Micromixing effects in air pollution modelling

A. Garmory, E. Richardson & E. Mastorakos
Engineering Department, University of Cambridge, UK

Abstract

Predicting the dispersion of reacting pollutants close to their source is a topic of importance in Air Quality Modelling. The conventional method of neglecting species concentration fluctuations is not valid for such small-scale problems. Various methods that incorporate segregation are reviewed here and their use for typical atmospheric dispersion problems is illustrated through numerical simulations of a simplified problem. By comparison with experimental data, it is found that micromixing can affect the evolution of the mean reaction rate and that the models presented here are more accurate than if segregation were not included. Further work should focus on the interfacing of these models with practical Air Quality calculations.

Keywords: segregation, turbulent reacting flows, air quality.

1 Introduction

A current goal of urban air quality studies is to predict as accurately as possible the pollution that humans actually experience. Grid models for cities must hence have enough resolution to track the pollution produced in street canyons or dispersed in the immediate vicinity of industrial sources. This necessitates novel approaches concerning the chemical reaction and its interaction with the atmospheric turbulence because the reactant segregation, or micromixing, cannot be neglected at such fine scales. The purpose of this paper is to demonstrate that this is indeed the case for typical small-scale dispersion problems, to review some of the previous work on this topic and to suggest methods by which segregation can be taken into account. Some new results from our own efforts in implementing advanced turbulent reacting flow theories in atmospheric dispersion problems are also presented.
2 Models for micromixing: a short review

2.1 The main problem

Consider the advection-diffusion equation describing the evolution of the instantaneous concentration $\phi$ of a pollutant ignoring deposition and emissions, but including chemical reaction. Solutions to this equation would virtually always use some sort of averaging, e.g. time averaging in a statistically-steady problem. For unsteady problems, we could think of the averaging as an ensemble or even as a volume average over, say, an Eulerian Grid cell or a cell in an LES calculation. After Reynolds decomposition and averaging, denoted by an overbar, we obtain

$$\frac{\partial \bar{\phi}}{\partial t} + \bar{u}_i \frac{\partial \bar{\phi}}{\partial x_i} = D \frac{\partial^2 \bar{\phi}}{\partial x_i^2} - \frac{\partial (\bar{u}'_i \phi')}{\partial x_i} \bar{w}$$  \hspace{1cm} (1)

where $\bar{w}$ is the chemical source term for $\phi$ and primed quantities represent the turbulent fluctuations. $u_i$ is the gas velocity and $D$ the molecular diffusivity. It is evident that the Reynolds averaging procedure brings in a new term, $u'_i \phi'$, which represents turbulent diffusion and requires modelling, as for example by the so-called “K-theory” [1]. The mean wind speed $\bar{u}_i$ can come from a Grid Model or LES or any other calculation solving (modelled) fluid mechanics equations. Understanding the nature of the micromixing problem for the evolution of the chemical reaction can be achieved by examination of the mean reaction rate $\bar{\dot{w}}$. Assume that we have the chemical reaction $A + B \rightarrow C$, then

$$\dot{\bar{w}} = \beta \phi_A \phi_B \exp \left(-\frac{T_{\text{act}}}{T}\right)$$

where $T_{\text{act}}$ is the activation temperature. Performing a Reynolds decomposition, we obtain

$$\dot{\bar{w}} = \bar{\dot{w}} + \dot{w}' = \beta (\bar{\phi}_A + \phi'_A)(\bar{\phi}_B + \phi'_B) \exp \left(-\frac{T_{\text{act}}}{T + T'}\right)$$ \hspace{1cm} (2)

If $T' = 0$, as is often the case in atmospheric problems, we can group the exponential and the pre-exponential constant $\beta$ to give the reaction rate constant $k$, and then only a product between the species concentration fluctuations appears:

$$\bar{\dot{w}} = k \left(\bar{\phi}_A \bar{\phi}_B + \phi'_A \phi'_B\right)$$ \hspace{1cm} (3)

Therefore, to calculate the mean reaction rate, one needs a model for $\phi'_A \phi'_B$. Moment methods aim to model this correlation (a higher moment) either in an ad hoc or semi-empirical manner or by solving a transport equation, which of course requires further modelling. Alternatively, the mean reaction rate may be calculated directly by other methods. We review some of the previous work on these topics next.

2.2 Low Damköhler numbers

The common practice in Air Quality Modelling is to completely neglect $\phi'_A \phi'_B$. As discussed by [2, 3, 4, 5, 6], this is acceptable if the chemistry is very slow.
compared to the turbulent timescales, since turbulence is the process by which the fluctuations $\phi_A'$ and $\phi_B'$ decay due to mixing. For illustration of this concept, consider a problem where the mean concentrations are constant in space, but with small-scale fluctuations (i.e. segregation) present. It can be shown that the equation for the variance $\sigma^2 = \overline{\phi^2}$ of the scalar is then given simply by [3, 7]

$$\frac{d\sigma^2}{dt} = -2 \frac{\sigma^2}{T_{eddy}} + 2\overline{\phi'} \overline{\phi'}$$

(4)

The first term in the r.h.s. of Eq. (4) represents the rate of decay of the fluctuations. It is called the scalar dissipation and has been modelled here following the conventional model that uses a large-eddy timescale $T_{eddy}$, which is equivalent to assuming that the scalar fluctuations decay at the same rate as the turbulence kinetic energy. The second term is due to the chemistry. For the first-order reaction $A \rightarrow B + C$, the chemical source term is $\dot{w}_A = -k\phi_A$, hence $\overline{\phi'} \overline{\phi'} = -k\sigma^2$. Equation (4) can be integrated to give $\sigma^2(t) = \sigma^2_0 \exp[-2(1 + Da)t/T_{eddy}]$, where the Damköhler number $Da = kT_{eddy}$. Hence, if $Da \ll 1$, turbulence is given enough time to kill the scalar fluctuations before the chemistry becomes important. In the general case where the chemistry is not linear, third-order correlations also appear in Eq. (4). Still, however, it can be argued that if the chemistry is very slow ($Da \ll 1$), the species will be well-mixed (i.e. $\sigma^2_{A,B} \rightarrow 0$, $\overline{\phi_A'} \overline{\phi_B'} \rightarrow 0$) before the reaction proceeds appreciably and hence neglecting segregation is not a problem.

When attention is focused on faster chemical phenomena at length scales close to the pollution sources, $Da$ may not be low and the well-mixed assumption, typical of urban Box Models, Eulerian Grid or Lagrangian codes, is flawed. Consider an urban street canyon, as an important small-scale problem [8]. A typical residence time of the pollutants generated by cars inside the canyon may be of the order of 100 s, which is comparable to the timescale of some reactions. Examples are the initial, fast conversion of $NO$ to $NO_2$ and the reactions between $VOC$ radicals and $NO_x$. Reactions with the hydroxyl radical are also considered to be fast [9]. If $Da = o(1)$ or $Da \gg 1$, the chemistry-turbulence interaction is important. The mean reaction rate calculated by ignoring segregation can then be out by an order of magnitude [4, 3, 6]. Despite the good resolution achieved by systematic grid refinements [10], this problem persists even at the smallest cell and even at the sub-grid scale, as concluded in Refs. [11] and [6] with LES studies. To predict such phenomena accurately, the mean reaction rate needs closure that includes the species small-scale inhomogeneities.

2.3 Intermediate and high Damköhler numbers

2.3.1 Very fast chemistry

The case of very high Damköhler numbers can be dealt with special concepts for the limit of infinitely-fast chemistry. These provide closure with a conserved scalar and its statistics in the turbulent mixing flow [5, 12]. Instead of solving Eq. (1) directly, equations for the first and second-moment of a conserved scalar are
solved, which then allow the construction of a conserved scalar Probability Density Function (PDF). Given how the reactive species are related to this conserved scalar, which can be found if the chemistry is very fast, their mean values can be calculated. This limit may not be very relevant to long-range atmospheric problems, but some reactants may fall in this regime [5, 6, 9]. The methods described next cover the full range of Damköhler numbers and are hence of quite general applicability.

2.3.2 Moment methods
Moment methods aim to provide a direct closure for $\phi_A^T \phi_B^T$. Historically, moment methods have not found much success in turbulent combustion due to the strong non-linearity of the reaction rates with temperature (Eq. 2). This, however, is less of a problem in atmospheric chemistry and some progress has been made. The books by Bourne and Baldyga [13] and Fox [14] contains a lot of references, mostly from the chemical engineering community, that present various models for $\phi_A^T \phi_B^T$ for simple reactions. In the atmospheric community, Ref. [3] also contains a good review. More recent work aims at a parametrization of the reaction rate as measured by LES calculations of the atmospheric boundary layer [11, 6, 15], which may then be used in conventional Eulerian Grid models. Moment methods with detailed chemistry has only recently been attempted [6], while some results are also presented in Ref. [3] for multiple reactions. Moment methods is an active area of research which, despite their age, probably have still significant contributions to make in Air Quality Modelling, especially if they are made to work with complex chemistry.

2.3.3 PDF methods
A method applicable to all turbulent reacting flows is the PDF approach [16], where a transport equation for the joint probability density function of the reacting scalars is considered. Its numerical implementation very often involves Monte Carlo methods. Very crudely, in the Monte Carlo approach the fluid is thought to be comprised of (virtual) particles. Their evolution in space is modelled by a random walk, representing turbulent dispersion (or macromixing). Their scalar concentrations are solved by deterministic or stochastic models, which include micromixing. In this way, segregation of the scalars is taken into account. The simplest of these models solves the following evolution equation for the scalars in particle $n$:

$$ \frac{d\phi_n^T}{dt} = -\frac{\phi_n^T - \bar{\phi}}{T_{\text{eddy}}} + \dot{\omega}_n $$

(5)

where the mean value $\bar{\phi}$ is calculated as the average over all particles at a particular point in space and $\dot{\omega}_n$ is the reaction rate of the $n$-th particle. The first term in the r.h.s. of Eq. (5) is called the “Interaction by Exchange with the Mean” (IEM) model and represents the approach of the scalar fluctuations towards the mean value $\bar{\phi}$ due to the scalar dissipation. More advanced models can be found in the literature [14, 17]. Note that the use of $T_{\text{eddy}}$ in Eq. (5) implies that passive and
reacting scalar fluctuations are dissipated at the same rate, an assumption that can be removed with more refined models [18]. The random walk in space for each particle may follow the simplified Langevin model [17]:

\[
\begin{align*}
    dx_i &= u_i dt \\
    du_i &= -\left( \frac{1}{2} + \frac{3}{4} C_0 \right) \frac{\overline{u_i - u}}{T_{\text{eddy}}} dt + (C_0 \epsilon)^{1/2} \xi(dt)^{1/2}
\end{align*}
\]  

(6)

where \( \epsilon \) is the dissipation of kinetic energy \( k \) so that \( T_{\text{eddy}} = \epsilon/k \), \( \xi \) is a random number following a normal distribution with zero mean and unity variance, and \( C_0 \) is a constant tuned by experiment to predict the correct mixing behaviour. More complete models are also available to take into account complicated flow fields [16, 17].

The PDF method has found some use in idealized atmospheric dispersion problems [19, 20]. The computational cost of this method with detailed chemistry is quite high [19] due to the large number of Monte Carlo samples needed to achieve statistical convergence. However, the PDF approach is a theoretically-sound method by which micromixing can be included to atmospheric dispersion codes at any spatial resolution, including LES [21]. There is no limitation on the Damköhler number and chemistry to any level of complexity can be used. A demonstration of this method for a simple plume problem is given in Section 3.

2.3.4 The Conditional Closure Moment method

Another method for micromixing, which like the PDF method by-passes the need to model the difficult \( \overline{\phi_A \phi_B'} \), is the Conditional Moment Closure (CMC) [22] that has been applied successfully to turbulent combustion. The CMC approach is a conserved-scalar method, which means that the reactive scalars (i.e. the species participating in the chemical reactions) are related to a non-reactive (conserved) scalar (i.e. a compound scalar that has no source term in its governing equation). In the high Damköhler number limit, these relations are supplied by assuming infinitely fast chemistry [12]. In CMC, these relations are conditional averages of the concentrations given a value of the conserved scalar and are calculated with modelled transport equations that can include finite-rate chemistry. The mean species concentrations are found by integrating the conditional averages over the conserved scalar PDF (usually of a presumed shape). Crudely speaking, macromixing is included in the turbulent large-scale transport of the conserved scalar, which affects the conserved scalar PDF, while micromixing is included in the CMC equations through the conditionally-averaged scalar dissipation rate. Chemistry is included only in the CMC equations and hence the effect of molecular mixing on the evolution of the chemical reaction is explicitly included in the model.

Brown and Bilger [23] successfully developed a formulation of CMC for the \( NO-NO_2-O_3 \) system in a wind-tunnel plume, an experiment that we will consider in more detail in Section 3. The use of CMC with more realistic chemistry, the CBM-IV mechanism, has been described in this series of Conferences [7]. It was
shown that segregation is important for power station plume problems in the early 30 minutes or so of their evolution. In particular, it was found that micromixing affects the species participating mostly in fast reactions, such as the OH and other radicals of the CBM-IV mechanism, consistent with [9]. Very slow species, such as \( CO \) or some \( VOC \)’s, are predicted accurately by the conventional method of neglecting fluctuations [7]. To fully examine the applicability of this approach to realistic problems, coupling with practical codes is necessary and research along these lines is currently underway at the University of Cambridge.

### 2.3.5 Stochastic Fields method

A new method that shows great promise in treating together turbulent mixing and reactions has been developed by Valiño [24]. This method starts from the transport equation for the scalar PDF and derives an equation akin to an unsteady-advection-diffusion-reaction equation, but with an additional random forcing term and a term representing micromixing. One would solve many such equations, each one corresponding to a different (virtual) “field” (crudely speaking, a different 3-D realization of the scalar field). The conservation equation for the scalar now becomes a stochastic partial differential equation:

\[
\begin{align*}
\frac{d\tau^n_i}{dt} &= -\bar{u}_k \frac{\partial \tau^n_i}{\partial x_k} dt + \frac{\partial}{\partial x_k} \left( K \frac{\partial \tau^n_i}{\partial x_k} \right) dt \\
&\quad + \dot{w} (\tau^n_1, \tau^n_2, \ldots, \tau^n_N) dt + (2K)^{1/2} \frac{\partial \tau^n_i}{\partial x_k} \xi(dt)^{1/2} - \frac{\tau^n_i - \bar{\tau}_i}{T_{eddy}} dt
\end{align*}
\]

where \( \tau^n_i \) is the concentration of the \( i \)-th species in the \( n \)-th field, \( \bar{\tau}_i \) the mean concentration of the scalar (calculated as an average over the fields), \( K \) the eddy diffusivity, and \( \xi \) is again a random number following a normal distribution with zero mean and unity variance. Details can be found in Ref. [24]. Each field evolves according to the mean velocity and an eddy diffusivity and uses a chemical source term calculated from the concentrations of scalars found in this field. It interacts with the other fields through the micromixing term, i.e. the last term in the r.h.s. of Eq. (7), which has been modelled as in the Monte Carlo PDF method discussed previously (Eq. 5) by the IEM model. Efforts to implement this equation in practical LES of atmospheric problems are underway in LITEC, Zaragoza [25]. Equation (7) has also been used here in some preliminary calculations for the experiment of Brown and Bilger [5], with very promising results as shown in Section 3.

### 3 Segregation in a reacting plume

#### 3.1 Description of the problem

In this Section, the experiment of Refs. [5, 23] is simulated by the PDF and the Stochastic Fields models described previously. Calculations are also done with Eq. (1) with the mean reaction rate evaluated at the mean concentrations (i.e.\( \langle r \rangle \)).
neglecting segregation). The aim is to demonstrate the improvement in the predictions by including micromixing.

The experimental arrangement consists of a point source of NO in a uniform turbulent flow of air doped with O₃. The flow is in a wind tunnel with grid-produced turbulence. The reaction $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ is expected to occur and measurements of the reactants and products were performed by fast-response probes. The mean velocity was $\bar{U} = 0.5$ m/s and the authors provide detailed information on the turbulence kinetic energy as a function of distance from the grid and on the large-eddy lengthscale. A constant value for the eddy diffusivity of $K = 0.0128\bar{U}M$ ($M$ is the turbulence grid spacing of 0.32 m) has been suggested [5]. Empirical expressions for the variation of velocity fluctuations are also given and from these, an expression for the variation of the turbulent timescale $T_{\text{eddy}}$ was derived. This timescale is about 4 s. The Damköhler number based on these large-eddy quantities is of order unity [5]. Mean species volume fractions are given as $\langle \Gamma_i \rangle$ and rms values by $\gamma_i'$. The inlet values for NO and O₃ were $\Gamma_{\text{NO},1} = 515$ ppm and $\Gamma_{\text{O}_3,2} = 1.07$ ppm.

3.2 Numerical methods

The PDF method is solved by a Lagrangian Monte Carlo approach, where each particle follows a random walk (Eq. 6) with a random velocity component added to the mean velocity $\bar{U}$. 1,000,000 particles are tracked and Eq. (5) is solved for each one. Average values of the scalars as a function of space are compiled over the particles that fall in the same cell of a grid spanning the domain of interest. Note that we do not solve any fluid mechanical equations here, as it is assumed that the mean velocity is uniform and the turbulence intensity and large-eddy timescale appearing in the Langevin model and in Eq. (5) are taken from the experimental results. Therefore the grid in physical space only serves to group the Lagrangian particles at each timestep.

The Stochastic Fields method is solved by an operator splitting technique. Equation (7) without the random forcing term is solved first with a standard finite-difference technique, since it is now a deterministic partial differential equation. Then, the outcome from this first step is updated for the random forcing term by a simple Euler method. Note that special techniques may be necessary for this step [26] to ensure accuracy, but these have not been implemented yet. About 500 fields have been used here because the chemical model is very simple as it involves only three species and one reaction. In a more realistic problem with detailed chemistry, fewer fields (10-100) would have to be used or the computational cost would be prohibitive. For simulating the experimental arrangement of Ref. [5], turbulent dispersion in the streamwise direction is neglected and, since there is no velocity component in the cross-stream directions, Eq. (7) is solved in an unsteady 2-D formulation over a $65 \times 65$ point grid. The variation with time represents the downstream evolution of the plume.
3.3 Results and discussion

The total value of \( NO_x = NO + NO_2 \) is a conserved scalar and hence its value can be used to characterize the inert mixing field. Figure 1 shows the \( NO_x \) values calculated by the Stochastic Fields model compared to experimental measurements at two downstream locations. It can be seen that using a constant value of \( K \) is a reasonable assumption, certainly over the region where experimental data is available, and that the actual value used is appropriate. The passive scalar rms (Fig. 2) is also predicted very accurately. This shows the accuracy of the IEM model for micromixing of a non-reacting scalar, which is not surprising given that this model has been widely validated against similar experimental data. More importantly, it shows that the Stochastic Fields model, that introduces a randomness in the whole of the spatial distribution of the scalar and then use these random distributions to get first and second moments at a point, has the correct behaviour. The good agreement shown in Figs. 1 and 2 also validates the numerical method used here.

![Figure 1: Radial profiles of mean \( NO_x \) at x/M = 11 & 15.5. Predictions using the Stochastic Fields method. Data from Ref. [5].](image)

Results for the mean and rms values of \( NO_2 \) (i.e. a reactive scalar) calculated from the Stochastic Fields method are shown in Figs. 3 and 4 respectively. Volume fractions have been normalized by the inlet \( O_3 \) concentration and radial position has been normalized by a characteristic plume width calculated from \( \sigma = \sqrt{2tK} \), where \( t \) is time \( (t = x/U) \). It can be seen that the calculations are reasonably close to the data, with an overprediction of \( NO_2 \) by about 20%. The rms profiles collapse onto each other when normalized as above, consistent with experiment (not shown). The actual values are very close to the data, as shown in Fig. 4.
consistent with the good agreement found for the variance of the passive scalar evident in Fig. 2 and in Ref. [24].

Calculations using only the mean concentrations, i.e. neglecting micromixing, and using the same values for turbulent diffusivity and inlet concentrations are also shown in Fig. 3. In the absence of micromixing, the production of $NO_2$ is overpredicted compared with the experimental data by about 30%. Hence only using mean values appears to give a reaction rate that is too high. If we consider Eq. (3), we can infer that the correlation coefficient $\phi'_{NO}\phi'_{O_3}$ is not negligible and takes a negative value. This is fully consistent with experimental data [5].

Results from the PDF method are also included in Figs. 3 and 4. The mean is predicted very accurately, while the rms is underpredicted by about 20%. The data from the PDF method are again much better than the predictions without any segregation. The better agreement of the PDF method than the Stochastic Fields method implies that the former predicts a more negative correlation between the species than the latter. We should not disregard the fact that the PDF method is at a more mature stage of development. The present data demonstrate possibly one of the first uses of the Stochastic Fields method for such a reacting flow problem and hence future improvements are to be expected.

We conclude that micromixing is important for the plume experiment of [5] and that the present models that include small-scale segregation can improve substantially the accuracy of the predictions relative to the conventional model of neglecting the correlation between the species fluctuations. Further work should focus on introducing these models to more practical Air Quality calculations.
Figure 3: Radial profiles of mean NO$_2$ at $x/M = 15$. Predictions with the stochastic fields and the PDF methods and with a calculation without segregation. Experimental data from Ref. [5].

Figure 4: Radial profiles of the rms of NO$_2$ at $x/M = 15$. Predictions with the stochastic fields and the PDF methods. Experimental data from Ref. [5].

4 Conclusions

Predicting the dispersion of reacting pollutants close to their source is a topic of importance for Air Quality Modelling. The conventional method of neglect-
ing species fluctuations is not valid for such small-scale problems because the Damköhler number is of order unity. In this regime, the interaction of the chemical reaction with the turbulence needs to be considered.

In the present paper, moment, PDF, CMC and the Stochastic Fields methods that have been developed as general theories for turbulent reacting flows have been reviewed and their use for typical atmospheric dispersion problems has been illustrated. By comparison with wind tunnel data, it is found that micromixing can affect the evolution of the mean reaction rate and that the models presented here can track the evolution of the pollutant. Further work should focus on the interfacing of these models with Eulerian Grid or LES codes applied to more practical situations of Air Quality Modelling.

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