A stochastic Lagrangian micromixing model for the dispersion of reactive scalars in turbulent flows: role of concentration fluctuations and improvements to the conserved scalar theory under non-homogeneous conditions.

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Abstract.

Several reaction schemes, based on the conserved scalar theory, are implemented within a stochastic Lagrangian micromixing model to simulate the dispersion of reactive scalars in turbulent flows. In particular, the formulation of the RDL (Reaction-Dominated Limit) reaction scheme is here extended to improve the model performance under non-homogeneous conditions (NHRDL scheme).

The validation of the stochastic model is obtained by comparison with the available measurements of reactive pollutant concentrations in a grid-generated turbulent flow. This test case describes the dispersion of two atmospheric reactant species (NO and O₃) and their reaction product (NO₂) in an unbounded turbulent flow. Model inter-comparisons are also assessed, by considering the results of state-of-the-art models for pollutant dispersion.

The present validation shows that RDL reaction scheme provides a systematic overestimation (relative error of ca. 85% around the centreline) in computing the local reactant consumption/production rate, whereas the NHRDL scheme drastically reduces this gap (relative error lower than 5% around the centreline). In terms of NO₂ production (or reactant consumption), neglecting concentration fluctuations determines overestimations of the product mean of around 100% and a NO₂ local production of one order of magnitude higher than the reference simulation. In terms of standard deviations, the concentration fluctuations of both the passive and reactive scalars are generally of the same order of magnitude or up to 1 or 2 orders of magnitudes higher than the corresponding ensemble mean values, except for the background reactant close to the plume edges.

The study highlights the importance of modelling pollutant reactions depending on the instantaneous instead of the mean concentrations of the reactants, thus quantifying the role of the turbulent fluctuations of concentration, in terms of scalar statistics (mean, standard deviation, intensity of fluctuations, skewness and kurtosis of concentration, segregation coefficient, simulated reaction rate). This stochastic particle method represents an efficient numerical technique to solve the convection-diffusion equation for reactive scalars and involves several application fields: micro-scale air quality (urban and street-canyon scales), accidental releases, impact of odours, water quality and fluid flow industrial processes (e.g. combustion).

Keywords.

Concentration fluctuations; Lagrangian stochastic models; micro-scale air quality; segregation coefficient; micromixing; reactive scalars; reactive pollutants.

1. INTRODUCTION

Turbulent fluctuations of concentration play a key role in several dispersion phenomena, especially in case the pollutant fly time (t_f) is smaller than the integral Lagrangian time scale (i.e. micro-scale dispersion or turbulence; Galmarini et al., 1995, [33]), in the presence of reactive pollutants where the reaction time scale is comparable with the turbulence time scales (some details are provided in the following of this section) and when damage is non-linear with respect to concentration. Several application fields are concerned: accidental releases (e.g. extra-ordinary emissions, flammable substances, explosions, terroristic attacks), reactive scalars/pollutants (e.g. any 2nd-order kinetics transformation), impact of odours (e.g. energy from waste and waste treatment, high enthalpy geothermal energy), micro-scale air quality (e.g. pollution from traffic or production/power plants), water quality (e.g. pollutant dispersion in water bodies; sewage treatment; perforation fluids) and several industrial processes (e.g. combustion, smoke treatment, fuel desulfurization, energy from sewage).

In this context, the Reynolds/ensemble average (Reynolds, 1985, [57]) of concentration is generally not adequate to represent the evolution of the instantaneous concentration field of a pollutant dispersed in a turbulent flow (the ensemble average is roughly equivalent to the concentration time average under stationary turbulence owe to the ergodic properties of turbulent flows; Monin & Yaglom, 1971, [49]; Galanti & Tsinober, 2004, [31]). Thus, numerical models would need to estimate the (Reynolds') ensemble probability density function of concentration (f_C or concentration pdf), or at least its first statistical moments.

In particular, one may refer to the mutual relationships between turbulent fluctuations and reactions to highlight their key role in the dispersion of reactive scalars in turbulent flows, as discussed in the following.

The balance equation of an instantaneous scalar (C) reads:

$$\frac{\partial C}{\partial t} + u_j \frac{\partial C}{\partial x_j} = D_M \frac{\partial^2 C}{\partial x_j^2} + T \quad (1.1)$$

where $\underline{u}$ is the velocity vector and D_M the molecular diffusion. Einstein notation applies to the subscript “j” hereafter, if not otherwise stated. From left to right, the terms in (1.1) represent the local rate of change of the instantaneous concentration, the advective term of C , the divergence of the molecular diffusion flux of C and the instantaneous reactive term (T). In the following, we consider the concentration of a reactive pollutant as representative of a generic scalar dispersed in a turbulent flow, without losing generality.

The balance equation of the Reynolds' average of a scalar provides:

$$\frac{\partial \bar{C}}{\partial t} + \bar{u}_j \frac{\partial \bar{C}}{\partial x_j} + \bar{u}_j' \frac{\partial \bar{C}'}{\partial x_j} = D_M \frac{\partial^2 \bar{C}}{\partial x_j^2} + \bar{T} \quad (1.2)$$

where the prime symbol denotes a turbulent fluctuation around the ensemble mean (over-bar symbol). From left to right, the terms in (1.2) are the local rate of change of the mean concentration, the advective term of $\bar{C}$, the divergence of the turbulent and the molecular diffusion fluxes of $\bar{C}$ and the mean reactive term.

The balance equation for the scalar variance (σ_C^2) reads:

$$\frac{\partial \sigma_C^2}{\partial t} + \bar{u}_j \frac{\partial \sigma_C^2}{\partial x_j} + \frac{\partial \bar{u}_j' (C')^2}{\partial x_j} = -2 \bar{u}_j' C' \frac{\partial \bar{C}}{\partial x_j} - 2 D_M \left(\frac{\partial \bar{C}'}{\partial x_j} \right)^2 + D_M \frac{\partial^2 \sigma_C^2}{\partial x_j^2} + 2 \bar{C}' T' \quad (1.3)$$

where the terms on the left hand side represent the local rate of change, the advective term and the divergence of the turbulent flux of the concentration variance, respectively. On the right-hand side,

(1.3) shows the production term of σ_c^2 (always non-negative), the dissipation rate of the concentration variance triggered by molecular diffusion (always non-positive), the divergence of the molecular diffusion flux of σ_c^2 and the reactive term ($\overline{R_2} \equiv 2\overline{C'T'}$).

Let us hereafter refer to a 2-reactant 2nd order kinetics, not to lose generality in the discussion. Thus $\overline{T} = -rR_r$, where r stands for the chemical reaction rate and R_r for the observed (or simulated) “reaction rate”, as defined by Brown & Bilger (1996, [14]) and representing Reynolds’ average of the reactant product. The mean reactive term assumes the following form:

$$\overline{T} = -\overline{rC_A C_B} = -r(\overline{C_A + C_A'})(\overline{C_B + C_B'}) = -r(\overline{C_A C_B} + \overline{C_A' C_B'}) \quad (1.4)$$

where the subscript “A” (elsewhere omitted) refers to the control pollutant and “B” to its co-reactant. The ratio between the last two terms of (1.4) is defined as the segregation coefficient (or intensity of segregation) and potentially ranges from -1 (i.e. instantaneous reactions or uncorrelated reactant concentrations) to infinity:

$$I_s = \frac{\overline{C_A' C_B'}}{\overline{C_A C_B}} = \frac{(\overline{C_A - C_A})(\overline{C_B - C_B})}{\overline{C_A C_B}} = \frac{\overline{C_A C_B} - 2\overline{C_A C_B} + \overline{C_A C_B}}{\overline{C_A C_B}} = \frac{\overline{C_A C_B}}{\overline{C_A C_B}} - 1 = \rho_{AB} i_{C,A} i_{C,B}, \quad (1.5)$$

$$i_{C,i} \equiv \frac{\sigma_{C_i}}{\overline{C_i}}, \quad \overline{T} = -r(1 + I_s)\overline{C_A C_B}$$

where ρ is the correlation coefficient and i_C the intensity of fluctuations.

Thus, the turbulent fluctuations generally affects the mean concentrations of the reactants and the product species, by means of the reactant concentration covariance in (1.4).

On the other side, let us preliminarily consider the influence of reactions on concentration fluctuations, at least in terms of concentration variances.

Reactions alter the concentration mean gradients of the control reactant and then relevantly affect the production term (P_{σ_C}) in the balance equation of σ_{CA}^2 :

$$P_{\sigma_C} = -2\overline{u_i' C'} \frac{\partial \overline{C}}{\partial X_i} \approx 2K_{T,i} \left(\frac{\partial \overline{C}}{\partial X_i} \right)^2 \quad (1.6)$$

where $\underline{K_T}$ represents the vector of the turbulent dispersion coefficients.

Further, scalar transformations activate the reactive term in the balance equation of σ_{CA}^2 , so that:

$$\overline{R_2} = -2r \left(\overline{C_A C_A' C_B} + \sigma_{C_A}^2 \overline{C_B} + \overline{(C_A')^2 C_B} \right) \quad (1.7)$$

This reactive term is quite complex and one may consider that the triple correlation term in (1.7) is not modelled by Eulerian RANS codes that assume strong and simplifying hypothesis.

In practise, turbulent fluctuations of concentration influence the mean concentrations of reactive pollutants only if the reaction time scale is comparable with the turbulence time scales, as discussed in detail by both Vila-Guerau de Arellano et al. (2004, [65]) and Sawford (2006, [59]). If the reaction time scale (t_r) is both smaller than (or equal to) the Lagrangian integral time scale (T_L) and higher than (or equal to) the Kolmogorov time scale (t_K), then turbulence influences the reactive mean concentrations (“moderate regime” of Vila-Guerau de Arellano et al., 2004, [65]; regime of the “Reaction-Dominated Limit” as described for example in Sawford, 2006, [59]). If $t_r > T_L$ and $t_r \approx T_L$, then turbulent fluctuations actually do not influence the reactive mean concentrations as the mean concentration gradients are very low (“slow regime” of Vila-Guerau de Arellano et al., 2004, [65]). If $t_r \gg T_L$, then reactions can be considered as frozen (regime of the “Frozen Limit” as described for

example in Sawford, 2006, [59]). If $t_r < t_K$ and $t_r \approx t_K$, then turbulent fluctuations could only influence the reactive mean concentrations at the smallest turbulence scales (“fast regime” of Vila-Guerau de Arellano et al., 2004, [65]). If $t_r \ll t_K$, then reactions are characterized by a very fast reaction time compared to the mass transfer time (regime of the “Equilibrium Limit” as described for example in Sawford, 2006, [59]). One may notice that, in the above discussion, T_L could be replaced by any Eulerian time scale of the turbulence largest scales. In this context, the Damkohler number (N_D) quantifies the ratio between a main flow time scale (which could refer to turbulence or advection at different scales) and the reaction time scale. Several definitions are available for this non-dimensional number. The formulation reported in Sawford (2006, [59]) involves an advection time scale and a 2nd order kinetics in grid turbulence (M being the grid spacing):
$$N_D \equiv \frac{rM(C_{A,max} + C_{B,max})}{u}.$$

From this brief dissertation on the relevant and reciprocal influences of concentration fluctuations and scalar reactions, concentration fluctuations turn out to play a key role and several numerical schemes have been developed to estimate them. They are based on Direct Numerical Simulations (DNS; e.g. Brethouwer et al. 1999, [12]), Large Eddy Simulations (LES) (e.g. Watanabe et al., 2015, [66]; Zhong et al., 2015, [69]; Le Ribault et al., 2014, [39]; Baker et al., 2004, [9]; Meeder & Nieuwstadt, 2000, [47]) possibly coupled with Lagrangian sub-grid schemes (Aguirre et al., 2006, [1]), pdf models (e.g. Garmory, 2006, [33]; Rembold et al., 2008, [56]; Fox, 2003, [29]; Heinz, 2003, [36]; Pope, 2000, [52]), Reynolds’ Average Navier-Stokes models (RANS; e.g. Efthimiou et al., 2011, [24]; Milliez & Carissimo, 2008, [48]; Andronopoulos et al., 2001, [8]; Mavroidis et al., [46]), reactive plume models (Galmarini et al., 1995, [33]), fluctuating and meandering plume models (e.g., Franzese, 2003, [30]; Ferrero et al., 2013, [27]; Gifford, 1959, [35]; Luhar et al., 2000, [43]; Yee & Wilson, 2000, [68]) and stochastic models for odour impact (Lo Iacono, 2009, [42]).

In this context, Lagrangian micromixing models (e.g. Sawford, 2004, [58]; Cassiani et al., 2009, [19]; Dixon & Tomlin, 2007, [23]; Amicarelli et al., 2011, [6]) seem to represent one of the most efficient approaches in terms of both accuracy and computational costs. These models evaluate the mean and the higher moments of concentration, coupling a macromixing scheme with a micromixing scheme. The first evaluates the trajectories of fictitious fluid particles, representing the turbulent transporting flow. The latter simulates the dissipative effects on concentration fluctuations. These are triggered by molecular diffusion (and driven by turbulence). The resulting governing equations represent a Lagrangian stochastic system, which is constrained to the balance equations of the concentration/scalar mean and variance.

Generally, Lagrangian micromixing models show several advantages, with respect to alternative numerical models for concentration fluctuations. They usually provide limited computational costs, do not need any computational mesh and use a unique system of equations to estimate any statistical moment of concentration and f_C . Further, they take into account the effects of the velocity autocorrelation function, the mixing time scale (i.e. the time scale of the dissipation rate of the concentration variance) depends on the fly time (in the near- and mid- field) and the chemical reactions are functions of the particle concentrations. In this context, instantaneous concentrations are approximately represented by means of “particle concentrations obtained from single realizations of one-point one-time scalar pdfs”. Hereafter, the expression “instantaneous-like concentrations” possibly replaces this definition, just for simplicity of notation. Only DNS can represent actual instantaneous concentrations as well as LES (if the reaction time scale is slow compared to the sub-grid mixing time scale).

On the other hand, the Lagrangian micromixing models are still poorly investigated, especially in 3D ([53], [54], [40]), also due to a general lack of open-field experimental data on concentration fluctuations ([37], [38], [67], [20]). These models need Eulerian velocity statistics of the main flow in input, as resulting from another code or a diagnostic tool. Nevertheless, they can be directly coupled to RANS models (either CFD -Computational Fluid Dynamics- tools or microscale meteorological models; e.g., Leuzzi et al., 2012, [40]).

As numerical models for concentration fluctuations are mainly devoted to passive scalars, modelling scalar reactions via instantaneous concentrations is a research topic, which is sparsely explored. Beyond DNS simulations, so far confined to very small domains, one may refer the reactive plume model of Galmarini et al. (1995, [33]), to the pdf model of Garmory (2006, [33]), the Lagrangian micromixing models of Sawford (2006, [59]) and Cassiani (2013, [17]). These three studies investigate the 2D dispersion of reactive scalars in decaying grid turbulence flows. Tartakowsky et al. (2012, [62]) highlight the key role of segregation coefficient by means of their 1D model, based on the “method of moment equations”. Beyond these kinds of model, other codes dealing with reactive scalars normally use tuned parameterizations to represent the segregation coefficient and thus the pollutant reactions.

According to the above dissertations, the Lagrangian micromixing models can be considered among the fastest models in representing the dispersion of reactive pollutants depending on concentration fluctuations with a direct estimation of the intensity of segregation (neither ad-hoc parameterization nor tuning is assumed for this parameter). Their computational time is ruled by the highest order statistics (as chosen by the user), which requires the highest number of particles to provide robust results. However, the algorithms associated with accurate micromixing schemes impose the adoption of an approximated reaction scheme of the Conserved Scalar Theory (CST; Bilger, 1991, [10]; Sawford, 2006, [59]): the Reaction-Dominated Limit (RDL). Unfortunately, this scheme suffers from a systematic overestimation of the reaction process under non-homogeneous scalar fields (Sawford, 2006, [59]).

This study presents a Lagrangian micromixing model for reactive scalars, based on the code LAGFLUM (Leuzzi et al., 2012). The present model drastically reduces the systematic errors of the RDL reaction scheme, while keeping the advantages of Lagrangian micromixing models. In particular, this study formulates and validates a new CST limit, which extends the RDL scheme under non-homogeneous conditions (the modified formulation is referred as “NHRDL”, just for simplicity of notation). Further, alternative CST reaction schemes are implemented and tested.

The validation of the present model is obtained by comparison with the experimental measurements of Brown & Bilger (1996, [14]; 1998, [15]), who represented the dispersion of two major atmospheric pollutants (NO and O₃) in a grid-generated air turbulent flow. To the best of our knowledge, it seems that this test case had not been explored by neither any accurate micromixing scheme (Sec.[2.2]) nor any CST reaction scheme. Model inter-comparisons are also assessed by considering the numerical results of Cassiani (2013, [17]) and alternative configurations of the presented model. A further inter-comparison is performed by using the chemical Lagrangian stochastic model of Alessandrini & Ferrero (2009, [1]).

2. THE NUMERICAL MODEL

The reference Lagrangian micromixing model simulates the dispersion of scalars/pollutants in a stationary turbulent flow and was validated in 2D and 3D neutral boundary layers in the presence of obstacles (e.g., Leuzzi et al., 2012, [40]; Amicarelli et al. 2012b, [7]). It represents a Lagrangian stochastic system of governing equations, which respects the balance equations for the ensemble mean and variance of the simulated scalar (or pollutant 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, Sec.2.1), and it robustly computes its mean concentrations 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, Sec.2.2). Finally, Reynolds' statistics of the species concentrations are computed on a background grid, using the particle (instantaneous-like) concentrations.

With this general algorithm available for passive scalars, we found convenient to implement simplified reaction schemes (Sec.2.3 and Sec.2.4), with no modification of the micromixing scheme for passive pollutants. Thus, the resulting model for reactive scalars is still characterized by two main phases. During the first ("conservative") phase, we only transport a fictitious passive scalar (the "mixture fraction" F_m , Sec.2.3). During the second ("non-conservative") phase, we use both the macromixing and the micromixing schemes to reproduce F_m particle values. They are used to compute the instantaneous-like concentrations of the reactants and the product species, according to the conserved scalar theory (Sec.2.3 and Sec.2.4). Further details on the model algorithm are provided in Sec.2.5.

The present model is a Lagrangian Monte-Carlo solver of the underlying Fokker-Planck equation (Pope, 1985, [50]; Pope, 2000, [52]; Fox, 2003, [29]; Heinz, 2003, [36]). In this frame, it is similar to other methods, such as Cui et al. (in press, [22]) which also represent the convection-diffusion equation. Having a very low numerical diffusion, these particle stochastic models do not show any shortcoming related to using a computational grid, contrarily to finite-difference and mesh-based Monte-Carlo methods.

Finally, the Lagrangian stochastic models available for the inter-comparisons of Sec.3.11 are briefly described in Sec.2.6.

2.1. Macromixing scheme

The macromixing scheme of the model was formulated by Thomson (1987, [63]) and is considered one of the most successful schemes for Lagrangian turbulence in stochastic numerical models (e.g. [45]). The vector of the particle position $\underline{X}$ is computed by integrating in time the vector of the particle velocity $\underline{U}$, according to Euler time integration scheme:

$$X_i(t+dt; \underline{x}_0, t_0) = X_i(t; \underline{x}_0, t_0) + U_i(t; \underline{x}_0, t_0)dt, \quad X_i(\underline{x}_0, t_0) = X_{0,i} \quad (2.1)$$

where the subscript "0" denotes the initial conditions. Thomson (1987, [63]) imposes the components of the increment of the particle velocity vector (dU_i) to be Markovian processes. In particular, they represent Harris chains, expressed according to the Ornstein-Uhlenbeck formalism:

$$dU_i = a_i dt + b_{ij} d\xi_j \quad (2.2)$$

Each of the three processes of (2.2) is composed by a deterministic term, proportional to the time step (dt), and a stochastic term, proportional to a Wiener process ($d\xi_i$). This is defined as a stochastic variable with Gaussian pdf, null mean and variance equal to dt .

The formulation (2.2) should be constrained to the fair representation of the Lagrangian structure function in the limit $dt \rightarrow 0$ (correctness of the autocorrelation function at the origin). On the other

hand, (2.2) should guarantee the correct reproduction of the mean and the variance of the Eulerian velocities (so-called “well mixed” condition; correctness of the probability density functions -pdfs-). In this frame, Thomson (1987, [63]) assumes Gaussian velocity pdfs.

Kolmogorov theory provides an estimation of the correlation of the velocity increments, for the time increment dt tending to zero. Computing the same quantity, under the definition of (2.2), Thomson (1987, [63]) derives a value for b_{ij} :

$$\overline{[U_i(t+dt) - U_i(t)][U_j(t+dt) - U_j(t)]} = \delta_{ij} C_0 \varepsilon dt, \quad dt \rightarrow 0 \Rightarrow b_{ij} = \delta_{ij} \sqrt{C_0 \varepsilon} \quad (2.3)$$

where C_0 is the Kolmogorov constant. The respect of the well-mixed condition implies a much longer demonstration (Thomson, 1987, [63]) and finally provides the value of $\underline{a}$, so that the system (2.2) assumes the following expression:

$$dU_i = \left\{ -\frac{C_0 \varepsilon}{2} V_{ik}^{-1} U_k' + \frac{1}{2} \frac{\partial V_{il}}{\partial x_i} + \frac{\partial \bar{u}_i}{\partial t} + \bar{u}_i \frac{\partial \bar{u}_i}{\partial x_i} + \left[\frac{1}{2} V_{lj}^{-1} \left(\frac{\partial V_{il}}{\partial t} + \bar{u}_m \frac{\partial V_{il}}{\partial x_m} \right) + \frac{\partial \bar{u}_i}{\partial x_j} \right] U_j' + \frac{1}{2} V_{lj}^{-1} \frac{\partial V_{il}}{\partial x_k} U_j' U_k' \right\} dt + \sqrt{C_0 \varepsilon} d\xi_i \quad (2.4)$$

where V_{ij} is the covariance matrix of the Eulerian velocity and V_{ij}^{-1} is the corresponding inverse matrix. In case of stationary regimes and diagonal covariance matrix, (2.4) assumes the following form:

$$\begin{aligned} dU &= \left[-\frac{U'}{T_{Lx}} + \frac{1}{2} \frac{\partial \sigma_u^2}{\partial x} + \frac{U'}{2\sigma_u^2} \left(U \frac{\partial \sigma_u^2}{\partial x} + V \frac{\partial \sigma_u^2}{\partial y} + W \frac{\partial \sigma_u^2}{\partial z} \right) + U \frac{\partial \bar{u}}{\partial x} + V \frac{\partial \bar{u}}{\partial y} + W \frac{\partial \bar{u}}{\partial z} \right] dt + \sqrt{C_0 \varepsilon} d\xi_u \\ dV &= \left[-\frac{V'}{T_{Ly}} + \frac{1}{2} \frac{\partial \sigma_v^2}{\partial y} + \frac{V'}{2\sigma_v^2} \left(U \frac{\partial \sigma_v^2}{\partial x} + V \frac{\partial \sigma_v^2}{\partial y} + W \frac{\partial \sigma_v^2}{\partial z} \right) + U \frac{\partial \bar{v}}{\partial x} + V \frac{\partial \bar{v}}{\partial y} + W \frac{\partial \bar{v}}{\partial z} \right] dt + \sqrt{C_0 \varepsilon} d\xi_v \\ dW &= \left[-\frac{W'}{T_{Lz}} + \frac{1}{2} \frac{\partial \sigma_w^2}{\partial z} + \frac{W'}{2\sigma_w^2} \left(U \frac{\partial \sigma_w^2}{\partial x} + V \frac{\partial \sigma_w^2}{\partial y} + W \frac{\partial \sigma_w^2}{\partial z} \right) + U \frac{\partial \bar{w}}{\partial x} + V \frac{\partial \bar{w}}{\partial y} + W \frac{\partial \bar{w}}{\partial z} \right] dt + \sqrt{C_0 \varepsilon} d\xi_w \end{aligned} \quad (2.5)$$

where $(x, y, z) = (x_1, x_2, x_3)$, $(U, V, W) = (U_1, U_2, U_3)$ and $(u, v, w) = (u_1, u_2, u_3)$.

The relationship between the Lagrangian integral time scale (T_L) and the dissipation rate (ε) of the turbulent kinetic energy (q) is provided by several authors (e.g. Thomson, 1987, [63]).

$$T_{L_i} = \frac{2\sigma_{u,i}^2}{C_0 \varepsilon} \quad (2.6)$$

where C_0 depends on the Reynolds number and usually varies between 2 and 6 (Sawford et al., 2008, [60]). Eq.(2.6) can be derived by comparing two alternative formulas of the plume spread (according to Taylor analysis). Each of them depends on either the Lagrangian structure function or the Lagrangian integral time scale (Cancelli et al., 2006, [16]).

In case of missing data, ε can be related to the turbulent kinetic energy and the mean velocity gradient, according to Leuzzi et al. (2012, [40]):

$$\varepsilon = 0.3q \sqrt{(\partial \bar{u}_i / \partial x_j)^2} \quad (2.7)$$

In synthesis, the system of equations (2.1), (2.5), (2.6) and (2.7) allow representing the trajectories of fluid particles in stationary turbulent neutral boundary layers, once provided the statistics of the Eulerian velocities (input data for the model). This macromixing scheme is used in both the

simulation phases of the numerical model. In case of different boundary layers, analogous formulations are available (e.g. [44]).

2.2. Micromixing scheme

A micromixing scheme represents the molecular diffusion phenomena, which quantify the dissipation term in the balance equation for the concentration variance (1.3).

The presented model adopts the IECM (Interaction by Exchange with the Conditional Mean) scheme for passive scalars, considering the formulation of Pope (1998, [51]). This is also used in Sawford (2004, [58]), whereas a more general version of IECM is reported in Fox (1996, [28]). The particle “instantaneous-like concentration” 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). Thus, the particle concentration tends to the value of the surrounding environment, due to the dissipative effects triggered by molecular diffusion:

$$dC / dt = -(C - \langle C | \underline{U} \rangle) / t_m \Rightarrow C(t_0 + dt) = C(t_0) e^{-dt/t_m} + \langle C | \underline{U} \rangle(t_0) (1 - e^{-dt/t_m}) \quad (2.8)$$

The mixing time scale t_m rules this process and is consistent with the asymptotic mixing constraints reported in Cassiani et al. (2005, [18]):

$$t_m = \mu [(3/2)^{1/2} \frac{\sigma_{z0}^{2/3}}{\varepsilon^{1/3}} + \sqrt{2T_L t_f}] \leq t_{m,\max} = \frac{2q}{C_\phi \varepsilon} \quad (2.9)$$

Here σ_{z0} represents the plume spread at source and μ the micromixing constant (Cassiani et al., 2005, [18]). Only when the plume length scale is comparable with the boundary layer depth, all the turbulent vortices contribute to the relative dispersion of particles and we adopt the threshold in (2.9), no matter about the fly time (C_ϕ represents a constant of proportionality between the scalar and the velocity times scales of turbulence; Pope, 2000, [52]).

The role of the mixing time scale t_m is hereafter analysed. When t_m tends to infinity, particles behave as conservative elements (“macromixing limit”). On the other hand, when t_m tends to zero, particle concentration tends to the conditional mean: concentration fluctuations are only determined by plume meandering phenomena (ruled by the largest turbulent vortices). In the following, the mixing time will be approximately computed as an ensemble mean of the instantaneous particle values.

The asymptotic behaviours of (2.9) are consistent with the similarity theory of relative dispersion in both the limits $t_m \rightarrow 0$ and $t_m \gg T_L$ (Cassiani et al., 2005, [18]). The same theory requires a linear

dependency of t_m in time, in the limit $\left(\frac{\sigma_0^2}{\varepsilon}\right)^{1/3} \ll t_m \ll T_L$. However, under this limit one needs the definition of the Richardson constant C_r . The choice of its value would introduce an uncertainty in the model formulation. Thus, this study prefers to keep a more approximated (but generic) formulation for the mixing time (2.9), reducing the uncertainty in the input data. Nevertheless, the reference simulation is also carried out with the linear formulation for t_m implemented in Amicarelli et al. (2015, [5]):

$$t_m = \mu \left[\left(\frac{3}{2}\right)^{1/2} \frac{\sigma_0^{2/3}}{\varepsilon^{1/3}} + \sqrt{\frac{3}{2}} (C_r)^{1/3} t_f \right] \quad (2.10)$$

Its practical equivalence to (2.9) for this test case is shown in Sec.3.12.

Considering the main properties of a micromixing scheme as defined by Pope (1998, [51]), IECM correctly reduces concentration fluctuations, as they would result from a macromixing model.

Further, it does not influence the mean, the conditional mean and the turbulent flux of a passive scalar (Sawford, 2004, [58]). The first two demonstrations are straightforward by simple averaging of (2.8). Furthermore, IECM provides concentration values in a limited range (concentrations are non-negative and not higher than the source instantaneous maximum values). However, IECM cannot guarantee a Gaussian f_C in case of a homogeneous field of the mean concentration.

The relationship between the IECM and the balance equation of the concentration variance is briefly recalled in the following.

Considering (1.3), the definition of the dissipation rate of the concentration variance reads:

$$\varepsilon_c \equiv -2D_M \overline{\left(\frac{\partial C'}{\partial x_i} \right)^2} \quad (2.11)$$

Assuming that reaction rates do not affect ε_c , (2.11) can be expressed as follows (Amicarelli et al., 2012a, [4]):

$$\varepsilon_c = 2C' \frac{dC}{dt} \quad (2.12)$$

The IECM scheme (2.8) can replace the Lagrangian derivative of the instantaneous concentration in (2.12), thus providing the following representation of the dissipation rate of the concentration variance:

$$\varepsilon_c = -2C' \overline{\left(\frac{C - \langle C|U \rangle}{t_m} \right)} = -2 \overline{\left(\frac{C' \bar{C}}{t_m} + \frac{\sigma_c^2}{t_m} - \frac{C' \langle C|U \rangle}{t_m} \right)} = -\frac{2}{t_m} \left[\sigma_c^2 - \overline{C' \langle C|U \rangle} \right] \leq 0 \quad (2.13)$$

Provided a reliable formulation of t_m , (2.13) seems to represent one of the best validated parameterizations of ε_c (Cassiani et al., 2005, [18]).

From (2.13) and (2.11), one can notice that the dissipation rate of the concentration variance depends on the square of the concentration fluctuation gradient, which is in turn linear in the concentration variance. The mixing time scale depends on several turbulent parameters, according to (2.9). Actually, it simply provides a time scale necessary to parameterize the gradient of the concentration fluctuation in a proper way. The molecular diffusion coefficient implicitly affects the micromixing constant in (2.9). The more concentration and velocity are correlated (or anti-correlated), the more the concentration variance keeps high, as fluid particles in contact within an instantaneous plume (with a similar velocity) have more similar concentrations, thus reducing the dissipation of the concentration variance (provided the same value of σ_c^2).

2.3. State-of-the-art formulations (limits) of the conserved scalar theory

Several reaction schemes, based on the “conserved scalar theory” (Dopazo & O’ Brien, 1973, [24]; Bilger et al., 1991, [10]; Sawford, 2006, [59]), are implemented in the reference code.

The main idea of the conserved scalar theory (CST) is that, in case of simple configurations, we can identify a single passive (conserved) scalar and represent its instantaneous field. From this, we can derive the concentration of the reactants and the product species, by means of approximated reaction formulas (or “limits”).

Consider a generic 2-reactant 2nd order kinetics. In this case it is very convenient to define the mixture fraction F_m (and its stoichiometric value $F_{m,s}$):

$$F_m \equiv \frac{C_A - C_B + C_{B,2}}{C_{A,1} + C_{B,2}}, \quad F_{m,s} = \frac{C_{B,2}}{C_{A,1} + C_{B,2}} \quad (2.14)$$

F_m represents the reference passive scalar for CST, being a normalized difference between the reactant concentrations added to a constant ($F_{m,s}$). $C_{A,1}$ and $C_{B,2}$ are the maximum concentrations of the reactants at the inlet section where pollutants are segregated. F_m is a passive scalar (independent from reactions), subjected to molecular diffusion (F_m changes along a trajectory).

The reactive term T in (1.1) is here rearranged and written in terms of F_m , according to (2.14):

$$T = -rC_A C_B = rC_A [C_A + (F_{m,s} - F_m)(C_{A,1} + C_{B,2})] \quad (2.15)$$

The strategy of this study relies on modelling F_m as a passive scalar and using its instantaneous values to determine the reactant and the product concentrations (C_A , C_B , C_C), according to alternative and approximated formulations («reaction limits») of the conserved scalar theory.

Let us consider a fixed time in a particle trajectory and the (instantaneous) value of F_m . One can write the solution for passive species concentrations (i.e. solution in the Frozen Limit -FL-, $r=0$; Bilger et al., 1991, [7]):

$$C_A = F_m C_{A,1}, \quad C_B = (1 - F_m) \quad (2.16)$$

The “reaction-dominated limit” (RDL) represents the most reliable CST limit. One may consider a fixed point in a fluid particle trajectory. To compute the instantaneous concentrations of the reactive pollutants from F_m , RDL strictly assumes that the two reactants had instantaneously mixed at the beginning of the trajectory (with the on-going passive FL concentrations as initial values) and that reaction has taken place within the fluid particle during the whole fly time, with no mass exchange with the surrounding environment. This hypothesis is practically flawless only in uniform F_m fields. Although it represented one of the best solution in modelling reactions, this limit provides a modest, but systematic overestimation of the effects of reaction processes, under non-homogeneous conditions. RDL formulation (Bilger et al. 1991, [10]) provides ($F_m \neq F_{m,s}$):

$$C_A = C_{A,1} F_m \frac{(F_{m,s} - F_m)}{F_{m,s}(1 - F_m) e^{[(F_{m,s} - F_m)r(C_{A,1} + C_{B,2})t_f]} - F_m(1 - F_{m,s})} \quad (2.17)$$

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

The last expression in (2.17) depends on the previous line and simply guarantees no alteration of the F_m field, according to (2.14).

The singularity ($F_m = F_{m,s}$) is treated by assuming the following expressions:

$$C_A = C_{A,1} \frac{F_{m,s}}{1 + F_{m,s}(1 - F_{m,s})r(C_{A,1} + C_{B,2})t_f}, \quad (2.18)$$

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

RDL represents the particular case of the Conditional Moment Closure model, where the conditional scalar dissipation is null (Brown, 1996, [13]; Sawford, 2006, [59]).

The “Equilibrium Limit” represents another relevant formulation in the conserved scalar theory. It is equivalent to RDL, with the Damkohler number (Sec.1) tending to infinity. In this case, the reaction time scale is much faster than the mass transfer time scale:

$$C_A = \begin{cases} C_A - C_B, & F_m > F_{m,s} \\ 0, & F_m \leq F_{m,s} \end{cases}$$

$$C_B = \begin{cases} 0, & F_m > F_{m,s} \\ C_B - C_A, & F_m \leq F_{m,s} \end{cases} \quad (2.19)$$

In any CST limit, the concentration of the product species is equal to the concentration reduction in each co-reactant:

$$C_C = C_{B,FL} - C_B = C_{A,FL} - C_A = F_m C_{A1} - C_A \quad (2.20)$$

The CST method can be extended up to three correlated reactants. This constrains the model to treat a limited number of reactive scalars, even though they could be effectively split in groups of three or two correlated species. To overcome this constraint, one should avoid using a 2-stage Lagrangian micromixing model and prefer a more complex and slower Lagrangian micromixing model with simultaneous (1-stage) computation of all the concentration moments. In this frame, an exact reaction scheme could be applied instead of CST.

Finally, one may notice that the conserved scalar theory is a bounded scheme as it correctly bounds the reactant concentration values C_A and C_B in the ranges $[0, C_{A,1}]$ and $[0, C_{B,2}]$, respectively.

2.4. Proposed variants for the conserved scalar theory

This study proposes a modified version of the Reaction-Dominated Limit, under non-homogeneous conditions. It relies on the same equations of RDL, but a corrected contact time replaces the fly time:

$$t_{NHRDL,I}(t_f^*) = \frac{\int_0^{t_f^*} C_{A,FL}|_{t_f} C_{B,FL}|_{t_f} dt_f}{\int_0^{t_f^*} C_{A,FL}|_{t_f^*} C_{B,FL}|_{t_f^*} dt_f} t_f^* = \frac{\int_0^{t_f^*} C_{A,FL}|_{t_f} C_{B,FL}|_{t_f} dt_f}{C_{A,FL}|_{t_f^*} C_{B,FL}|_{t_f^*}} \quad (2.21)$$

In this section, t_f^* simply represents the on-going fly time (i.e. the fly time of the computational particle at the on-going step) and the integration in (2.21) is performed along the particle trajectory. Then, the contact (or reaction) time is computed as a modified fly time, which is modulated on the actual product of the reactant instantaneous concentrations, as recorded along the particle trajectory. On the other hand, RDL scheme only depends on the FL values at the current end of the particle trajectory. The acronym “NHRDL” simply stands for “Non-Homogenous Reaction-Dominated Limit”, while the subscript “I” in (2.21) represents an integral formulation (i.e. a formulation in the continuum). In a discrete domain, (2.21) becomes:

$$t_{NHRDL}(t_f^*) = \frac{\sum_{l=0}^{n_{step}(t_f^*)-1} C_{A,FL}|_{(t_f^*-l \cdot dt)} \cdot C_{B,FL}|_{(t_f^*-l \cdot dt)} \cdot dt|_{(t_f^*-l \cdot dt)}}{C_{A,FL}|_{t_f^*} \cdot C_{B,FL}|_{t_f^*}} \quad (2.22)$$

Here dt is a constant time step and n_{step} is the time step number of the on-going computational particle, since its release in the domain. The definition (2.22) replaces the fly time in (2.17) and (2.18), thus defining the NHRDL. Eq.(2.22) permits to define a contribution to the simulated reactive term T , which is directly proportional to the instantaneous FL values of the reactant concentrations, at any trajectory point. This property is valuable under non-uniform conditions, as T is directly proportional to the product $C_A C_B$. Under uniform conditions, NHRDL is equivalent to RDL.

This will improve the RDL performance under non-homogeneous conditions (Sec.3), avoiding systematic and appreciable overestimations of the scalar reactions for anti-correlated reactants. The

proposed correction (2.22) does not reduce the applicability fields of the RDL scheme; in particular, no constraint is imposed in terms of travel time and source configuration. This study also explores another limit, lying between RDL and NHRDL. During the non-conservative phase of each simulation, the model can release particles from upstream plume edges, instead of the inlet section, thus automatically reducing the fly time during a period when the reactant product is zero. We refer to this solution as a Reaction-Dominated Limit with fly time starting when particles cross the plume edges (“RDLP”, just for simplicity of notation). Finally, a further limit (NFRDL: RDL with “No Fluctuations”) is defined and investigated. This allows quantifying the role of concentration fluctuations in estimating the mean concentration of a reactive scalar, by comparison with NHRDL. NFRDL relies on NHRDL formulation, but the instantaneous values are replaced by their associated mean values: F_m is substituted by its mean value both in (2.17) and (2.18), as well as the fly time is replaced by its mean value ($X/\bar{u}$ in this study). In the frame of the CST, NFRDL is equivalent to use NHRDL, but modelling $\left(-r\overline{C_A C_B} = -r\overline{C_A} \overline{C_B}\right)$ instead of $\overline{T} = -r\overline{C_A C_B} = -r\left(\overline{C_A C_B} + \overline{C_A' C_B'}\right)$, in the balance equation for the reactant mean concentrations.

2.5. Model algorithm and boundary conditions

The model integrates a macromixing scheme, a micromixing model and alternative reaction CST schemes (Figure 2.1). In the following, consider the dispersion of two reactants (the main reactant “A” and the background reactant “B”) as well as their product species “C”.

A generic run starts with the input management. The model requires the following data on the main flow: the Eulerian statistics of velocity, the dissipation rate of the turbulent kinetic energy (if available), the Kolmogorov constant, the micromixing constant and the prevailing flow direction (if any). The code also reads the domain size and the position of both the obstacles/buildings and the monitoring lines. The scalar input data are introduced in the following list: the source position and flow rate of the main reactant, the concentrations of both the reactants at the inlet section (where the pollutants are segregated), the reaction rate r and the selected reaction scheme (among the alternative solutions of Sec.2.3 and Sec.2.4). Other numerical parameters are required: the number of particles to simulate in the conservative (n_{p1}) and the non-conservative (n_{p2}) phases, the spatial resolutions of the background grid (dx, dy, dz), which is a reference frame to count the ensemble statistics of the particle concentrations. The time step dt is constant, much smaller than the reaction time scale, the Lagrangian integral time scale, the mixing time and the ratio dx/U^* , where U^* is the mean velocity scale. Each simulation is then characterized by two sequential phases (Figure 2.1).

During the conservative phase, particles can be released only from the source of the main reactant and transport the passive scalar F_m . In fact, the mixture fraction is zero elsewhere within the inlet section and conservative particles with null F_m do not contribute to the mean concentration field of F_m . During this phase, the particle trajectories are computed according to the macromixing scheme (Sec.2.1) and the ensemble concentration means and conditional means, as well as the mixing time (Sec.2.2), are evaluated. At the end of this phase, the model computes the plume spread, as described by $\bar{F}_m$, and detects the edges of the mean plume, depending on the mean flow direction.

Then, the simulation runs again from the beginning (non-conservative phase). Particles are now released from the upstream edges of the plume (not only from the source) and move according to the macromixing scheme (Sec.2.1). The mean values of F_m and t_m , already available, are used by the micromixing scheme (Sec.2.2) to represent the molecular diffusion processes. During each time step, the reaction scheme uses the instantaneous/particle value of the mixture fraction to estimate the instantaneous-like values of the reactant and the product concentrations, according to the conserved scalar theory (Sec.2.3 or Sec.2.4). The ensemble moments of concentration are then updated.

Figure 2.1. Simplified algorithm of the numerical model.

The numerical implementations of this study refer to the new (red) and the modified (yellow) parts of the algorithm.

During both the numerical phases, particle initial conditions are randomly assigned. They are constrained to the respect of the velocity pdf in the corresponding cell. The model uses Euler scheme for time integration and does not need more complicated schemes, commonly used to solve stochastic differential equations (Przybylowicz & Morkisz, 2014, [55]).

At the very end of the simulation, the model counts the following ensemble statistics: mean, standard deviation, intensity of fluctuations, skewness and kurtosis for all the scalars (reactants, product species and mixture fraction). Further, the code estimates the segregation coefficient and the simulated reaction rate, as defined by Brown & Bilger (1996, [14]). According to Figure 2.1, the model computes the ensemble statistics of reactive scalars when the second, third and fourth moments are saved, but the instantaneous-like concentrations are no longer available. At that stage standard deviation, skewness and kurtosis are expressed as functions of the available concentration moments, according to the standard relationships between centred and not centred moments (Monin & Yaglom, 1971, [49]).

At this stage, the simulated reaction rate is computed (Brown & Bilger, 1996, [14]):

$$r = \frac{\overline{C_A C_B}}{C_{B,2}^2} = \frac{I_s \cdot \overline{C_B} \cdot \overline{C_A} + \overline{C_A} \cdot \overline{C_B}}{C_{B,2}^2} \quad (2.23)$$

The treatment of boundary conditions concern the inlet and outlet sections, and the particle interactions with obstacles and wall boundaries, as described in the following.

During both the simulation phases, the particles leaving the domain are replaced by new particles generated at the inlet section (the pollutant source or the plume edges), in order to continuously model the whole turbulent flow. We notice that the particles should represent the motion of the whole fluid mass inside the domain, for several realizations of the same experiment. In fact, under the hypothesis of Reynolds' decomposition, Lagrangian micromixing models simultaneously reproduce a great number of realizations (N) of the turbulent flow. The number of particles should be large enough to guarantee that in each cell of the underlying grid all the computed concentration statistics are robust (this grid is not a computational mesh). In this frame, the source mass flow rate of a generic passive pollutant is provided as an input parameter:

$$Q_s = C_s U_s A_s \quad (2.24)$$

where U_s is the mean value of the velocity magnitude at the source location, A_s the source area and C_s the source concentration. The source should be located in a cell centre, otherwise the spatial discretization would potentially alter the concentration fields around the source itself. Then, the model attributes a pollutant mass m_p to each particle during the conservative phase:

$$m_p = Q_s dt \quad (2.25)$$

As the particles are conservative, we do not need to initialize their concentration values. With the definition (2.25), the number of virtual realizations (N) is equal to the number of particles released (at the source) during the conservative phase (in case of point sources).

During the second phase, particles are uniformly distributed within the domain. Now N simply represents the number of particle traces in the cell, where the model computes the ensemble statistics. Further, the code can simply initialize the particle concentrations at the inlet section according to the cell conditional means, without setting any pollutant mass.

Wall boundaries are represented by symmetric conditions. A particle crossing a solid wall of an obstacle or a domain frontier (e.g. the ground) is mirrored back into the computational domain: its position is overturned with respect to the boundary and the model changes the sign of the velocity component aligned with the frontier normal. This very simple treatment is consistent with keeping the mean velocity component, which is aligned with the frontier normal, equal to zero at the very solid frontier and does not change the standard deviations of velocity in the on-going cell.

The following discussion finally recalls the reason why the first phase of a model run only needs a macromixing scheme to estimate the mean concentration of a passive scalar. In fact, in case of high Reynolds numbers (turbulent regimes), molecular diffusion does not affect concentration mean (e.g., Monin & Yaglom, 1971, [49]; Pope, 1998, [51]). Thus, we can neglect molecular diffusion when writing the Reynolds' average of the balance equation of C :

$$\overline{\frac{dC}{dt}} = 0 \quad (2.26)$$

The model is allowed to use conservative particles (with constant concentration along the trajectory) to represent passive pollutants (like F_m), as they satisfy (2.26):

$$\frac{dC}{dt} = 0 \Rightarrow \overline{\frac{dC}{dt}} = 0 \quad (2.27)$$

However, the resulting particle concentrations are not representative of the instantaneous concentrations of the passive scalar in the first phase, as particle concentrations should be affected by molecular diffusion processes. In fact, a stand-alone macromixing scheme (i.e. in the absence of a micromixing scheme) would provide highly overestimated concentration fluctuations.

2.6. Other Lagrangian stochastic models available for inter-comparisons

2.6.1. The chemical Lagrangian stochastic model of Alessandrini & Ferrero (2009)

The state-of-the-art Lagrangian stochastic model (Thomson, 1987, [63]) coupled with the chemical scheme of Alessandrini & Ferrero (2009, [3]; 2011, [2]) is here used to provide unpublished results, which are used for inter-comparison purposes (Sec.3.11). At each time step, this model updates the particle position using a stochastic model equation, then the concentrations of each substance is calculated over a static Eulerian grid. For every grid cell, the concentrations of each species are

updated following (2.28), as described hereafter. The new concentrations are then used to update the particle masses inside every cell, as suggested by Chock & Winkler (1994, [21]). The chemical reaction considered in this model is (1.4) and its discretized form of the chemical equation (also used for the other compounds) is:

$$\overline{c(NO)} = \overline{c^*(NO)} - r\Delta t \left(\overline{c^*(NO)} \right) \left(\overline{c^*(O_3)} \right) (1 + I_s) \quad (2.28)$$

where c represents an Eulerian concentration and the symbol “*” indicates the value of c in the cells after the turbulent dispersion but before the chemical reaction. For including the O_3 background concentration, the new specie deficit of concentration is introduced, as described in Alessandrini & Ferrero (2009, [3]). This avoids filling the whole domain with particles with a huge increase of computational time. This model adopts a parameterization for the segregation coefficient (I_s), based on the Brown & Bilger (1996, [14]) wind tunnel data-set (Alessandrini & Ferrero, 2009, [3]).

2.6.2. The Lagrangian micromixing model of Cassiani (2013)

The published results of the model of Cassiani (2013, [17]) are used for inter-comparison purposes (Sec.). This code represents a 2D Lagrangian micromixing model. The macromixing scheme is implemented according to Sec.2.1. A simplified micromixing scheme (i.e. the “Volumetric Particle Approach”) replaces the IECM scheme of Sec.2.2. The Volumetric Particle Approach is characterized by solving the balance equations for the numerical particle volumes. Thanks to this approach, the model can estimate concentration fluctuations by simulating only those particles passing through the pollutant sources. This guarantees a higher computational speed than other micromixing models. Further, the peculiar algorithm of this approach allows implementing an exact reaction scheme, as an alternative to the formulations of the Conserved Scalar Theory.

3. RESULTS

The model of Sec.2 is validated on the experimental test case of Brown & Bilger (1996, [14]; 1998, [15]). It describes the dispersion of two atmospheric reactant species (NO and O₃) and their reaction product (NO₂) in an unbounded turbulent flow (grid decaying turbulence). The test case is 2D, due to the symmetry with respect to the x-axis; however, the model simulations still adopt 3D configurations.

A first model inter-comparison is provided where the numerical results of Cassiani (2013, [17]) are available. Cassiani (2013, [17]) model was validated by comparisons with the experimental measurements of Brown & Bilger (1996, [14]), in terms of concentration mean and variance of the reactant species.

The results are presented as described in the following. Sec.3.1 reports the experimental test case and the numerical settings. The following sections show the model validation and inter-comparisons in terms of mean (Sec.3.2), standard deviation (Sec.3.3), intensity of fluctuations (Sec.3.4), skewness (Sec.3.6) and kurtosis (Sec.3.7) of the mixture fraction, the reactant and product species, as well as the plume spread (Sec.3.2), the segregation coefficient and the simulated reaction rate R_r (both in Sec.3.5). Sec.3.8 reports an inter-comparison of the newly implemented reaction schemes (RDL, FL, RDL, EL, NFRDL). Sec.3.9 and Sec.3.10 describe the sensitivity analysis on the micromixing constant and the number of particles, respectively. Sec.3.11 reports a valuable inter-comparison with the chemical Lagrangian stochastic model of Alessandrini & Ferrero (2009, [3]), by considering a region of the domain not explored in other publications. Finally, Sec.3.12 discusses an alternative model formulation, which assumes a linear mixing time.

3.1. Experimental test case and numerical settings

The experimental set-up represents the dispersion of reactive scalars in a decaying grid turbulence flow, in presence of a point source emission of the main reactant (NO), a background reactant (O₃) and a product species (NO₂). The experiment is widely described in Brown & Bilger (1996, [14]; 1998, [15]) and is related to point source emissions of reactive pollutants in the atmospheric boundary layer (e.g. Limem et al., 2014, [41]; Gariazzo et al., 2004, [32]).

The velocity turbulent fluctuations in the main flow direction can be neglected with respect to $\bar{u}$ = 0.5m/s and the following expression represents the other standard deviations of velocity:

$$\sigma_v^2 = \sigma_w^2 = A * 0.041 * \bar{u}^2 \left(\frac{x - x_g}{M} \right)^{-c}, \quad c = 1.27, \quad A = 1 \quad (3.1)$$

in agreement with Brown & Bilger (1996, [14]). Here x represents the distance from the source, M(=0.320m) the grid spacing and x=x_g=-3M the grid location. Under these conditions, the dissipation rate of the turbulent kinetic energy is equal to (Brown-Bilger 1996, [14], Sawford, 2004, [58]):

$$\varepsilon = -\frac{3}{2} \frac{\partial \sigma_w^2}{\partial t} = \frac{3}{2} \frac{c}{t} (0.0041 A) \bar{u}^2 \left(\frac{x - x_g}{M} \right)^{-c} = \frac{3}{2} \sigma_w^2 \frac{\bar{u}}{(x - x_g)} \quad (3.2)$$

The NO source is located at $\underline{x}_s = (0, L_x/2, L_z/2)$ where L_x, L_y and L_z are the sizes of both the experimental and the computational domain, aligned with the reference axis. Since the NO concentration at source is 515ppm and the source diameter is D=31.5mm, the scalar discharges are Q_s(NO)=0.2007ppm*m³/s and Q_s(F_m)=3.89·10⁻⁴m³/s. The background O₃ concentration is equal to 1.00ppm. The formula NO+O₃→NO₂+O₂ represents the only permitted reaction, with reaction rate r=0.37ppm·s⁻¹, in mean that the experiment is performed in a dark environment (no O₃ dissociation takes place).

The background mesh has a spatial resolution of $dx=M/10$. $L_y=L_z=4\sigma_{w,max}\cdot t_{f,max}=2.176m$ allows reproducing an unbounded domain with $170\times68\times68$ cells ($L_x=17M$), where the maximum fly time is $t_{f,max}=L_x/\bar{u}=3.4s$. The model uses $1\times10\times10$ velocity classes (for its three components, respectively) to estimate the conditional mean concentrations.

Combining (3.1) and (3.2), the Lagrangian integral time scale assumes the following form:

$$T_L = \frac{2\sigma_w^2}{C_0\varepsilon} = \frac{4}{3} \frac{t_f}{cC_0} \quad (3.3)$$

with a source value $T_L(x=0)=0.753s$. At the same position, the value of t_m is 0.59s (minimum) and $\varepsilon=2.43\cdot10^{-3}m^2/s^3$.

The input parameters of the reference solution are set to $n_{p1}=7.0\cdot10^6$ (number of particle released during the conservative phase), $n_{p2}=7.0\cdot10^7$ (number of particle released during the non-conservative phase), $dt=0.0032s$, $C_0=2.0$, $\mu=0.45$ and the reactive scheme is NHRDL (Sec.2.4).

The reference value of the Kolmogorov constant (C_0) is chosen according to the previous validations of the model (Leuzzi et al. 2012, [40]; Amicarelli et al. 2012b, [7]). This value is close enough to the arithmetic average of the Lagrangian micromixing reference values adopted in grid turbulence ($C_0=2.7$), with C_0 varying from 1.4 (Sawford, 2006, [59]) to 4.9 (Sawford 2004, [58]).

The reference value of the micromixing constant is chosen according to a common practice in Lagrangian micromixing modelling (since Sawford -2004, [58]- to Cassiani -2013, [17]-), motivated by the absence of a consolidated literature. Then, μ value is tuned in order to minimize the errors in estimating the concentration variance of a passive tracer (i.e. F_m in our case) along a single profile. This calibration provides $\mu=0.45$, which is close to the same value of Cassiani (2013, [17]): $\mu=0.38$, obtained with a simplified micromixing model ("Particle Volume Approach"). However, a sensitivity analysis on μ is also provided in Sec.3.9.

3.2. Mean scalars and plume spread

The reference simulation computes the stationary ensemble mean values of both the mixture fraction and the concentrations of the reactive pollutants.

The mean field of the mixture fraction (Figure 3.1, top left panel; Figure 3.2, left panel) shows its absolute peak at the NO source and exponentially decreases with x , along the centreline. Its transversal

profiles show a bell shape, which approximately goes with $e^{-\frac{1}{2}d^2}$, as already observed by Brown & Bilger (1998, [15]), where d represents the distance from the plume centreline. Hereafter, let equivalently consider the Frozen Limit of NO or the mixture fraction, as $C_{NO,FL} = F_m C_{NO,1}$, according to (2.16). Validations against the available measurements (still affected by non-negligible instrumental and ensemble errors, as in Figure 3.2, left panel) demonstrate the very good performance of the model in reproducing the mean mixture fraction. Cassiani's results (2013, [17]) show a similar model performance.

The reference simulation can estimate the plume spread from the mean field of F_m (Figure 3.2, right). According to Taylor analysis, the plume spread is linear in x close to the origin and goes with the root square of x far enough from the source, as reported by the model. Validation and inter-comparison (Figure 3.2, right panel) show the good reliability of the model in reproducing the plume spread: the slight underestimation with respect to the numerical curve of Cassiani (2013, [17]) is negligible when considering the experimental errors.

The spatial evolution of $\bar{C}_{NO}$ is very similar to the mean mixture fraction (Figure 3.1, top right panel; Figure 3.3, left column). Comparing Figure 3.2 (left panel) and Figure 3.3 (top left panel), one can appreciate the decrease in NO mean concentration due to chemical oxidation. The model provides good estimation of $\bar{C}_{NO}$ along the plume centreline and Profile 1, whereas an appreciable underestimation is recorded at the end of the domain (Profile 2). However, the reference solution

1 provide much better results than the simulation with the RDL scheme, which over-predicts the effects
 2 of NO oxidation much more than NHRDL. Cassiani (2013, [17]) provides better results along Profile
 3 2, but slight overestimations along the centreline.
 4 The mean concentration of O_3 is null at the NO source, rapidly increases with x along the plume
 5 centreline up to a peak value (at around $x/M=2$). $\bar{C}_{O_3}$ then slightly reduces and tends to a constant
 6 value, as the effects of the turbulent transport from the plume edges are approximately balanced by
 7 the chemical reaction. The transversal profiles of $\bar{C}_{O_3}$ show an upside down Gaussian bell shape, with
 8 a minimum at the plume centreline (Figure 3.1, bottom left panel; Figure 3.3, left column). The
 9 reference solution provides reliable results both along the centreline and transversal profiles, if
 10 compared to the available measurements. Nevertheless, a slight overestimation at $y=0$ is visible, but
 11 still negligible with respect to the experimental errors. Cassiani (213) results (not available along the
 12 centreline) slightly over-predict $\bar{C}_{O_3}$ at the centre of the domain, with opposite minor
 13 underestimations towards the plume edges. RDL simulation noticeably under-predicts the ozone
 14 levels, due to a systematic overestimation of the reactive process.
 15 The mean concentration of NO_2 (Figure 3.1, Figure 3.4) rapidly increases with x from its null value
 16 at source and exponentially tends to a plateau, which is established in the experimental “Region Of
 17 Interest” (R.O.I.: $7 \leq x/M \leq 17$; Brown & Bilger -1996, [14]-). Here the chemical production of $\bar{C}_{NO_2}$
 18 is approximately balanced by the turbulent transport towards the plume edges. The transversal
 19 profiles present a bell shape, qualitatively similar to $\bar{C}_{NO}$. The reference simulation provides reliable
 20 estimations of $\bar{C}_{NO_2}$ both along the centreline and transversal profiles, which are located at the two
 21 boundaries of R.O.I. No numerical data is available from Cassiani (2013, [17]), whereas RDL
 22 simulation overestimates the mean concentration of NO_2 .
 23

24 Figure 3.1. Mean fields of the mixture fraction and the reactive pollutant concentrations.
 25 Top left: F_m (extreme values: 0-0.99), the monitoring centreline and profiles. Top right: NO (extreme values: 0ppm-
 26 515ppm). Bottom left: O_3 (extreme values: 0ppm-1.00ppm). Bottom right: NO_2 (extreme values: 0ppm-0.93ppm).

Figure 3.2. Model validation and inter-comparisons along the centreline ($x,y=0,z=0$). Left: mean concentration of NO in the Frozen Limit (equivalent to F_m). Right: plume spread $\sigma_z(x)$. Legend: + reference simulation; x measurements (Brown & Bilger 1996, 1998a); * numerical results of Cassiani (2013).

Figure 3.3. Model validation and inter-comparisons. Mean concentration of NO (left column) and O3 (right column) at the monitoring centreline (first row), Profile 1 (central row) and Profile 2 (bottom row). Legend: + reference simulation; x measurements (Brown & Bilger 1996, 1998a); * numerical results of Cassiani (2013); □ reference simulation with RDL replacing NHRDL.

Figure 3.4. Model validation and inter-comparisons. Mean concentration of NO₂. Left: centreline (x,y=0,z=0). Right: profile 1 (x=7M,y=0,z) and profile 2 (x=17M,y=0,z). Legend (left panel): + reference simulation; × measurements (Brown & Bilger 1996, 1998a); * reference simulation with RDL replacing NHRDL. Legend (right panel): + reference simulation (profile 1); × reference simulation (profile 2); * measurements (Brown & Bilger 1996, 1998a; profiles 1 and 2); □ reference simulation with RDL replacing NHRDL (profile 1).

3.3. Standard deviations of passive and reactive scalars

The standard deviation of the mixture fraction (Figure 3.5, top left panel; Figure 3.6) is null at source (controlled release) and explosively increases with x , as the background air ($F_m=0$) easily mixes with the most polluted air ($F_m=1$) where the plume is very thin. In this region ($0 < x/M < 0.4$), the production term P_{σ_c} of σ_{F_m} is very high (like the mean scalar gradient) and remains the only term in (1.3) to increase the local rate of change of σ_{F_m} . Then σ_{F_m} exponentially decreases with x , due to molecular diffusion processes and the turbulent transport towards the plume edges. This typical centreline spatial evolution is similar to analogous profiles of other experimental studies (e.g. Fackrell & Robins, 1982, [26]). The shape of the transversal profiles of σ_{F_m} sensitively changes with the plume spread, since it is related to the location of the maximum of the production term of σ_{F_m} , depending on the mean scalar gradient. Where the plume is narrow enough (Profile 1 in Figure 3.6), P_{σ_c} has two peaks close to the centreline. Combined to the effect of the transversal turbulent transport, they cause the establishment of a plateau of maximum values of σ_{F_m} (Figure 3.6, right panel, Profile 1). Far enough from the source (Profile 2 in Figure 3.6), the two maxima of P_{σ_c} are more distant from the centreline, where there is no production of σ_{F_m} and a relative minimum can establish. In the lateral regions of the plume (within the R.O.I.), σ_{F_m} is approximately linear in both y and z . Here, the divergence of the turbulent transport flux is close to zero and the dissipation rate of the mixture fraction variance (ε_c) is approximately balanced by the combined effects of the non-homogenous production term P_{σ_c} and the advective term of σ_{F_m} .

Both the reference solution and the numerical model of Cassiani (2013, [17]) calibrates the micromixing constant on the profile of Figure 3.6 (left panel). Here, we can only notice that the spatial evolution of σ_{F_m} is well reproduced by both the models. The reference solution provides satisfactorily results along the transversal profiles, if compared to the measured values, which are still affected by non-negligible ensemble errors (Figure 3.6, right panel). The reference solution can reproduce the plateau of maximum values around the centreline (Profile 1) and the minimum of Profile 2. Both these features are much less appreciable in the numerical curves of Cassiani (2013, [17]).

1 The spatial pattern of the standard deviation of NO is very similar to σ_{F_m} (Figure 3.5). Comparing
2 Figure 3.7 (left panel) with Figure 3.6 (left panel), one can notice that the reactive term $\overline{R_2}$ has small
3 effects on NO close to the source, as already observed by Brown & Bilger (1996, [14]). As far as the
4 ozone concentration is negligible with respect to NO, the oxidation process is limited by O₃ and the
5 NO reduction cannot be appreciable with respect to NO levels. Validation still reveals a reliable
6 performance of the model in the R.O.I., where reactions play a noticeable role.
7 The standard deviation of ozone concentration (Figure 3.5, bottom left panel; Figure 3.7, right panel)
8 explosively grows from zero (source value) to its centreline peak value ($\sigma_{C,O_3}=0.4\text{ppm}$) at around
9 $x/M=0.5$ and then exponentially decreases with x along the centreline, keeping its values higher than
10 0.27ppm. The transversal profiles generally show two relevant peaks, located where the ozone mean
11 gradient is the highest, and a minimum centreline value. As a simplifying assumption, σ_{C,O_3} is set to
12 zero out of the mean plume, where computation is frozen. Validation, by comparison with the
13 available measurements, shows a good performance of the model, despite a slight and systematic
14 overestimation of σ_{C,O_3} .
15 The field of the standard deviation of NO₂ concentration (Figure 3.5, bottom right panel; Figure 3.8)
16 is very similar to σ_{C,O_3} , but close to the source, where the centreline peak ($\sigma_{C,NO_2}=0.35\text{ppm}$) occurs at
17 around $x/M=2$. Validations demonstrate the model reliability both along the centreline and the
18 transversal profiles, despite a slight and systematic overestimation of σ_{C,NO_2} . The reference simulation
19 well reproduces the transversal shape of σ_{C,NO_2} : the two symmetric peaks, are recorded where NO₂
20 mean gradient is the highest and a centreline minimum is obtained. Here σ_{C,NO_2} is not produced, but
21 only transported by the main flow.
22

23 Figure 3.5. Fields of the standard deviation of the mixture fraction and the reactive pollutant concentrations.
24 Top left: F_m (extreme values: 0-0.34). Top right: NO (extreme values: 0ppm-164ppm). Bottom left: O₃ (extreme values:
25 0ppm-0.44ppm). Bottom right: NO₂ (extreme values: 0ppm-0.43ppm).

Figure 3.6. Model validation and inter-comparisons. Standard deviation of NO in the Frozen Limit. Left: centreline ($x, y=0, z=0$). Legend: + reference simulation; $\times$ measurements (Brown & Bilger 1996, 1998a); * numerical results of Cassiani (2013). Right: Profile 1 ($x=7M, y=0, z$) and Profile 2 ($x=17M, y=0, z$). Legend: + reference simulation (Profile 1); $\times$ reference simulation (Profile 2); * measurements along Profile 1 and Profile 2 (Brown & Bilger 1996, 1998a); $\square$ Profile 1 and Profile 2 of Cassiani (2013).

Figure 3.7. Model validation. Standard deviations along the plume centreline ($x, y=0, z=0$). Left: NO. Right: O_3 . Legend: + reference simulation; $\times$ measurements (Brown & Bilger 1996, 1998a).

Figure 3.8. Model validation for the standard deviation of NO_2 . Left: centreline ($x, y=0, z=0$). Legend: + reference simulation; $\times$ measurements (Brown & Bilger 1996, 1998a). Right: Profile 1 ($x=7M, y=0, z$) and Profile 2 ($x=17M, y=0, z$). Legend: + reference simulation (Profile 1); $\times$ reference simulation (Profile 2); * measurements along Profile 1 and Profile 2 (Brown & Bilger 1996, 1998a).

3.4. Intensities of fluctuations

The intensity of fluctuations $i_{C,i} \equiv \frac{\sigma_{C,i}}{C_i}$ is considered as a relevant index to quantify the relative importance of concentration fluctuations with respect to the mean. Although no experimental

Figure 3.9. Fields of the intensity of fluctuations for the mixture fraction and the reactive pollutant concentrations. Top left: F_m (extreme values: 0-933). Top right: NO (extreme values: 0-36). Bottom left: O_3 (extreme values: 0-2.1). Bottom right: NO_2 (extreme values: 0-21).

Figure 3.10. Intensity of fluctuations for the mixture fraction and the reactive pollutant concentrations (reference simulation). Left: centreline ($x,y=0,z=0$). Right: Profile 1 ($x=7M,y=0,z$). Legend: + F_m ; $\times$ NO; * O_3 ; $\square$ NO_2 .

estimation of this parameter is available for the explored test case, the numerical estimations of i_c are discussed in the following.

All the analysed scalars (Figure 3.9) show the same centreline pattern of i_c , which is null at the NO source (controlled release), rapidly grows with x up to a maximum, then exponentially decreases and finally tends to a constant value (Figure 3.10, left panel). This behaviour was already reported by other authors for elevated point source emissions of passive scalars in the absence of obstacles (e.g. Fackrell & Robins, 1982, [26]) and is here confirmed for reactive pollutants too. The ozone intensity of fluctuations reaches its peak ($i_{C,O_3}=6.2$) at around $x/M=0.25$. The other scalars shows lower centreline maximum values: $i_{F_m}=1.9$ at $x/M=1.7$; $i_{C,NO}=1.6$ at $x/M=2.0$; $i_{C,NO_2}=0.7$ at $x/M=2.0$. These curves seems to achieve an almost constant centreline value at the end of the domain, where i_{F_m} , $i_{C,NO}$

1 , i_{C,O_3} and i_{C,NO_2} are equal to 0.6, 1.0, 0.8 and 0.4, respectively (but i_{F_m} is still slightly decreasing with
2 x).
3 Considering a generic transversal profile, the intensity of fluctuations of F_m , NO and NO_2 (Figure 3.9;
4 Figure 3.10, right panel) shows a minimum on the plume centreline and non-linearly increases with
5 z. At the plume edges, i_{F_m} , $i_{C,NO}$ and i_{C,NO_2} reach levels one order of magnitude higher than the
6 centreline. In these regions, the scalar turbulent fluctuations, due to the mixing of air with very
7 different scalar values, are relevantly higher than the corresponding mean values (let also consider
8 that the absolute maxima of i_{F_m} , $i_{C,NO}$, i_{C,O_3} and i_{C,NO_2} are 933, 36, 2.1 and 21, respectively; Figure
9 3.9). On the other hand, the mean transversal profile of O_3 has an upside down shape with respect to
10 the other scalar means, as the peak lies outside the mean plume. For this reason, i_{C,O_3} shows a
11 maximum at the centreline and decreases towards the plume edges.
12 Comparing F_m and NO fields and curves in Figure 3.9 and Figure 3.10, and considering that
13 $i_{C,F_m} = i_{C,NO,FL}$, one can appreciate that the chemical reaction improves the centreline intensity of
14 fluctuations of NO, which is instead lowered towards the plume edges, where the local maximum of
15 i_C is noticeably displaced towards the centre of the plume. In other words, the oxidation reduces both
16 NO mean and standard deviation. However, the proportional reduction of the mean is higher/lower
17 along the plume centreline/edge than the decrease in the NO standard deviation.
18 In conclusion, the standard deviation of both the passive and reactive scalars is generally of the same
19 order of magnitude or up to one order of magnitude higher than the corresponding ensemble mean
20 values, except for the background reactant (O_3) close to the plume edges (i_{C,O_3} approaches zero), and
21 the mixture fraction at the very plume edges (where σ_{F_m} is two order of magnitudes higher than $\bar{F}_m$).

22
23

24 3.5. Segregation coefficient and simulated reaction rate

25 The reactive term $\bar{r}$ in the balance equation of the reactant mean concentration (1.4) depends on the
26 covariance of the reactants and the product of their means. The relationships between these two terms
27 can be analysed both considering the segregation coefficient (their ratio, I_s) and the reaction rate (their
28 sum, R_r), as defined by Brown & Bilger (1996, [14]).

29 The segregation coefficient (Figure 3.11) shows a discontinuity at source, where it is equal to zero
30 (reactant are never simultaneously available at the NO source, where O_3 is constantly null). Along
31 the centreline profile, I_s immediately reaches its minimum value (-1), which corresponds to the
32 minimum value of the reactant correlation coefficient ($\rho=-1$): NO and O_3 are exactly anticorrelated,
33 very close to the source.

34 The segregation coefficient exponentially grows with x until the experimental R.O.I., where it
35 approximately equals a uniform value of around $I_s=-0.55$ (Brown & Bilger, 1996, [14]). Its transversal
36 profiles generally show a maximum along the centreline, two minima located where the species are
37 highly anti-correlated (i.e. over the peaks of the reactant mean gradients) and grows again towards
38 the plume edges, where the mean gradients zero as well as the covariance of the reactants.

39 The numerical model provides reliable estimations in the experimental R.O.I., where NHRDL results
40 fairly match the available measurement of I_s (Figure 3.11, right panel). The numerical results of
41 Cassiani (2013, [17]) provide a comparable representation of the segregation coefficient, even if they
42 systematically underestimate I_s , with respect to the reference simulation. The model also provides
43 comparative results using different CST limits (Sec.2.3 and Sec.2.4). Consider the noticeable
44 improvement provided by the NHRDL scheme (reference simulation), with respect to the RDL
45 scheme, which systematically overestimates the effects of the chemical reactions for anti-correlated
46 scalars. Only a minor part of this improvement relates to the fly time

Figure 3.11. Left: field of the segregation coefficient (extreme values: -0.98-0.00).

Right: centreline values ($x,y=0,z=0$) of the segregation coefficient; legend: + reference simulation; $\times$ measurements (Brown & Bilger 1996, 1998a); * numerical results of Cassiani (2013); $\square$ reference simulation with RDL replacing NHRDL; $\blacksquare$ reference simulation with RDL replacing NHRDL; $\circ$ reference simulation with EL replacing NHRDL; $\bullet$ reference simulation with NFRDL replacing NHRDL.

Figure 3.12. Reaction rate as defined by Brown & Bilger (1996). Left: Profile 1 ($x=7M, y=0, z$), Right: Profile 2 ($x=17M, y=0, z$). Legend: + reference simulation; $\times$ measurements (Brown & Bilger 1996, 1998a); * numerical results of Cassiani (2013); $\square$ reference simulation with RDL replacing NHRDL.

reductions, due to particles released from the plume edge, instead of the inlet section (i.e. appreciable, but slight improvement of RDL with respect to RDL). The “Equilibrium Limit” represents instantaneous reactions so that NO and O₃ are never simultaneously recorded ($I_s=-1$). Figure 3.11 (right panel) also shows the importance of modelling concentration fluctuations, even only for the estimation of the mean concentration of a reactant. In fact, in case of “no fluctuations” (NFRDL), the segregation coefficient is always null. This means that the reactant covariance is set to zero even if it represents the 50% up to the 100% the value of the product of the reactant means, which is the only reactive term considered by NFRDL.

The profiles of the reaction rate R_r (Figure 3.12) highlight the reliability of the model in reproducing this parameter, despite a slight underestimation of the experimental values along Profile 1. The reaction rate is directly proportional to the mean NO₂ production. Its maximum is located at the plume centreline and linearly decreases towards the plume edge, down to zero. The numerical results of Cassiani (2013, [17]) provide a better curve along Profile 1 but noticeably overestimate the central values of Profile 2, with respect to the present model and the available measurements. Once again, the improvement of NHRDL (reference solution) with respect to the RDL scheme is much relevant. Although RDL still represented a valid CST formulation (Sawford, 2006, [59]), it provides a systematic overestimation (relative error of ca. 85% around the centreline) in computing the local reactant consumption/production rate, whereas the NHRDL drastically reduces this gap (relative error lower than 5% around the centreline; Figure 3.12).

This validation shows the reliability of the present model in estimating the segregation coefficient (or intensity of segregation). The direct estimation of this parameter does not need any ad-hoc tuning or parameterization. This feature represents a key point in assessing the reactant mean concentrations

and their turbulent fluctuations, with respect to other Lagrangian (Sec.1, Sec.3.11) and Eulerian models (Sec.1). The simultaneous reliability in computing both I_s and the reactant consumption/production rate (or the reactant means, as described in Sec.3.2), implies the correctness of the simulated reactant covariance.

3.6. Scalar skewness

The scalar skewness provides a quantitative assessment of the concentration pdf asymmetry, by especially weighting the development its lateral tails.

Figure 3.13. Fields of the skewness for the mixture fraction and the reactive pollutant concentrations. Top left: F_m (extreme values: -0.1-270). Top right: NO (extreme values: -5.9-449). Bottom left: O_3 (extreme values: -85-6.3). Bottom right: NO_2 (extreme values: -6.0-231). The extreme values cited in this caption are the very absolute maxima/minima of the simulated values, no matter about the strong statistical noise, which affect them.

Figure 3.14. Scalar skewness along the plume centreline ($x, y=0, z=0$). Left: NO. Right: O_3 . Legend: + Frozen Limit (left) or NHRDL reference simulation (centre and right); x measurements (Brown & Bilger 1996, 1998a); * reference simulation with Frozen Limit replacing NHRDL; □ measurements in the Frozen Limit (Brown & Bilger 1996, 1998a).

The skewness of the mixture fraction and the reactive pollutant concentrations (Figure 3.13 and Figure 3.14) highlights the relevant role of the scalar pdf physical bounds (e.g. NO, F_m and O_3 cannot exceed the corresponding source or background values; concentrations cannot be negative) on the sign of the skewness itself. When the mean is close to the highest scalar bound (e.g. ozone far from the centreline; the other scalars in the very wake of the NO source), the ensemble skewness is negative. Contrarily, when the mean is close to the lowest scalar bound (e.g. ozone along the centreline; the other scalars almost all over the domain), the scalar skewness is positive (Figure 3.13). Then ozone skewness decreases towards the plume edges, contrarily to the other scalars. Except for the small zone of negative values (close to the source), the centreline profile of $S_{k,C,NO(FL)} (= S_{k,F_m})$ rapidly grows up to a peak of 3.2 at $x/M=3.8$ (Figure 3.14, left panel) and then monotonically decreases. It would reach the limit value of zero, under uniform scalar conditions (downstream and outside the numerical domain). Considering the reactive NO, the absolute value of the skewness is higher, due to the selective behaviour of a 2nd-order kinetics reaction, when applied to anticorrelated reactants: transformations involving medium values of the reactant concentrations are more intense than reactions involving extreme values. This implies that the instantaneous scalars around the mean are subjected to a higher consumption than the extreme values of the same scalar, thus causing a skewness increase. In this context, one notice that NO concentration would never reach homogenous conditions (reactive case), but the NO concentration skewness has already attained a constant value ($S_{k,C,NO}=3.6$) along the centreline (Figure 3.14, left panel). S_{k,C,O_3} field is very similar to the field of S_{k,C,NO_2} , when changed of sign. In particular, S_{k,C,O_3} and S_{k,C,NO_2} are very close to zero along the plume centreline (Figure 3.13 and Figure 3.14), in the experimental R.O.I. (their absolute value lies between 0.1 and 1.0): here O_3 and NO_2 concentration pdfs are almost symmetric.

The validation of the skewness of a reactive scalar represents a hard task and, unfortunately, only one measurement per parameter is here available (Brown & Bilger: 1996, [14]; 1998, [15]). In this limited context, the model seems to over-estimate the skewness of around 2 times for a passive scalar ($S_{k,F_m} = S_{k,C,NO(FL)}$) and of around 3 times for a reactive scalar ($S_{k,C,NO}$), with respect to the only available measurement. The very low value of skewness of the background reactant (S_{k,C,O_3}) in the experimental R.O.I. (centreline) is underestimated of around 4 times. Beyond the lack of experimental data for a complete validation, the main reasons of the model shortcomings are related to its sensitiveness on the micromixing constant, when estimating skewness and kurtosis, as demonstrated in Sec.3.9.

3.7. Scalar kurtosis

The concentration kurtosis is here defined as $K_{u,C} \equiv \frac{\overline{(C - \bar{C})^4}}{\sigma_C^4}$, provides a relative measurement of the fourth central moment of the scalar pdf, quantifies the pdf spread around the mean value and the presence of the pdf heavy tails (Figure 3.15).

The kurtosis of the passive scalar (equivalently either F_m or NO in the Frozen Limit) shows very low values in the source wake (around 1) and then increases along the plume centreline up to a peak of $K_{u,C,F_m}=17$, at $x/M=5.5$ (Figure 3.16). It follows a slow decrease until a value of $K_{u,C,F_m}=10$, at the end of the domain, whereas the theoretical value under uniform scalar conditions (downstream, far from the domain outlet) would be 3 (i.e. Gaussian scalar pdf). Considering the analogous curve of the reactive NO (Figure 3.16), the chemical reaction improves the scalar kurtosis. This effect is due to the selective behaviour of a second order reaction for anticorrelated reactants, with respect to their instantaneous concentrations, as analogously observed for the skewness (Sec.3.6). After $x/M=3$, the reactive NO concentration kurtosis slightly keeps increasing and reaches a value of $K_{u,C,NO} = 24$ at the end of the domain. $K_{u,C,NO}$ raises towards the plume edges, where it generally reaches 10^2 , with local

Figure 3.15. Fields of the kurtosis for the mixture fraction and the reactive pollutant concentrations.

Top left: F_m (extreme values: $0-93 \cdot 10^3$). Top right: NO (extreme values: $0-270 \cdot 10^3$).

Bottom left: O_3 (extreme values: $0-217 \cdot 10^3$). Bottom right: NO_2 (extreme values: $0-217 \cdot 10^3$).

Values outside the mean plume are not computed, but simply shown as the lowest bound of the legend interval. The extreme values cited in this caption are the very absolute maxima/minima of the simulated values, no matter about the strong statistical noise, which affect them.

Figure 3.16. Scalar kurtosis along the plume centreline ($x, y=0, z=0$). Left: NO. Right: O_3 . Legend: + Frozen Limit (left) or NHRDL reference simulation (right); $\times$ measurements (Brown & Bilger 1996, 1998a); * reference simulation with Frozen Limit replacing NHRDL; $\square$ measurements in the Frozen Limit (Brown & Bilger 1996, 1998a).

peaks up to 10^5 (Figure 3.15, top right panel). This lateral increase is not monotonic and we can appreciate two symmetric zone of relative maxima aligned with the centreline.

The concentration kurtosis of O_3 and NO_2 are very similar (Figure 3.15; bottom panel) and share the same patterns as NO and F_m field (Figure 3.15; bottom panel), but with lower centreline values. After an irregular behaviour (with a peak of 41) close to the source, the centreline K_{u,c,O_3} is approximately constant since $x/M=2$ and ranges from 1.3 to 1.6, thus revealing a very narrow ozone pdf in the domain centre.

The lack of measurements is demonstrated by the only presence of one experimental value for each available parameter ($K_{u,c,NO}$, K_{u,c,O_3} , K_{u,c,F_m}). From this very limited validation, the model seems to overestimate the passive scalar kurtosis (F_m or NO Frozen Limit) of a factor of 3 and over-predicts

the reactive NO kurtosis of a factor of 5. On the other hand, K_{u,c,o_3} is under-estimated of 47%, which would represent a good relative error in computing a scalar kurtosis (high order statistics).

3.8. Inter-comparisons of the reaction schemes

Comparing the results reported in Figure 3.17 and Figure 3.11 (right panel), together with RDL results of Sec.3.2 and Sec.3.4, one can order the CST limits of Sec.2.3 and Sec.2.4, according to their NO₂ production (increasing order).

- Frozen Limit (FL; Sawford, 2006, [59]; Bilger, 1991, [10]): no reaction takes place.
- Non-Homogeneous Reaction-Dominated Limit (NHRDL): new scheme (reference simulation), which improves the performance of the RDL scheme.
- Reaction-Dominated Limit with fly time starting when particles cross the plume edge (RDLP): RDL scheme with a slight improvement provided by the fly time reduction, due to particles released on the plume edges instead of the inlet section.
- Reaction-Dominated Limit (RDL; Sawford, 2006, [59]; Bilger, 1991, [10]): the most used CST scheme, which provides reliable results, but also a modest, but systematic overestimation of reactions under non-homogeneous conditions (e.g. for anticorrelated reactants).
- Equilibrium Limit (EL; Sawford, 2006, [59]; Bilger, 1991, [10]): reactions are immediate so that the reactant species never coexist.
- No-Fluctuation Reaction-Dominated Limit (NFRDL): RDL with no turbulent fluctuations.

The new scheme (NHRDL) noticeably improves the performance of the RDL scheme, in case of non-homogeneous conditions, thus avoiding systematic overestimations of the reaction processes (Figure 3.17).

The automatic improvement provided RDLP to the RDL scheme is also appreciable, but plays a minor role if compared to the advantages given by NHRDL.

The reactant covariance lowers the reactive term $\bar{T}$ in (1.2). The result is that, in case of no turbulent fluctuations (NFRDL; Figure 3.17), the production of NO₂ is higher than the Equilibrium Limit (where reactions are instantaneous). This noticeable behaviour highlights the relevant role of concentration fluctuations, also in the estimation of the mean concentrations of reactive scalars.

3.9. Sensitivity on the micromixing constant

According to a reference procedure adopted in Lagrangian micromixing literature (since Sawford - 2004, [58]- to Cassiani -2013, [17]-), the micromixing constant μ is calibrated on a unique reference measured profile, related to the standard deviation of a passive scalar. All the other profiles and parameters are estimated by keeping the micromixing constant unchanged. This procedure is motivated by a general lack of reference values for this constant (both experimental and numerical). This study strictly adopts this procedure, with the reference measured profile of σ_{F_m} reported in Figure 3.18 (top left panel). The optimized value found for the micromixing constant is then $\mu=0.45$, which characterizes all the results presented in the other sections.

Comparing the plots of Figure 3.18, one can briefly recall some effects of the micromixing constant on the reference solution. Increasing μ , the model increases the mixing time (2.9), which implies a decrease in the molecular diffusion processes, responsible for the dissipation of concentration fluctuations. This means that the instantaneous field of the reactant concentrations is less homogeneous, with two clear effects: the turbulent fluctuations of the reactant and passive scalars are increased and the NO₂ production lowers. In fact, a 2-reactant 2nd-order kinetics provides the highest efficiency with no turbulent fluctuations, as already observed in Sec.3.8.

Figure 3.17. Inter-comparisons of the CST limits.

Left: mean concentration of O_3 along Profile 1 ($x=7M, y=0, z$). Centre: mean concentration of NO_2 along Profile 2 ($x=17M, y=0, z$). Right: reaction rate along Profile 1 ($x=7M, y=0, z$).

Legend: + reference NHRDL simulation; $\times$ measurements (Brown & Bilger 1996, 1998a); * reference simulation with FL replacing NHRDL; $\square$ reference simulation with RDLP replacing NHRDL; $\blacksquare$ reference simulation with RDL replacing NHRDL; $\circ$ reference simulation with EL replacing NHRDL; $\bullet$ reference simulation with NFRDL replacing NHRDL.

Figure 3.18. Sensitivity analysis on the micromixing constant μ . Scalar statistics along the plume centreline ($x, y=0, z=0$).

Top left: standard deviation of NO concentration in the Frozen Limit (equivalent to F_m). Top right: skewness of NO concentration in the Frozen Limit (equivalent to F_m). Bottom left: kurtosis of the NO concentration in the Frozen Limit (equivalent to F_m). Bottom right: mean concentration of NO_2 .

Legend: + measurements (Brown & Bilger 1996, 1998a); $\times$ reference simulation (with NHRDL and $\mu=0.45$); * reference simulation, except for $\mu=0.40$; $\square$ reference simulation, except for $\mu=0.65$.

The differences between the reference simulation ($\mu=0.45$) and the run with $\mu=0.40$ are almost negligible in estimating the standard deviation of F_m , whereas they provide a relative difference up to 100% for the kurtosis of the mixture fraction (Figure 3.18). In particular, the simulation with $\mu=0.45$, which is not exactly the optimum solution for σ_{F_m} , matches the skewness and kurtosis of the mixture fraction much better than the reference solution. As anticipated in Sec.3.6 and Sec.3.7, the sensitivity of these higher order statistics on the choice of the micromixing constant is the main cause of the overestimations of S_{k, F_m} , $S_{k, NO}$, K_{u, F_m} and $K_{k, NO}$, as Figure 3.18 demonstrates.

Figure 3.19. Sensitivity analysis on the number of particles. Scalar kurtosis along Profile 1 ($x=7M, y=0, z$). Left: NO. Right: O_3 . Legend: + fast simulation; $\times$ reference simulation; * long simulation.

The sensitivity analysis on the micromixing constant shows that the dependency on μ strongly grows with the scalar statistics order (Figure 3.18). The analysis suggests calibrating the micromixing constant on one experimental kurtosis (or skewness) profile (instead of a σ_c profile) of a passive scalar dispersed within the investigated domain. However, in the lack of kurtosis (and skewness) profiles (e.g., there is only one kurtosis/skewness value for the present test case and no estimation of its error), it is unreliable to adopt the suggested procedure above.

The sensitivity analysis on the micromixing constant also shows that the discrepancies between the simulated kurtosis/skewness and its unique associated measurement could be simply related to the choice of the micromixing constant.

3.10. Sensitivity on the number of particles: proofs of convergence

This study explores a wide range of values for the number of particles. In this frame, let briefly define the extreme and the reference solutions: the “fast simulation” ($n_{p1}=n_{p2}=7.0 \cdot 10^6$), the “reference simulation - NHRDL” ($n_{p1}=7.0 \cdot 10^6$, $n_{p2}=7.0 \cdot 10^7$) and the “long simulation” ($n_{p1}=2.0 \cdot 10^7$, $n_{p2}=2.0 \cdot 10^8$).

For the configuration explored in this study, the number of particles demanded is ruled by the less robust statistics (kurtosis), where it shows the highest transversal gradients (the plume edges). In terms of robustness, the most challenging profiles are reported in Figure 3.19. The differences between the fast and the reference simulation are appreciable, even if limited. At the same time, the discrepancies between the long and the reference simulation are negligible.

This analysis then proves that the main simulation of this study (the reference-NHRDL solution) converges with respect to the number of particles. Here convergence is simply intended in terms of statistics robustness (i.e. the model does not require any convergence algorithm).

As a general strategy to reduce the simulation uncertainties due to the model resolution, one may consider the following procedure. Run a simulation by activating only the conservative phase, with a very low value of n_{p1} . Increase this value until the mean scalar converges and fix the last value of $n_{p1}(=n_{p1,1})$. Now run a simulation by activating both the conservative and non-conservative phases with $n_{p1}=n_{p2}=n_{p1,1}$ and assume 10 velocity classes for each velocity component. Alternatively increase n_{p1} and n_{p2} until the higher simulated statistics converges on both these parameters. Now, reduce the number of velocity classes without deteriorating the results.

3.11. Comparisons with a state-of-the-art Lagrangian stochastic model

The reference simulation of this study, as defined and validated in Sec.3.1-3.11, is compared with the numerical results obtained by the Lagrangian stochastic model with a chemical scheme, described in Alessandrini & Ferrero (2009, [3]; Sec.2.6). The corresponding curves are noted as “Spray” (name of the associated numerical code). Both the models have been validated in terms of mean

concentrations of the reactants. Since the model have been already separately validated at the section $x/M=7$ and $x/M=17$ (Sec.3.2-3.10; Alessandrini and Ferrero, 2009), here are considered the transversal profiles at $x/M=12$, which represents an unexploited region for both the models, even though the experimental values were available only along the centreline. Looking at the Figure 3.20, it can be observed that the two models show the same spatial evolution of the mean concentration of NO, both in the reactive case and the Frozen Limit. Their numerical results are very close to the measured values, also considering that the experimental uncertainty on NO levels is not negligible (Figure 3.20, left panel). The reference simulation provides slightly higher NO levels than the state-of-the-art model, but in the Frozen Limit, around the centreline. As the macromixing schemes of both the models should behave in a similar way in this simple turbulent flow, the differences in the profile of the FL of NO should mainly refer to the choice of the Kolmogorov constant (C_0) and the estimation of dissipation rate (ε) of the turbulent kinetic energy (or alternatively the Lagrangian integral time scale $-T_L$). The “reference simulation” uses the theoretical formula for the dissipation rate of the turbulent kinetic energy in decaying grid turbulence (3.2), whereas the “state-of-the-art model” estimates the Lagrangian integral time scale, based on the far field formulation for the turbulent dispersion coefficient (Taylor analysis). This is related to the experimental fitting (limited to the experimental region of interest) for the plume spread, as reported in Brown & Bilger (1996, [14]). The differences in the model performances slightly increase when estimating NO levels, in the reactive case (Figure 3.20, left panel). Although they both considered the reactant covariance, the two reaction schemes of the compared models are very different. The reference simulation uses the NHRDL of the conserved scalar theory (Sec.2.3-2.4), whereas the state-of-the-art model adopts an Eulerian reaction scheme. The particle concentration of the “state-of-the-art model” represents mean concentrations and the segregation coefficient is defined according to the experimental formula proposed by Brown & Bilger (1996, [14]), which considers measured values along the centreline, in the experimental region of interest (between $x/M=7$ and $x/M=17$). On the other hand, the “reference simulation” reproduces “instantaneous-like” concentration values (thanks to the IECM micromixing scheme) and computes the field of the segregation coefficient.

The two numerical profiles of the mean concentration of O_3 are very close each other (Figure 3.20, right panel) and show a modest overestimation of the centreline measurement. The results of the “state-of-the-art model” seem to show a rougher spatial resolution than the “reference simulation”. However, the values of the first model are extracted from a finer background grid.

Figure 3.20. Model inter-comparison. Mean concentration of NO (left column) and O_3 (right column) at $x/M=12$. Legend: + reference simulation; $\times$ Spray/state-of-the-art model (Sec.2.6.1); * centreline measurements; $\square$ reference simulation with FL replacing NHRDL; $\blacksquare$ FL of Spray/state-of-the-art model (Sec. 2.6.1); $\circ$ FL for the centreline measurements.

3.12. Comparisons with a numerical solution based on a linear mixing time

The reference simulation of this study is based on the mixing time formulation (2.9). Here it is compared with an analogous simulation, which assumes a linear mixing time (2.10) with a

Figure 3.21. Inter-comparisons of the mixing time formulations.

Left: mean concentration of NO along the centreline. Centre: standard deviation of NO in the Frozen Limit along the centreline. Right: reaction rate along Profile 1 ($x=7M, y=0, z$).

Legend: + reference NHRDL simulation; $\times$ measurements (Brown & Bilger 1996, 1998a); * numerical results of Cassiani (2013); $\square$ reference simulation with a linear mixing time.

micromixing constant $\mu=0.38$ and $C_r/C_0=1.5$ (according to an approximated relationship for Lagrangian micromixing models; Cassiani et al. 2005, [18]).

Owing to the practical equivalence of the two formulations for the mixing time on this test case (Figure 3.21), this study prefers to use a more approximated (but generic) t_m formulation, which does not require any assumption on the Richardson constant.

4. CONCLUSIONS

The study describes the implementation and validation of several reaction schemes, based on the conserved scalar theory (CST), into a 3D Lagrangian micromixing model to simulate the dispersion of reactive scalars in turbulent flows. In particular, a modified version of the RDL (Reaction-Dominated Limit) scheme is defined (NHRDL: Non-Homogeneous RDL) and validated to improve the model performance, under non-homogeneous conditions.

Validations refer to comparisons with the experimental test case of Brown & Bilger (1996, [14]; 1998, [15]), which describes the 2D dispersion of two reactant species (NO and O₃) and the product (NO₂) of their 2nd order kinetics reaction, in an unbounded turbulent flow (grid decaying turbulence). Validations highlight the reliability of the model in estimating several statistics of the mixture fraction (a support passive scalar) and of the reactive pollutant concentrations: mean, standard deviation, intensity of fluctuations, segregation coefficient and reaction rate (as defined by Brown & Bilger, 1996, [14]). Numerical skewness and kurtosis were more difficult to assess due to the lack of experimental data. At the same time, the study demonstrates that these statistics are very sensitive on the choice of the micromixing constant, which is simply and automatically chosen, according to the procedure described by several authors (since [59] to [17]).

Model inter-comparisons are widely discussed, first considering the available results of Cassiani (2013, [17]), who developed a 2D simplified micromixing model (i.e. the “Volumetric Particle Approach”, alternative to IECM -Interaction by Exchange with the Conditional Mean-) coupled with an exact reaction scheme (alternative to the CST formulations). The performance of the present model is comparable with the faster model of Cassiani (2013, [17]): the first also represents higher order statistics and releases particles from whole the mean plume edge; the latter adopts a simplified micromixing scheme, with particles only released from the pollutant source.

The quantification of the differences between the CST limits (NHRDL, RDL, FL -Frozen Limit-, RDLP -RDL with Plume edge detection-, EL -Equilibrium Limit-, NFRDL -No Fluctuation RDL-) in estimating a 2nd order reaction of anticorrelated reactants is also considered. NHRDL scheme noticeably improves the performance of the RDL scheme, thus correcting the modest, but systematic overestimations of the reactant consumption, under non-homogeneous conditions. The present validation shows that RDL provides a systematic overestimation (relative error of ca. 85% around the centreline) in computing the local reactant consumption/production rate, whereas the NHRDL drastically reduces this gap (relative error lower than 5% around the centreline). The absence of concentration fluctuations (NFRDL scheme) artificially improves the reaction process more than reproducing an instantaneous chemistry (i.e. Equilibrium Limit).

Far enough from the source ($x > 4M$), one can avoid a direct estimation of the product statistics, which can be simply calculated from the mixture fraction mean and the background reactant statistics ([14]). The present model is also compared with a state-of-the-art chemical Lagrangian stochastic model (Alessandrini & Ferrero, 2009, [3]) to provide a further assessment in a region of the domain not explored in other publications. The state-of-the-art model is faster than the present model because it only estimates mean concentrations (and releases particles uniquely from the source). It adopts a state-of-the-art Lagrangian stochastic model (Thomson, 1987, [63]) and a hybrid Lagrangian-Eulerian reaction scheme with an experimental parameterization of the segregation coefficient. The inter-comparison show the reliability of both the models in reproducing the mean concentrations of reactive scalars and highlights their relative differences in terms of numerical schemes and input data. Lagrangian micromixing models represent an alternative method to pdf models or DNS (Direct Numerical Simulations), in treating scalar reactions depending on the instantaneous-like concentrations (e.g. direct estimation of the segregation coefficient). Other models (e.g. RANS -Reynolds-Averaged Navier Stokes-, Lagrangian macromixing codes, LES -Large Eddy Simulations-) usually neglect the effects of concentration fluctuations in reactive scalar dispersion, or use ad-hoc parameterizations for the segregation coefficient. Nonetheless, neglecting scalar fluctuations in the sub-grid scale of a LES model is a much more acceptable assumption than adopting analogous approximations in the framework of other approaches (e.g., RANS). On the other hand, LES are much

1 slower than other codes, like Lagrangian stochastic models, which are also very suitable to
2 parallelization. In any case, concentration fluctuations are non-negligible, even if one just focuses on
3 the mean concentrations of reactive pollutants. According to Pope (1998, [51]), only the mean values
4 of passive scalars could be modelled using conservative particles and do not need concentration
5 fluctuations. Here, in terms of NO₂ production (or reactant consumption), neglecting concentration
6 fluctuations determines overestimations of the product mean of around 100% and a NO₂ local
7 production of one order of magnitude higher than the reference simulation. In terms of standard
8 deviations, the concentration fluctuations of both the passive and reactive scalars are generally of the
9 same order of magnitude or up to 1 or 2 orders of magnitudes higher than the corresponding ensemble
10 mean values, except for the background reactant close to the plume edges.

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