the background pollutants into the puff can not follow the Gaussian distribution in equation [2], as their concentration distribution in the puff should verify two conditions,
a) the pollutant concentration at the external region of the puff (near the background air) must be equal to the background concentration,
b) if there is an effective reduction of the background pollutant into the puff (i.e., because of chemical reactions), the pollutant concentration at the center of the puff must be less than the background concentration. But, its minimum value is zero.

**Mechanism A**

\[ \begin{align*} 
O_3 + NO & \longrightarrow NO_2 + O_2 & k_1 = 2.2 \times 10^{-12} \exp(-1430 / T) \\
2NO + O_2 & \longrightarrow 2NO_2 & k_2 = 1.5 \times 10^{-40} \exp(1780 / T) \\
NO_2 + h\nu & \longrightarrow NO + O & k_{31} = 8.9 \times 10^6 G / C_{O_2} \\
O + O_2 + M & \longrightarrow O_3 + M & k_{32} = 6 \times 10^{-34} (T / 300)^{-2.3} \\
NO_2 + O_3 & \longrightarrow NO_3 + O_2 & k_4 = 1.2 \times 10^{-13} \exp(-2450 / T) 
\end{align*} \]

Table 1. Basic NOx-O3 cycle (M=N2 or O2). Units in molec/cm^3 and seconds.

**Mechanism B**

\[ \begin{align*} 
O_3 + NO & \longrightarrow NO_2 + O_2 & k_1 = 2.2 \times 10^{-12} \exp(-1430 / T) \\
2NO + O_2 & \longrightarrow 2NO_2 & k_2 = 1.5 \times 10^{-40} \exp(1780 / T) \\
NO_2 + h\nu & \longrightarrow NO + O & k_{31} = 8.9 \times 10^6 G / C_{O_2} \\
NO_2 + O_3 & \longrightarrow NO_3 + O_2 & k_4 = 1.2 \times 10^{-13} \exp(-2450 / T) \\
O + O_2 + M & \longrightarrow O_3 + M & k_5 = 6 \times 10^{-34} (T / 300)^{-2.3} \\
O_3 + h\nu & \longrightarrow O_3(D) + O_2 & k_6 = 0.0028 k_3 \\
(O_3(D) + M & \longrightarrow O + M & k_7 = 2.9 \times 10^{-11} \\
O_3(D) + H_2O & \longrightarrow 2OH & k_8 = 2.2 \times 10^{-10} \\
CO + OH & \longrightarrow CO_2 + H \cdot & k_9 = 2.2 \times 10^{-13} \\
HO_2 + NO & \longrightarrow NO_2 + OH \cdot & k_{10} = 3.7 \times 10^{-12} \exp(240 / T) \\
OH + NO_2 & \longrightarrow HNO_3 & k_{11} = 1.1 \times 10^{-11} \\
HCHO + h\nu & \longrightarrow 2HO_2 \cdot + CO & k_{12} = 8.9 \times 10^{-3} \\
HCHO + h\nu & \longrightarrow H_2 + CO & k_{13} = 2.7 \times 10^{-5} \\
HCHO + OH \cdot & \longrightarrow HO_2 \cdot + CO + H_2O & k_{14} = 3.5 \times 10^{-5} 
\end{align*} \]

Table 2. NOx-O3-VOCs mechanism considered (M=N2 or O2). Units in molec/cm^3 and seconds.

So, a different expression for background pollutants concentration in the puff, \( c_{BP} \) is assumed,
where $c_p$ is a "virtual concentration" defined by the expression [2], for the pollutant $p$. When the net production of pollutant $p$ in the plume is positive, $c_p$ can take negative values.

The reactive-adaptive puff (RAP) model has been implemented in FORTRAN 77, and it runs on a Fujitsu VP2400/10 installed at the Centro de Supercomputación de Galicia (CESGA).

In a complete three-dimensional Eulerian grid model (Dabdub and Seinfeld, 1994), that includes more than 70 chemical reactions, the amount of CPU time spent in the chemistry model can reach up to 90% of the total, because the chemical mechanism must be solved in all the grid cells. As a Lagrangian model, the RAP model can reduce the amount of CPU time spent in both processes, transport and chemistry.

3 The chemical mechanisms

The chemical mechanism included in the RAP model was focused in the photochemical reactions of NO$_x$ (NO, NO$_2$), O$_3$ and VOCs, as the main chemical force in the transformation of NO$_x$ emitted from a power plant. Two mechanisms have been implemented,

a) a four reactions mechanism (table 1), for the NO$_x$-O$_3$ cycle (Finlayson Pitts and Pitts, 1986), as the basic cycle that includes NO, NO$_2$ and O$_3$ production-destruction.

b) a fourteen reactions mechanism (table 2), that includes some VOCs and H$_2$O too (Seinfeld, 1986), as an extension of the NO$_x$-O$_3$ cycle, usually applied to compare the influence of different VOCs in this cycle.

On tables 1 and 2, the chemical reactions and their kinetic coefficients, $k_b$, are shown. This information is applied to define the $n$ differential equations as [1], for the $n$ chemical species considered.

4 Results

The reactive-adaptive puff model (RAP) was applied on a 60 x 60 km$^2$ real environment (figure 2) around As Pontes Power Plant, to simulate the transport and chemical transformation of NO-NO$_2$ inside the plume emitted from the power plant. This utility is a 1400 MWe coal fired power plant located at Galicia, in the NW of Spain, an Atlantic region with complex terrain and sea influence.

Seventeen ground level concentration (glc) stations with automatic sensors for SO$_2$, NO, NO$_2$ and solid particles are located 30 km around the power plant. At F-2 and B-2 stations, O$_3$ automatic sensors are installed too.

In order to obtain an estimation of the computational cost of the RAP model at the same meteorological conditions, a set of scalar runs was
performed for the three model versions (non-reactive, mechanism A and mechanism B), using constant wind, atmospheric stability and solar radiation. As the size and the number of puffs can vary widely due to the stability conditions, the simulations were done using unstable, neutral and stable conditions. The results are shown on table 3.

Figure 2. As Pontes Power Plant air pollution monitoring network (30 km around), as the simulation environment considered.

The speed-up of the model varies due to the stability conditions, with a minor influence of the chemical mechanism. This can be explained because the speed-up depends on the number of puffs that the model needs to represent the continuous plume; in unstable conditions, puffs grow faster than in stable conditions, so unstable puffs are bigger. Less than 60 puffs were required to represent a 30 km plume in unstable conditions, but in stable conditions the number of puffs was 150. Comparing stable and unstable speed-up reductions, the computational cost of the chemical mechanisms is higher in stable conditions, because the number of puffs (reactive volumes) is higher. So, if the plume simulation tries to cover longer distances (so the number of puffs increases), the computational cost of the chemical mechanism grows. The
relative influence of the chemical mechanisms in the speed-up of the model can only be evaluated against the same stability conditions.

<table>
<thead>
<tr>
<th>SPEED-UP</th>
<th>non-reactive</th>
<th>mechanism A</th>
<th>mechanism B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stable</td>
<td>29.28</td>
<td>23.39 (20%)</td>
<td>21.74 (26%)</td>
</tr>
<tr>
<td>Neutral</td>
<td>48.50</td>
<td>39.51 (19%)</td>
<td>37.02 (24%)</td>
</tr>
<tr>
<td>Unstable</td>
<td>90.50</td>
<td>79.96 (12%)</td>
<td>76.76 (15%)</td>
</tr>
</tbody>
</table>

Table 3. Speed-up of the RAP runs and speed-up reduction ratio (%) for the reactive runs, referred to the non-reactive runs with different atmosphere stability conditions; all runs using constant meteorological conditions.

If the chemical mechanism is more complex, there is a decrease in the speed-up, i.e., in neutral conditions, for the mechanism A (4 reactions) is of 19%, and for the mechanism B (14 reactions) is of 24%. So, it is possible to include more reactions (probably, up to 100 reactions) before the speed-up reduction reaches 100%, that is, the chemical mechanism needs as CPU time as the wind & transport model.

<table>
<thead>
<tr>
<th>CPU time</th>
<th>non-reactive</th>
<th>mechanism A</th>
<th>mechanism B</th>
</tr>
</thead>
<tbody>
<tr>
<td>25/Jun/1996</td>
<td>7 min 59 s</td>
<td>10 min 29 s</td>
<td>11 min 15 s</td>
</tr>
</tbody>
</table>

Table 4. Total CPU time to simulate the real plume transport (and reaction) around As Pontes Power Plant, along 25/Jun/1996.

The three versions of the RAP model were applied to the simulation with real data along one day (25/Jun/1996). Emission and meteorological data as time averages were provided every 5 minutes to the RAP model, in order to represent quick changes in the boundary conditions (specially, wind and stability). The CPU time is shown on table 4.

The increment in CPU time from non-reactive to reactive runs is due mainly to the calculation of the mean puff concentrations to estimate the reaction rates, as it is described on section 2.2. This computational cost depends on the number of chemical species considered, for the same meteorological conditions.

Figure 3 shows the NO₂/NOₓ ratios estimated by the model at F-2 station (25/Jun/1996). This ratio for mechanism A is 100% (no NO is left). But, it is
well known that the influence of other species (mainly, VOCs) in the cycle NO\textsubscript{X}-O\textsubscript{3} usually causes lower NO reduction, because VOCs (as NO) can react with O\textsubscript{3} too. In fact, measured NO\textsubscript{2}/NO\textsubscript{X} ratios can get down to 80 % (Méndez et al., 1997). Applying a more complex mechanism B (that includes CO and HCHO), some NO left at F-2, following the real behaviour. This mechanism B needs less than 1 min of extra CPU time (see table 4). More complex chemical mechanisms, including other VOCs, can obtain more NO (as real measurements) and, in the RAP model, the CPU time would only be doubled.

![NO\textsubscript{2}/NO\textsubscript{X} vs Time (LST)](image)

Figure 3. NO\textsubscript{2}/NO\textsubscript{X} ratios estimated at the same distance as F-2 station, along 25/Jul/1996.

Conclusions

A Lagrangian reactive & adaptive puff model (RAP) to simulate the transport and chemical reactions of a pollutants plume at short distances (less than 100 km) in the atmospheric boundary layer, has been developed. Different runs (non reactive and reactive) have been done in order to compare the computational cost of the transport and chemical parts of the model.

The analysis of several runs applying different atmospheric stability conditions shows that the speed-up decreases mainly because of the introduction of a chemical mechanism, and the reduction in the speed-up from 4 to 14 reactions is less significant. From these results, it is expected that the RAP model including up to 100 chemical reactions only need twice as much CPU time as the case of non-reactive run. Typical Eulerian grid models need up to 90 % of the total CPU time to simulate the chemical reactions.

The simulation with real emission and meteorological data indicates that a more complex chemical mechanism should be included in the model, in order...
to represent the dynamic behaviour of NOx and O3. CPU time results on a
Fujitsu VP2400/10 show that the implementation of this mechanism is feasible.

Future work includes the reactions involving other VOCs, SO2 and H2O2 in
the Lagrangian model, and the use a regional model to estimate the
concentration of background species, as O3, that affect the plume reactions.

Acknowledgments

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