

**16th International Conference on  
Harmonisation within Atmospheric Dispersion Modelling for Regulatory Purposes  
8-11 September 2014, Varna, Bulgaria**

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**MODELLING POLLUTANT REACTIONS DEPENDING ON INSTANTANEOUS  
CONCENTRATIONS: A DIRECT ESTIMATION OF THE SEGREGATION COEFFICIENT**

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**Abstract:** We have implemented a reaction scheme, based on the conserved scalar theory, into a Lagrangian micromixing model (LAGFLUM, Leuzzi et al.). This coupled solution is tested in decaying grid turbulence to represent the dispersion of reactive pollutants. We report preliminary validations, obtained by comparisons with available measurements and analytical solutions, as well as several model inter-comparisons. We underline the difference between modelling pollutant reactions depending on the instantaneous instead of the mean concentrations of the reactants (effects of the segregation coefficient). Finally, we have implemented and tested a new limit for the scalar conserved theory, which tries to improve the reaction-dominated limit (RDL) in non-homogeneous conditions.

**Key words:** pollutant reactions; segregation coefficient; accidental releases; urban scale and street-canyon modelling; concentration fluctuations; Lagrangian micromixing modelling; conserved scalar theory; reaction-dominated limit.

## INTRODUCTION

Modelling pollutant reactions in the atmospheric boundary layer represents a key point in air quality modelling. The kinetic formulas depend on the instantaneous concentrations of the reactants, but air quality models usually represent (Reynolds') mean concentrations. This shortcoming is so relevant that modellers introduce additional and parameterized terms (e.g. the segregation coefficient) in the reaction formulas to fill this gap, especially at the micro-scale. On the other hand, Lagrangian micromixing models can reproduce instantaneous-like concentrations. However, the state-of-the-art of these models for reactive pollutants only counts very few studies (Sawford, 2006; Cassiani, 2013). In this frame, we have implemented a simplified reaction scheme within the Lagrangian micromixing model LAGFLUM (Leuzzi G. et al.) to estimate the chemical reactions depending on instantaneous concentrations, so that the segregation coefficient is directly computed with no parameterization. Further, we have formulated, implemented and tested a new limit ("NHRDL") for the scalar conserved theory, which improves the reaction-dominated limit in non-homogeneous conditions. In the following, we describe the model (Sec.2), some preliminary validations (Sec.3 and Sec.4) and conclusions (in Sec.5).

## THE NUMERICAL MODEL

The reference Lagrangian micromixing model simulates the dispersion of scalars pollutants in a turbulent stationary flow. It represents a Lagrangian stochastic system of governing equations, which respects the balance equations for the ensemble mean and variance of the scalar concentration. During the first numerical phase, the model reproduces a large number of trajectories of conservative fictitious fluid particles transporting a passive scalar, according to a macromixing scheme (Lagrangian turbulence), and it robustly computes its mean concentration and other auxiliary parameters. In the second phase, it similarly reproduces the motion of the same main fluid, but using non-conservative particles, subjected to molecular diffusion processes (micromixing scheme). Finally, Reynolds' statistics of the species concentrations are computed on a background grid, using the particle concentrations. During the simulation, the time step is constant (much smaller than all the time scales of the phenomenon).

With this general algorithm for passive scalars, we find convenient to implement a simplified reaction scheme, still keeping a micromixing scheme for passive pollutants. In the first phase, we only transport a useful passive scalar (the mixture fraction). In the second phase, we reproduce its instantaneous values and simultaneously compute the same parameters for the reactants, according to the conserved scalar theory (original and new formulas). Finally, we estimate the concentration statistics.

Further details of the numerical model are discussed in Amicarelli et al. (in revision).

### Macromixing scheme

The macromixing scheme reproduces the fluid particle trajectories in turbulent flows. It represents a Lagrangian Stochastic System (with a Harris chain -Markov process- for  $\underline{U}$ ; Thomson 1987):

$$\underline{X}(t + dt) = \underline{X}(t, \underline{x}) + \underline{U}(t)dt, \quad \underline{X}(t = 0) = \underline{X}_0$$

$$dU_i = \left\{ -\frac{\delta_{ij} C_0 \varepsilon}{2} V_{jk}^{-1} U_k + \frac{1}{2} \frac{\partial V_{ij}}{\partial x_i} + \overline{u_i} \frac{\partial \overline{u_i}}{\partial x_i} + \frac{\partial \overline{u_i}}{\partial t} + \left[ \frac{1}{2} V_{ij}^{-1} U_j \left( \frac{\partial V_{ij}}{\partial t} + U_m \frac{\partial V_{ij}}{\partial x_m} \right) \right] \right\} dt + \sqrt{C_0 \varepsilon} d\xi_i, \quad i = 1, 2, 3 \quad (1)$$

$\underline{X}$  and  $\underline{U}$  represent the Lagrangian particle position and velocity vectors (respectively),  $dU$  the velocity increment during a time step  $dt$ ,  $d\xi_i$  is a Gaussian Wiener process with mean zero and variance  $dt$ . Einstein notation works for all the subscripts but “ $i$ ”,  $C_0$  is the Kolmogorov constant,  $\varepsilon$  the dissipation rate of the turbulent kinetic energy,  $V_{ij}$  the one-point velocity covariance matrix. Capital and lower case letters represent Lagrangian and Eulerian velocities, respectively. Over-bar symbol denotes Reynolds’ averages.

This formulation is well constrained with respect to the Lagrangian structure function in the limit  $dt \rightarrow 0$  (correctness of the autocorrelation function, according to Kolmogorov theory). On the other hand, it guarantees that the Eulerian statistics of the Lagrangian velocities (in case of a domain uniformly filled with particles) be equal to the Eulerian statistics of the Eulerian velocities (so-called “well mixed” condition; correctness of the probability density functions -pdfs-). This formulation assumes independent Gaussian velocity pdfs. The system (1) then allows representing fluid particle trajectories, once provided the statistics of the Eulerian velocities (input data for of the model).

### Micromixing scheme

The micromixing scheme here represents molecular diffusion phenomena. The reference model adopts the IECM passive scheme (Pope, 1998; Sawford, 2004). The particle “instantaneous” concentration  $C$  evolves in time, according to the difference between  $C$  and the mean concentration conditioned to velocity (representative of the concentration of the instantaneous plume around the particle). Then the particle concentration tends to the value of the surrounding environment, due to molecular diffusion:

$$dC/dt = -(C - \langle c | \underline{U} \rangle) / t_m \Rightarrow C(t_0 + dt) = C(t_0) e^{-dt/t_m} + \langle c | \underline{U} \rangle (1 - e^{-dt/t_m}) \quad (2)$$

The mixing time scale  $t_m$  rules this process and is consistent with the asymptotic mixing constraints:

$$t_m = 0.8(3/2)^{-1/2} [(3/2)^{1/2} \frac{\sigma_{z0}^{2/3}}{\varepsilon^{1/3}} + \sqrt{2T_L t_f}] \quad (3)$$

Here  $T_L = \frac{4q}{3C_0 \varepsilon}$  is the Lagrangian time scale,  $\sigma_{z0}$  the plume spread at source and  $t_f$  the fly time.

### Conserved scalar theory: original formulas and improvements

We have implemented a reaction scheme based on the “conserved scalar theory” (Bilger 1991 et al.; Sawford, 2006), first briefly recalled. Let consider a generic 2nd order 2-species (A and B) kinetics and define the mixture fraction ( $F_m$ ) and its stoichiometric value ( $F_{m,s}$ ):

$$F_m = \frac{C_A - C_B + C_{B,2}}{C_{A,1} + C_{B,2}}, \quad F_{m,s} = \frac{C_{B,2}}{C_{A,1} + C_{B,2}} \quad (4)$$

$C_{A,1}$  and  $C_{B,2}$  are the maximum concentrations of the reactants (segregated pollutants at inlet section).  $F_m$  is a passive scalar (independent from reactions) subjected to molecular diffusion ( $F_m$  changes along a trajectory). The reactive term in the balance equation for the instantaneous concentration provides:

$$\frac{dC_A}{dt} = -r C_A C_B = r C_A \left[ C_A + (F_{m,s} - F_m) (C_{A,1} + C_{B,2}) \right] \quad (5)$$

Let consider a fixed time in a particle trajectory and the (instantaneous) value of  $F_m$ . We simply know the passive species concentrations in the frozen limit (FL:  $C_A = F_m C_{A,1}$ ,  $C_B = (1 - F_m) C_{B,2}$ ). On the other hand, the “reaction-dominated limit” (RDL) of the conserved scalar theory assumes that the two species have instantaneously mixed at the beginning of the trajectory (with initial values from the current FL) and react according to the fly time. This hypothesis is exactly satisfied only in uniform  $F_m$  fields. Although it represented one of the best solution in modelling reactions, this limit systematically overestimates the reaction processes, if the species are initially segregated. RDL (Bilger et al. 1991) provides ( $F_m \neq F_{m,s}$ ):

$$C_A = C_{A1} F_m \frac{(F_{m,s} - F_m)}{F_{m,s} (1 - F_m) e^{[(F_{m,s} - F_m)k(C_{A1} + C_{B,2})k_f] - F_m (1 - F_{m,s})}}, C_B = C_{B,2} \left[ \frac{(F_{m,s} - F_m)}{F_{m,s}} + \frac{(1 - F_{m,s}) C_A}{F_{m,s} C_{A1}} \right] \quad (6)$$

The second equation of (6) depends on the first and simply guarantees no alteration of  $F_m$  fields. In the study of Amicarelli et al. (in revision), we also propose, implement and validate an alternative limit (“non-homogenous reaction-dominated limit”, “NHRDL” just for simplicity of notation). It relies on the same equation of RDL, but we replace the fly time with a corrected contact time ( $n_{\max}$  is the time step number of the on-going computational particle, since its release in the domain):

$$t_{\text{NHRDL}}(t_f) = \frac{\sum_{i=0}^{n_{\max}-1} C_{A,FL}(t_f - 1 \cdot dt) \cdot C_{B,FL}(t_f - 1 \cdot dt) \cdot dt (t_f - 1 \cdot dt)}{C_{A,FL}(t_f) C_{B,FL}(t_f)} \quad (7)$$

We also explore another limit, lying between RDL and NHRDL. In fact, in the second phase of the simulation (when the micromixing scheme is active), we can release particles from the plume edges, instead of the inlet section. This way, we automatically reduce the fly time. We refer to this solution as a reaction-dominated limit corrected by plume initialization (“RDLP”).

### REACTIVE DISPERSION MODELLING IN GRID TURBULENCE (POINT SOURCE)

We validate the model on the experimental test case of Brown and Bilger (1996). It describes the dispersion of two reactant species (NO and O<sub>3</sub>) and their reaction product (NO<sub>2</sub>) in an unbounded turbulent flow (grid decaying turbulence). We here report a brief description of the test case and some preliminary results. A complete validation is available in Amicarelli et al. (in revision).

#### Experimental test case and numerical set-up (point source)

The experimental set-up is described in Brown and Bilger (1996). The velocity turbulent fluctuations in the main flow direction can be neglected with respect to  $\bar{u} = 0.5\text{m/s}$ , while Cassiani (2013) reports:

$$\sigma_v^2 = \sigma_w^2 = A * 0.041 * \bar{u}^{-2} \left( \frac{x - x_g}{M} \right)^{-c}, \quad c = \begin{cases} 1.7, & \frac{x}{M} \leq 10, & A = 2.68 \\ 1.27, & 10 \leq \frac{x}{M} \leq 17, & A = 1 \end{cases} \quad (8)$$

Here  $x$  represents the distance from the source,  $M (= 0.320\text{m})$  the grid spacing and  $x_g = -3M$  the grid location. Under these conditions, the dissipation rate of the turbulent kinetic energy is equal to:

$$\varepsilon = -\frac{3}{2} \frac{\partial \sigma_w^2}{\partial t} = \frac{3}{2} \sigma_w^2 \frac{c \bar{u}}{(x - x_g)} \quad (9)$$

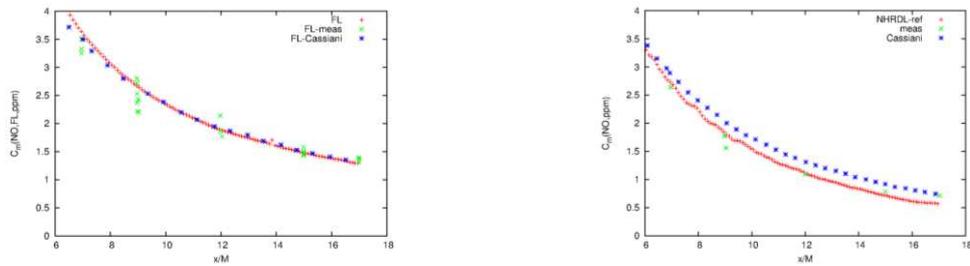
The NO source is located at  $\underline{x}_s = (0; L_y/2; L_z/2)$ . The NO concentration at source is 515ppm and the source diameter is  $D = 31.5\text{mm}$ . The background O<sub>3</sub> concentration is 1.0ppm. The only permitted reaction is:



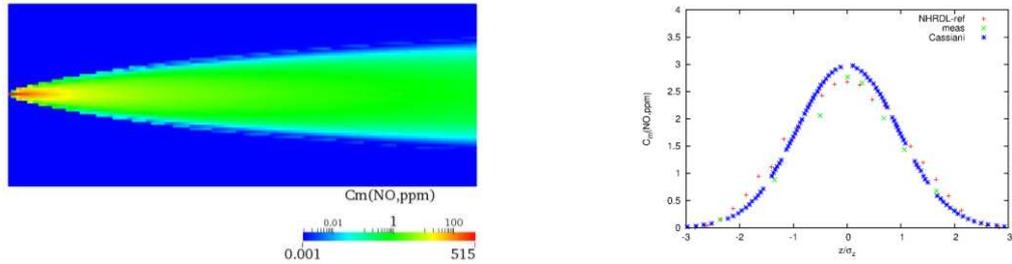
with a reaction rate  $r = 0.37(\text{ppm} * \text{s})^{-1}$ . The numerical setup is characterized by the following parameters. We use first attempt values for  $C_0 (= 2, \text{reference choice for Lagrangian micromixing models})$  and Cassiani (2013) value for  $\Gamma (= 0.46)$  with no tuning process. The background mesh has a spatial resolution of  $dx = M/10$ , while  $dt = 0.001\text{s}$ . The domain dimensions are  $L_x * L_y * L_z$ .  $L_y = L_z = 2 * \Gamma_{w,\max} * t_{f,\max} = 2.176\text{m}$  allows reproducing an unbounded domain with  $170 * 68 * 68$  cells ( $L_x = 17M$ ). We use  $1 * 10 * 10$  velocity classes (for its three components, respectively) to estimate the conditional mean concentrations.

#### Results. Mean concentration fields (point source).

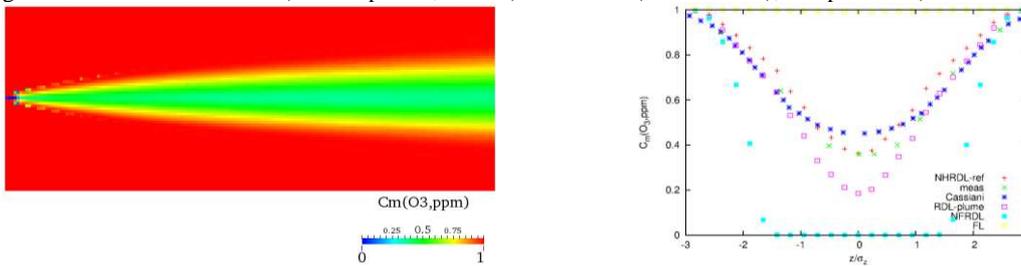
This section reports some preliminary results for the mean concentration fields. Validation are performed by comparison with the measurements of Brown and Bilger (1996), also available in Cassiani (2013). First, we validate the RDL solution, here improved with the RDLP limit. Then we compare it with the new NHRDL limit (the reference model hereafter). Further, we show the results of our simulation in the FL, to quantify the effect of reactions. Furthermore, we model this test case with the same reaction scheme, now based on the mean values of  $F_m$  (“no-fluctuation reaction-dominated limit”: NFRDL). This is equivalent to neglecting the segregation coefficient. Its comparison with the reference solution quantifies the importance of modelling the turbulent fluctuations of concentration in estimating the mean concentration of reactive pollutants. We finally compare our estimations with Cassiani’s results (2013).



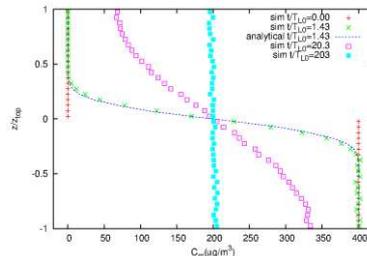
**Fig.1.** Centreline NO mean concentrations ( $y=L_y/2, z=L_z/2$ ). Validation (vs. measures) and inter-comparisons (vs. Cassiani, 2013). Passive (left) and reactive (right) test cases.



**Fig.2.** Left. Mean concentration of NO (vertical section aligned with the mean velocity, passing for the point source). Right. NO mean concentration (vertical profile,  $x/M=7$ ): validation (vs. measures), comparisons (vs. Cassiani 2013).



**Fig.3.** Left. Mean concentration of  $O_3$  (vertical section aligned with the mean velocity, passing for the point source). Right.  $O_3$  mean concentration (vertical profile,  $x/M=7$ ): validation (vs. measures) and inter-comparisons (vs. Cassiani -2013- and our simulations using the FL, RDLP and NFRDL limits).



**Fig.4.** Vertical profiles of the mean concentration of the bottom source pollutant (frozen limit) at different distances (or normalized fly times) from the source. Validation vs. analytical solution at  $t_{f,rit}/T_{L,0}=1.43$ .

Fig.1 reports the centreline mean concentration of NO in the passive (left) and in the reactive case (right); Fig.2 (right) and Fig.3 (right) show the reference cross-flow profiles at  $x/M=7$ . We then report the reference vertical sections of the 3D domain for the reactant mean concentration fields in Fig.2 (left) and Fig.3 (left). These preliminary validations of the reference model (NHRDL-ref) show a very good agreement with measurements and at least a similar performance than Cassiani (2013). On the other hand, RDLP limit shows a slight underestimation of the reaction processes, due to the bias introduced by the RDL limit in homogeneous conditions. We also notice that neglecting the segregation coefficient (NFRDL) drastically underestimates the  $O_3$  centreline mean concentration up to 100%.

Finally, the model compute the fields of the main concentration statistics (mean, variance, skewness and kurtosis) for the mixture fraction, the two reactants and the reaction product, together with the plume spread and the segregation coefficient. A detailed study is available in Amicarelli et al. (in revision).

## REACTIVE DISPERSION MODELLING IN GRID TURBULENCE (SURFACE SOURCES)

The experimental test case of Bilger (1991) represents the dispersion of two reactant species and their reaction product in a bounded turbulent flow (grid decaying turbulence), with two surface pollutant sources, each one covering a half of the inlet section. So far, we have just used a simplified macromixing model and we simply report a brief description of the test case and some preliminary results.

### Experimental test case and numerical set-up (surface sources)

This grid-generated turbulence flow interests the whole height of the channel is 0.200m, in stationary regime. The mean flow is homogeneous and 1D ( $\bar{u}=6.2\text{m/s}$ ) and we can apply Taylor's transformation ( $X=Ut_f$ ). Then the vertical velocity variance and  $\varepsilon$  take the following expressions:

$$\sigma_w^2(x) = \sigma_w^2(0) \left(1 + \frac{t_f}{t_0}\right)^{-m} = \sigma_w^2(0) \left(1 + \frac{x}{Ut_0}\right)^{-m}, \quad \varepsilon = -\frac{3}{2} \frac{d\sigma_w^2}{dt} = \left(\frac{3m}{2t_0}\right) \sigma_w^2(0) \left(1 + \frac{t_f}{t_0}\right)^{-m-1} \quad (11)$$

At the source  $\sigma_w^2(0) = 0.049\text{m}^2/\text{s}^2$ ,  $m=1.26$  (constant),  $t_0=0.168\text{s}$  a reference time scale. The two surface sources (of NO and O3) are located down-flow the grid, at  $x=0$ . The phenomenon is 2D (homogeneous along y direction). The time step is  $dt=0.004\text{s}$  ( $dx=0.002\text{m}$ ), the pollutant mass of each of the 500'000 numerical particles is  $m_p=1\mu\text{g}$  and  $dz=0.002\text{m}$  (100 cells along the vertical direction).

### 1D macromixing model for surface pollutant sources in grid turbulence

In this frame, we only need a simplified 1D macromixing scheme, but treating surface sources. We refer to Thomson (1987) grid turbulence-like solution:

$$dW = \left[ -\frac{W}{T_L} + \frac{WU}{2\sigma_w^2} \frac{\partial \sigma_w^2}{\partial x} \right] dt + \sqrt{C_0 \varepsilon} d\xi_w = \left[ -\frac{W}{T_L} + \frac{W}{2\sigma_w^2} \frac{d\sigma_w^2}{dt} \right] dt + \sqrt{C_0 \varepsilon} d\xi_w, \quad \bar{U} = \frac{dX}{dt} \quad (12)$$

### Results. Mean concentration of a passive pollutant (surface sources)

We report only preliminary results for the mean concentration of the bottom pollutant (frozen limit). They are successfully compared (Fig.4) with the analytical solution ("an") of Sawford (2006).

## CONCLUSIONS

We have implemented a reaction scheme (RDLP), based on the conserved scalar theory, within a Lagrangian micromixing model to represent the dispersion of reactive pollutants. The numerical coupling shows a good performance in modelling dispersion phenomena with reactive pollutants in grid-generated turbulence. Preliminary validations refer to comparisons with measured values and an analytical solution, while several model inter-comparisons are reported. Further, we underline the relevant difference between modelling reactions according to instantaneous instead of mean concentration values. Finally, we have formulated, implemented and tested a new limit (NHRDL) for the scalar conserved theory, which here improves the reaction-dominated limit (RDL and RDLP) in non-homogeneous conditions.

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