

# A Lagrangian particle model with chemical reaction

Stefano Alessandrini<sup>1</sup>

Enrico Ferrero<sup>2</sup>

Gianni Belfiore<sup>3</sup>

CESI RICERCA

1. CESI RICERCA, ITALY
2. UNIVERSITA' PIEMONTE ORIENTALE, ITALY
3. ISAC CNR, ITALY



# Introduction

- ◆ Needs of estimating plume secondary pollutants like  $\text{NO}_2$
- ◆ A lagrangian one particle model can compute only the average concentrations and not correlation between reactants
- ◆ To know average concentrations we refer to a finite volume in an eulerian frame
- ◆ To simulate the chemical reactions an eulerian scheme has been introduced, that make use of a fixed grid concentration computation
- ◆ How to simulate the background  $\text{O}_3$  concentration filling the whole domain

# Lagrangian model description

- ◆ SPRAY (Ferrero and Anfossi, 1998) is a Lagrangian stochastic particle model for complex terrain based on three Langevin equations for the random velocities (Thomson, 1987):

$$\begin{aligned} du &= a(x, u)dt + b(x, u)dW(t) \\ dx &= (U + u)dt \end{aligned}$$

**U is the mean wind velocity,**

$$a(x, u)dt$$

**is a deterministic term depending on  $P_E(x, u)$ ,**

$$b(x, u)dW(t)$$

**is a stochastic term**

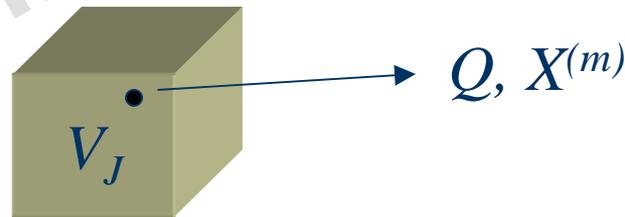
$$dW(t)$$

**is the incremental Wiener process.**

# Concentration computations

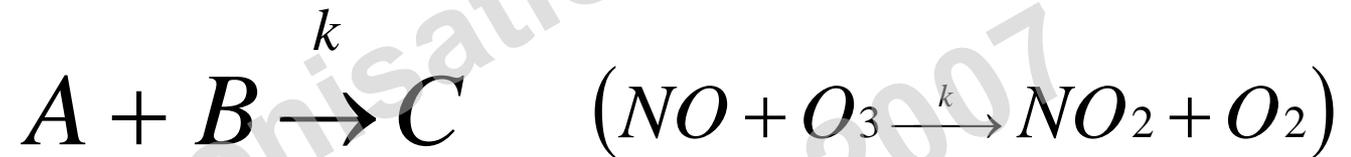
- ◆ The concentration are computed in an Eulerian Grid
- ◆ Concentration in the cell of volume  $V_j$ , is computed considering the total mass of the particles contained

$$\langle c(x_j, t) \rangle = \frac{1}{V_j} \sum_{m=1}^M \int_{\Gamma_j} Q \delta(x' - X^{(m)}(t)) dx'$$



# Algorithm for chemical reactions

The simple chemical reaction is considered :



The chemical kinetic follows:

$$\frac{\partial c_A}{\partial t} = \frac{\partial c_B}{\partial t} = -\frac{\partial c_C}{\partial t} = -k c_A c_B$$

# Algorithm for chemical reactions

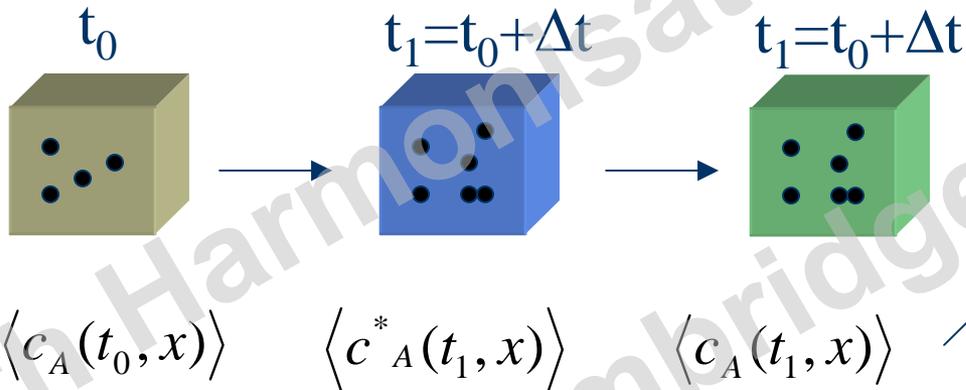
- ◆ Based on the papers of Chock and Winkler, 1994a, 1994b
- ◆  $\mathbf{C}_{A,B,C}(\mathbf{x}, t_0)$  is the concentration at the time  $t_0$
- ◆ After the turbulent displacements we have at the time  $\mathbf{t}_1 = \mathbf{t}_0 + \Delta t$ ,  $\mathbf{C}_{A,B,C}^*(\mathbf{x}, t_1)$
- ◆ After the chemical reactions we have  $\mathbf{C}_{A,B,C}(\mathbf{x}, t_1)$  from the following :

$$\langle c_A(\mathbf{x}_j, t_1) \rangle = \langle c_A^*(\mathbf{x}_j, t_1) \rangle - k\Delta t \langle c_A^*(\mathbf{x}_j, t_1) \rangle \langle c_B^*(\mathbf{x}_j, t_1) \rangle$$

$$\langle c_B(\mathbf{x}_j, t_1) \rangle = \langle c_B^*(\mathbf{x}_j, t_1) \rangle - k\Delta t \langle c_A^*(\mathbf{x}_j, t_1) \rangle \langle c_B^*(\mathbf{x}_j, t_1) \rangle$$

$$\langle c_C(\mathbf{x}_j, t_1) \rangle = \langle c_C^*(\mathbf{x}_j, t_1) \rangle + k\Delta t \langle c_A^*(\mathbf{x}_j, t_1) \rangle \langle c_B^*(\mathbf{x}_j, t_1) \rangle$$

# Algorithm for chemical reactions



$$\langle c_A(t_0, x) \rangle$$

$$\langle c_A^*(t_1, x) \rangle$$

$$\langle c_A(t_1, x) \rangle$$

**If**  $\langle c_A^*(t_1, x) \rangle \neq 0$

$$M_A^{(n)}(t_1) = M_A^{(n)}(t_0) \frac{\langle c_A(t_1, x) \rangle}{\langle c_A^*(t_1, x) \rangle}$$

**If**  $\langle c_A^*(t_1, x) \rangle = 0$

$$M_A^{(n)}(t_1) = \langle c_A(t_1, x) \rangle \frac{V}{N}$$

# The segregation coefficient

- ◆ Following the Reynolds hypothesis:

$$c_A = \langle c_A \rangle + c_A'$$

$$c_B = \langle c_B \rangle + c_B'$$

$$\langle c_A c_B \rangle = \langle c_A \rangle \cdot \langle c_B \rangle + \langle c_A' c_B' \rangle$$

$$\langle c_A c_B \rangle = \langle c_A \rangle \cdot \langle c_B \rangle \left( 1 + \frac{\langle c_A' c_B' \rangle}{\langle c_A \rangle \langle c_B \rangle} \right)$$

$$k \langle c_A c_B \rangle \leq k \langle c_A \rangle \cdot \langle c_B \rangle$$

For this reaction is  $\leq 0$

# How to account for the segregation

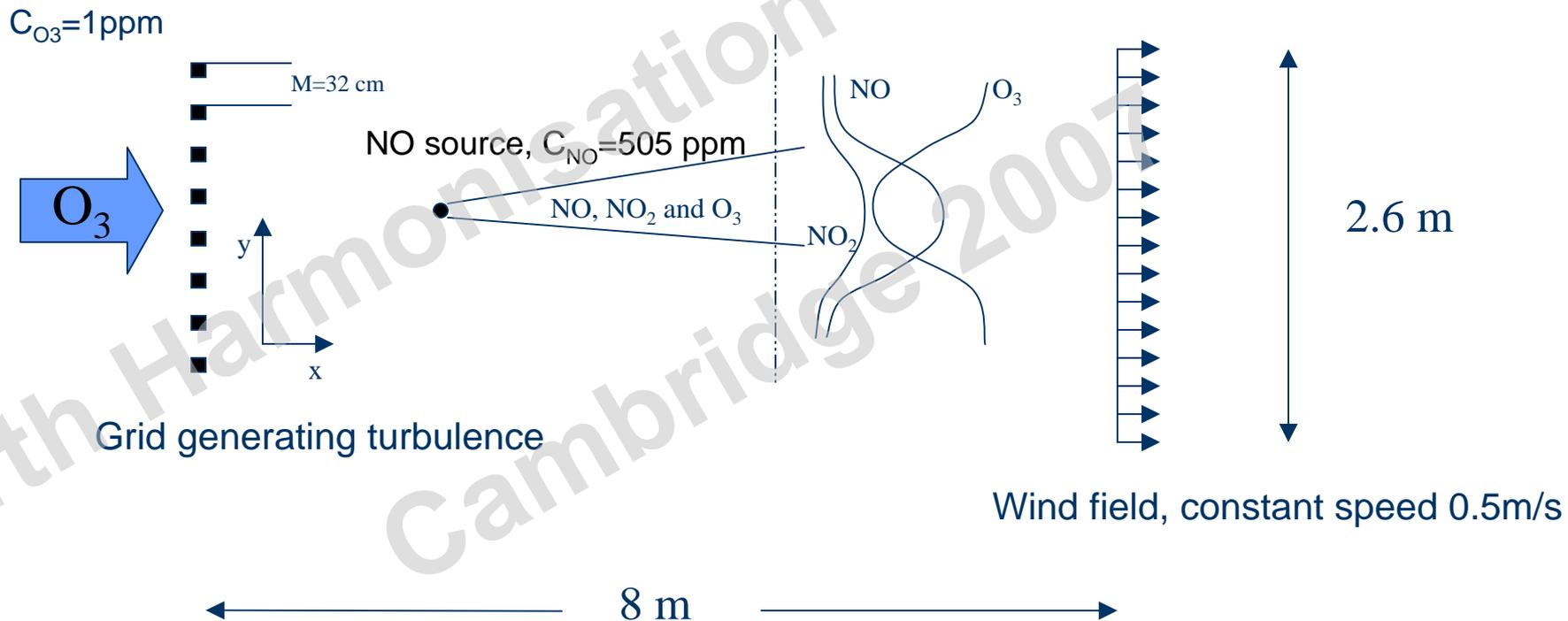
- ◆ Neglecting  $\alpha$  the kinetic of the chemical reaction is overestimated
- ◆ Two possibilities: two particles model (Crone 1999, van Dop 2001) that still meet some limit in the application to real atmospheric non homogeneous conditions

- ◆ The segregation coefficient

$$\alpha = \frac{\langle c_A' c_B' \rangle}{\langle c_A \rangle \langle c_B \rangle}$$

can be parameterised according to experimental data

# Wind tunnel experiment: Bilger et al. 1996



# Wind field simulation: RAMS

- Simulation period: 500 sec
- Time step: 0.01 sec
- Domain dimensions (x,y,z): 8 x 8 x 8 m<sup>3</sup>;
- Grid dimensions (x,y,z): 0.1x0.2x0.3 m<sup>3</sup>;
- Velocity component along x: 0.5 m/s;
- Average velocity along y and z: 0 m/s;

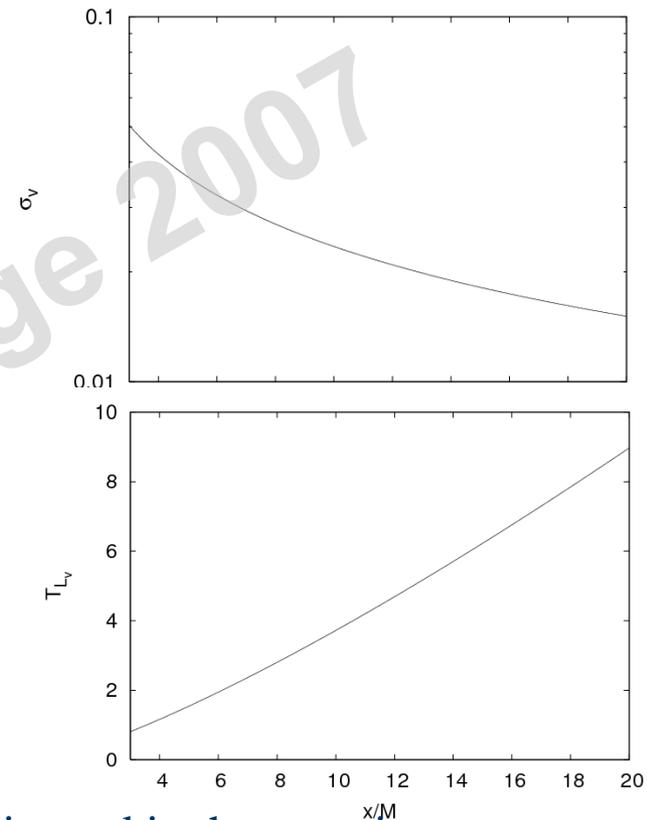
# Turbulence parameterisation

- The velocity variances and the lagrangian time scales are derived from the measurements (Bilger, 1996)

$$\overline{\sigma_u^2} = 0.173 \cdot \overline{U}^2 \left( \frac{x}{M} \right)^{-1.37}$$

$$\overline{\sigma_{v,w}^2} = 0.041 \cdot \overline{U}^2 \left( \frac{x}{M} \right)^{-1.27}$$

$$T_{Lx,y,z} = \frac{D}{\sigma_{u,v,w}^2} = \frac{0.002048}{\sigma_{u,v,w}^2}$$



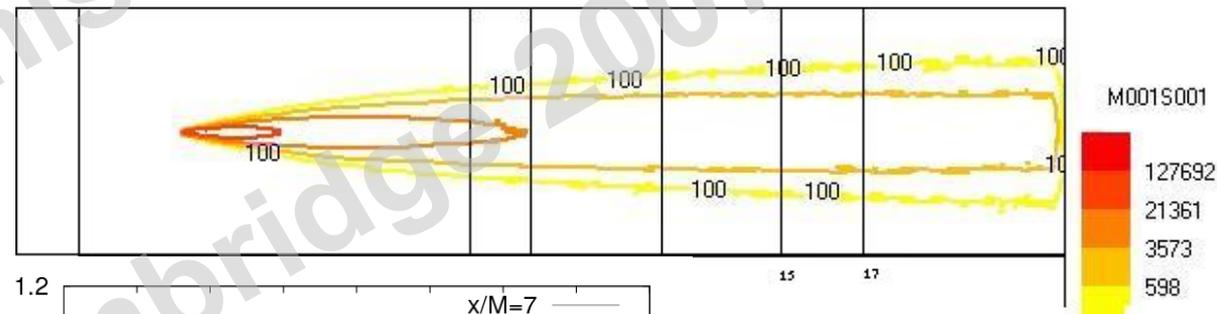
where D is the diffusivity and its value was estimated in the experiment

# SPRAY simulation characteristic

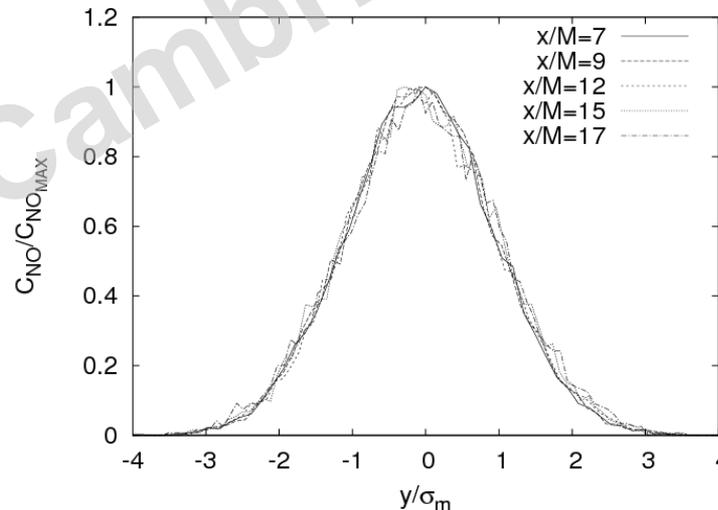
- Source dimension (x,y,z): 0.01x0.03x0.03 m<sup>3</sup>;
- NO concentration at the source : 505 p.p.m.;
- Background O<sub>3</sub> concentration: 1 p.p.m.;
- Reaction rate k: 0 (s p.p.m.)<sup>-1</sup> o 0.44 (s p.p.m.)<sup>-1</sup> ;
- Time step: 0.1s;
- Number of emitted particles every time step: 1000 for NO ;
- Boundary conditions at the top and bottom boundaries: Total reflection;
- Number of iterations: 5000
- Concentration grid dimensions (DX, DY, DZ): 0.1, 0.02, 0.02 m
- Average concentrations computed between the time steps 2000 and 5000, saving the temporary concentrations every 50 time steps

# SPRAY simulation: frozen case

- NO concentration along horizontal section in the frozen case ( $k=0$ ). The lines indicates the sections where the concentration distributions have been computed (at  $x/M=7, 9, 12, 15, 17$ ) and consequently the plume width  $\sigma_m$

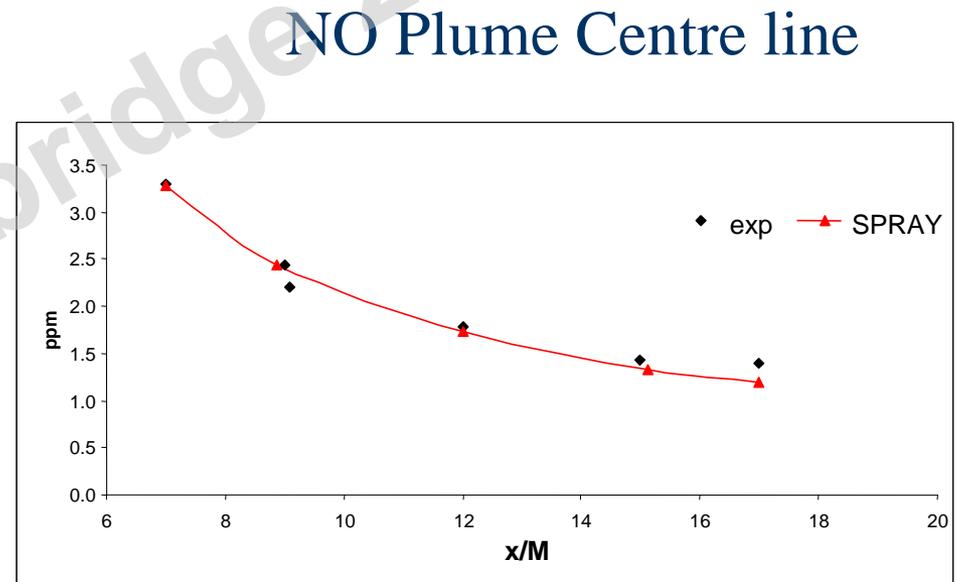
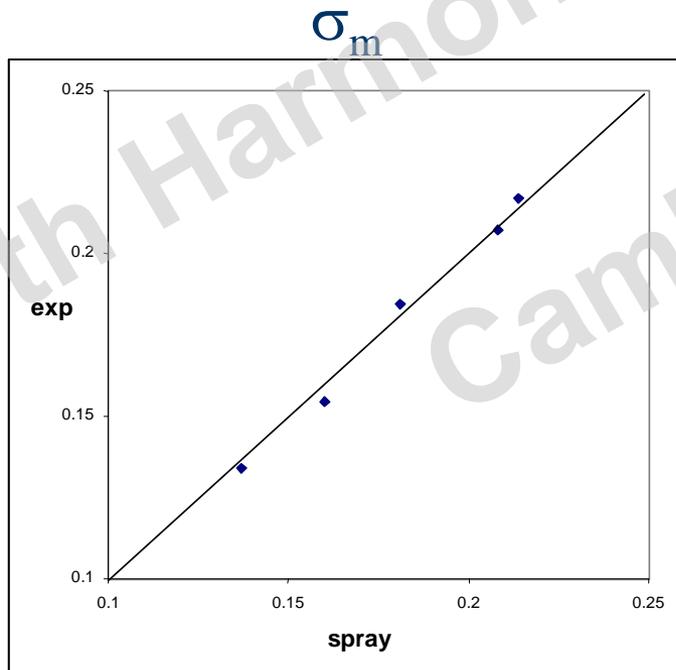


$$\bar{C} = \bar{C}_c \exp\left(-\frac{1}{2}\left(\frac{r}{\sigma_m}\right)^2\right)$$



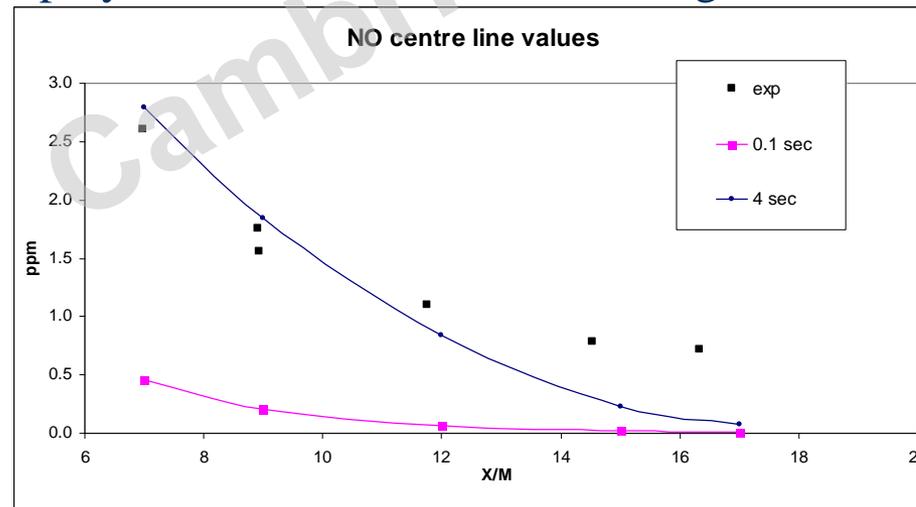
# Frozen case: comparison with experimental data

- Comparison between measured and simulated values of  $\sigma_m$  (left), and between measured and simulated plume centre line values at different distances  $x/M$ , ( $M=0.32$  m) from the source (right)



# Constant background O<sub>3</sub> case

- ◆ Damköhler is defined as 
$$N_D = \frac{kMC_{O_3}}{U}$$
- ◆ It represents the ratio between the time scales of turbulence and chemical reactions, in this experiment  $N_D = 0.24$  so the turbulence is faster than the chemistry
- ◆ The turbulence should be able to restore the original background value of 1 ppm reduced by the chemical reaction
- ◆ Coloured line: Spray with the chemical reaction algorithm is activated every 0.1 sec and 4 sec



# Segregation coefficient parameterisation

- Two kind of simulations have been performed considering the background  $O_3$  diffusion:
  - the segregation coefficient has been neglected ( $\alpha = 0$ )
  - the following parameterisation, obtained interpolating experimental measurements of the covariance performed in the wind tunnel experiment, is proposed

$$k \cdot \langle c_A c_B \rangle = k \langle c_A \rangle \cdot \langle c_B \rangle \left( 1 + \frac{\langle c_A' c_B' \rangle}{\langle c_A \rangle \langle c_B \rangle} \right)$$

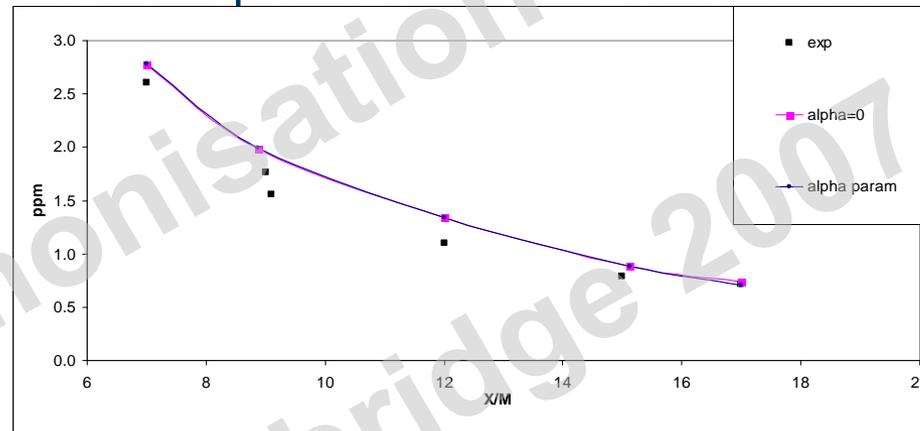
$$k \langle c_A \rangle \cdot \langle c_B \rangle (1 + \alpha)$$

$$\alpha = -0.77 \cdot e^{-\frac{0.106 x}{N_D x_s}} \quad \begin{matrix} N_d = 0.24 \\ x_s = 20M \end{matrix}$$

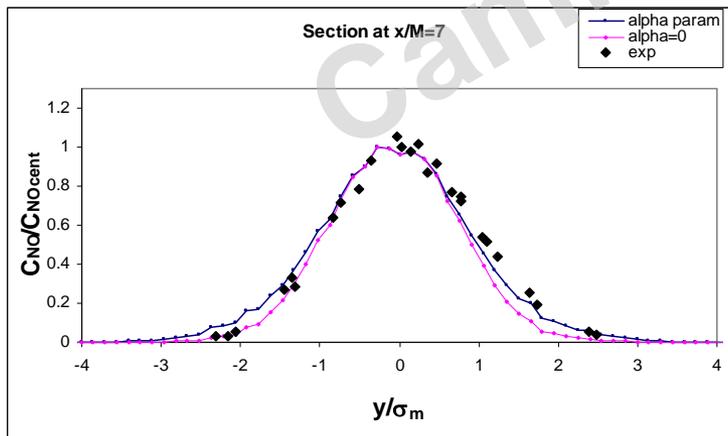
where  $x_s$  is the stochiometric distance and  $N_d$  the Damköhler number

# Background O<sub>3</sub> simulated with particles: comparison with the measurements

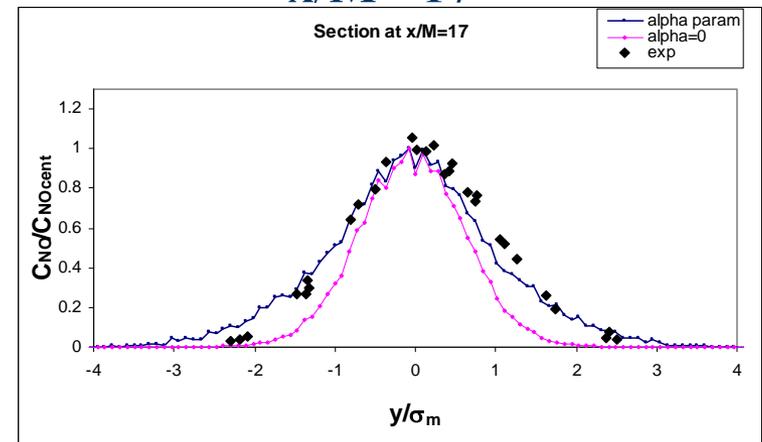
NO: trend of the plume centre line concentrations



NO: section x/M= 7

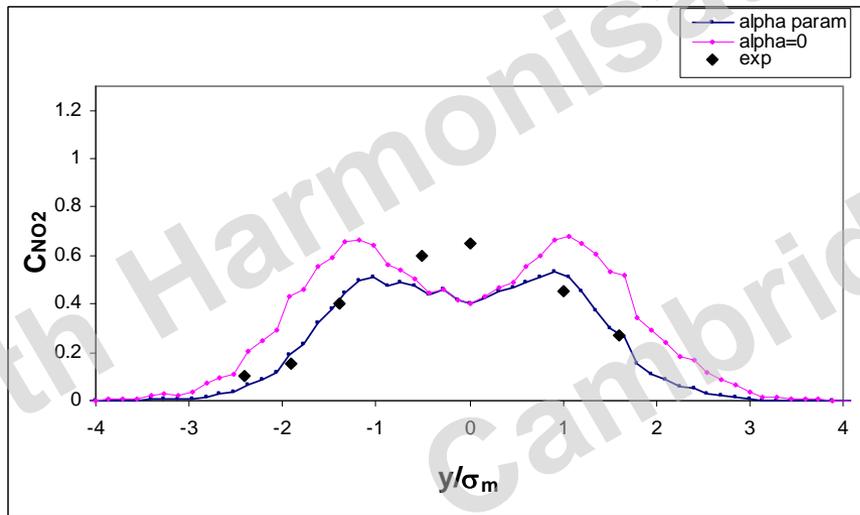


x/M= 17

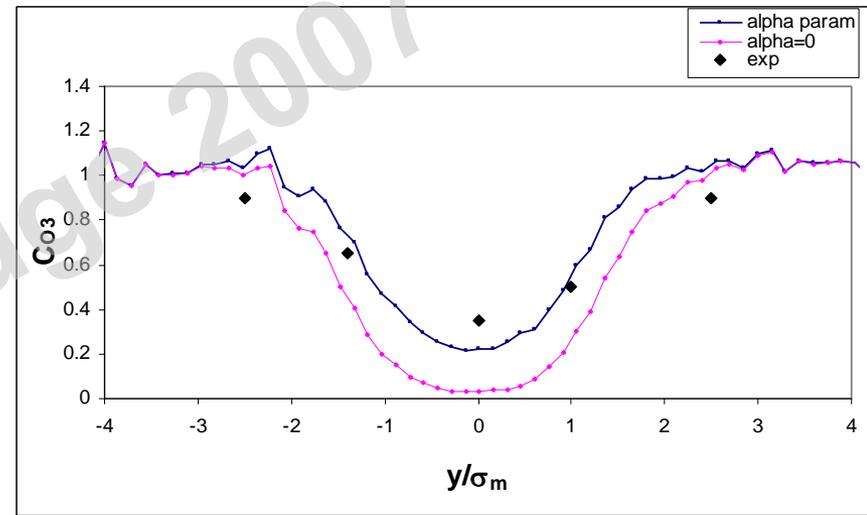


# Background O<sub>3</sub> simulated with particles: comparison with the measurements

NO<sub>2</sub> at x/M=7

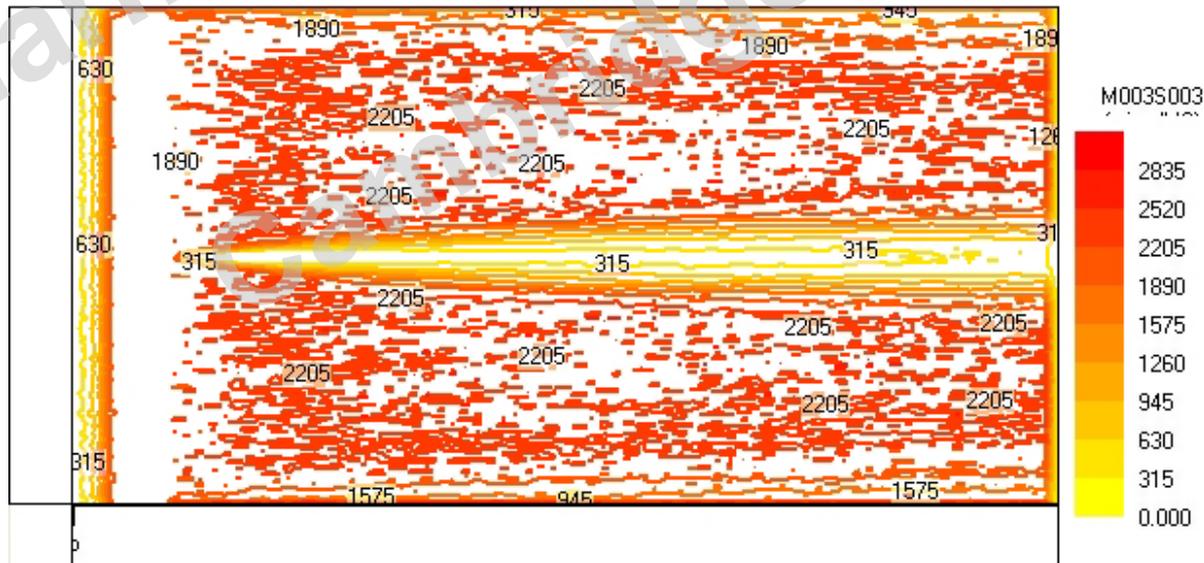


O<sub>3</sub> at x/M=7



# Background O<sub>3</sub> simulated with particles

- ◆ Number of particles released every time step (0.1 sec): 1000 for NO, 80000 for O<sub>3</sub> (12 hours of computational time for a 5 minutes long simulation)
- ◆ The NO plume is described with more accuracy than the background O<sub>3</sub>



# Background O<sub>3</sub> simulated with holes

- ◆ The decreasing of the O<sub>3</sub> background concentration happens only in the presence of NO and hence only inside the plume
- ◆ It is not useful simulating the O<sub>3</sub> diffusion where NO is absent because its concentration remains constant (well mixed condition)
- ◆ We have adopted the scalar:

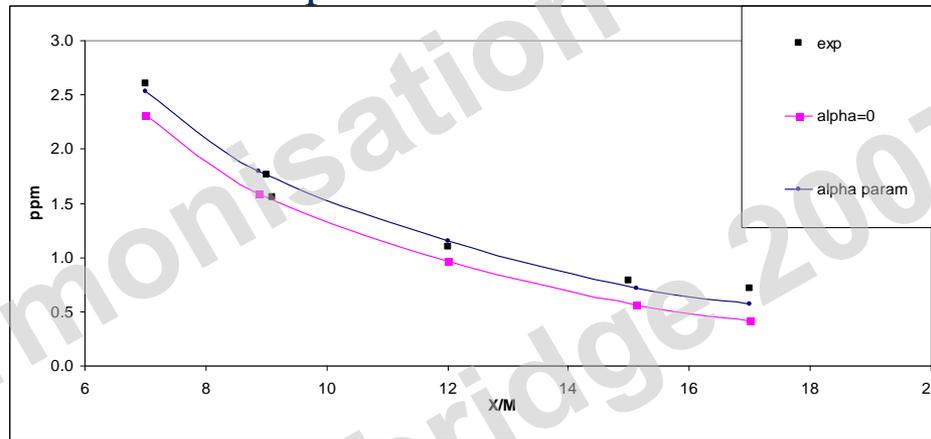
$$C_{O3hole} = C_{O3back} - C_{O3}$$

where  $C_{O3back}$  is in our case constant equal to 1 ppm

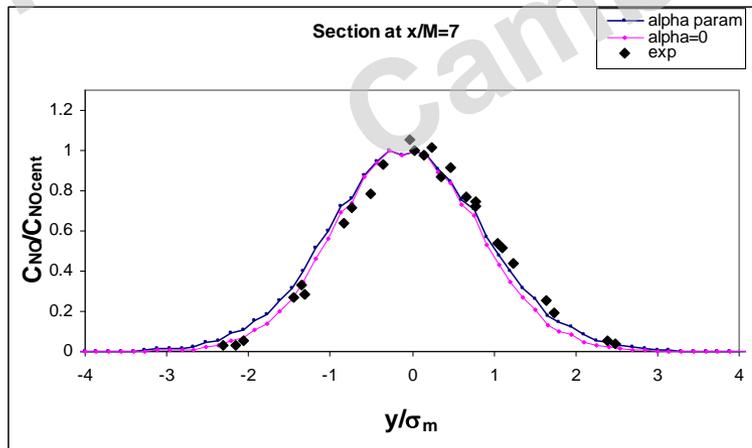
- ◆ The scalar  $C_{O3hole}$  is released only by the point source together with NO requiring no other particles than those of the plume to be well represented
- ◆ Then the actual  $C_{O3}$  is computed before the chemical reaction, therefore the algorithm remains unchanged

# Background O<sub>3</sub> simulated with holes: comparison with the measurements

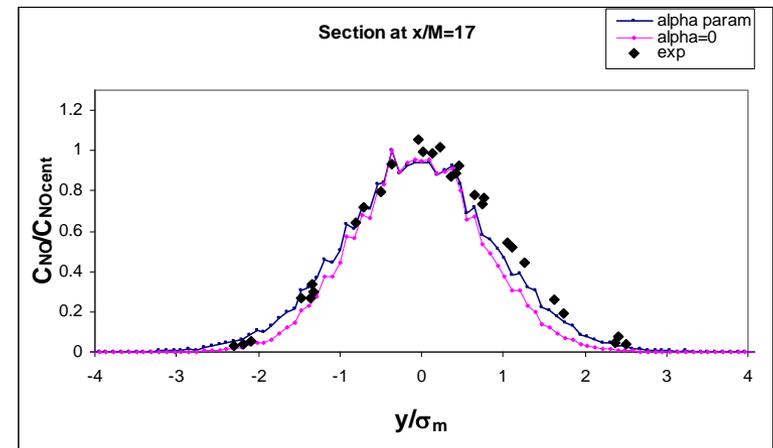
NO: trend of the plume centre line concentrations



NO: section  $x/M=7$



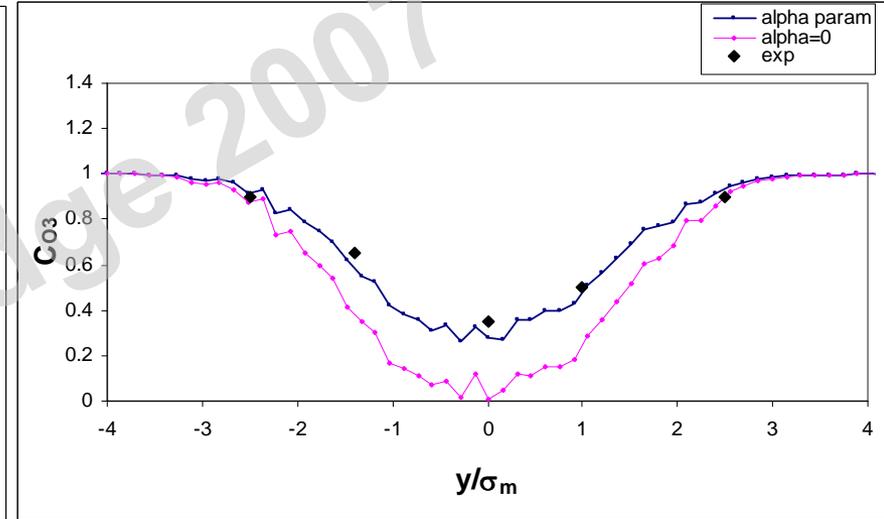
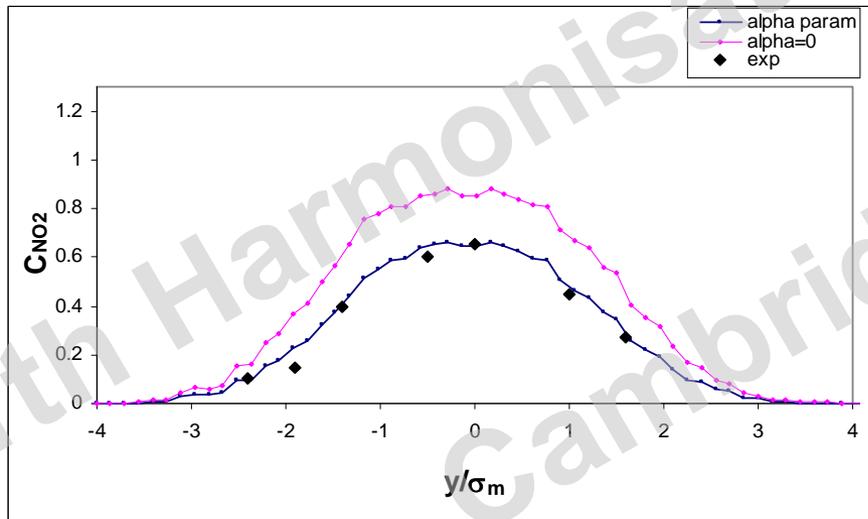
$x/M=17$



# Background O<sub>3</sub> simulated with holes: comparison with the measurements

NO<sub>2</sub> at x/M=7

O<sub>3</sub> at x/M=7

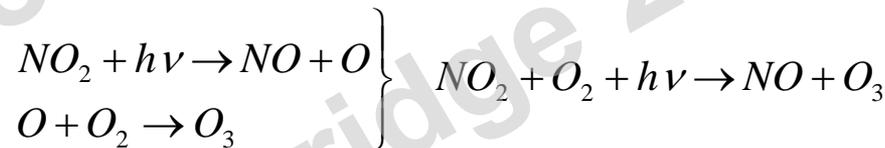


# Conclusions

- ◆ The O<sub>3</sub> depletion inside the plume needs to be simulated
- ◆ Simulating the background O<sub>3</sub> diffusion by emitting particles filling the domain requires extremely high computational time and does not guarantee enough accuracy.
- ◆ Simulating the background O<sub>3</sub> by means of “holes” yields better results requiring much less computational time
- ◆ The segregation effect should be considered to avoid the NO<sub>2</sub> overestimation and O<sub>3</sub> underestimation

# Future developments

- ◆ Application in real atmosphere testing the results with experimental data
- ◆ In diurnal condition the chemical module must be changed adding the following reaction system



- ◆ Development of an adaptive grid to increase the resolution of the 3-D concentration fields near the source