A lagrangian particle model with chemical reactions: application in real atmosphere

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Outline

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- Eulerian chemical scheme
- Treating the background (O_3) concentration
- Preliminary test on a laboratory experiment
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Introduction

- Needs of estimating plume secondary pollutants like NO_2 for regulatory purposes
- Estimating short term non-equilbrium concentration in a plume with chemical reactions
- The lagrangian particle model is particularly suitable to simulate the dispersion at the small scale
- Two critical point: 1) how to simulate the background concentrations (how many particles); 2) how to simulate chemical reactions (eulerian scheme)
- In this work we have applied the model to a case in real atmosphere evaluating the dispersion of pollutants released by a power plant located in the North of Italy
- the model considers the photolysis of NO_2 due to solar radiation

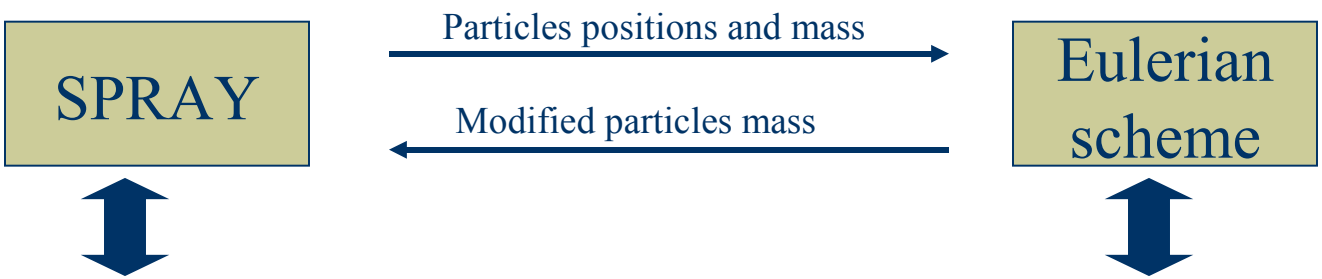
Previous work

- This is the prosecution of the work presented at the Harmo 11 conference
- We have presented an application of a lagrangian particle model with chemical reactions to a wind tunnel experiment
- The model was able to estimate a secondary pollutant like NO_2 due to the only oxidation reaction: $NO + O_3 \xrightarrow{k} NO_2 + O_2$

- The average concentrations were computed in a finite volume in an eulerian frame using a fixed grid
- The background O_3 concentration filling the whole domain has been simulated by using the "deficit" method
- The model was validated against a wind tunnel data-set

Model Scheme

- The Eulerian model is included inside the lagrangian model, SPRAY, following the simple scheme:



•Particles emission
•Lagrangian particle displacements
•Final concentration computation

•Temporary concentration computation on a 3D grid
•Chemical reactions performed on the same grid
•New particles mass of different species computation

Algorithm for chemical reactions

- The set of chemical reactions considered is:

$$NO + O_3 \xrightarrow{k} NO_2 + O_2$$

$$NO_2 + O_2 + h\nu \xrightarrow{J} NO + O_3$$

- The chemical kinetic follows:

$$\frac{\partial c_{NO}}{\partial t} = \frac{\partial c_{O_3}}{\partial t} = -\frac{\partial c_{NO_2}}{\partial t} = -k \cdot c_{NO} \cdot c_{O_3} + j \cdot c_{NO2}$$

- k depends on temperature and is around 0.4 $ppm^{-1}sec^{-1}$ while J depends on solar radiation and ranges between 0 during the night and 0.4 min^{-1} in the full sunlight

- the O_2 concentrations are neglected because this substance is always present in excess and his variation in time and space does not influence the kinetic J of the reaction

Algorithm for chemical reactions

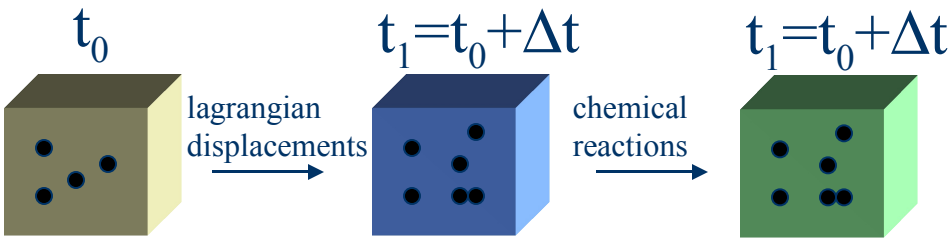
- Extension of the Chock and Winkler (1994a, 1994b) scheme
- $\mathbf{C_{NO,NO2,O3}(x,t_0)}$ is the concentration at the time t_0
- After the turbulent displacements we have at the time $\mathbf{t_1=t_0+\Delta t}$, $\mathbf{C^*_{NO,NO2,O3}(x,t_1)}$
- After the chemical reactions we have $\mathbf{C_{NO,NO2,O3}(x,t_1)}$ from the following :

$$\left\langle c_{NO}(\mathbf{x}_j,t_1)\right\rangle = \left\langle c^*_{NO}(\mathbf{x}_j,t_1)\right\rangle - k\Delta t\left\langle c^*_{NO}(\mathbf{x}_j,t_1)\right\rangle\left\langle c^*_{O_3}(\mathbf{x}_j,t_1)\right\rangle + j\Delta t\left\langle c^*_{NO_2}(x_j,t_1)\right\rangle$$

$$\left\langle c_{NO_2}(\mathbf{x}_j,t_1)\right\rangle = \left\langle c^*_{NO_2}(\mathbf{x}_j,t_1)\right\rangle + k\Delta t\left\langle c^*_{NO}(\mathbf{x}_j,t_1)\right\rangle\left\langle c^*_{O_3}(\mathbf{x}_j,t_1)\right\rangle - j\Delta t\left\langle c^*_{NO_2}(x_j,t_1)\right\rangle$$

$$\left\langle c_{O_3}(\mathbf{x}_j,t_1)\right\rangle = \left\langle c^*_{O_3}(\mathbf{x}_j,t_1)\right\rangle - k\Delta t\left\langle c^*_{NO}(\mathbf{x}_j,t_1)\right\rangle\left\langle c^*_{O_3}(\mathbf{x}_j,t_1)\right\rangle + j\Delta t\left\langle c^*_{NO_2}(x_j,t_1)\right\rangle$$

Algorithm for chemical reactions: particles mass



$\langle c_A(t_0,x)\rangle$ $\langle c^*{}_A(t_1,x)\rangle$ $\langle c_A(t_1,x)\rangle$

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 $\langle c^*{}_A(t_1,x)\rangle = 0$

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

Background O_3 simulation

- Treating background species as static fields (as O_2) is not a reasonable approximation in the case of O_3
- O_3 concentration variation inside the plume need to be taken into account (Hegg et al. 1977).
- The changes of the O_3 background concentration occur only in presence of $NO_{x,}$ hence outside the plume, O_3 concentration remains constant (well mixed condition)
- It is not useful simulating the diffusion where NO is absent

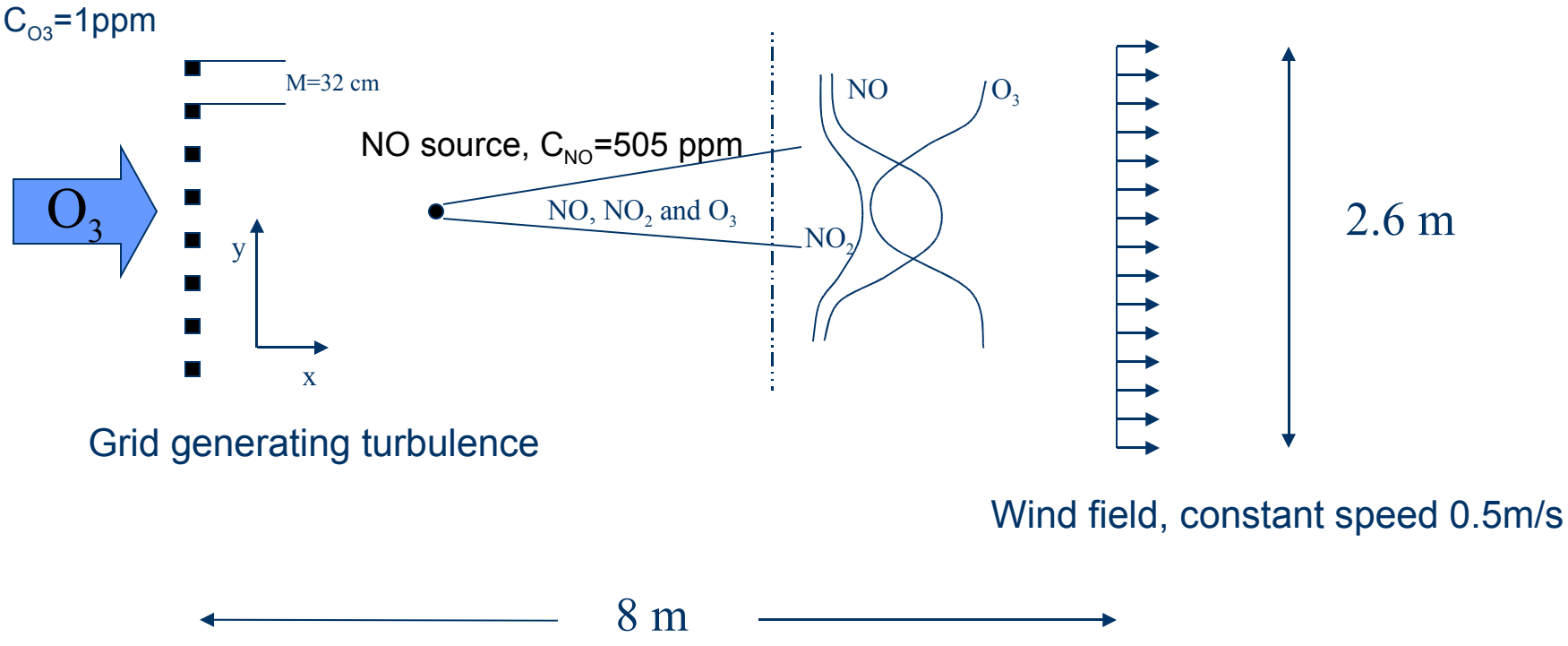
A new scalar: “deficit”

- The following new scalar is introduced:

$$C_{O3deficit} = C_{O3back} - C_{O3}$$

  where C_{O3back} is the background homogeneous concentration value
- Every emitted particle carries a “deficit” of concentration
- The scalar $C_{O3deficit}$ is released only by the point source together with NO requiring no more particles than those of the plume
- The actual C_{O3} is computed before the chemical reaction, therefore the chemical algorithm remains unchanged

Preliminary qualitative comparison



Wind tunnel experiment: Bilger et al.1996

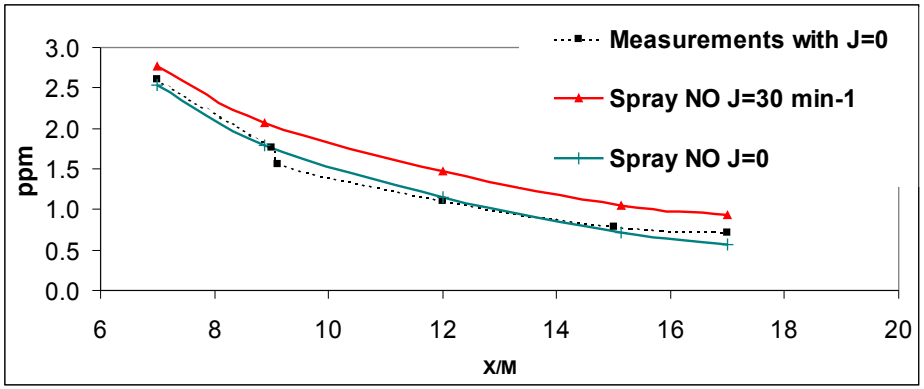
Preliminary qualitative comparison: results

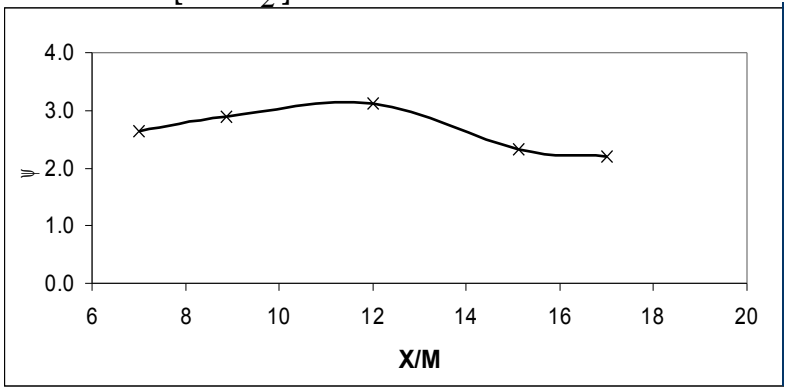
NO trend along plume centre line

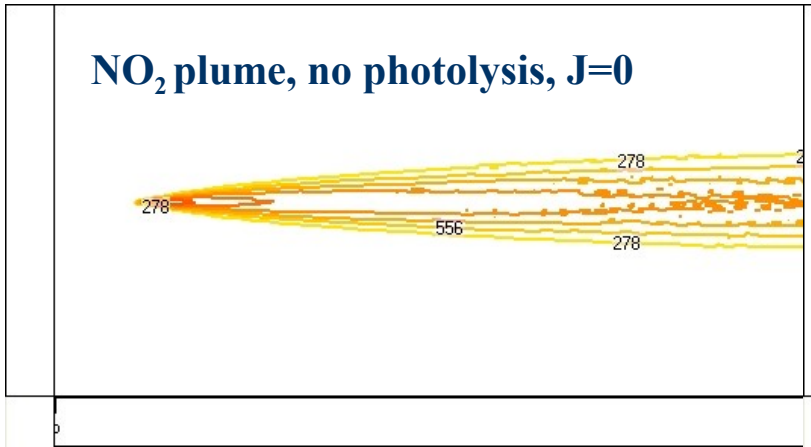
$$\psi = \frac{k[NO][O_3]}{J[NO_2]}$$

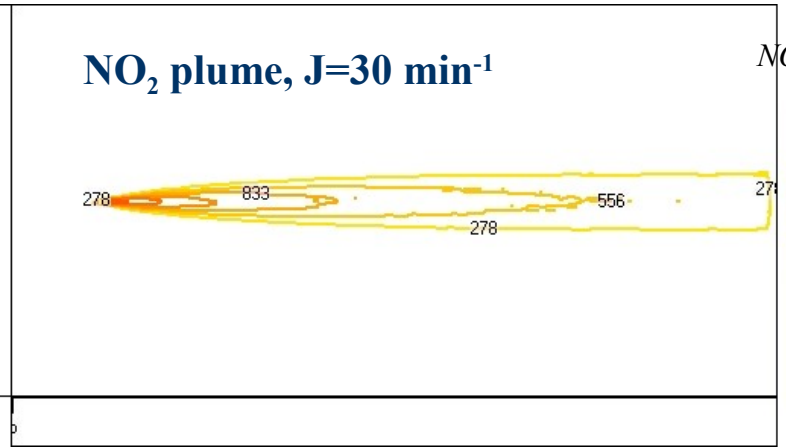
k=0.44 min^{-1}

J=30 min^{-1}



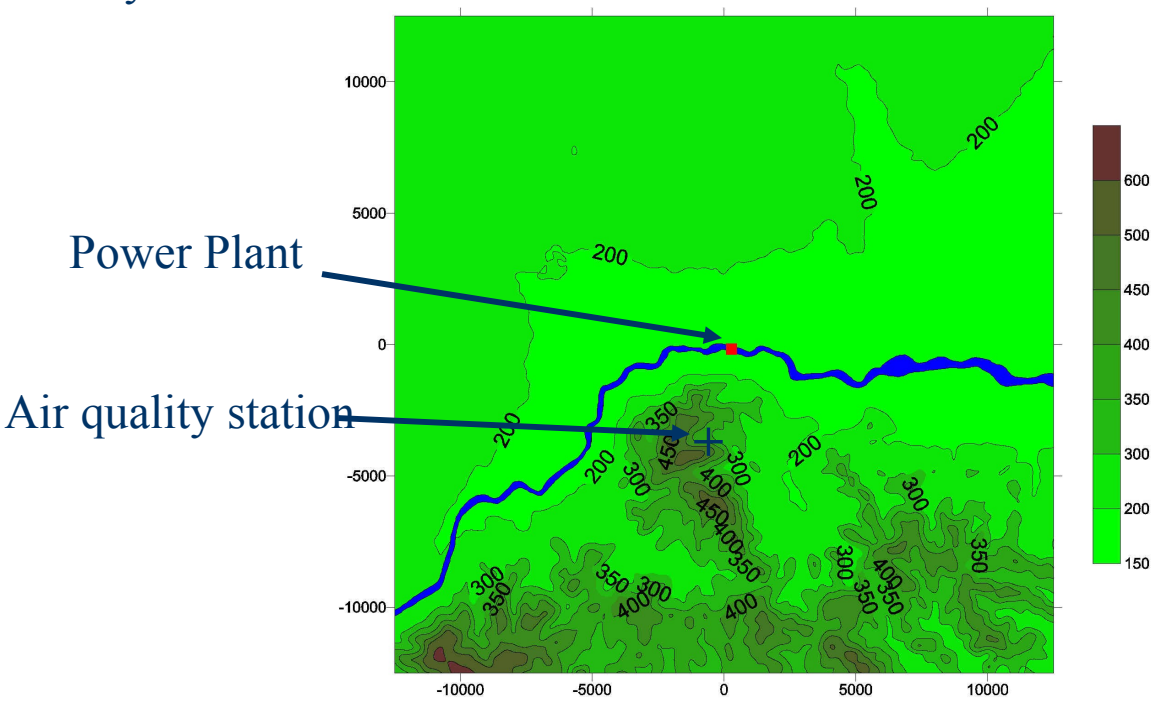






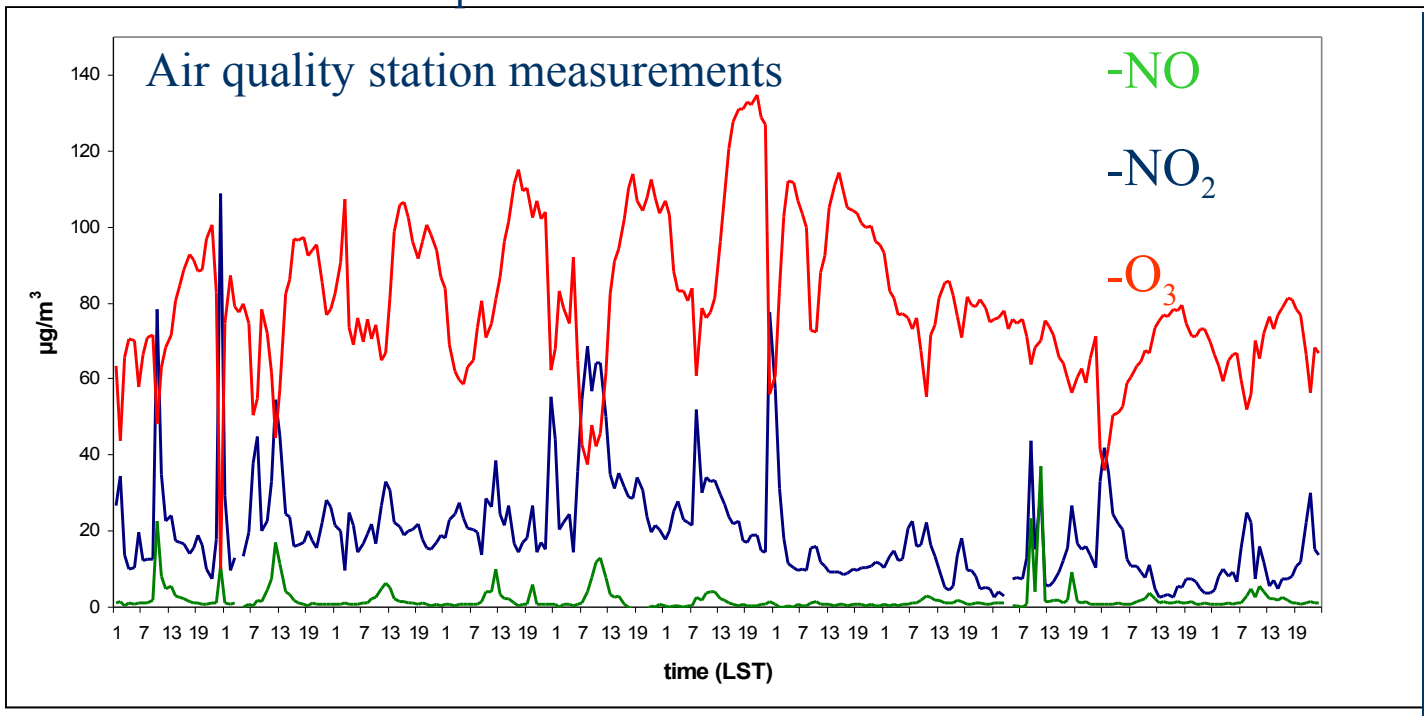
Real case application: topography and power plant position

- the station is located in a rural area surrounded by a small village in the south, located on a hill 300 m higher than and 3 km far from the power plant
- the power plant NO_x contribution is isolated from the others, with Northerly, North-Eastelry wind



Real case application: measured concentration

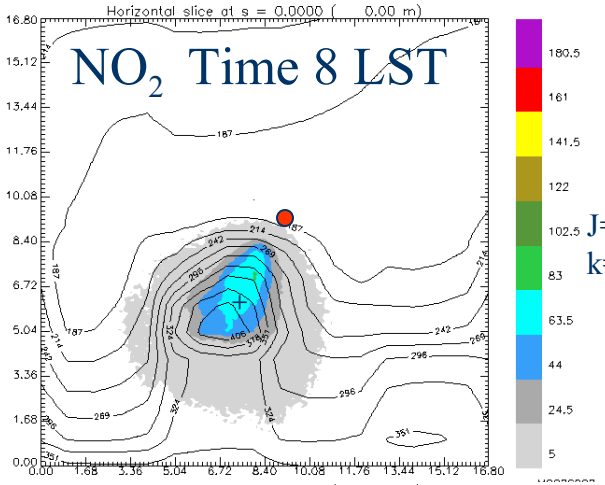
- A period lasting 10 days, from the 12th to 22th of March 2007, has been chosen because several plume transits over the station, usually between 6 and 11 LST, were observed and, in general, clear sky and high-pressure conditions occur.
- The background O_3 concentration for the simulation has been evaluated by the measurements before the plume transit



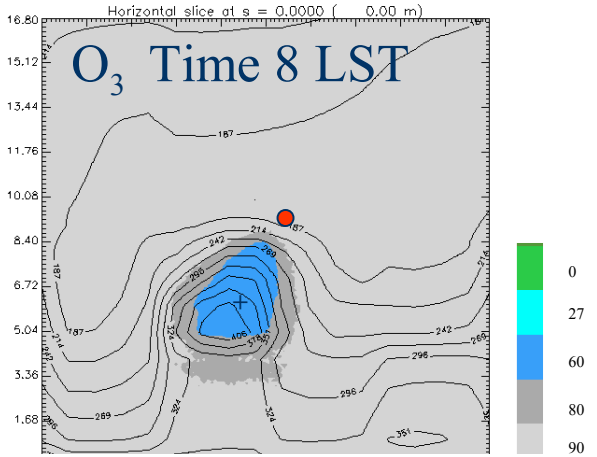
Real case application: numerical simulation

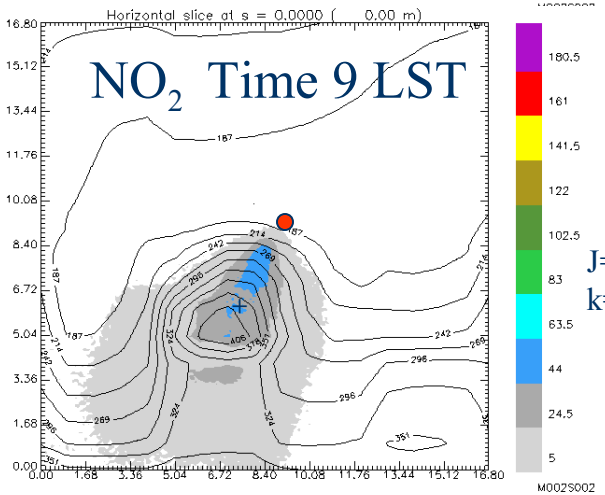
- The wind and turbulence fields have been built by the model system RAMS 6.0-MIRS, using the ECMWF analysis fields as boundary conditions
- 4-d var data assimilation with the meteorological measurements of two ground stations located close to the power plant and the air quality gauges.
- Three nested grids have been used with a grid spacing of 12, 4 and 1 km respectively; dispersion domain: inner grid is 17x17 km^2
- A variable time step for the lagrangian particles displacement; constant time step (20 s) for the chemical reactions.
- The cells for the concentrations computation have been set equal to 100 x 100 x 50 m^3 and constant all over the domain.

Concentration field: an example

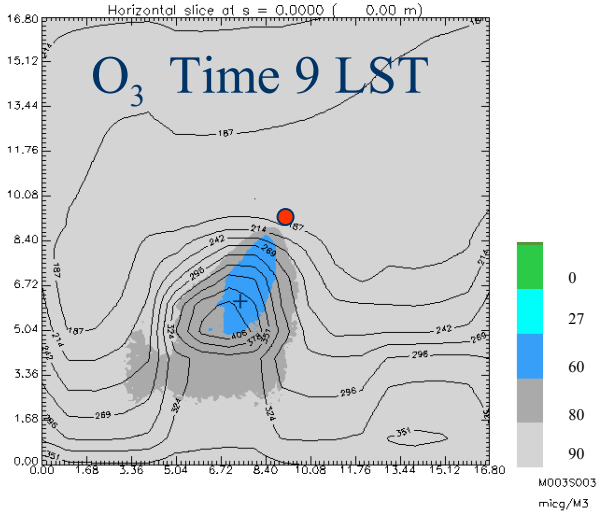


$J=0.07\ min^{-1}$
$k=0.38\ ppm^{-1}\ sec^{-1}$





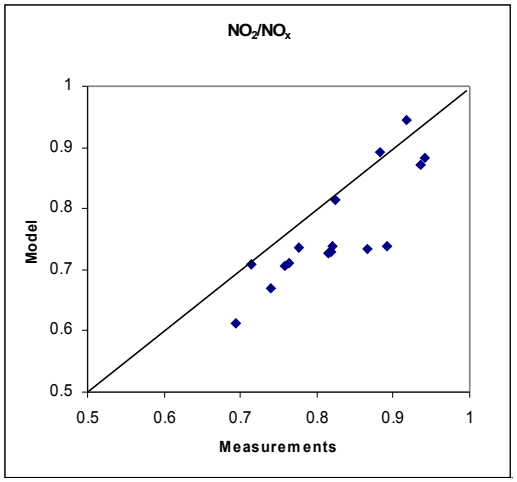
$J=0.22\ min^{-1}$
$k=0.38\ ppm^{-1}\ sec^{-1}$



Real case application: comparison with the measurements

- NO_2/NO_x hourly computed ratios are compared with the measurements considering only the diurnal significant situations in order to highlight the chemical scheme performances.
- Only the Northerly and North-Easterly wind have been chosen to consider only the episodes caused by the plume transits (16 hours) over the gauge

	Mean	Sigma	Bias	Nmse	Cor	Fa2	FB	fas
Measurements	0.82	0.076	0	0	1	1	0	0
Spray	0.76	0.088	-0.059	0.0091	0.85	1.0	0.075	-0.15



Real case application: comparison with the measurements

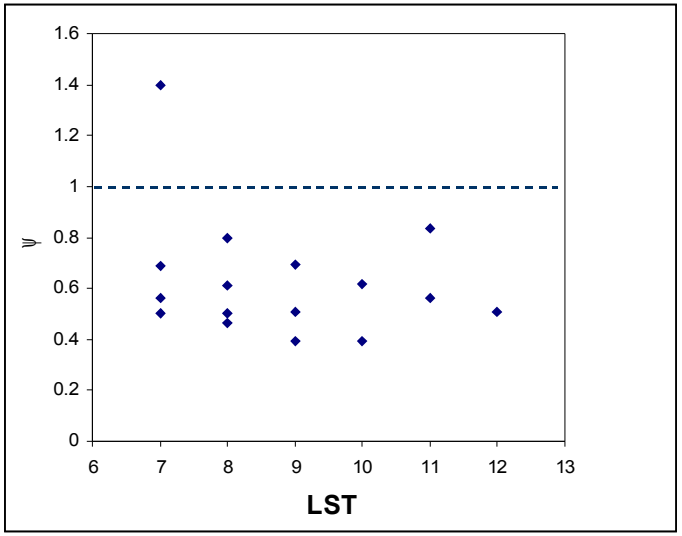
- The values of $\psi = \frac{k[NO][O_3]}{J[NO_2]}$ should be ≥ 1 inside a plume (Hegg et al. 1977)
- In this case, considering that the ground station is far from the emission, values of $\Psi \cong 1$ should be expected
- In the figure are presented the values of ψ computed by the measured concentrations and with k and j used in the simulation from (IUPAC 2005 and Parrish et al. 1983) assuming clear sky conditions:

$$k = 3.1 \cdot 10^{3} \cdot \exp(-1450/T)$$

where T is the air temperature from RAMS

$$J = 0.01305 \cdot \exp(-0.36/\cos(\alpha))$$

where α is the complementary of the solar elevation angle

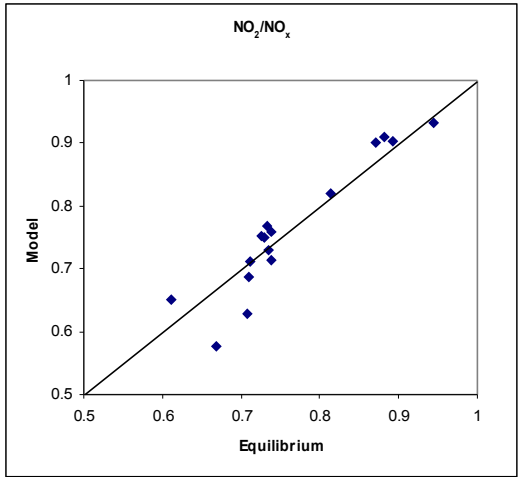


Real case application: comparison with the photo-stationary equilibrium

- Model results are also compared with the NO_2/NO_x of the photo-stationary equilibrium, where ψ=1, at the station location

- Following Seinfeld (1986), the NO_2/NO_x equilibrium values were computed using the NO_x concentrations by Spray and the background O_3 value

	Mean	Sigma	Bias	Nmse	Cor	Fa2	FB	fas
Equilibrium	0.76	0.10	0	0	1	1	0	0
Spray	0.76	0.088	0.0011	0.0024	0.94	1.0	-0.0014	0.16



Conclusions

- A new lagrangian model including the main chemical reaction involving NO_x and O_3 has been developed
- The mean concentration are calculated on an eulerian grid
- The O_3 background concentration are computed through “deficit”
- The qualitative comparison with wind tunnel data gives reasonable results
- Real case data comparison shows a general agreement although a slight NO_2/NO_x under estimation occurs due to the lack of cloud cover information
- The model correctly predict NO_2/NO_x equilibrium concentration even if is able to reproduce non-equilibrium condition

SPRAY simulation characteristic

- Source dimension (x,y,z): 0.01x0.03x0.03 m^3;
- NO concentration at the source : 505 p.p.m.;
- Background O_3 concentration: 1 p.p.m.;
- Reaction rate k: 0.44 $(s\ p.p.m.)^{-1}$, j=30 min^{-1} ;
- Time step: 0.1 s;
- 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

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):

$$du = a(\mathrm{x},\mathrm{u})dt + b(\mathrm{x},\mathrm{u})dW(t)$$

$$d\mathrm{x} = (\mathrm{U} + \mathrm{u})dt$$

U is the mean wind velocity,

$$a(\mathrm{x},\mathrm{u})dt$$

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

$$b(\mathrm{x},\mathrm{u})dW(t)$$

is a stochastic term

$$dW(t)$$

is the incremental Wiener process.

- The PDF is assumed to be Gaussian for u,v, and non-gaussian for w

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

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